

Thermal Analysis in Practice

Dr. Matthias Wagner

The information contained in this handbook is based on the current knowledge and experience of the authors. The handbook presents a large number of carefully selected application examples. The experiments were conducted and evaluated with the utmost care using the instruments specified in the description of each application.

This does not however absolve you from personally testing the suitability of the examples for your own work and purposes. Since the transfer and use of an application is beyond our control, we cannot of course accept any responsibility.

When chemicals, solvents and gases are used, the general safety rules and the instructions given by the manufacturer or supplier must be observed.

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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.

Thermal Analysis in Practice is a further publication in the Collected Applications series. The aim of the handbook 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. The results were evaluated using the **STAR**[®] software.

Many of the application examples have been taken from previous Collected Applications handbooks such as "Thermoplastics", "Elastomers", "Thermosets", and "Validation in Thermal Analysis", or from "UserCom", the biannual METTLER TOLEDO technical customer journal. Back issues of this applications-oriented periodical can be downloaded from the Internet at www.mt.com/ta-usercoms.

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.

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Dr. Matthias Wagner, Editor

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1 Introduction to Thermal Analysis

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1.1 Definitions

An earlier definition proposed by the **ICTAC**, the International Confederation for Thermal Analysis and Calorimetry, was:

“Thermal analysis covers a group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample is programmed. The sample is kept in a specified atmosphere.

*The **temperature program** may involve heating or cooling at a fixed rate of temperature change, or holding the temperature constant, or any sequence of these.”*

Various objections were later raised and various recommendations put forward to clarify certain points. For example:

- The distinction between a thermoanalytical technique and a thermoanalytical procedure. Thermal analysis means the whole thermoanalytical method. It covers both the thermoanalytical technique (measurement of a change in a sample property) and the thermoanalytical investigation procedure (evaluation and interpretation of the measured values).
- Analysis therefore means more than just monitoring.
- In many cases, the change in the sample property is monitored and not the sample property itself.
- In most cases, the temperature of the environment is programmed rather than the temperature of the sample.
- Atmosphere is an operational parameter and is not essential for the definition.

This finally led to the most recent ICTAC definition of thermal analysis put forward in 2004.

This defines thermal analysis simply as:

“Thermal Analysis is a group of techniques that study the relationship between a sample property and its temperature.”

The definition clarifies key words used in this definition as follows:

- **Group** – thermal analysis comprises a diverse range of techniques and experimental types that may be considered collectively if the total measurement conforms to the total definition.
- **Techniques** – a technique is characterized by the property that is under investigation.
- **Study** – implies that time is an integral part of the thermal analysis experiment and the total experiment, and the interpretation and discussion of the measured data are included.
- **Relationship** – implies that either the sample property can be measured as a function of temperature (controlled-temperature program), or the temperature can be measured as a function of the sample's property (sample-controlled heating).
- **Sample** – the material under study during the entire experiment (starting material, intermediates and final products) and its close atmosphere. This is equivalent to the thermodynamic system.
- **Property** – any physical or chemical property of the sample.
- **Temperature** – which can be directly programmed by the user, or controlled by a property of the sample. The program may include an increase, or decrease in temperature, a periodic change, or a constant temperature or any combination of these.

The data produced in a thermal analysis experiment is displayed as a thermoanalytical curve in a thermoanalytical diagram. Frequently, several different measured signals are displayed at the same time (referred to as **simultaneous measurement**).

The thermoanalyst is usually interested in so-called **thermal effects** in which the measured signal changes more or less abruptly.

Often the objective is to measure physical quantities outside thermal effects, for example the specific heat capacity, the expansion coefficient or the elastic modulus.

Note: The term “thermogram” is dated and should not be used. It is nowadays reserved for the graphical representation of the surface temperature distribution of objects.

The terms currently used are thermoanalytical curve or diagram, measurement curve, for example a DSC curve, a TMA diagram, etc.

1.2 A Brief Explanation of Important Thermal Analysis Techniques

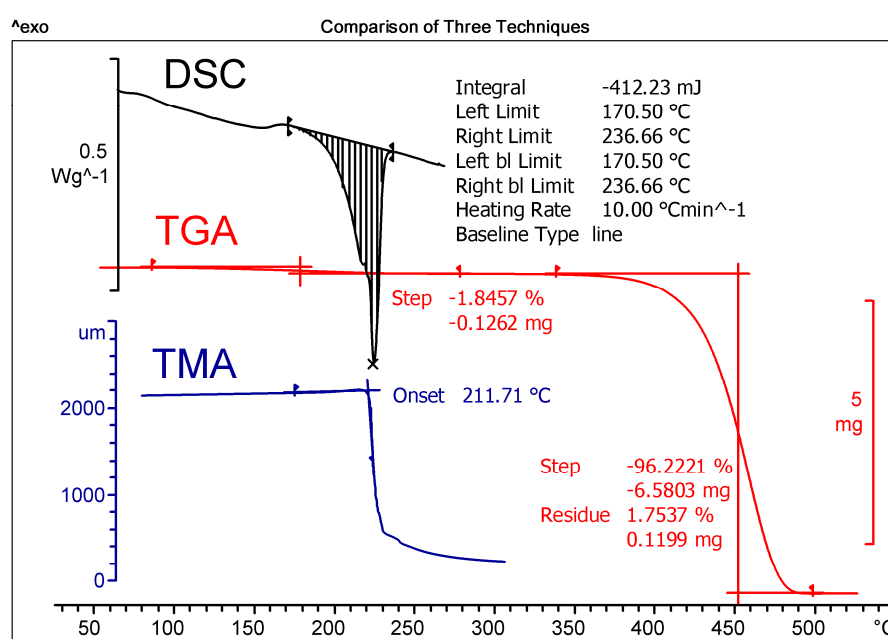


Figure 1.1. The three techniques used to measure polyamide 6 show different thermal effects. DSC: melting peak of the crystalline part; TGA: drying and decomposition step; TMA: softening under load.

DTA, Differential Thermal Analysis. In DTA the temperature difference between the sample and an inert reference substance is measured as a function of temperature. The DTA signal is °C or K. Previously, only the thermocouple voltage in mV or μ V was displayed.

SDTA, Single DTA. This term was patented by METTLER TOLEDO and is a variation of classical DTA that is particularly useful when used simultaneously with thermogravimetric analysis. The measurement signal represents the temperature difference between the sample and a previously measured and stored blank sample.

DTA (and SDTA) allows you

- to detect endothermic and exothermic effects, and
- to determine temperatures that characterize thermal effects.

DSC, Differential Scanning Calorimetry. In DSC, the heat flow in and out of a sample and a reference material is measured as a function of temperature as the sample is heated, cooled or held isothermally at constant temperature. The measurement signal is the energy absorbed by or released by the sample in milliwatts.

DSC allows you to

- detect endothermic and exothermic effects,
- determine peak areas (transition and reaction enthalpies),
- determine temperatures that characterize a peak or other effects, and
- measure specific heat capacity.

TGA, Thermogravimetric Analysis. TGA measures the weight and hence mass of a sample as a function of temperature. The acronym **TG** was previously used. Nowadays TGA is preferred in order to avoid confusion with T_g , the glass transition temperature.

TGA allows you to

- detect changes in sample mass (gain or loss),
- determine stepwise changes in mass, usually as a percentage of the initial sample mass, and
- determine temperatures that characterize a step in the mass loss or mass gain curve.

EGA, Evolved Gas Analysis. EGA is the name for a family of techniques by means of which the nature and/or amount of gaseous volatile products evolved from a sample is measured as a function of temperature. Important analysis techniques are mass spectrometry and infrared spectrometry. EGA is most often used in combination with a TGA because volatile compounds are eliminated in every TGA effect (mass loss).

TMA, Thermomechanical Analysis. TMA measures the deformation and dimensional changes of a sample as a function of temperature. In TMA, the sample is subjected to a constant force, an increasing force, or a modulated force, whereas in **dilatometry** dimensional changes are measured using the smallest possible load.

Depending on the measurement mode, TMA allows you to

- detect thermal effects (swelling or shrinkage, softening, change in the expansion coefficient),
- determine temperatures that characterize a thermal effect,
- determine deformation step heights, and
- to measure expansion coefficients.

DMA, Dynamic Mechanical Analysis. In DMA, the sample is subjected to a sinusoidal mechanical stress and the force amplitude, displacement (deformation) amplitude and phase shift are determined.

DMA allows you to

- detect thermal effects based on changes in the modulus or damping behavior.

The most important results are

- temperatures that characterize a thermal effect,
- the loss angle (the phase shift),
- the mechanical loss factor (the tangent of the phase shift),
- the elastic modulus or its components the storage and loss moduli, and
- the shear modulus or its components the storage and loss moduli.

TOA, Thermo-optical Analysis. By TOA we mean the visual observation of or the measurement of the optical transmission of a sample, for example in a thermo-microscope. Typical applications are the investigation of crystallization and melting processes as well as polymorphic transitions.

TCL, Thermochemiluminescence. TCL is a technique that allows you to observe and measure weak light emission that accompanies certain chemical reactions.

1.3 Application Overview

Property, application	DSC	DTA	TGA	TMA	DMA	TOA	TCL	EGA
Specific heat capacity	...	.						
Enthalpy changes, enthalpy of conversion	...	.						
Melting enthalpy, crystallinity	...	.						
Melting point, melting behavior (liquid fraction)	...	.		.		...		
Purity of crystalline nonpolymers	...		...			.		
Crystallization behavior, supercooling	...	.				...		
Vaporization, sublimation, desorption	...	.	...			...		...
Solid–Solid–transitions, polymorphism	...	...		.		...		
Glass transition, amorphous softening	...	.		...	...	.		
Thermal decomposition, pyrolysis, depolymerization, degradation	.	.	...	.		.		...
Temperature stability	.	.	...	.		.		...
Chemical reactions, e.g. polymerization	...	.	.				.	
Investigation of reaction kinetics and applied kinetics (predictions)	...	.	...					.
Oxidative degradation, oxidation stability	...	...	...	.			...	
Compositional analysis	...		...					...
Comparison of different lots and batches, competitive products	...	.	...	.	.	...	.	...
Linear expansion coefficient				...				
Elastic modulus				.	...			
Shear modulus					...			
Mechanical damping					...			
Viscoelastic behavior				.	...			

Table 1.1. Application overview showing the thermoanalytical techniques that can be used to study particular properties or perform certain applications. ... means "very suitable", . means "less suitable".

1.4 The Temperature Program

A sample is subjected to a temperature program in order to **measure** the processes that occur or to subject the sample to defined **thermal treatment**, for example annealing, erasing thermal history or creating a defined thermal history.

According to ICTAC, the **temperature program**

"may involve heating or cooling at a fixed rate of temperature change, or holding the temperature constant, or any sequence of these".

The elements making up such sequences are called **segments**.

The temperature program usually begins at the start temperature from a state of isothermal equilibrium in which no measurement data is collected. As soon as the start temperature is reached, the measurement begins with the first segment of the temperature program.

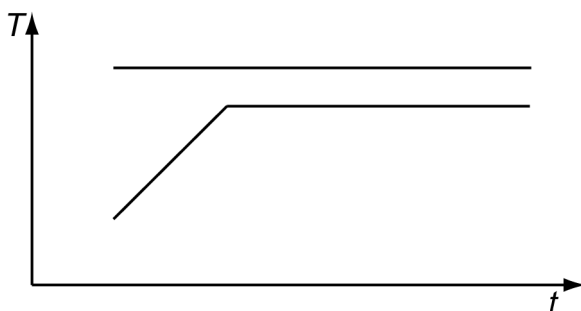


Figure 1.2. Isothermal measurement. Above: Insertion of the sample into the measurement cell that has already been programmed to the isothermal temperature (purely isothermal program). Below: Insertion of the sample at room temperature followed by dynamic heating (or cooling) to the measurement temperature.

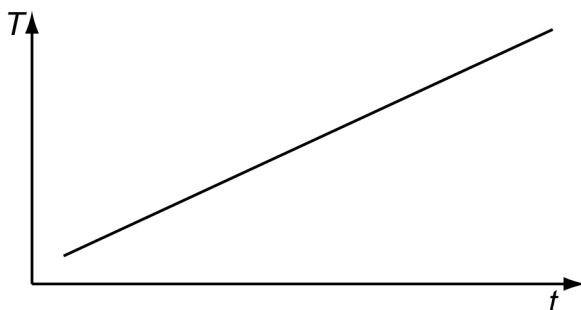


Figure 1.3. Dynamic measurement at a constant heating rate. This is the usual operating mode for most measurements. With DSC, low heating rates result in good temperature resolution but small effects, whereas high heating rates give poor temperature resolution and large effects. Low heating rates are 0.5 to 5 K/min, medium rates 5 to 20 K/min, and high rates >20 K/min.

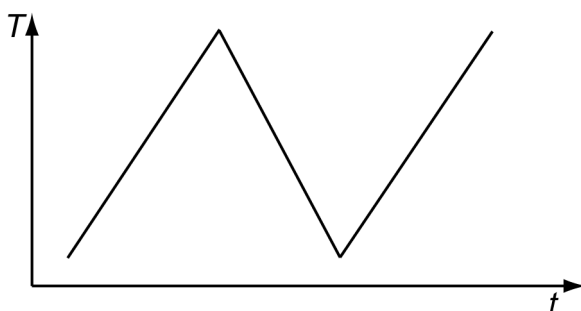


Figure 1.4. Dynamic heating, followed by cooling and a second heating segment. This is often very useful for interpreting measurement curves.

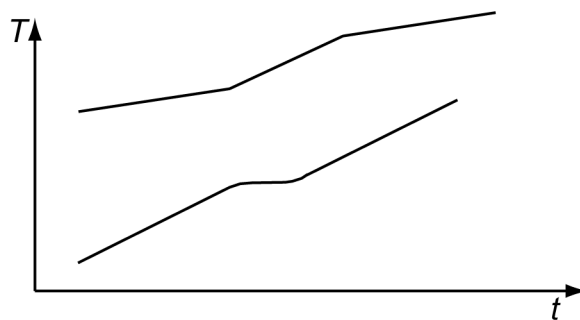


Figure 1.5. Dynamic measurements at different heating rates to save time. Above: A DSC In-AI check. Below: MaxRes[®] used with TGA: The resolution remains good - the heating rate is automatically decreased parallel to the increasing reaction rate of the sample. As soon as the reaction rate slows, the heating rate increases again.

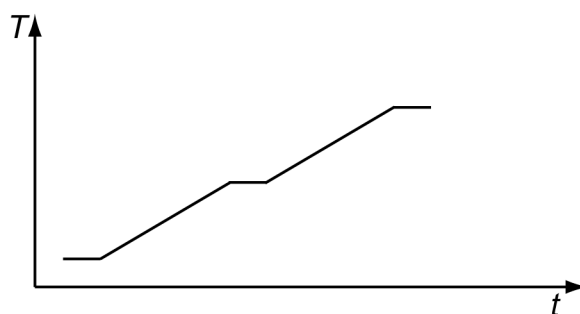


Figure 1.6. The isothermal-dynamic-isothermal temperature program is mainly used for the measurement of the specific heat capacity with DSC and for IsoStep[®].

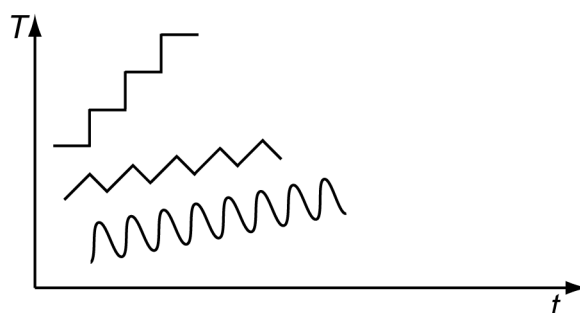


Figure 1.7. Periodic temperature programs. Top: A series of isothermal steps, mainly for safety investigations of chemical reactions, for equilibrium-melting, and for IsoStep[®]. Middle: The saw-tooth program illustrates a version of alternating DSC (ADSC). Bottom: The sinusoidal modulation (below) is the current version of our ADSC technique. ADSC can separate certain effects. The phase shift that occurs between the heating rate and the heat flow is an additional piece of information.

The heating rate chosen applies to a so-called reference position*) because the real sample can exhibit first order phase changes (e.g. melting) in which the heating rate cannot be controlled. This type of temperature control of the sample environment is known as **isoperibolic**. In fact, the temperature of the sample advances compared to that of the reference during exothermic processes and lags behind in endothermic processes. Depending on the thermal contact of the sample (thermal resistance), the sample temperature can deviate from the reference temperature by several tenths to several °C (K).

*) In the case of TGA/SDTA, DMA/SDTA und TMA/SDTA, this corresponds to a fictive inert sample during the blank run, whereas in DSC it is a reference crucible during the measurement.

References and Further Reading

[1] ICTAC Nomenclature of Thermal Analysis, at <http://www.ictac.org>

2 A Brief History of Thermal Analysis

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Thermal methods were used long before anyone talked about chemistry or material sciences. Even in antiquity, many substances were subjected to a “heat test” to verify their identity and authenticity.

Nowadays, most of these tests have been replaced by other physical-chemical test methods.

In the 18th century, thermometers and temperature scales were developed, for example that of Anders Celsius in 1742. The thermal expansion of materials was used to indicate the temperature. Conversely, measurements of the change in length of materials as a function of temperature (dilatometry) had already been performed at this time.

The manufacture of ceramic products is closely connected with the development of thermal analysis. For example, even today, so-called Seger cones are still used to indicate the temperature reached at the position in the furnace where they are placed. A set of these consists of several triangular pyramids cones made of clay and oxide mixtures of increasing softening temperature. When they reach a particular temperature, they deform under the influence of their weight.

In the 19th century, it became possible to measure heat quantities. This was after the difference between temperature and heat content or enthalpy had been clarified using thermodynamic principles.

In 1887, Le Chatelier [1] performed the first actual thermoanalytical measurements as we understand them by putting a thermocouple in a sample of clay and heating the sample in a furnace. The heating curve was recorded on a photographic plate using a mirror galvanometer.

In 1899, Roberts-Austen [2] significantly improved the sensitivity and meaningfulness of such measurements through the introduction of two differential thermocouples connected in opposition. This allowed him to measure the temperature difference between the sample and an inert reference. He is therefore regarded as the inventor of differential thermal analysis, DTA.

In 1915, Honda [3] published the first thermogravimetric measurements in which the mass of the sample was almost continuously measured. Before this, it had only been possible to measure the mass difference after a thermal experiment by back-weighing.

In 1955, Boersma [4] invented the present-day heat flow DSC with his idea of placing the thermal resistance outside the crucible. The development of power-compensated DSC was first described in a publication by Watson et al. [5] in 1964.

Dynamic mechanical measurements with a constant selectable frequency have only recently become possible. Before this, similar measurements were performed using a torsion pendulum at resonance frequencies.

Robert MacKenzie [6] studied the history of thermal analysis in great depth and published many articles on this subject.

In more recent years, thermal analysis has profited greatly from the availability of powerful computer hardware and software. This has had an enormous influence on the development of thermoanalytical methods. Before 1980, measurement curves were recorded with linear pen recorders and evaluated manually. Selection of the wrong measurement range meant that the measurement had to be repeated using a more suitable range. Nowadays, the measured curve is saved, then displayed in an optimal fashion for interpretation and if necessary automatically evaluated.

2.1 Thermal Analysis at METTLER TOLEDO

Erhard Mettler, the founder of the company, had been very successful with his analytical and precision balances. In 1960, he began looking for possible additions to expand the range of products.

TA1: Hans-Georg Wiedemann came forward with his ideas for the commercialization of his “thermobalance” just at the right time. A development group was quickly set up to modify the purely mechanical semi-micro balance using electromagnetic force compensation so that the balance signal could be recorded graphically on a pen recorder. At the same time, furnaces, temperature sensors and controllers were developed to enable temperature programs to be performed. Vacuum technology also had to be developed before in 1964 the first TA1 “recording vacuum thermoanalyzer” was introduced. The TA1 Thermal Analysis System could simultaneously perform TGA, DTG and DTA measurements. Soon any reputable laboratory engaged in materials science research had to have a TA1 even though the cost of such a system at that time was very high, about 120,000 to 200,000 Swiss Francs, depending on the particular version. The most important application areas of the TA1 were inorganic compounds and ceramic materials.

FP1: At about the same time, an instrument for the automatic determination of the melting point of organic substances was developed. An additional measuring cell for the dropping point of edible oils and lubricant greases and a hot stage for the observation of samples under the microscope completed the system.

TA2000: In 1971, an instrument followed for quantitative differential thermal analysis, as the earlier versions of the present-day heat flow DSC were called at the time. Soon a temperature range of -170 to +500 °C was available, which was ideal for the investigation of organic compounds and the increasingly important polymer plastic materials. At the same time, the first successful trials began with computer (PDP11) evaluation techniques following digitization of the analog measurement data. From 1973 onward, the first programmable desk top computers appeared on the market and automatic evaluations became an economical proposition for normal customers.

TA3000: 1981 saw the introduction of the TA3000 System with its new method concept. This was the first commercial instrument for the automatic measurement and evaluation of thermoanalytical data. Routine measurements enabled efficient quality control tasks to be performed. In addition to the DSC and TGA measuring cells, the **TMA40** Thermomechanical Analyzer was introduced. This was revolutionary at the time because its programmable sample load enabled dynamic load TMA (DLTMA) to be performed for the first time.

STAR[®] concept: Thermal analysis has benefited enormously from the availability of powerful but inexpensive personal computers. The **STAR[®]** System was the result of the development of the **TA4000** (1987) and then the completely new **TA8000** (1992). Some of its most important features were its

- modular design,
- excellent measurement performance,
- unique calibration with FlexCal[™],
- fully automatic through to result assessment, and
- integrated relational database.

The innovative **DMA/SDTA861[®]** Dynamic Mechanical Analyzer was introduced in 2002. Its modular design means that additional measuring modules can be developed in the future as required and integrated into the system using the **STAR[®]** software.

Finally, 2007 saw the introduction of the Thermal Analysis Excellence line comprising the TGA/DSC 1 with its innovative SDTA, DTA and DSC sensors sample holders and the DSC 1.

Both the performance and the operating convenience of the instruments were greatly improved. High priority was given to ergonomics and optimum ease of use. For example, the instruments can be operated using the intuitive touchscreen display or by actuating the hands-free SmartSens infrared sensors.

The new TGA and DSC models offer a choice of several different detectors. The TGA-DSC sensors simultaneously detect both weight and enthalpy changes with great accuracy. They differ in their maximum sample size and performance. The unique TGA-DSC sensor measures heat flow using six thermocouples and is very sensitive.

The instruments can be connected to a computer directly via TCP/IP, or via a network. This is an important advantage in a larger laboratory where several analysts operate different instruments and computers.

Finally, in 2009 the HP DSC 1 replaced the HP DSC 827^e. It can be equipped with a PC10 gas controller which allows the cell pressure to be controlled. DSC microscopy is now available for both high-pressure DSC and standard DSC.

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3 Polymers

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3.1 Introduction

Polymers (or macromolecules) are extremely large organic molecules made up of very many smaller units (monomers). They are widely used in materials such as rubber, plastics, and adhesives to name a few. The length of an individual macromolecule is typically 10 nm to 1000 nm and the molar mass is more than 10,000 g/mol. Polymers always consist of mixtures of macromolecules of different size and are therefore characterized by their average molar mass.

At low temperatures, polymers are glassy solids. Above their glass transition temperature, they become more or less soft and elastic. There are several ways to classify polymers, for example based on the polymerization process used to produce them, on their structure (linear, branched, or network) or as below on their properties (thermoplastics, elastomers or thermosets).

- **Thermoplastics** are linear or branched uncrosslinked molecules. The thread-like macromolecules are joined together through entanglement and intermolecular forces. Thermoplastics soften or melt on heating and can therefore be molded and recycled. On cooling they may form a glass below the glass transition temperature. If the polymer chains are uniformly built up and mostly free of side chains, they may partially crystallize, giving rise to amorphous (non-crystalline) and crystalline regions. Above the crystallite melting temperature they melt and are liquid. Many linear polymers are soluble in certain solvents and can be cast as films from solution.
- **Thermosets** are network polymers that are heavily crosslinked to form a dense three-dimensional network. Thermosets cannot melt on heating and decompose at higher temperatures. They are therefore normally rigid and cannot be plastically molded or dissolved. Their starting materials are more or less liquid and cure to the finished polymer during the molding process. Above the glass transition temperature, they become somewhat rubbery and soft.
- **Elastomers** are network polymers that are lightly cross-linked. On cooling, elastomers become glassy. On heating, they cannot melt or flow because of their crosslinks. If their glass temperature is below room temperature, they are soft and rubbery at normal temperatures. Under mechanical stress, elastomers undergo marked deformation, but regain their original shape almost completely when the stress is removed. Since the polymer chains are chemically linked through crosslinking (vulcanization), elastomers cannot be molded or dissolved. Molding is therefore performed prior to vulcanization of the thermoplastic starting material.

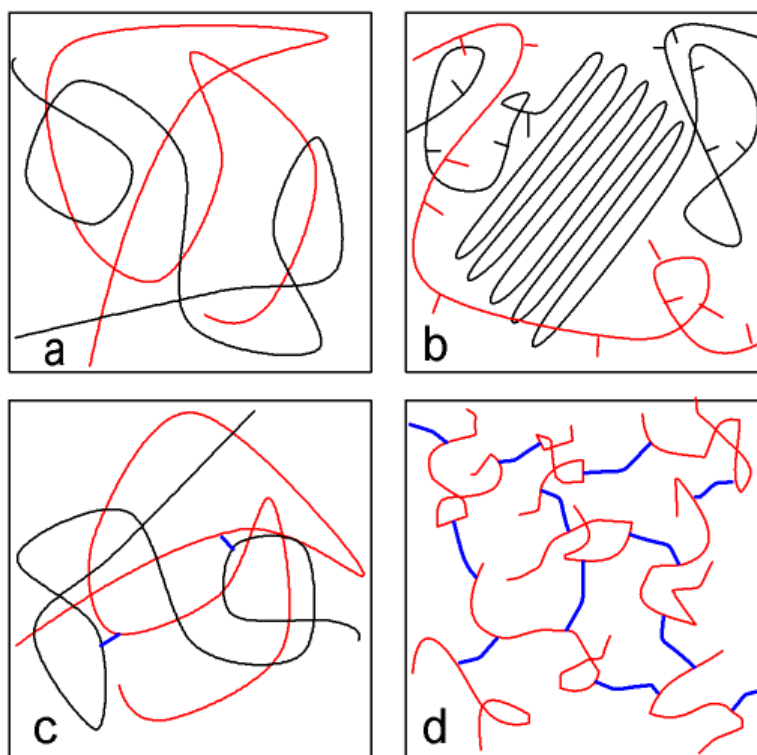


Figure 3.1. Schematic diagrams of different polymer molecules.

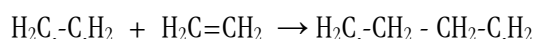
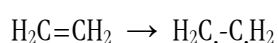
- a: Amorphous thermoplastic. The two macromolecules are shown in different colors in order to distinguish them more easily.
 b: Semicrystalline thermoplastic. In the center of the diagram is a chain folded crystallite. The remainder of the molecule and the red colored molecule are not able to crystallize because of the randomly occurring side groups.
 c: Elastomer. The two macromolecules are linked at two points (colored blue).
 d: Thermoset. The red molecules (resin) are three-dimensionally crosslinked by the blue curing agent.

3.2 Synthesis of Polymers

Polymers are formed when very many (up to several thousand) monomer units are linked together end to end by covalent bonds. The monomer units are reactive molecules that possess at least one bond that can be relatively easily cleaved. This allows the monomer units to be joined together through a chemical reaction.

Polymerization

In polymerization, the macromolecules are produced through successive linking of the same or similar individual monomer molecules to form a chain molecule. If there is only one type of chemical repeat unit (monomer) the corresponding polymer is a homopolymer; if more than one type of monomer is involved, it is a copolymer. A typical example is the formation of polyethylene, which has one of the simplest molecular structures. The basic monomer unit for polyethylene is the ethylene molecule (C_2H_4), whose two carbon atoms are joined through a covalent double bond. Under favorable conditions of pressure and temperature and in the presence of a suitable free-radical initiator such as benzoyl peroxide, the double bond of the C atoms is transformed into a single bond, leaving each C atom with an unpaired electron. As a free radical it can then form a bond with another ethylene molecule.



As can be seen, the resulting dimer is also a free radical so that further monomers can become attached.

Although the most important chain reactions are those involving free radicals, there are also other mechanisms. The reactive center at the growing end of a polymer can be ionic in character. Ionic polymerization is subdivided into cationic and anionic mechanisms. If the monomer has a non-organic atom (e.g. vinyl chloride $\text{CH}_2=\text{CHCl}$) or a side group (e.g. propylene $\text{CH}_3-\text{CH}=\text{CH}_2$), the side groups can occur randomly in the macromolecule (atactic polymer, little tendency for crystallization) or stereoregular (syndiotactic, on alternate sides; or isotactic, on the same side).

Copolymers: The properties of a copolymer depend not only on the content of the individual monomer units but also on their distribution. A random copolymer exhibits only one glass transition, whereas block and especially graft copolymers show transitions that correspond to the constituent homopolymers.

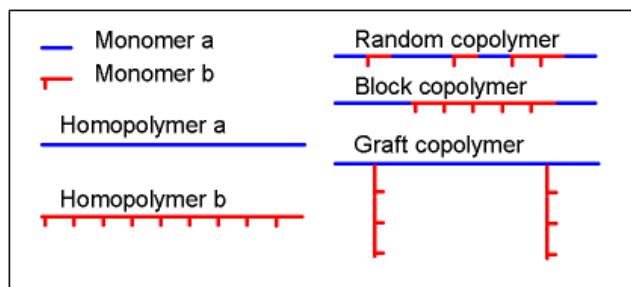
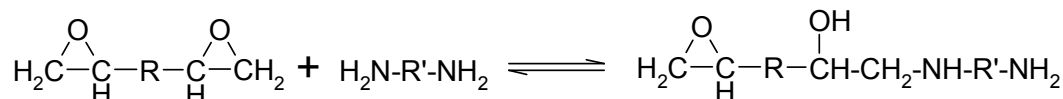


Figure 3.2. The monomers can be randomly distributed in the copolymer molecule or be present in blocks. Side chains can also be grafted onto the main chain.

Polyaddition

In polyaddition polymerization reactions, macromolecules are produced through the chemical reaction of low molecular weight compounds with reactive groups, such as hydroxyl, amino, acid, isocyanate or epoxy groups. The monomers are joined to each other by means of the oxygen or nitrogen atoms. For example, the reaction of an epoxy resin with an amine begins according to the following equation:



The reaction continues without stopping due to the remaining reactive group of each monomer. Three-dimensional crosslinking to form a thermoset is only possible because the secondary amine hydrogen can also react with an epoxy group. Each molecule of the amine therefore has four possible points of attachment.

In general, molecules with two points of attachment form linear polymers, and those with three or more points of attachment, three-dimensional crosslinked polymers.

Polycondensation

In polycondensation polymerization reactions, the same or different types of monomer molecules are joined together with the elimination of a substance of low molecular mass (usually water). A well-known example is the polymerization reaction of hexamethylenediamine (1,6-diaminohexane) and adipic acid (hexanedioic acid) to form polyamide 66 (PA 66) or nylon 66.

As shown in Figure 3.3, an H atom of the hexamethylenediamine reacts with an OH group of the adipic acid thereby eliminating a molecule of water. The reaction continues at both ends of the new molecule and leads to the formation of a long chain. The numbers in the name polyamide 66 (nylon 66) refer to the number of carbon atoms in the two monomers.

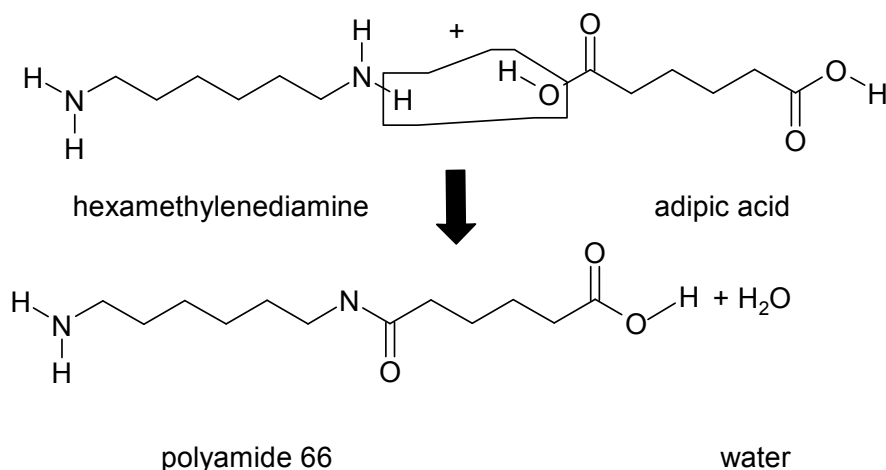


Figure 3.3. Polycondensation of hexamethylenediamine and adipic acid to polyamide 66.

3.3 Thermoplastics

In thermoplastics, the polymer chains are held together by weak bonding forces (van der Waals forces) and entanglement; there are no crosslinks. The chains can therefore easily turn and stretch under load. Semicrystalline thermoplastics contain both amorphous and crystalline regions. The latter disappear on melting. The properties of thermoplastics are very temperature dependent.

Below the glass transition temperature (T_g), thermoplastics are rigid glass-like materials. At the T_g , the thermoplastic becomes leathery, at higher temperatures rubbery, and finally more or less fluid. For this reason, many thermoplastics are easy to mold and can be recycled. The influence of temperature on the elastic modulus (Young's modulus) of an amorphous thermoplastic is shown schematically in Figure 3.4. The melting and glass transition temperatures of a number of different thermoplastics are summarized in Table 3.1.

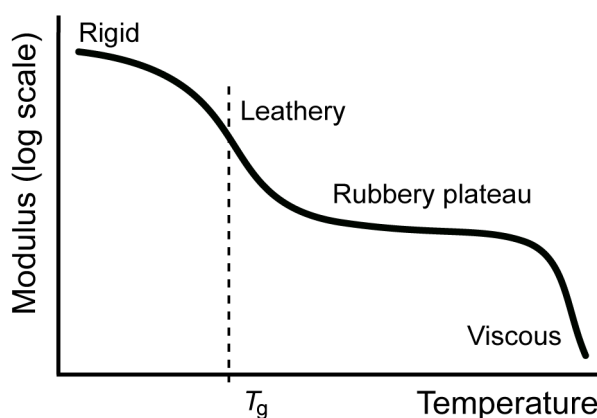


Figure 3.4. Influence of temperature on the elastic modulus and the behavior of a thermoplastic.

Polymer	Glass transition temperature	Melting temperature
Polyethylene (low density)	-120 °C	115 °C
Polyethylene (high density)	-120 °C	137 °C
Polyvinylchloride (PVC)	87 °C	175–212 °C
Polystyrene (PS)	85–125 °C	240 °C
Polypropylene (PP)	-16 °C	168–176 °C
Polyester (PET)	75 °C	255 °C
Polyamide (PA 66)	50 °C	265 °C

Table 3.1. Glass transition temperature and melting temperatures of various thermoplastics.

Some semicrystalline thermoplastics are polymorphous and can exist in different crystalline forms (e.g. PTFE). The degree of crystallinity of a thermoplastic depends on a number of factors. Simple polymers such as polyethylene crystallize most easily because there are no bulky groups present to prevent regular arrangement in a lattice. The degree of crystallinity of a thermoplastic also depends on how the material has been cooled from the melt. Slow cooling allows the macromolecules sufficient time to form a crystal lattice and leads to a high degree of crystallinity. On the other hand, shock-cooled polymers tend to retain an amorphous structure.

Deformation behavior of thermoplastics

Thermoplastics undergo both elastic and plastic deformation under the action of mechanical force. The deformation depends on the duration of the stress and on the rate at which the stress is applied. Figure 3.5 shows a typical tensile stress–strain curve for polyamide 66.

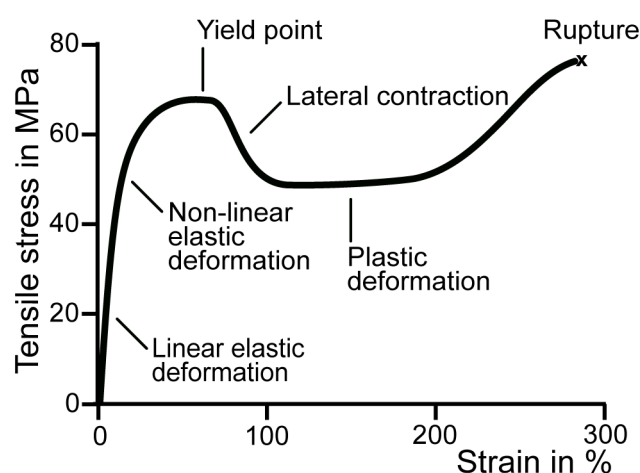


Figure 3.5. Typical tensile stress–strain curve of polyamide 66.

In the region of elastic deformation, two main mechanisms are in effect. On the one hand, the entangled chains are elastically stretched and return to their original position again after the tensile stress has been removed. On the other hand, entire sections of the chains can be shifted with respect to one another. These shifts are reversible in the elastic deformation region but the characteristic time constants for the relaxation can be hours or even months. This behavior, which is known as viscoelasticity, determines the deformation in the non-linear region of elastic deformation. If the polymer is subjected to a tensile stress above the yield point (elastic limit) the phenomenon of cold drawing occurs. The molecular structure changes permanently and permanent plastic deformation occurs. The chains are partially disentangled, stretched and simultaneously oriented parallel to each other. This process of cold drawing leads to localized lateral contraction or the formation of a neck (so-called necking). The neck region spreads until the entire specimen has been drawn into the new shape. Once the polymer is fully drawn, it is stronger than during the necking propagation. The chains are now aligned and more densely packed. This leads to an increase of the effective bonding forces between the chains and thus to a final upswing in the stress-strain curve. When the maximum tensile strength that the material can withstand is reached, it ruptures or breaks.

Viscous behavior and viscoelasticity

Polymeric materials behave both as viscous fluids and elastic solids; they are viscoelastic materials and their mechanical properties depend on time and temperature. The extent to which mechanical stresses cause chain slippage and plastic deformation depends on the temperature and the rate at which the stress is applied. If the stress increases slowly or at high temperatures, the chains react and adapt to the force exerted on them. If the stress is exerted rapidly or at low temperatures, the slipping and stretching process does not have sufficient time to adapt to the stress and the material is brittle and breaks. The viscosity of the polymer is a measure of the slippage of its chains and is therefore a property that characterizes deformation behavior of the material. In the case of thermoplastics, a marked temperature dependence of the viscosity according to the equation $\eta = \eta_0 \exp(Q_A/RT)$ is observed. Here Q_A is the activation energy for the slipping process of the chains and η_0 a constant.

The time-dependent deformation of a material under an applied stress is called creep [1]. A purely elastic material responds instantaneously to the stress and recovers its initial shape when the stress is removed. A viscous liquid, however, will deform as long as the stress is applied. The response of a viscoelastic material is in between the two. In amorphous thermoplastics, the activation energy of chain slippage and the viscosity are relatively small; the polymer undergoes deformation even with low stresses. At constant tensile stress, the polymer first of all reacts with rapid stretching. In contrast to metals, the expansion does not attain a constant end value. Rather the polymer continues to stretch slowly. This creeping of the material increases with increasing stress and with increasing temperature.

Another phenomenon that is also due to the viscoelastic properties of polymers is the stress relief in polymers that have been stretched by a fixed amount. For example, the stress in a rubber band that has been placed around a pile of books used to hold them together decreases with time.

Thermoplastic elastomers

Thermoplastic elastomers are a subgroup of thermoplastics that have been developed to combine the processing advantages of thermoplastics with the properties of elastomers. The elastic behavior of thermoplastic elastomers is however not due to crosslinking (as with elastomers) but is a result of the special segmented chain structure of the macromolecule. This consists of alternate, mutually incompatible, hard and soft segments or blocks. The hard blocks tend to aggregate in domains that act as crosslinking points. The crosslinking usually takes place through thermally labile physical interactions. The result is that thermoplastic elastomers flow at elevated temperatures and can be processed and molded in the same way as thermoplastics.

Further information on thermoplastics can be found in the METTLER TOLEDO “Thermoplastics” Handbook [2].

3.4 Thermosets

Thermosets are heavily crosslinked, close-meshed, three-dimensional polymers. Because of their close-meshed crosslinking, thermosets as a whole resemble a single giant molecule rather than a material made up of individual macromolecules. In fact, the individual macromolecules can hardly move. The result is that thermosets are hard and brittle materials with great structural strength. Fillers are often added to influence their mechanical properties. Thermosets are insoluble but can swell. Once thermosets have been crosslinked (cured) they can no longer be thermally molded. They do not melt and cannot be recycled.

Important types of thermosets are

- phenolic resins for electric insulation boards (printed circuit boards) and tubing,
- melamine-formaldehyde resins for furniture,
- unsaturated polyester resins for boats, travel trailers, aircraft parts and car bodies, and
- epoxy resins for molding and adhesive resins, as well as for printed circuit boards.

Thermosets are mostly used as composites. The addition of glass fibers, or even better, carbon fibers, yields very stiff components of low density, such as are used in Formula 1 racing cars.

Further information on thermosets can be found in the METTLER TOLEDO “Thermosets” Handbook [3].

3.5 Elastomers

Elastomers are lightly crosslinked linear chain molecules that form a wide-meshed three-dimensional network. Elastomers are also glass-like and brittle at low temperatures (i.e. in the range -10 °C to -80 °C). At higher temperatures, they largely retain their shape thanks to the crosslinking. They do not melt but begin to degrade and decompose if the temperature is too high. For this reason they cannot be recycled.

Elastomers are amorphous and show very little crystallization during processing. They can be elastically stretched without permanent plastic deformation occurring.

The starting material for the production of elastomers is natural rubber (caoutchouc) or synthetic rubber. By rubber, we mean an uncrosslinked polymer that can be crosslinked in a process called vulcanization and which has certain rubbery elastic properties and can undergo plastic deformation. Crosslinking is achieved using a vulcanizing agent. This reacts at suitable positions on the macromolecules and joins different chains together (see Figure 3.1c). The oldest and most widely used vulcanizing agent is sulfur.

The hardness or modulus of the elastomer can be influenced by the amount of vulcanizing agent used: small amounts of sulfur (typically 1%) lead to soft elastomers. Larger amounts of sulfur produce a hard elastomer.

The composition of an individual elastomer is very complex and is matched to the specific demands put on the material. Besides the actual rubber, an elastomer contains numerous ingredients such as vulcanizing agents, vulcanizing accelerators, activators, vulcanizing retarders, fillers, plasticizers, stabilizers, oxidation inhibitors, antiaging agents, pigments, and so on.

An example showing the typical composition of the tread of an automobile tire is given in Table 3.2.

Ingredient	Content in %
Natural rubber	39%
Filler (carbon black)	35.1%
Plasticizer (mineral oil)	19.4%
Processing agent	1.2%
Antiaging agent	1.5%
Vulcanizing agent (sulfur)	0.8%
Vulcanizing accelerator	0.7%
Dispersing agent (stearic acid)	0.8%
Vulcanization activator (zinc oxide)	1.5%

Table 3.2. Typical composition of the tread of an automobile tire.

Natural rubber (caoutchouc) is obtained as the milky emulsion of rubber particles known as latex from the tropical rubber tree (*Hevea brasiliensis*). The other ingredients are produced synthetically.

Synthetic rubbers are produced from very different starting materials such as butadiene, styrene, acrylonitrile, chloroprene, ethylene, propylene and so on.

Elastomers are classified according to the type of rubber used.

Some important elastomers are

- natural rubber, NR, for articles of daily use such as shoes, sponges, seals, automobile tires, tubing,
- styrene-butadiene-rubber, SBR, for automobile tires,
- butyl rubber, IIR, wherever low gas permeability and good heat and resistance to aging are required (e.g. automobile hoses),
- ethylene-propylene rubber, EPM/EPDM, seals,
- acrylonitrile-butadiene rubber, NBR, seals, tubing,
- fluorine elastomer, FPM, seals, molded parts, cable insulation, and
- chlorosulfonated polyethylene elastomers, CSM, wherever good stability toward light (UV), ozone, weather and fire is required.

Further information on elastomers can be found in the METTLER TOLEDO “Elastomers” Handbook [4].

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

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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 $\mu\text{V/K}$. See also detection limit.

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

$$y = A + Bx + Cx^2 \dots \quad (4.1)$$

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 $0.5\ \mu\text{V}$ pp (i.e. $0.1\ \mu\text{V}$ rms), or $0.01\ ^\circ\text{C}$ pp (i.e. $0.002\ ^\circ\text{C}$ rms).

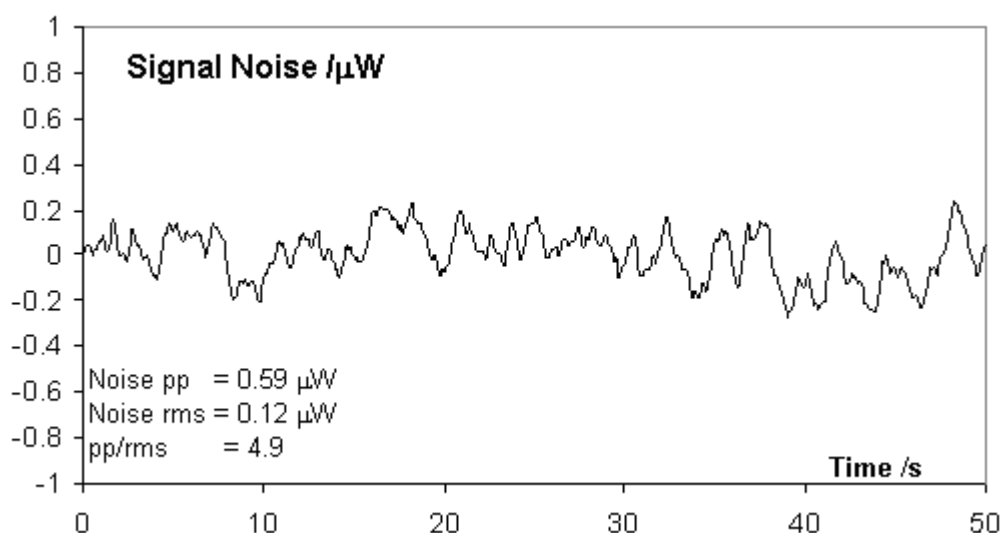


Figure 4.1. Calculation of peak-to-peak (pp) and root-mean-square (rms) values from random noise.

The effective rms value can be calculated from the equation:

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

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 $R_{th}C$ corresponds to the time constant, τ (tau), of this sensor:

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

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.

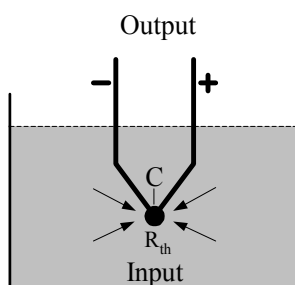


Figure 4.2. A thermocouple attempts to measure the true temperature of a water bath. The heat flows from the water across a thermal resistance R_{th} to the soldered junction, which has a certain heat capacity, C .

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.)

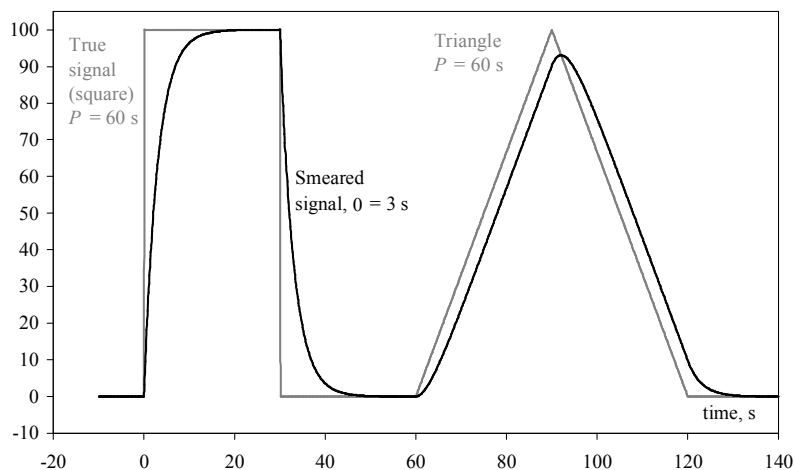


Figure 4.3. The true signal at the input is shown gray (left rectangular, right triangular, both with a period of 60 s; the output signal (black) of the RC element is somewhat smeared with a time constant of 3 s. The limiting frequency in this setup is 0.05 Hz, the limiting period 19 s.

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

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

So that the limiting period is given by

$$P_g = 2\pi\tau \quad (4.5)$$

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:

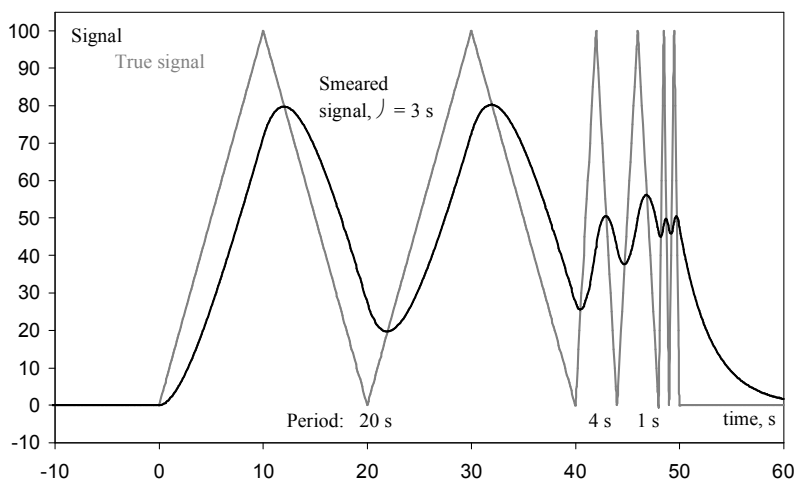


Figure 4.4. The two triangular input signals of 0 to 40 s corresponding to the limiting period of this sensor. They are well resolved and hardly damped. Those with significantly shorter periods (4, and 1 s) are strongly damped and the amplitude is reduced to about 5%.

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.

Temperature scales

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,

$$y = A + Bx + Cx^2 \dots \quad (4.1)$$

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.

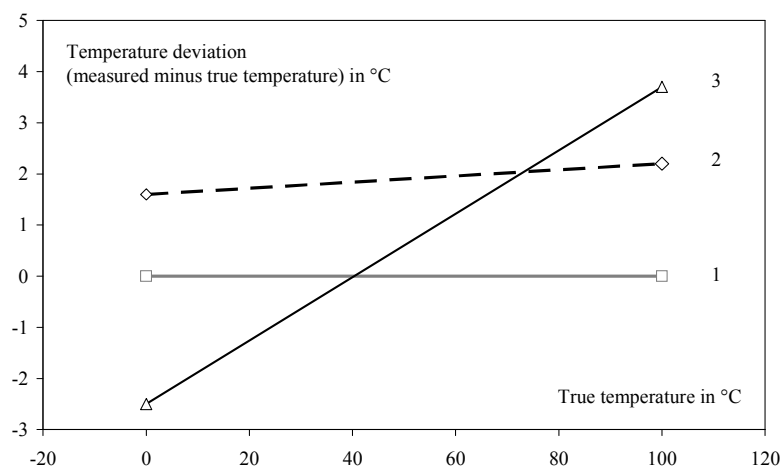


Figure 4.5. Plot of the measurement error of a thermometer.

1: The thermometer shows the expected temperatures. No adjustment is necessary.

2: The measured values are about 2 °C too high. If the value of the ordinate intercept, A , is adjusted by about 1.9 °C, a new measurement should give acceptable values of -0.3 °C and 100.3 °C.

3: In this case, both A and the slope, B , have to be adjusted. A test measurement afterward gives the correct result shown in Case 1.

This means that after adjustment, a new characteristic sensor curve is obtained. To facilitate adjustment, modern instruments include software that automatically calculates the new parameters A and B (and possibly others). The result of the adjustment should be checked by performing a new calibration (i.e. at least a one-point measurement).

4.9 The Most Important Electrical Temperature Sensors

In thermal analysis instruments, temperatures are nearly always measured with resistance thermometers and thermocouples. **Resistance thermometers** depend on the temperature dependence of the resistance of electrical conductors or semiconductors. Very often the Pt100 sensor is used whose resistance at 0 °C is about 100 Ω . In the range -180 °C to +700 °C, its electrical resistance, R , is given by the equation:

$$R = 100\Omega + 0.3908\Omega K^{-1} \cdot T + -58.02 \cdot 10^{-6} \Omega K^{-2} \cdot T^2 \quad (4.6)$$

The Pt100 sensor made of coiled platinum wire exhibits excellent long-term stability. Above 700 °C, there is the risk of recrystallization processes occurring which could change the resistance at 0 °C.

Thermocouples consist of two different metal wires that are joined together (soldered or welded) at both ends to form a circuit. If the two junctions are at different temperatures, a continuous current flows in the thermoelectric circuit. If the circuit is broken at the center, an electrical voltage can be measured that is proportional to the temperature difference and the nature of the two metals. Thermocouples are therefore ideal for measuring temperature differences, for example, at a thermal resistance to measure the heat flow through the resistance. Actual temperatures are measured by holding the second junction at a constant temperature (a reference temperature or comparison temperature, or also electronically generated).

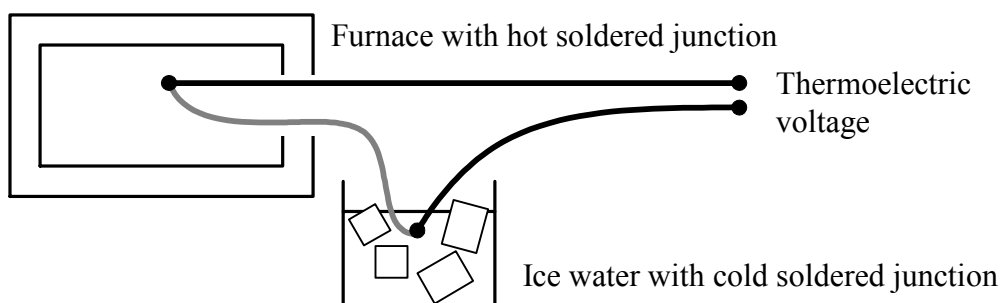


Figure 4.6. Measurement of the air temperature in a furnace using thermocouples. The platinum wires are drawn black and the platinum-rhodium wire gray.

The sensitivity or slope, S , of the thermocouple is expressed in $\mu\text{V/K}$. S is temperature dependent and in general increases with increasing temperature. Important types of thermocouple are for example:

- Copper-Constantan (Type T) from $-250\text{ }^{\circ}\text{C}$ to $+400\text{ }^{\circ}\text{C}$, $S_{0\text{ to }100\text{ }^{\circ}\text{C}} \sim 42\text{ }\mu\text{V/K}$.
- Iron-Constantan (Type J) from $-250\text{ }^{\circ}\text{C}$ to $700\text{ }^{\circ}\text{C}$, iron rusts easily, $S_{0\text{ to }100\text{ }^{\circ}\text{C}} \sim 54\text{ }\mu\text{V/K}$.
- Nickel-Chromium, practically identical to the Chromel-Alumel (Type K) from $-200\text{ }^{\circ}\text{C}$ to $1300\text{ }^{\circ}\text{C}$ (in non-oxidizing atmospheres) or to $600\text{ }^{\circ}\text{C}$ in oxygen-containing atmospheres.
- $S_{0\text{ to }100\text{ }^{\circ}\text{C}} \sim 41\text{ }\mu\text{V/K}$.
- Platinum-Platinum 10% Rhodium (Type S) from 0 to $1600\text{ }^{\circ}\text{C}$. Note that certain substances, so-called platinum poisons, change the thermoelectric properties, especially in reducing atmospheres.
- $S_{0\text{ to }100\text{ }^{\circ}\text{C}} \sim 6.4\text{ }\mu\text{V/K}$.
- Gold-Gold Palladium from $-200\text{ }^{\circ}\text{C}$ to $750\text{ }^{\circ}\text{C}$, $S_{156\text{ }^{\circ}\text{C}} \sim 9\text{ }\mu\text{V/K}$.

4.10 Temperatures in Thermal Analysis

A temperature difference, ΔT , that depends on the thermal resistance is necessary for heat to flow from the furnace to the reference point and to the sample. In METTLER TOLEDO designs, this is achieved by **increasing the furnace temperature** by the same value of ΔT . The time difference between T_c and T_r is equal to the time constant, τ_{lag} , independent of the heating rate. The heating rate, β , is equal to the slope of the triangle shown in the enlarged circular section of the diagram in Figure 4.7:

$$\beta = \Delta T / \tau_{\text{lag}}$$

From this, it follows that

$$\Delta T = \beta \tau_{\text{lag}} \quad (4.7)$$

At the beginning of each heating segment, the calculated temperature increase, ΔT , is added to the set value of the furnace temperature.

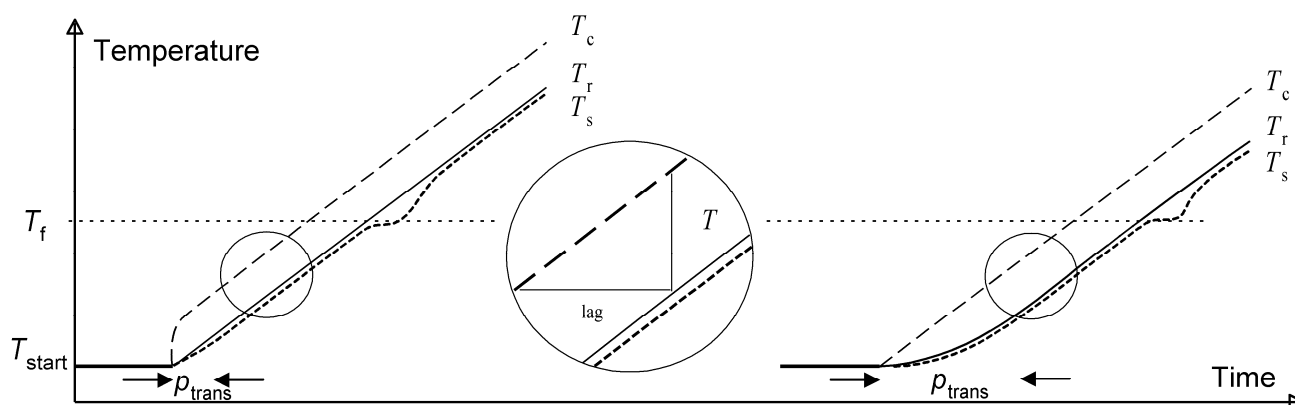


Figure 4.7. The three important temperatures are the furnace temperature, T_c ; the temperature of the reference point, T_r ; and the sample temperature, T_s . At T_f , a thermal event occurs (melting). The enlarged section shows the relationship between the heating rate, the lag time constant and ΔT . In the temperature program shown on the left, an increased temperature that exactly compensates ΔT is applied at the beginning of the dynamic segment. The diagram on the right shows the usual temperature program without the temperature increase. p_{trans} is the transition period that lasts from the start of the temperature program until dynamic equilibrium is reached (the DSC signal has stabilized).

Why do we use the increased temperature?

- It shortens the transient period (or settling time), p_{trans} , that is, the time taken to reach dynamic equilibrium (the reference and sample have assumed the heating rate of the furnace).
- It linearizes the temperature program of the reference point. Since τ_{lag} depends on the temperature, only the furnace temperature is linear in the usual temperature program.
- It makes the reference temperature independent of the heating rate.
- τ_{lag} and its temperature function ($\tau_{\text{lag}} = A + BT + \dots$) is usually taken into account using Total Calibration.

5 General Thermal Analysis Evaluations

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This chapter deals with the evaluation of curves obtained from the different thermal analysis measurement techniques. Specific evaluations can be found in the sections dealing with the particular measurement technique.

The first part discusses various graphical display possibilities. The section on curve comparison focuses on the important topic of the simultaneous presentation of several curves.

The second part covers generally applicable evaluations that give numerical results.

5.1 The Optimum Coordinate System

It pays to consider in advance which ordinate and abscissa is best for a particular task. For example, it makes no sense to evaluate DSC curves that are displayed with respect to time and then afterward decide to change the abscissa to the reference temperature and thereby lose all previous evaluations.

5.2 Editing Diagrams

This includes cutting out, copying and inserting text, changing the sample size (correcting weighing errors or referencing the evaluations to the active or dry mass of the sample), the sample name (e.g. typing mistakes), the color, the type of line and the font. If necessary, lines or arrows can be inserted to clarify particular features (Figure 5.1).

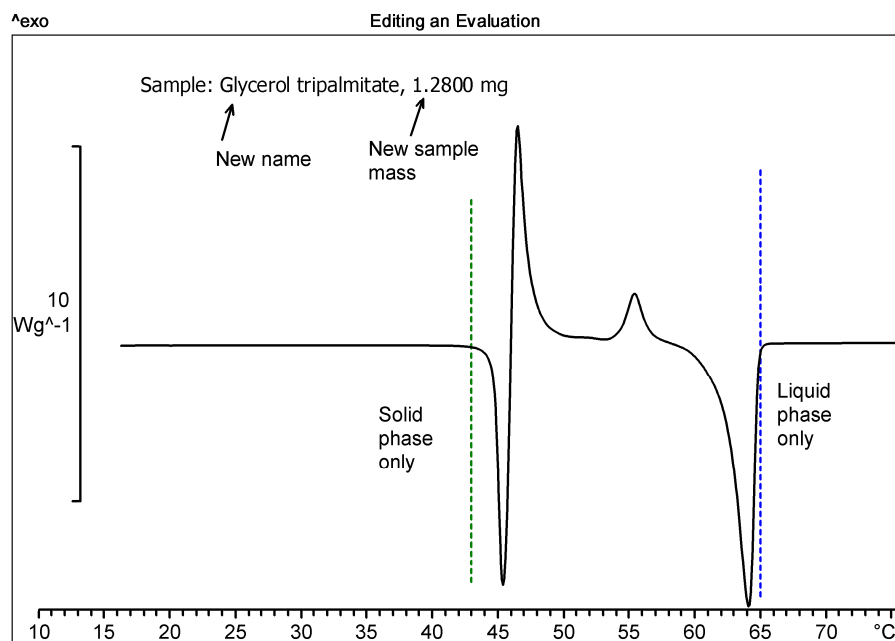


Figure 5.1. A typing error in the sample name has been corrected and sample mass after measurement (i.e. without the volatile content) has been entered for later calculations. Arrows and lines are drawn to illustrate different points. Important text is highlighted by using large characters. The DSC curve shows the polymorphic behavior of a fat recorded at 5 K/min.

5.3 Displaying Information from the Database

Examples: Name of the method, the sample, the customer, type of gas used, adjustment parameters, temperature program (shown graphically).

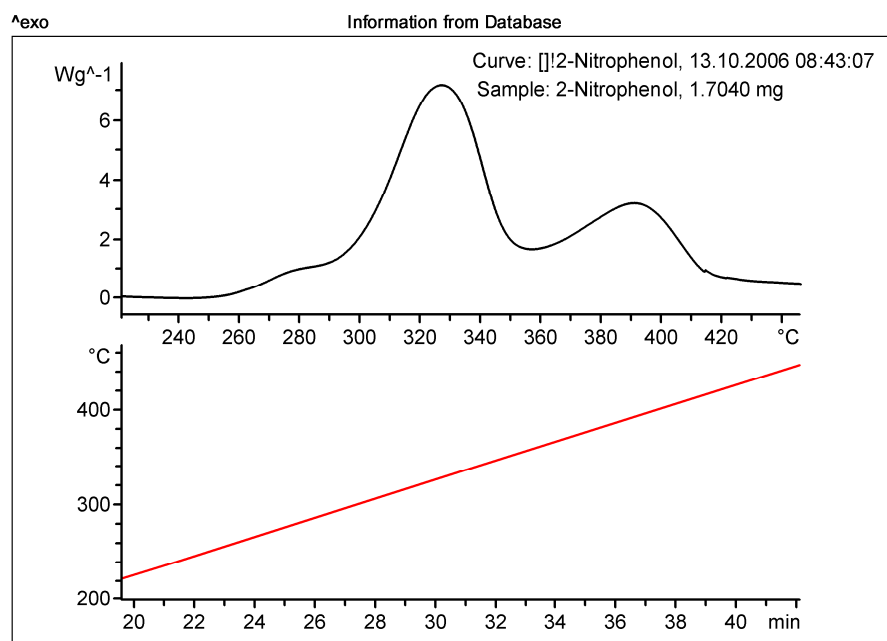


Figure 5.2. Different information from the database. Above: The curve name (possibly with symbols that indicate changes: for example [] means that it is a section of the curve and ! means sample mass normalization) with the date of the measurement and sample name with sample weight. Below: The temperature program. The curve shows the thermal decomposition of 2-nitrophenol in a DSC high-pressure crucible (heating rate 10 K/min).

5.4 Optimizing the Presentation of a Diagram

This includes the following:

- Automatic scaling (displays the entire curve in the diagram).
- Zooming (displays a desired section of the curve on an expanded scale).
- Displaying more than one coordinate system in the diagram, either as desired or exactly superimposed.
- Configuring the coordinate system:
linear or logarithmic axes, with or without gridlines, entry of numerical limits so that a diagram can be displayed exactly like a template.
- Displaying the y -axis relatively as in the upper curve of Figure 5.3 or absolutely.
- Defining units of time (s, min, h) and temperature ($^{\circ}\text{C}$, K).

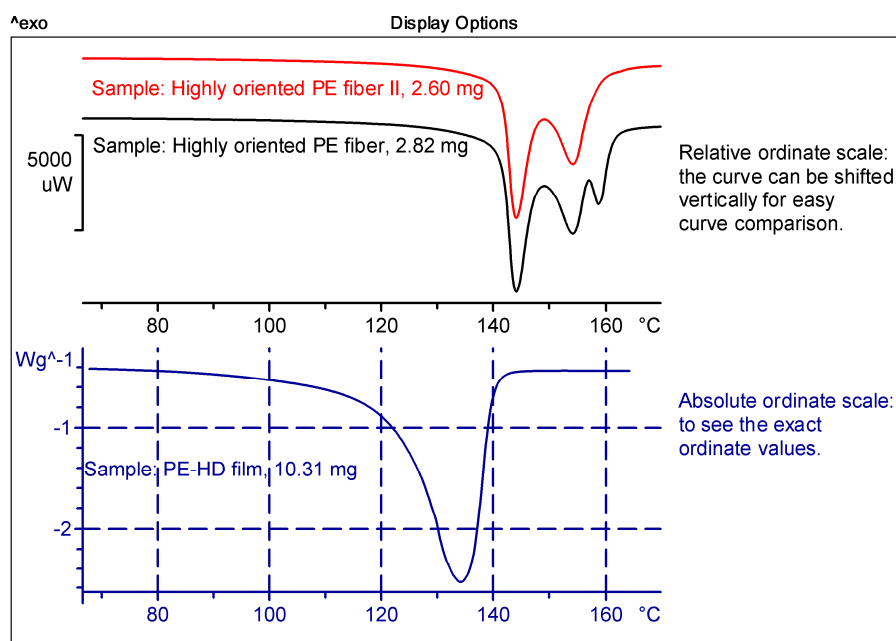


Figure 5.3. The two coordinate systems are not displayed in full width so that there is room to enter notes on the right. The two abscissas automatically correspond exactly. The upper coordinate system shows the DSC curves in heat flow units; the lower is normalized with respect to sample mass in W/g. The lower coordinate system has gridlines. The figure shows the DSC melting curves of different polyethylene samples.

5.5 Normalizing Measurement Curves to Sample Mass

When measurement curves are normalized, the ordinate unit changes from mW to W/g (Figure 5.3), from mg to % (TGA) and from μm to % (TMA). Normalization allows you to more easily compare curves recorded using different amounts of sample. The curves are not identical because larger samples produce broader effects.

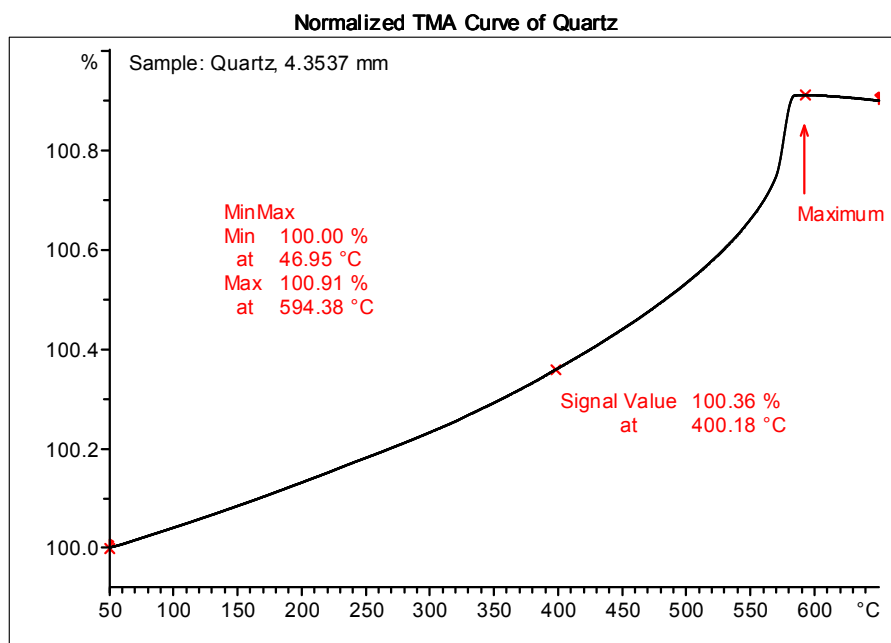


Figure 5.4. The expansion curve of a small piece of quartz with the display normalized with respect to length. The point of inflection at 577 °C is due to the transition of α -quartz to β -quartz.

5.6 Displaying Curves with Respect to Time, Reference Temperature or Sample Temperature

The reference temperature is normally used for the abscissa (default). In certain cases, the other possibilities are also valuable especially for comparing curves.

Note: DSC curves displayed with respect to sample temperature can sometimes be “non-monotonic”, i.e. they can show more than one ordinate value at a particular abscissa value. Such curves cannot be directly evaluated.

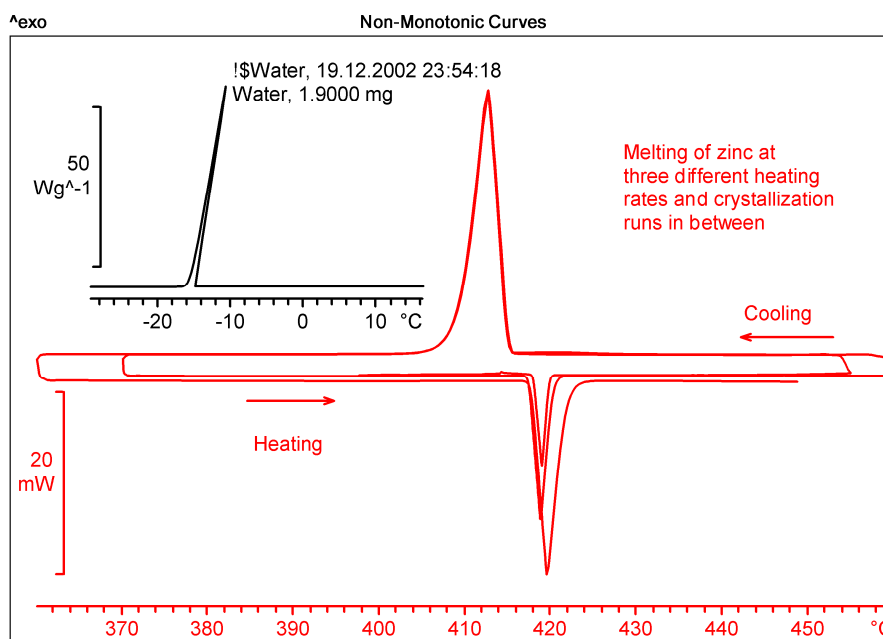


Figure 5.5. Two examples of DSC curves displayed with respect to sample temperature. Above left: The inserted diagram shows the crystallization of water on cooling at 10 K/min. Crystallization does not begin until about -15 °C due to marked supercooling. The enthalpy of crystallization released from the sudden crystallization results in a momentary increase in the sample temperature. This is why the peak has an unusual slope. The main diagrams show the repeated melting (heating rates 2, 5 and 10 K/min) and crystallization of zinc, which does not show any appreciable supercooling. In this case, the crystallization peak does not slope.

5.7 Sample Temperature as a Function of Time

If the thermal effects are strong, the sample temperature does not exactly follow the temperature program. This is evident from the display of sample temperature versus time (Figure 5.6).

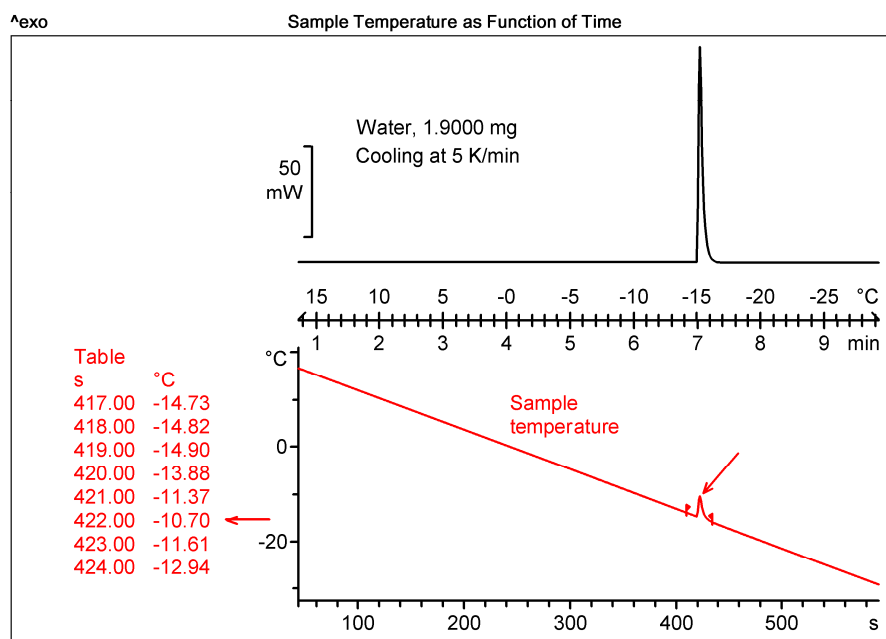


Figure 5.6. Above: The DSC cooling curve of water. Below: The sample temperature displayed using the same abscissa. The sample of 1.9 mg water enclosed in a hermetically sealed standard aluminum crucible was cooled at 5 K/min and crystallized at about -15 °C (due to supercooling). The enthalpy of crystallization causes the sample temperature to increase. The small amount of sample is not sufficient for it to reach the melting point of 0 °C. Nevertheless, the sample temperature increases to -10.7 °C (see Table on the left).

5.8 Curve Correction Using a Baseline Segment

An artifact in a measurement curve can be simply replaced by a segment of the baseline. The “Spline” baseline type is most often used.

Advanced users use this possibility to discuss hypotheses when reactions overlap.

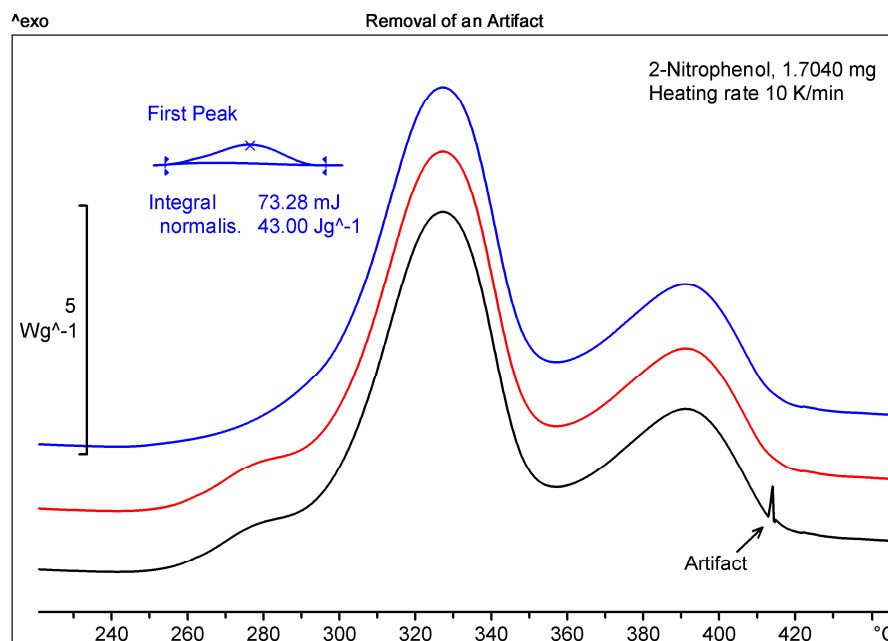


Figure 5.7. Applications showing the replacement of part of a DSC curve by a baseline: The black curve shows the decomposition of 2-nitrophenol in a high-pressure crucible. The measurement was disturbed (arrow at 413 °C) by closing a drawer in the laboratory bench. Instead of repeating the measurement, the artifact was cut out and replaced using the Spline baseline to give the red curve. The first small peak in the red curve was then removed and replaced by a Spline baseline to obtain the blue curve. The blue curve was then subtracted from the red curve in order to obtain the difference peak (First Peak, above left).

5.9 Mathematical Evaluations

These include the following:

- The calculation of the integral curve (Figure 5.8).
- The calculation of the first and second derivatives (each of these curves can be evaluated or a further derivative calculated (Figure 5.8)).
- Cutting out the curve outside the range of interest to omit unimportant details.
- Smoothing of curves using smoothing polynomial with a selectable width of window and order. This allows you to select the degree and type of smoothing (Figure 5.9).
- Adding a constant to the selected curve in order to shift the zero point of the curve.
- Multiplying and dividing a selected curve by a constant.
- Adding, subtracting, multiplying or dividing curves.
- Separating measurement curves of complicated temperature programs into the individual segments.
- Calculating the upper and lower envelope curves of periodic curves.
- Subtracting a hand-drawn line (straight line or polygonal line) from a measurement curve (Figure 5.10).
- Polynomial fit: for example when validating a method, the results can be entered as a function of the actual values in order to display them graphically and to fit them. The polynomial fit is also used to calculate a DSC curve from the DTA curve.
- Fast Fourier transformation for periodic curves such as occur in ADSC measurements.

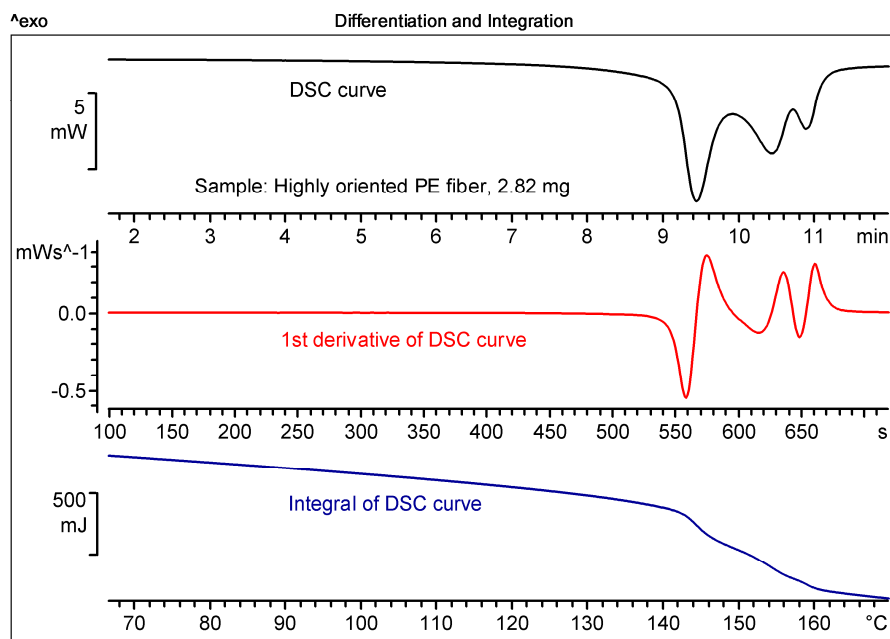


Figure 5.8. Top: The DSC curve of a Dyneema fiber (top) followed by the first derivative of the DSC curve (middle) and the integral curve (bottom). The first derivative curve often shows small changes in the measurement signal more clearly than the original curve. The integral corresponds to the amount of heat transported to the sample assuming that the DSC curve on which it is based has been blank corrected.

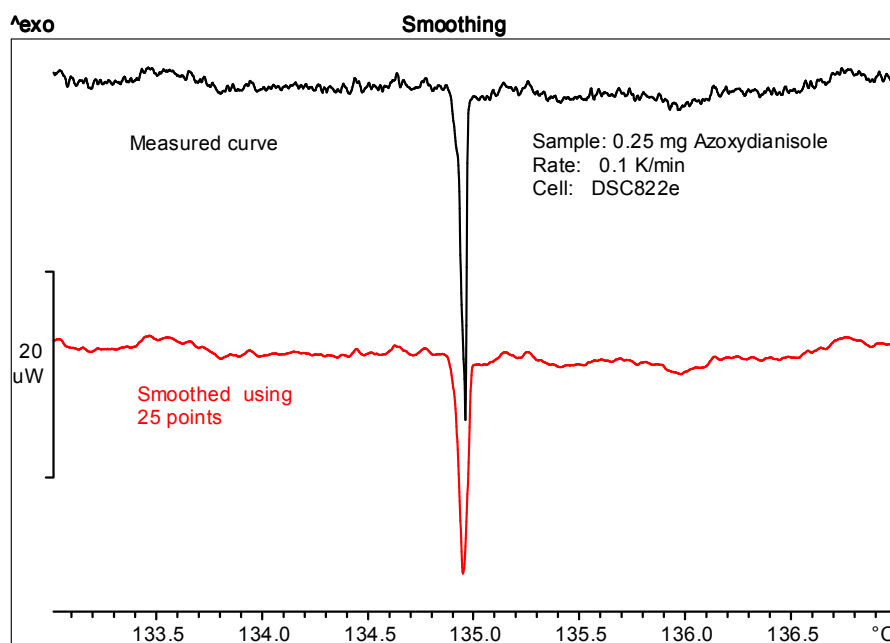


Figure 5.9. Curve smoothing: The figure shows the nematic-isotropic transition of a small sample of a liquid crystal measured at a very low heating rate. Under these conditions, the transition peak is very small and the highly expanded DSC curve is noisy (above). If first order smoothing is applied to the curve with a window of 25 points, the high-frequency noise disappears. The peak shape is, however, noticeably deformed.

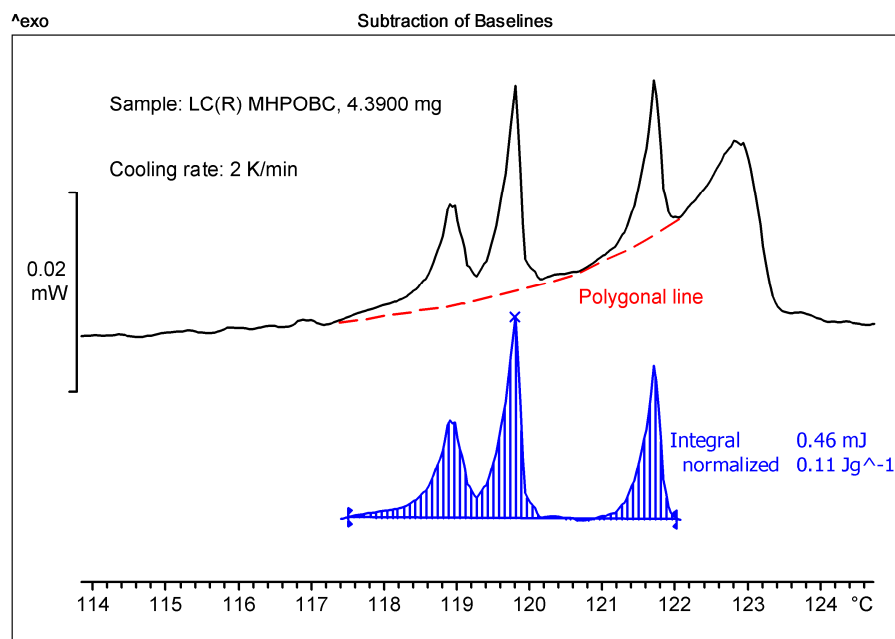


Figure 5.10. Polygon subtraction: The figure shows the cooling curve of a liquid crystal. Assuming that the three sharp DSC peaks lie on the shoulder of the last peak, the shoulder can be drawn as a polygonal line (red dashed). The polygon is now subtracted from the DSC curve and the difference curve (blue) is obtained. This can then be integrated using a straight baseline.

5.10 Curve Comparison

In thermal analysis one often wants to display several curves in one diagram.

5.10.1 In One Single Coordinate System

Curves with identical ordinate and abscissa units are automatically displayed in a coordinate system (Figure 5.11). The curves can be moved vertically with respect to one another so that they do not cross (Figure 5.12).

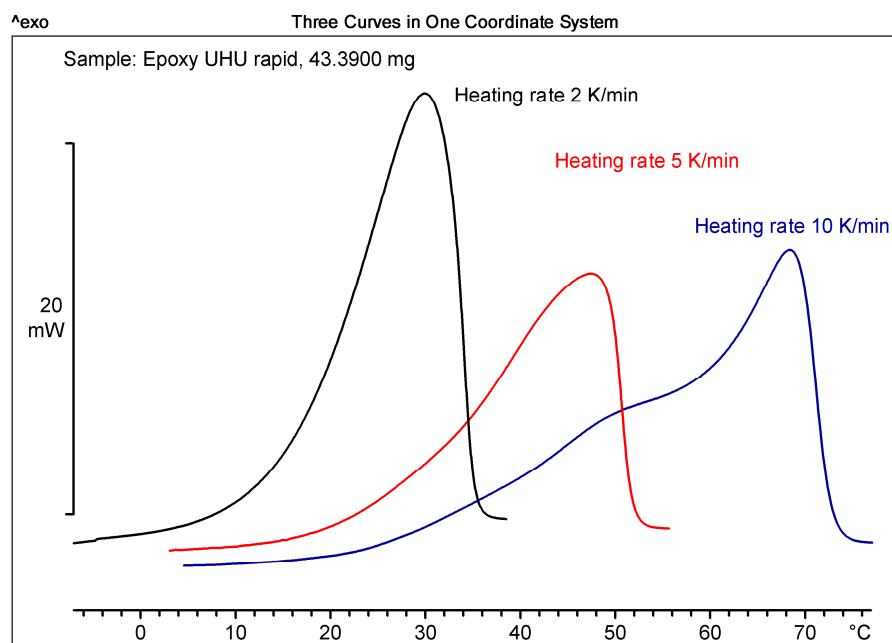


Figure 5.11. If three dynamic DSC curves are opened, they appear in a single coordinate system. The example shows the epoxy curing reaction of UHU Rapid.

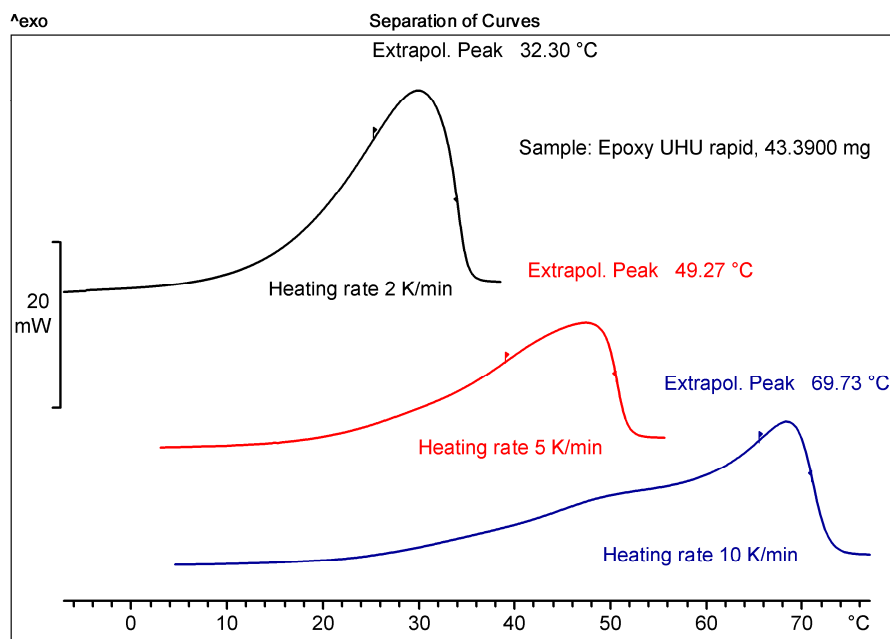


Figure 5.12. The three curves from Figure 5.11 can be separated vertically using the mouse. The mW-axis can be moved to any free position in the diagram. Furthermore, the extrapolated peak temperatures are evaluated to show how the peak temperature of a reaction peak depends on the heating rate.

It is also possible to zoom and display particular details of a survey curve (Figure 5.13).

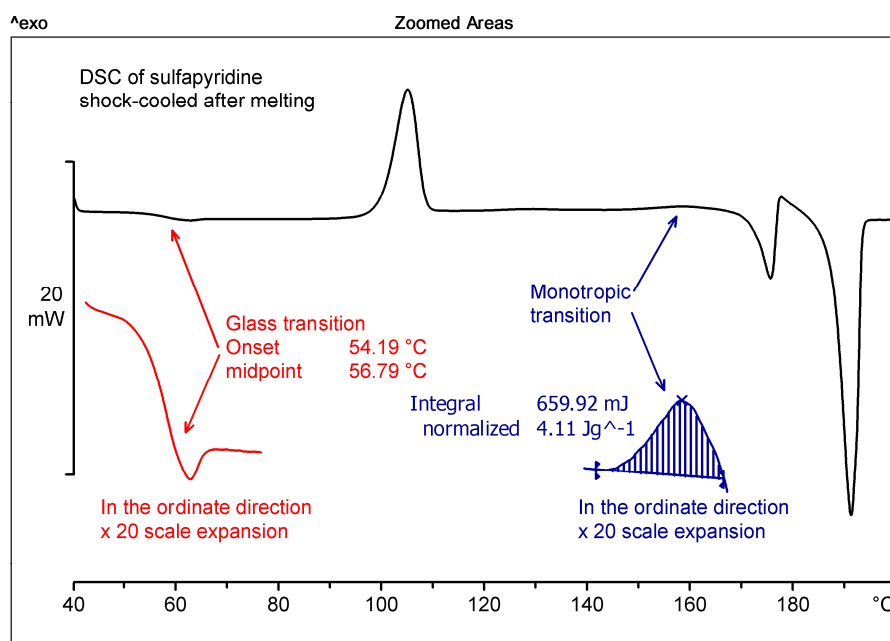


Figure 5.13. The upper DSC curve is a survey run. Below: The sections of interest are zoomed 20 times in the ordinate direction. In this example, the sections are the glass transition and the monotropic solid-solid transition, both of which can hardly be seen in the survey curve. Prior to measurement, the sulfapyridine was melted and then shock cooled so that it solidified to form a glass. The heating rate was 5 K/min.

5.10.2 Multi-Coordinate Systems

In multi-coordinate systems several coordinate systems of course appear. This occurs

- if curves from different measurement techniques are compared, e.g. TGA/DTA (Figure 5.14) or
- if a curve and its derivative are displayed (Figure 5.15).

If you want to view both the complete survey curve and two-dimensionally zoomed details in the same diagram, you first open it twice. After you have cut out the desired region, you can change the ordinate or abscissa units of the zoomed curve (ordinate normalized or the abscissa displayed against time, see Figure 5.16). The two coordinate systems can also be displayed one on top of the other (Figure 5.15) and next to one another (Figure 5.17).

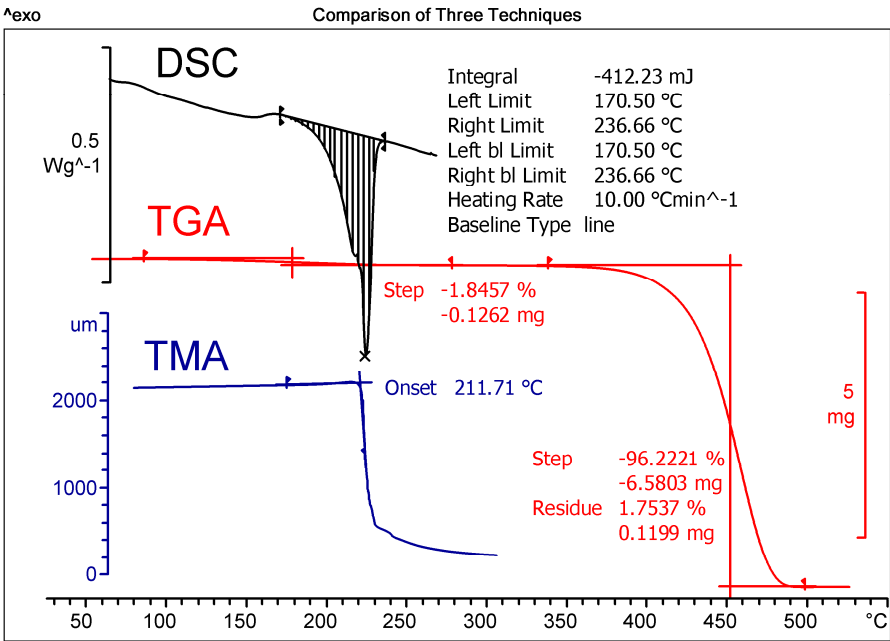


Figure 5.14. The figure shows three different measurement curves displayed with respect to the reference temperature. The main features of each curve have already been selected. The ordinate scales for this type of comparison are not so important and are therefore not shown.

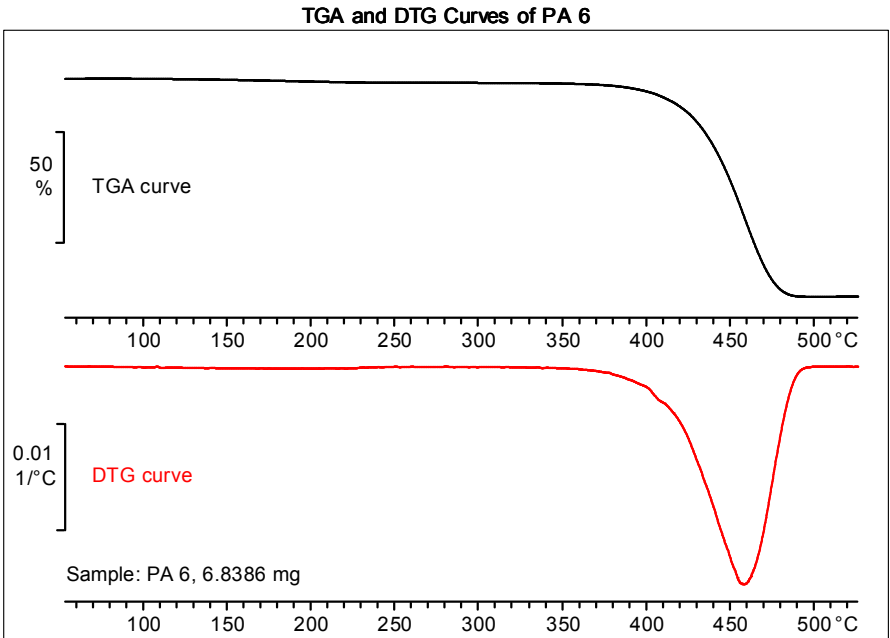


Figure 5.15. This is an elegant way to automatically split the diagram. You can do this with any number of coordinate systems.

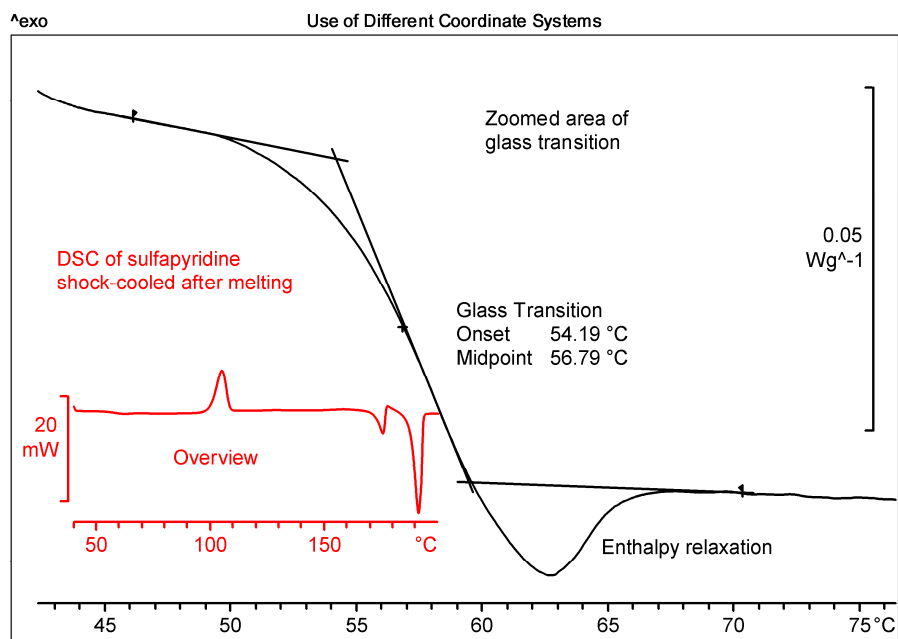


Figure 5.16. In this example, an interesting part of a curve (here the glass transition) is zoomed and evaluated. The complete curve is displayed in the lower left corner. A TGA curve can of course be displayed in the same way. In principle, there is no limit to the number of coordinate systems in a diagram. However, with four or more coordinate systems the diagram becomes overcrowded. Figure 5.8 shows an example with three systems.

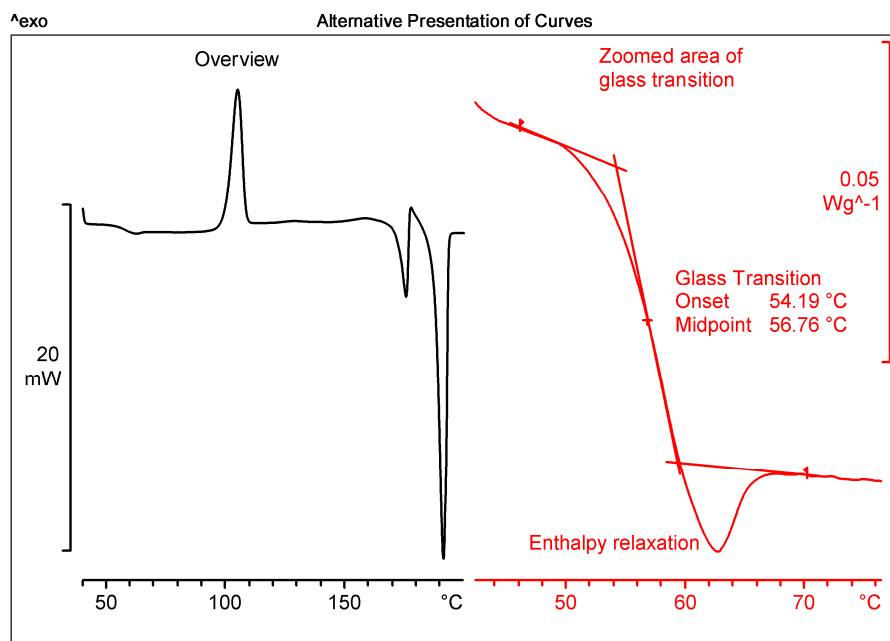


Figure 5.17. The two curves from Figure 5.16 can also be displayed next to each other.

5.11 Numerical Evaluations

Note: Area determination (integration) is used mostly for DSC and is therefore covered in Section 7.6. The step determination is also described in the same section.

5.11.1 Onset

One of the most frequent evaluations made in thermal analysis is to determine the extrapolated starting temperature or “onset”. This is the point of intersection of the baseline before a thermal effect and a tangent (often the inflectional tangent at the steepest part of the curve). More information about the onset can be found in Section 7.6.

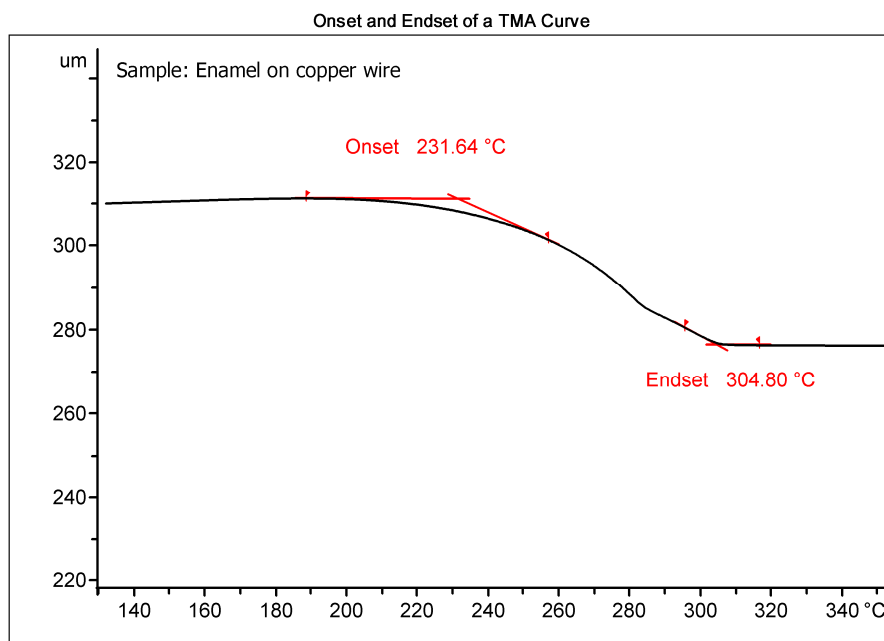


Figure 5.18. An insulated copper wire is heated in the TMA at 10 K/min in an air atmosphere. In this example, the decomposition region of the insulation layer is of interest. You can use the onset and endset evaluations for this.

5.11.2 Endset

As the word suggests, it means the extrapolated end of a reaction of the sample, that is, the point of intersection of the tangent with the baseline after the effect. The endset is the mirror image of the onset.

5.11.3 Onset and Endset

Step-like effects can be elegantly evaluated as shown in Figure 5.19.

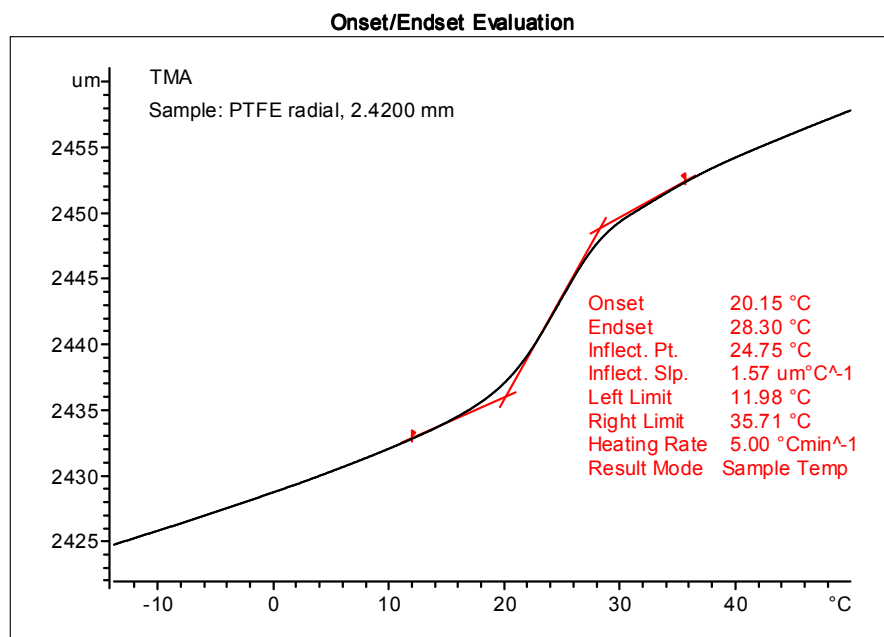


Figure 5.19. The TMA measurement shows the polymorphic transition of Teflon in the radial direction at room temperature. The standard default results are the onset and the endset. The temperature at the point of inflection, the slope at the point of inflection, the evaluation limits, the heating rate and the result mode are available as options.

5.11.4 Logarithmic Onset, Endset, Peak, Logarithmic Step Horizontal/Tangential

These evaluations all have in common that the tangents or baselines are drawn to a measurement curve and points of intersection are evaluated. In a logarithmic display, which for example is often used for the elastic modulus, a straight line of constant slope would be curved. These special evaluations yield straight line tangents in logarithmic displays.

The results of the linear and logarithmic presentations are of course not identical. For example, the onset of the glass transition of an epoxy resin in a linear presentation is 104.5 °C, and in a logarithmic presentation 110.7 °C.

5.11.5 Peak

The tangents are drawn to the measurement curve at the evaluation limits. Their point of intersection is the extrapolated peak. Optionally available are

- the left and right evaluation limits,
- the heating rate,
- the ordinate and abscissa value at the extreme point (peak value and peak). These results are relatively insensitive to evaluation limits that are not quite right.
- the normalized ordinate value at the extreme point, and
- the result mode (sample temperature, segment time or abscissa unit).

“Automatic limits” mode: the evaluation limits define the range for the automatic search routine to locate the steepest tangent (Figure 5.20, left).

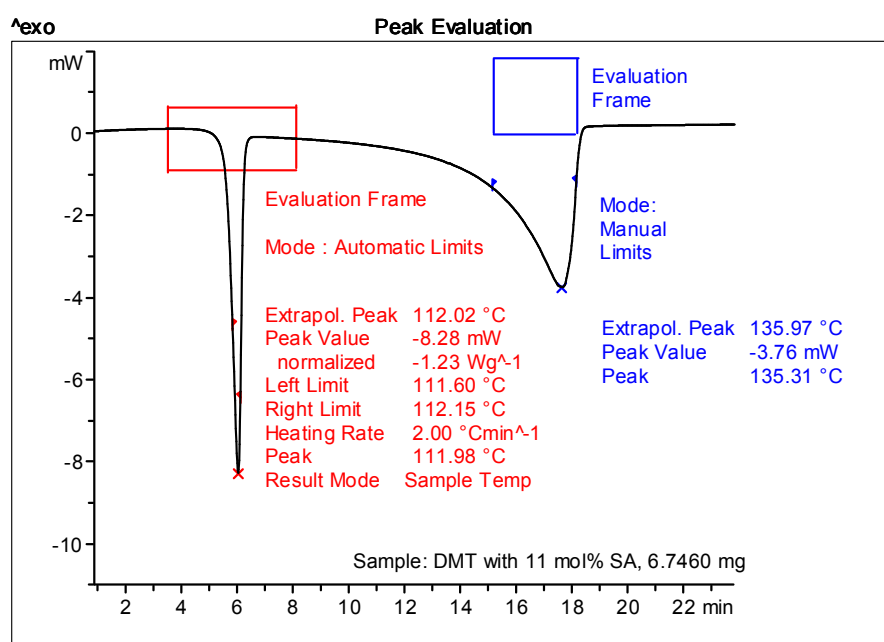


Figure 5.20. Left: The Automatic Limits mode determines the steepest tangents in the working range of the frame. Right: In the Manual Limits mode (right), tangents are drawn (not shown here) exactly at the frame limits, which of course influences the value of the extrapolated peak. Although the diagram is displayed as a function of time, sample temperatures appear as results because the Result Mode has been appropriately selected. The diagram shows the DSC melting peak of dimethyl terephthalate (DMT) contaminated with 11 mol% salicylic acid (SA).

5.11.6 Tables

In certain cases, one wants to display values from a curve in the form of a table. Some important tables are

- enthalpy-temperature functions,
- c_p temperature functions, and
- conversion as a function of time or temperature.

Temperature functions are usually shown with the same temperature increments. With conversion curves, a table with equidistant conversion increments is preferred. Finally, according to ASTM D3850, decomposition temperatures at 10, 20, 30, 50, and 75% conversion are calculated.

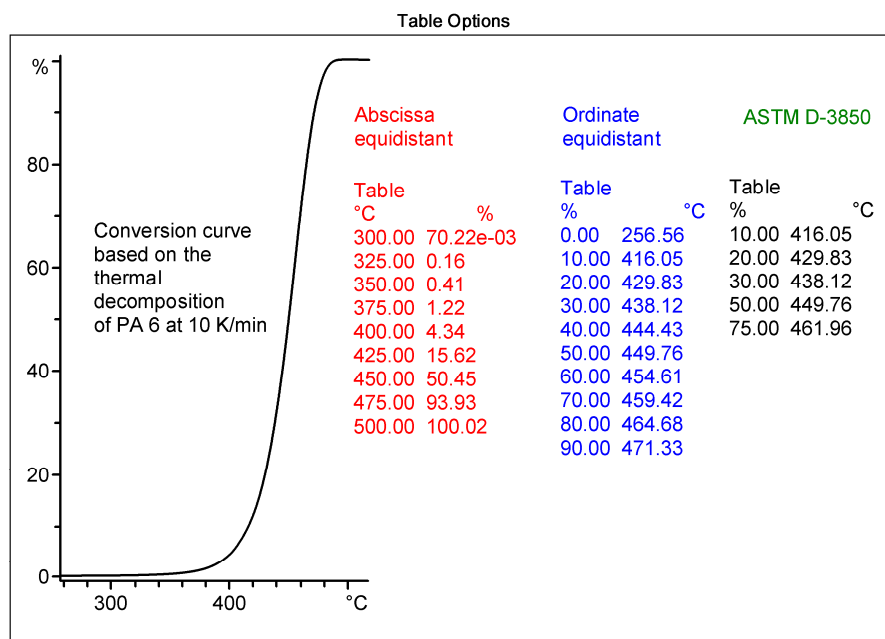


Figure 5.21. Left: The conversion curve calculated from a TGA curve of the thermal decomposition of PA 6. Right: The conversion data is displayed numerically in three different tables.

5.11.7 Minimum-Maximum

MinMax displays the minimum and maximum ordinate values of an entire curve or that within the selected working range (Figure 5.4). The abscissa values are also displayed. Optional results: evaluation limits.

5.11.8 Signal Value

Signal Value displays the ordinate value of a curve at any desired point on the curve (Figure 5.4). Optional result: the abscissa value corresponding to the ordinate value.

6 General Measurement Methodology

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6.1 Usual Coordinate Systems of Diagrams

6.1.1 Abscissa:

Thermoanalytical measurement data can be plotted against time, the temperature of the reference point or the sample temperature. Each type of abscissa presentation has its advantages and disadvantages:

- **Time:** suitable for mixed (dynamic and isothermal segments) and simple orientation (especially with inserted temperature program). The newest values are always to the right of the older data. It only makes sense to overlay curves recorded with the same temperature program. In this respect, comparison of the first and second measurement runs is often very informative.
- **T_r :** Temperature is the most important thermoanalytical physical quantity; curves measured using different temperature programs are always correctly overlaid. With cooling segments, the (time) display is from right to left. Isothermal segments practically disappear (the measured values are plotted vertically over the temperature). Measurement curves with just one dynamic segment look the same as a display proportional to time (T_r is proportional to time).
- **T_s :** One might think that the sample temperature is the best type of display because the sample temperature is usually of interest. However, the display of measurement curves during a first order transition is distorted (T_s is not proportional to time).

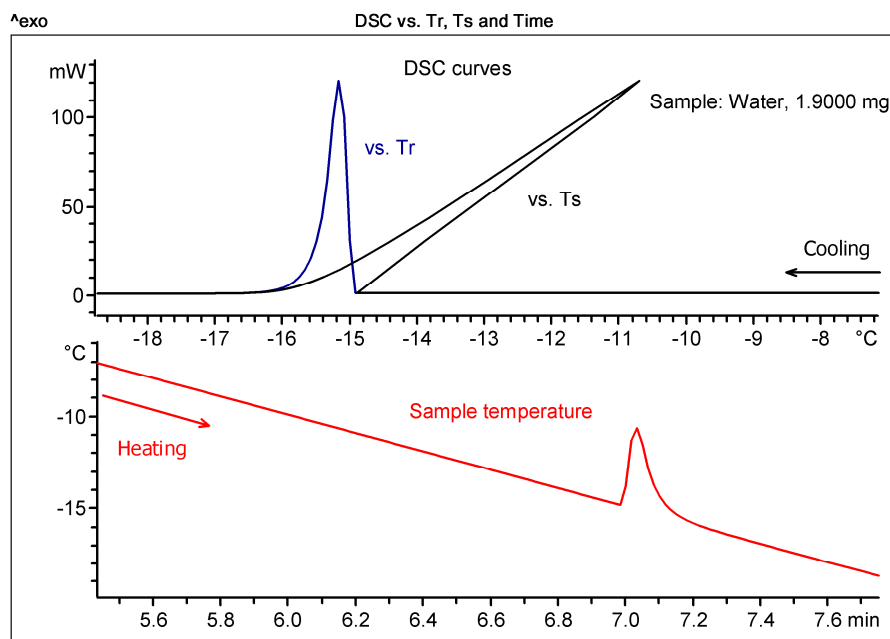


Figure 6.1. Above: Two different presentations of the same crystallization curve of water measured at a cooling rate of 5 K/min. The curve (blue) plotted against the reference temperature T_r , which is proportional to time, shows the usual crystallization peak. However, when the curve is plotted against the sample temperature T_s , it is "non-monotonic", for example at -12 °C there are three ordinate values (black). Below: To explain this effect, the sample temperature, T_s , is displayed as a function of time (red curve). At -15 °C , the water begins to crystallize. The crystallization enthalpy of the 1.9 mg sample is not sufficient to heat the sample and crucible to 0 °C , but nonetheless -10.7 °C is reached.

6.1.2 Ordinate:

Possibilities for normalized presentation:

- **DSC**

Normalized to sample mass: Ordinate in W/g for curve comparison.

Normalized to rate: Ordinate in J/K (= heat capacity) as well as sample mass and rate: Ordinate in $\text{Jg}^{-1}\text{K}^{-1}$ (= specific heat capacity), for the correct comparison of curves measured at different rates with respect to area (Figure 6.2).

- **TGA**

Normalized to sample mass: Ordinate in %, DTG in % per abscissa unit, that is, %/K for the correct comparison of curves measured at heating rates $\neq 0$, or %/min for isothermal measurements.

- **TMA**

Normalized to the original length (thickness), ordinate in % for the comparison of curves.

1st derivative of the TMA curve, ordinate in % (or ppm) per abscissa unit, that is, %/K or ppm/K (the expansion coefficient) for the correct comparison of curves measured at heating rates $\neq 0$, or %/min for isothermal measurements.

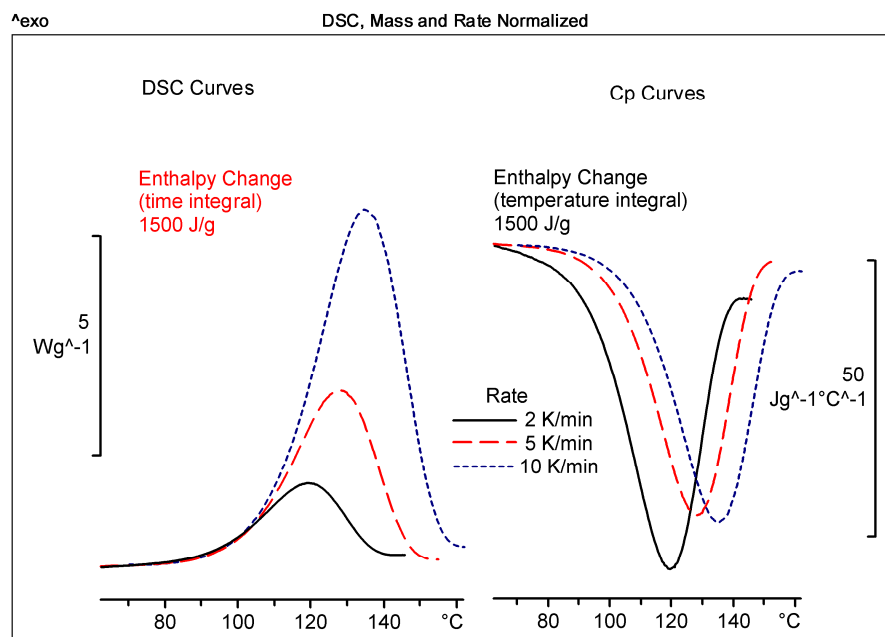


Figure 6.2. Comparison of measurement curves of a chemical reaction measured at different heating rates.

The figure shows **DSC curves** measured at 2, 5 and 10 K/min. The peak areas appear to be quite different because visually you integrate the heat flow with respect to temperature. The **STAR^e** software of course integrates the curve correctly with respect to time using “TA Integration”:

$$\Delta H = \int_{t_1}^{t_2} \Phi \, dt \quad (6.1)$$

Division by the heating rate yields the **specific heat capacity**. In this presentation, the areas are identical. Integration with respect to the abscissa is also possible using the **STAR^e** software “Mathematical Integration” program.

$$\Delta H = \int_{T_1}^{T_2} c_p \, dT \quad (6.2)$$

6.2 The Atmosphere in the Measuring Cell

In practically all thermoanalytical measurements, it is necessary to have a defined atmosphere in the sample chamber. In most cases, this is achieved by purging the measuring cell with a **purge gas** at a particular flow rate. The atmosphere can be either **inert**, **reactive** or **corrosive**.

- Inert: no reaction with the sample or the crucible.
- Reactive: chemical reaction with the sample is expected, e.g. air, O₂, NH₃ (flammable!).
- Corrosive: chemical reaction with the sample is expected, risk of reactions with the crucible and parts of the measuring cell, e.g. HCl, Cl₂, SO₂. The measuring cell may suffer damage.

Most measurements are performed at constant pressure (atmospheric pressure). A gas tight measuring cell can be operated at reduced pressure (partial vacuum) or at over pressures. Such applications in the range to 10 MPa are possible with the high-pressure DSC.

The measurement curve is influenced by the type of gas, the pressure and the flow rate of the gas in the measuring cell.

6.2.1 Flow Rate and Purity of the Atmosphere

The flow rate must of course be measured. This can be done using a flowmeter based on the rotameter principle or an electronic “mass flow” meter. This makes sure that the purge gas is flowing and prevents an excessively large gas flow from blowing the sample out of the crucible or from cooling the measuring cell. Typical flow rates are 20 to 100 mL/min. Flow rates in this range do not affect measurement as long as the flow remains constant. Thermogravimetric measurements in particular are disturbed by flow rates that fluctuate. For example, a pressure-reducing valve whose pressure slowly oscillates between two extreme values generates sinusoidal artifacts on the TGA curve. The pressure reducing valves used must therefore show no tendency to oscillate.

6.2.2 How are Low Oxygen Conditions Achieved?

The rate at which residual air is purged from the measuring cell depends on the flowrate. Exponential purging can be assumed if the cell is gas tight and if there is no dead volume (parts of the system separated from the sample chamber but not hermetically sealed, for example tubing or bore holes that are not purged):

$$c = c_0 \exp -t \frac{V}{\Delta V/\Delta t} \quad (6.3)$$

where c is the concentration; c_i the initial concentration and t the purge time,

V the volume being purged; $\Delta V/\Delta t$ the purge rate.

Example: An air-filled furnace chamber of 50 mL volume is purged with nitrogen at 50 mL/min. How quickly does the oxygen concentration decrease ($c_0 = 20\%$):

t	0	1	2	5	10 min
c	20%	7.4%	2.7%	0.13%	0.0009% (9 ppm)

This means that in the ideal case the oxygen concentration decreases to just a few ppm within 10 min. The situation is however adversely affected by

- oxygen absorbed on parts of the measuring cell,
- the existing oxygen concentration of the purge gas. Nitrogen of 99.999% purity can still contain up to 10 ppm oxygen. This means that the 9 ppm obtained in the calculation will never be achieved.
- dead volumes from which oxygen diffuses,
- small leaks, and
- long lengths of plastic tubing for gas supply (oxygen diffuses through plastic walls).

Test for oxygen purity:

- TGA: After purging sufficiently long, maintain activated carbon isothermally at 700 °C. A maximum combustion rate of 10 µg/min due to residual oxygen is a reliable limiting value.
- DSC: Heat several milligrams of unstabilized polyethylene (packaging film) in an open crucible at 10 K/min from 100 to 300 °C. Any oxygen present will give rise to an exothermic peak above 200 °C.

A very desirable side-effect of the purge gas is that it protects the sensor and the measuring cell against corrosive decomposition products from the sample. Sensitive sensors in particular, such as a microbalance or the TMA measuring cell, require a separate supply of **protective gas**. This should also flow **between and after the measurements**.

Decomposition reactions with volatile reaction products proceed differently depending on whether the volatile component is flushed away from the sample surface or remains in contact with the sample. In the latter case, the sample is almost in equilibrium with its decomposition products and a **self-generated atmosphere** is produced. Such conditions are most easily obtained using a hermetically sealed crucible with a pinhole (e.g. 50 µm) in the lid to restrict diffusion.

6.2.3 Commonly Used Purge Gases

The atmospheres most frequently used in measuring cells are

Air, occasionally also static air (stationary atmosphere). Air is often used for calibration. Since the main component of air is nitrogen, its physical properties are very much the same as those of nitrogen. Air can be inert or reactive (oxidizing) depending on the type of sample. It is inert toward most inorganic samples in the temperature range up to about 300 °C, for example for the melting of indium or dehydration of calcium sulfate. In contrast, air is reactive toward plastic materials such as polyethylene. Furthermore, metals such as tin or zinc oxidize on melting in air. This causes the DSC melting peak to change noticeably in repeated measurements.

In many cases, ambient air can be used that is supplied using an aquarium pump via a flowmeter. It then obviously contains a certain amount of moisture. In contrast, “synthetic air” from a pressure bottle contains practically no water and no carbon dioxide.

Nitrogen is used for measurements under oxygen-free (actually low-oxygen) conditions. Purity requirements: maximum 10 ppm O₂. Nitrogen is the most frequently used “inert gas”. At high temperatures, nitrogen is however by no means inert toward many metals (nitride formation).

Oxygen is used for the determination of the oxidation and combustion behavior. The purity requirements for oxygen are usually not high, the cheapest quality is adequate for OIT measurements.

Argon is used as an inert purge gas for the TGA-MS combination if carbon monoxide is of interest. Nitrogen is unsuitable in this case because it has the same molar mass (28 g/mol).

Helium has a much better thermal conductivity than the above gases. This makes it interesting as a heat transfer medium for TMA measurements and also for DSC measurements to reduce the signal time constant. Helium is also an ideal gas with no tendency to condense even below -180 °C. It is therefore often used for low temperature measurements. Its high thermal conductivity makes it difficult to reach temperatures above 1300 °C.

Carbon dioxide can be used for carboxylation reactions.

Carbon monoxide is not only flammable (see hydrogen) but also poisonous. The purge gas (and decomposition products of samples) must be trapped in cold traps or by specific filters. For risk of explosion, see hydrogen.

Inertized hydrogen is hydrogen that has been diluted to such an extent (for example with argon) that it cannot form explosive mixtures with air. Argon can be obtained ready mixed with 4% hydrogen by suppliers of compressed gases. This minimizes the possible risk of an explosion. We strongly recommend that you **do not** produce mixtures of argon and hydrogen yourself by mixing the two gases on-line at corresponding flow rates. Applications: reactions in **reducing** atmospheres, for example to suppress the formation of oxide layers in dilatometric measurements, and for the thermogravimetric reduction of metal oxides.

Pure hydrogen is very dangerous. When mixed with air it forms explosive mixtures over a wide range of concentrations.

Only specialists with experience in the handling of flammable gases should work with hydrogen. This also applies to other **flammable or poisonous** gases such as CH₄, CO, NH₃, H₂S, SO₂). Additional requirements are

- a gastight measuring cell, and
- an automatic hydrogen detector close to the measuring cell, which sounds an alarm when a concentration of 0.1% H₂ is reached in the laboratory air.

The main dangers include for example:

1. Leaks in the supply tubing (from the valve of the gas bottle to the flowmeter).
2. Leaks at the connection to the measuring cell (flowmeter to connection nipple).
3. Leaks within the measuring cell (leaky valve, nipple, weld seams, connecting holes, cracks, dirty O-rings, measuring cell not completely closed).
4. The formation of explosive mixtures in the sample chamber. Explosive mixtures can be prevented by evacuating to about 100 Pa, flooding with inert gas, re-evacuating to 100 Pa before and after filling with hydrogen. Instruments with a motor-driven furnace opening should be protected against unintentional opening above 100 °C, for example if a fault in the electronics occurs (risk of explosion following the ingress of oxygen!).
5. Purge gas outlet, vacuum pump outlet (how to dispose of the hydrogen?).

Since hydrogen is a very small molecule, it diffuses through plastic tubing and plastic parts in the gas switching device.

If all these safety measures are adhered to, it is possible to work with hydrogen. We have demonstrated this in an application study of the hydrogenation of sunflower oil in the high-pressure DSC [1].

METTLER TOLEDO however denies all responsibility if flammable, explosive, corrosive or poisonous purge gases are used.

6.2.4 Reduced Pressure and Overpressure

In some cases, better separation of a physical transition from a chemical reaction can be achieved under **reduced pressure** (i.e. partial vacuum): For example, volatile plasticizers in plastics vaporize before the thermal decomposition of the main components (at normal pressure both effects may possibly occur in the same temperature range, see Chapter 9, Thermogravimetric Analysis).

High-pressure DSC: If an oxygen-free atmosphere is required, the information given above under low-oxygen conditions applies.

In principle, the high-pressure DSC can also be operated at reduced pressure. At the same time, the heat transfer from the DSC sensor to the sample crucible is strongly pressure dependent below 1 kPa. This makes it difficult to interpret the DSC curves. Besides this, the diameter of the tubing is not optimal for vacuum operation; it can take several minutes to reach the desired end pressure. The pressure meter should not be in the suction line to the vacuum pump but connected to a different connection in order to obtain realistic values.

6.3 Crucibles in Thermal Analysis

Crucibles serve as containers for the samples during thermoanalytical measurements [2]. The type of crucible used for the measurement influences the results. A few considerations before the measurement often help to save time later on when evaluating the curve.

In nearly all DSC and TGA/SDTA experiments, the sample is measured in a crucible.

- The crucible should be inert, that is, the crucible material should not react with the sample in the temperature range of interest. Exceptions: The “copper stability” of polyolefines or lubricant greases and oils is determined in copper crucibles, and certain reactions are measured in catalytically active platinum crucibles. The crucible material should not undergo any physical transitions in the temperature range used and the melting point must be sufficiently high.
- The crucible protects the measuring cell against direct contact of the sample, which prevents contamination of the DSC measurement sensor or TGA/SDTA crucible holder.
- The type of crucible (crucible shape, heat capacity) to some extent determines the specifications of the measurement system, such as for example the calorimetric sensitivity and the signal time constant. A short time constant yields sharp DSC peaks and hence good resolution and separation of close-lying effects.
- Crucibles made of materials of high thermal conductivity and with a flat base enable optimum heat transfer between the sample holder and the sample with minimum temperature gradients.

Solids that remain solid over the entire temperature range can be measured without using a crucible, for example, the transition temperatures of 4- to 5-mm disks of metals or ceramic materials.

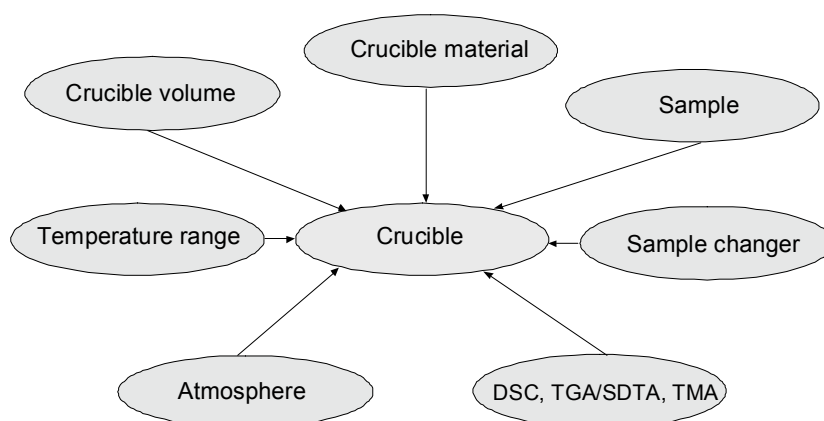


Figure 6.3. Factors influencing the choice of crucible.

6.3.1 Contact between the Sample and the Atmosphere of the Measuring Cell

In general, we distinguish between three different conditions:

- Hermetically sealed, pressure-resistant crucibles (if necessary with auxiliary external pressure in a high-pressure DSC).
- A “self-generated atmosphere” where volatile products from the sample remain in the crucible. The sample is in equilibrium with its volatile products without a large increase in pressure occurring. The “diffusion barrier” is achieved by piercing a very small hole in the crucible lid (crucible lids with a 50- μm hole are available). An even more effective diffusion barrier is obtained by scattering about 1 mg aluminum oxide powder on the rim of the standard aluminum crucible before sealing (cold welding). This creates fine channels through which gas can diffuse.

In a self-generated atmosphere, decomposition reactions are shifted to higher temperatures, resulting in better separation. The boiling point can also be easily determined in this way because premature evaporation is suppressed.

- Free access to the furnace atmosphere in an open crucible: For practical reasons, a lid with a hole is often used, for example to protect the measuring cell against samples that creep out or sputter out of the crucible. For this purpose, the lid of the aluminum crucible is pierced several times with a needle on a clean rubber surface before sealing (hole diameter about 1 mm).

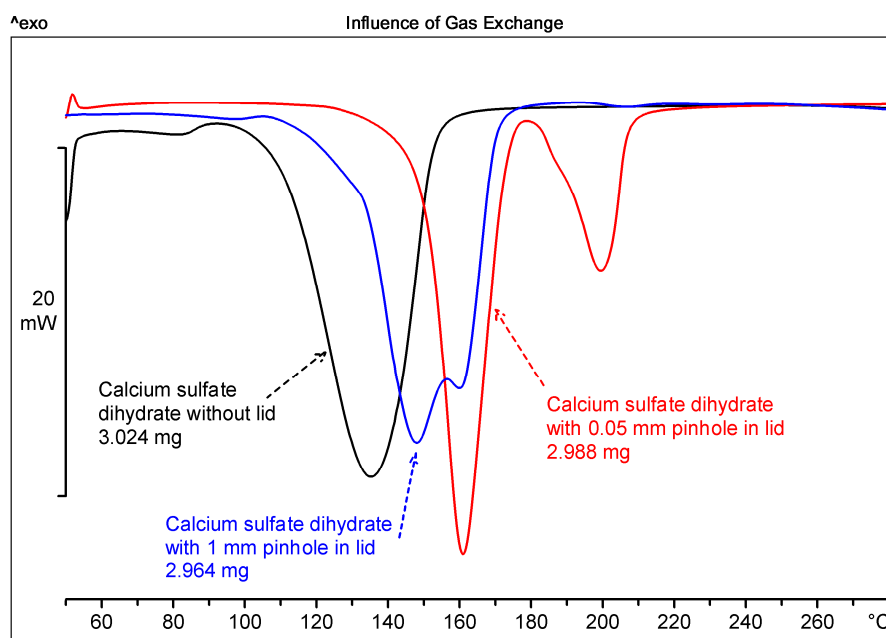
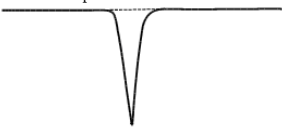
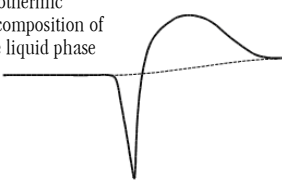
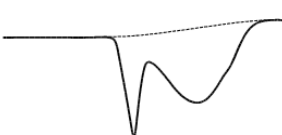
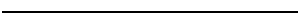
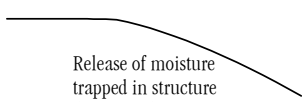
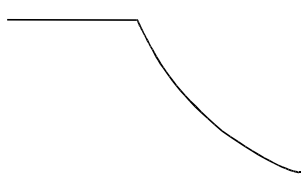
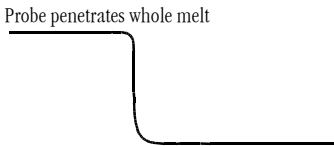
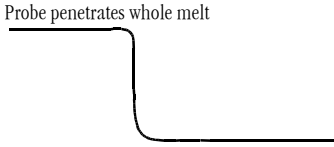
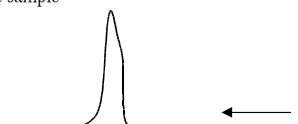
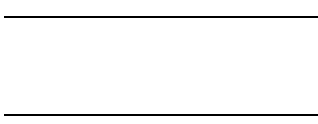
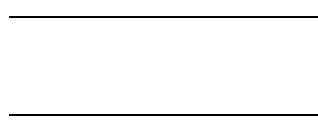
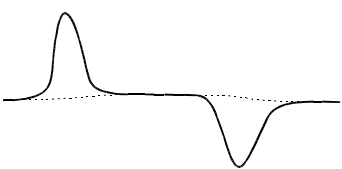
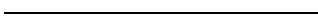
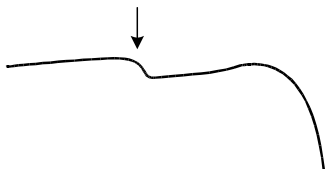
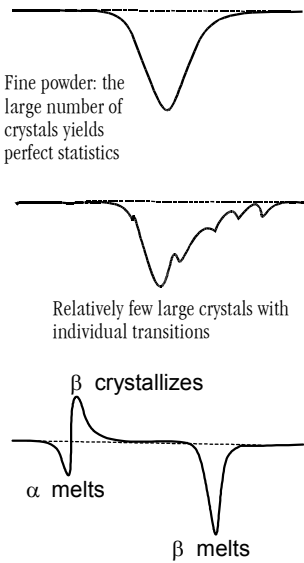
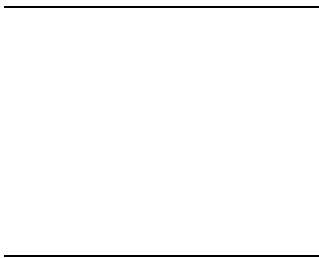
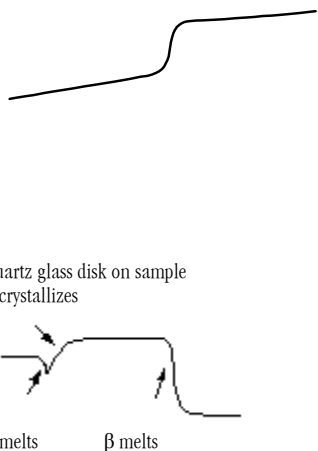
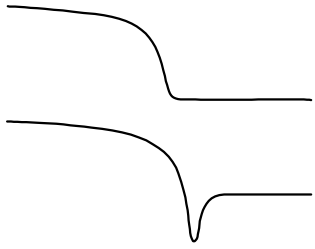
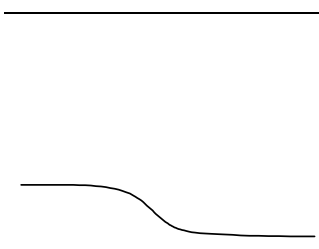
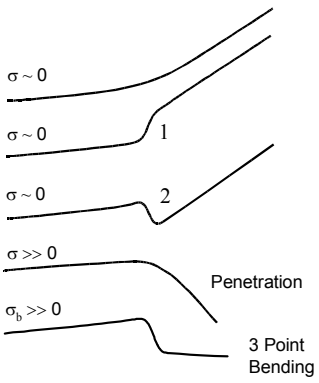
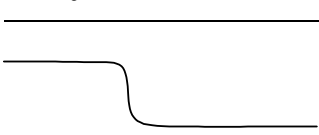


Figure 6.4. DSC curves showing the elimination of water of crystallization from calcium sulfate dihydrate (gypsum) measured in an open crucible, in a crucible with 1-mm hole in the lid, and in a self-generated atmosphere. In an open crucible, the water vapor formed escapes from the measuring cell. In the latter two measurements, the water vapor remains more or less inside the crucible. This causes the decomposition reaction to shift to higher temperatures and the successive losses of $1\frac{1}{2}$ H_2O and $\frac{1}{2}$ H_2O are separated. In a self-generated atmosphere, it is for example possible to determine small amounts of the dihydrate in the hemihydrate by TGA [3].

6.4 Overview of Thermal Effects

If the measurement signal of a thermoanalytical curve changes more or less abruptly, it is referred to as a thermal effect. Thermal effects are caused by physical transitions or chemical reactions occurring in the sample. We distinguish between peak-like and step-like effects. The following table summarizes the physical effects. For chemical reactions, see Interpretation DSC, TGA.

Thermal effect	DSC (DTA)	TGA	TMA
Melting Melting of organic compounds with decomposition	No visible decomposition  Exothermic decomposition of the liquid phase  Endothermic decomposition of the liquid phase 	Low vapour pressure  Volatile melt  Release of moisture trapped in structure during melt  Volatile decomposition products 	Probe penetrates whole melt  Probe penetrates whole melt 
Crystallization from the melt on cooling (one drop) (many small droplets)	The crystallization front moves through the whole sample  Each droplet supercools to a different extent before it crystallizes 		
Cold crystallization of an amorphous sample on warming, followed by melting	 Crystallization Melting		Volume change during crystallization  Probe penetrates into melt

Thermal effect	DSC (DTA)	TGA	TMA
Polymorphism Enantiotropic solid-solid transition of the low temperature form Liquid-liquid-solid transition of the metastable α -form	 Fine powder: the large number of crystals yields perfect statistics Relatively few large crystals with individual transitions β crystallizes α melts β melts		Measure only one small crystal!  Quartz glass disk on sample β crystallizes α melts β melts
Glass transition	 with enthalpy relaxation		 $\sigma \sim 0$ $\sigma \sim 0$ 1 $\sigma \sim 0$ 2 $\sigma \gg 0$ $\sigma_b \gg 0$ Penetration 3 Point Bending 1, 2: Disturbances during the first measurement
Ferromagnetic Curie-transition		Without magnet  Permanent magnet below furnace 	 Change of slope
Evaporation, drying, desorption, sublimation		 Sometimes volatile compounds are released during the transition	 Volume decrease due to drying

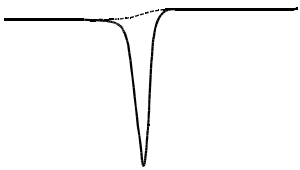
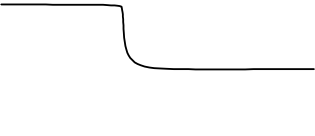
Thermal effect	DSC (DTA)	TGA	TMA
Boiling of a liquid in a crucible with a small hole in the lid, (self-generated atmosphere)			-

Table 6.1. The most important physical thermal effects.

6.5 Calibration and Adjustment

6.5.1 Some Definitions

- Calibration:** Determines the difference of a measured value from a reference value. This procedure is also called a “check”.
- Adjustment:** Adjusts the instrument parameters so that the measured value agrees with the reference value.
- Reference substance:** A substance with known properties used for calibrations.
- Error limits:** Acceptable (maximum) difference of the measured from the reference value.

6.5.2 Purpose of Calibration

The results must be within the acceptable error limits.

The calibration provides information about the current state of the instrument. Adjustments are only made if the deviation is unacceptable.

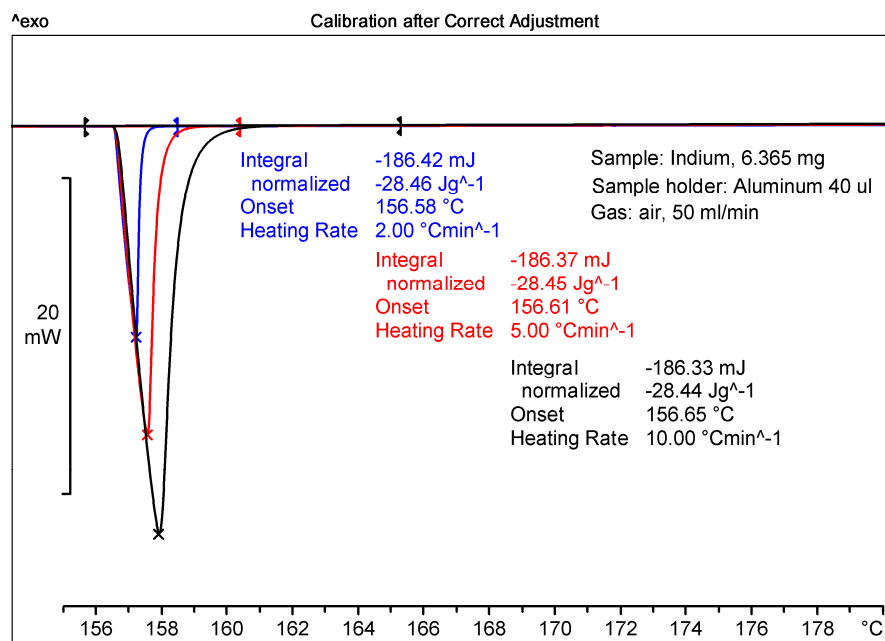


Figure 6.5. After adjustment, the instrument gives results that are within the permissible error limits. Three DSC curves measured at different rates are used to demonstrate that the correct enthalpy of fusion (normalized integral) and melting point (onset) are obtained.

6.5.3 Requirements for Reference Substances

- The properties of the reference substances used must be known (reliable literature values). Sources are: STAR^e database for the reference substances suggested by METTLER TOLEDO Internet, e.g. <http://webbook.nist.gov>
- The reference substance must not react with the crucible and/or the atmosphere. Unfortunately most metallic reference substances form a low melting eutectic with the aluminum pan when in intimate contact. Remedy: Do not press the metal into the pan!
- For heat flow calibrations there should be no change in heat capacity or only a very small change in heat capacity at the phase transition used
- Practical information, such as stability (shelf life and thermal stability), toxicity, availability.

Certified reference samples are available from the Laboratory of the Government Chemist, UK at <http://www.lgc.co.uk> or at the National Institute of Standards and Technology (NIST), USA at <http://ts.nist.gov/srm>

METTLER TOLEDO markets the reference substances needed for calibration and adjustment. The following reference substances are traceable to the manufacturer:

Substance		T_f	ΔH_f	Order Number
Indium	In	156.6 °C	28.5 J/g	ME 00 119 442
Tin	Sn	231.9 °C	60.1 J/g	ME 51 140 621
Lead	Pb	327.5 °C	23.0 J/g	ME 00 650 013
Zinc	Zn	419.6 °C	107.5 J/g	ME 00 119 441
Aluminum	Al	660.3 °C	397.0 J/g	ME 51 119 701
Gold	Au	1064.2 °C	63.7 J/g	ME 51 140 816
Palladium	Pd	1554.0 °C	162.0 J/g	ME 51 140 817

Table 6.2. Reference substance available from METTLER TOLEDO.

6.5.4 Properties Requiring Calibration in Thermal Analysis

The measured signal (ordinate) and the physical properties in conjunction with the abscissa of a diagram need to be calibrated.

Ordinate

- Heat flow, peak area (DSC)
- Mass (TGA, automatically performed in the electronic microbalance)
- Length (displacement) and force (TMA and DMA).

Abscissa

- Temperatures
- τ_{lag} , which makes the temperature independent of the heating rate (at the sample crucible position)
- Time (e.g. for isothermal measurements); since it is derived from the quartz clock of a microprocessor, it is extremely accurate.

6.5.5 Procedures in STAR^e

Measurement combinations

Any combination of a measuring module, type of crucible and atmosphere can be used to perform calibrations and adjustments. The calibration parameters are stored in the database. Example methods are available in the database for the most important standard combination (e.g. DSC, 40- μ L Al crucible, air). If DSC measurements are performed in a combination that has not been adjusted, the calorimetric results obtained are expected to be less accurate because the calibration data of the standard combination is extrapolated using empirical factors.

Error limits

The error limits depend on the application, for example for the determination of onset temperatures, the error limits of the DSC heat flow can be 10% or higher. Often, the goal of TGA is to determine the mass loss step; the temperature range in which this occurs is less important. The error limits can for example be 5 K for such applications.

The error limits used in the ready-to-use check methods are based on the instrument specifications and are thus rather small.

Calibration Interval

Initially we suggest a calibration interval of once a month. If the results are repeatedly within acceptable error limits, this interval can be doubled. If several measurements with unacceptable results are obtained, the interval should be reduced to half.

After an adjustment, one should always perform a calibration to verify that correct values are obtained.

Calibration

The ready-to-use checks, for example the In and the Zn check for DSC, have the advantage of automatic evaluation including the automatic validation of the results (pass or fail). The error limits used in these check methods are based on the instrument specifications and are thus rather small.

Calibration methods can of course also be used for this purpose. They show the measured results and it is the user's decision whether to accept the results as they stand or to use them to adjust the instrument if the deviation is considered to be unacceptable [4] [5].

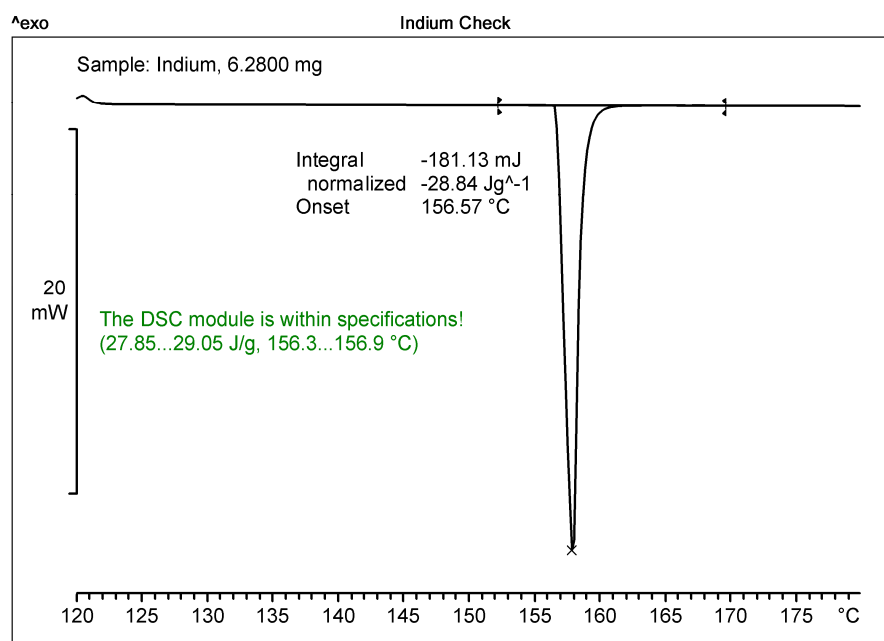


Figure 6.6. The results of this DSC calibration are within the permissible error limits. An adjustment is not necessary.

Adjustments

The usual way to perform adjustments is to use the METTLER TOLEDO Total Calibration method. There are also specific ready-to-use calibration methods.

Temperature calibration methods using one or several reference substances are available for all techniques.

After a check or another measurement with a reference material, the data obtained can be entered manually into the calibration menu of the Module Control Window to perform the adjustment.

Comment: Reference substances should be chosen in such a way that they cover the temperature range needed for measurements. Extrapolation is less accurate than interpolation [4].

6.5.6 FlexCal™

Conventional thermal analysis instruments are adjusted for specific conditions only. Whenever the experimental conditions change, the instrument has to be readjusted.

The STAR^e FlexCal™ system keeps the instrument properly adjusted under all conditions. For example for:

All heating rates

With FlexCal™, the temperature at the sample position becomes independent of the heating rate when τ_{lag} has been properly adjusted.

All types of crucible

Details of the various crucibles with their different geometry and mass are stored in the database. This information is automatically taken into account.

All atmospheres

Details of the different gases and their different heat conductivities are stored in the database. The information is automatically taken into account.

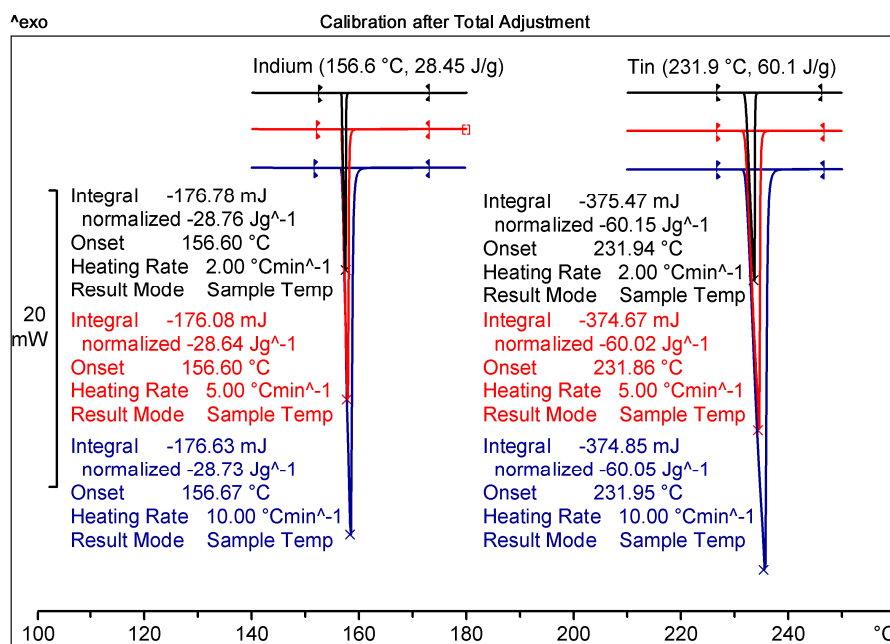


Figure 6.7. After adjustment, the DSC module gives correct results for indium and tin. Both the enthalpy of fusion (normalized integral) and the melting point (onset) of indium (156.6 °C) and of tin (231.9 °C) agree with literature values and are independent of the heating rate used (2, 5 and 10 K/min).

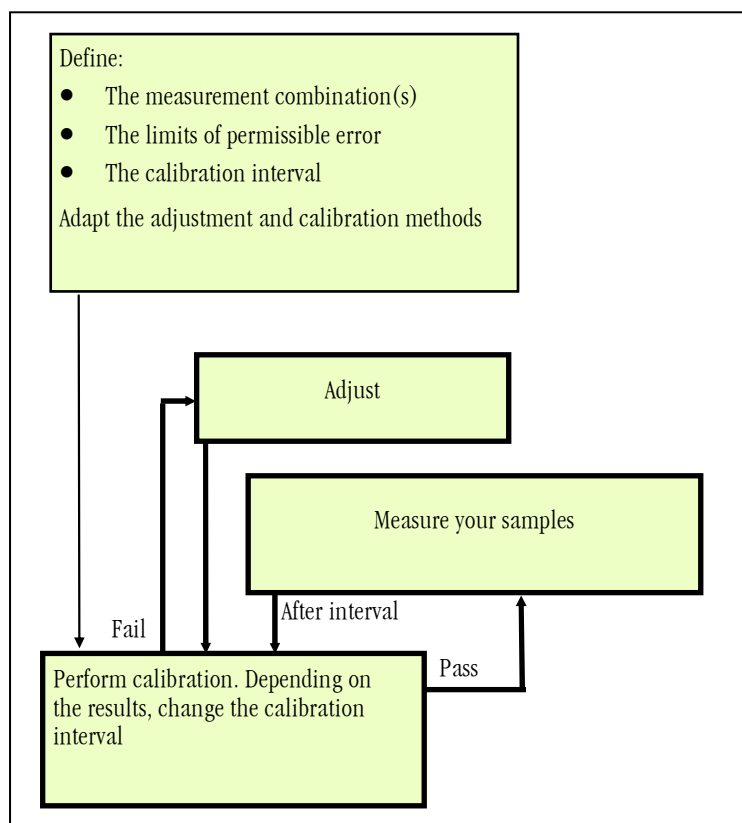


Figure 6.8. Flow chart for measurements and calibration.

References and Further Reading

- [1] METTLER TOLEDO Collected Applications Handbook: “Food”, Melting Behavior and Hydrogenation, p. 38.
- [2] METTLER TOLEDO Brochure “Crucibles for Thermal Analysis”.
- [3] M. Schubnell, Determination of calcium sulfate dihydrate and hemihydrate in cement, METTLER TOLEDO Thermal Analysis UserCom 26, 16–17.
- [4] Calibration, METTLER TOLEDO Thermal Analysis UserCom 6, 1–5.
- [5] Low-temperature calibration, METTLER TOLEDO Thermal Analysis UserCom 9, 1–4.

UserCom: Many of the application examples in this chapter have been taken from UserCom, the METTLER TOLEDO technical customer journal that is published twice a year. Back issues of UserCom can be downloaded as PDFs from the Internet at www.mt.com/ta-usercoms.

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7.1 Introduction

A differential scanning calorimeter measures the heat flow that occurs in a sample when it is heated, cooled, or held isothermally at constant temperature. The technique is also called differential scanning calorimetry, DSC. It allows you to

- detect endothermic and exothermic effects,
- measure peak areas (transition and reaction enthalpies),
- determine temperatures that characterize the peak or other effects, and
- determine specific heat capacity.

Physical transitions and chemical reactions can be quantitatively determined. Some properties and processes that are frequently measured are

- the melting point and enthalpy of fusion,
- crystallization behavior and supercooling,
- solid–solid transitions and polymorphism,
- the glass transitions of amorphous materials,
- pyrolysis and depolymerization,
- chemical reactions such as thermal decomposition or polymerization,
- reaction enthalpies,
- the investigation of reaction kinetics and predictions about the course of reactions,
- safety investigations of chemical reactions,
- oxidative decomposition, oxidation stability (OIT),
- comparison of different batches of a product, and
- measurements under pressure or with poisonous or flammable gases in a high-pressure DSC. Under pressure, the rate of heterogeneous reactions increases significantly and the vaporization of volatile components occurs at considerably higher temperatures.

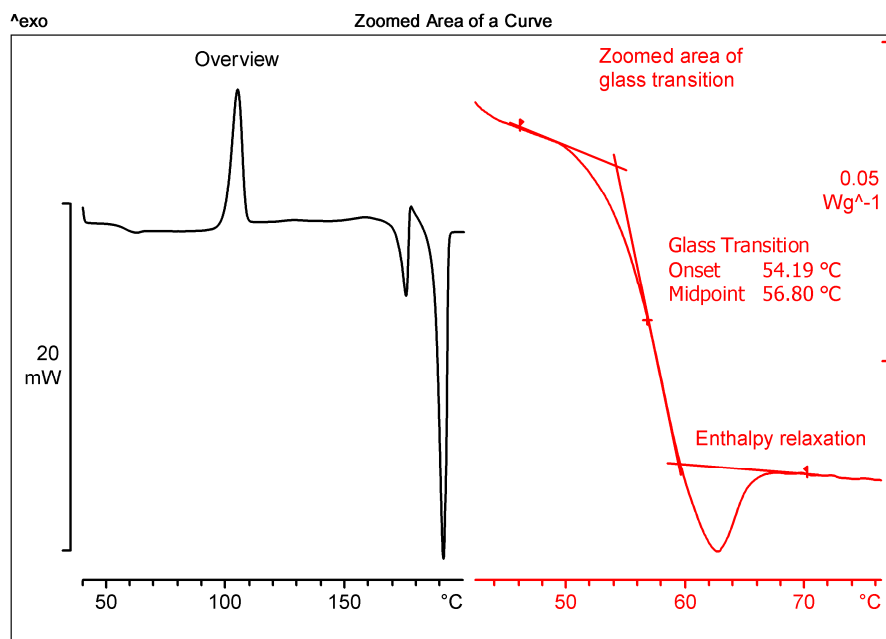


Figure 7.1. A typical DSC curve. Sample: 8 mg of an organic substance, heating rate 5 K/min. Left: Survey run from 40 to 200 °C showing different effects. Right: The glass transition with ordinate and abscissa scale expansion.

7.2 Design and DSC Measurement Principle

In 1955, S. L. Boersma introduced a quantitative DTA cell, which thereby led to the development of present-day heat flow DSC.

The current METTLER TOLEDO heat flow DSC measuring cell with ceramic sensors exhibits the following features [1],:

- Very small furnace made of pure silver with electrical flat heater.
- Pt100 temperature sensor with excellent long-term stability.
- Exchangeable FRS5 and HSS7 DSC sensors with a star-shaped arrangement of thermocouples underneath the crucible positions that measures the difference between the two heat flows. Connection of the thermocouples in series results in high calorimetric sensitivity.
Recesses ground into the underside of the sensor disk provide the necessary thermal resistance. The thermal resistance is very small and the heat capacity beneath the crucible is low because much of the material has been removed in the grinding process. The resulting signal time constant is therefore also very small.
The disk-shaped sensor is connected vertically from below thereby minimizing horizontal temperature gradients.
- Various cooling options (air cooling, circulator cryostat, IntraCooler, liquid nitrogen).
- The same furnace and DSC sensor is incorporated in a high-pressure DSC system, the HP DSC high-pressure DSC cell, usable up to 10 MPa [2].

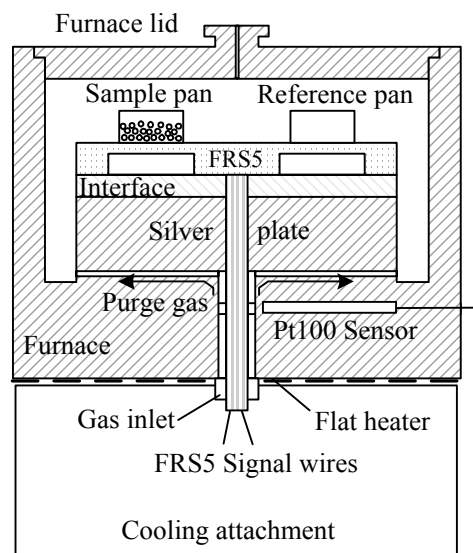


Figure 7.2. Simplified cross-section of a DSC measuring cell equipped with an FRS5 sensor. The sample and the reference crucible (usually empty) lie exactly over the recesses ground into the sensor disk. A thin disk of glass ceramic material (interface) connects the sensor with the silver plate of the furnace. The purge gas conditioning is shown in the lower part. The Pt100 measures the temperature of the furnace, T_c . The cooling attachment is shown below the flat heater. The two gold FRS5 signal wires and the purge gas inlet are located in the center under the FRS5 sensor.

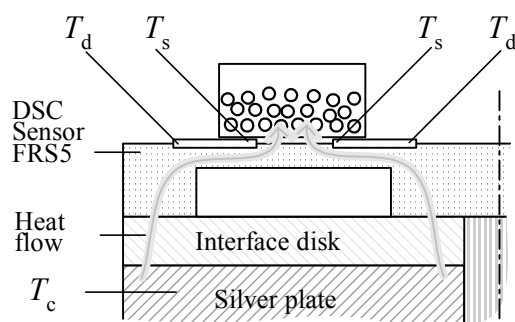


Figure 7.3. Expanded section of the sample side of Figure 7.2. The paths taken by the heat flow are colored gray, starting from the silver plate of the furnace across the glass ceramic interface disk, the DSC sensor (along the radially arranged thermocouples for the temperature difference $T_s - T_d$) and through the crucible base into the sample. The measured $T_s - T_d$ signal is proportional to the heat flow on the sample side. On the right side of the sensor, $T_r - T_d$ is measured in the same way. This temperature difference is proportional to the heat flow on the reference side.



Figure 7.4. The MultiSTAR™ FRS5 and HSS7 DSC sensors.

7.2.1 How Is the Heat Flow Measured?

The heat flow, Φ , flows radially through thermal resistance R_{th} of the FRS5 and HSS7 sensors. The thermal resistance is in the form of a ring under each of the two crucible positions. As already mentioned, the temperature difference across this thermal resistance is measured by the radially arranged thermocouples.

From Ohm's law it follows that the heat flow on the left side (composed of the heat flow to the sample crucible and to the sample) is given by

$$\Phi_l = \frac{T_s - T_c}{R_{th}} \quad (7.1)$$

and similarly on the right side (heat flow to the empty reference crucible)

$$\Phi_r = \frac{T_r - T_c}{R_{th}} \quad (7.2)$$

The DSC signal, Φ , the heat flow to the sample, corresponds to the difference between the two heat flows

$$\Phi = \Phi_l - \Phi_r = \frac{T_s - T_c}{R_{th}} - \frac{T_r - T_c}{R_{th}} \quad (7.3)$$

The thermal resistances on the left and right sides are identical due to the symmetrical arrangement. The same is true for T_c . The equation for the determination of the DSC signal can therefore be simplified to

$$\Phi = \frac{T_s - T_r}{R_{th}} \quad (7.4)$$

Since the temperature differences are measured by thermocouples, we still need the equation that defines the sensitivity of a thermocouple, $S = V/\Delta T$, where V is the thermoelectric voltage. From this, it follows that

$$\Phi = \frac{V}{R_{th} S} = \frac{V}{E} \quad (7.5)$$

where V is the sensor signal. The product $R_{th} S$ is called the calorimetric sensitivity E of the sensor. R_{th} and S are temperature dependent. The temperature dependence of E is described by means of a mathematic model.

In DSC curves, a peak area for example, is the integral of the heat flow over time and corresponds to the change in enthalpy, ΔH , of the sample.

7.2.2 How Is the Sample Temperature Measured?

Figure 7.2 shows that the furnace temperature, T_c , is measured using a Pt100 sensor. Basically, the Pt100 sensor is a resistance made of platinum wire that has an electrical resistance of 100 Ω at 0 °C. The relationship between resistance and temperature T is described by a polynomial:

$$R = A + BT + CT^2 \quad (7.6)$$

In a DSC measurement, the heating rate selected refers to the reference temperature because the sample can undergo first order phase transitions during which the heating rate cannot be controlled.

A temperature difference, ΔT , that depends on the thermal resistance is necessary for heat to flow from the furnace to the reference crucible. In METTLER TOLEDO instruments, this is achieved by **increasing the furnace temperature** by the same value of ΔT . Independent of the heating rate, the time difference between T_c and T_r is equal to the time constant, τ_{lag} . The heating rate, β , is equal to the slope of the triangle shown in the expanded scale section in Figure 7.5. It follows that

$$\beta = \Delta T / \tau_{lag} \quad \text{or} \quad \Delta T = \beta \tau_{lag}. \quad (7.7)$$

During the dynamic segment, the calculated temperature increase, ΔT , is added to the set value of the furnace temperature so that the reference temperature exactly follows the temperature program.

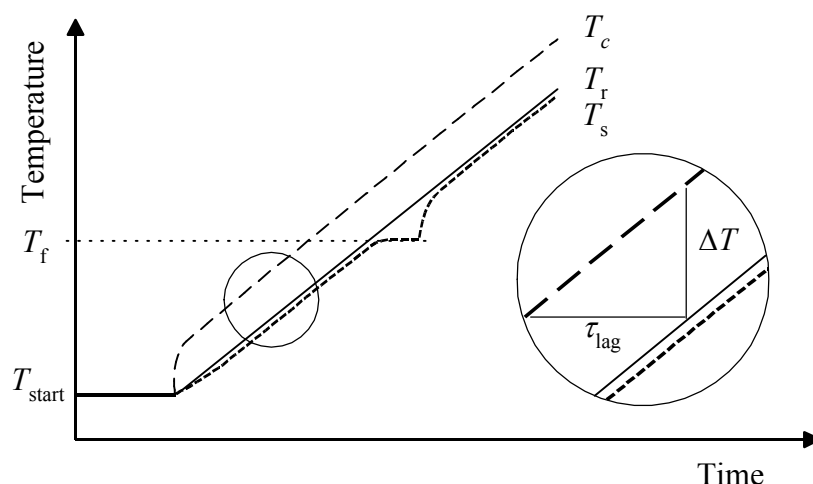


Figure 7.5. The three important temperatures are the furnace temperature T_c , the reference temperature T_r , and the sample temperature T_s . A thermal effect occurs (sample melting) at T_f . The enlarged section of the diagram shows the relationship between the heating rate (slope), β , the lag time constant, τ_{lag} , and the temperature advance, ΔT .

The furnace temperature is increased by ΔT at the beginning of the dynamic segment.

As shown in Figure 7.5, there is a difference between T_s and T_r , especially during thermal effect. It corresponds to the sensor signal in eq 7.1, which can be solved for T_s :

$$T_s = T_r + \Phi R_{th} = T_r + \Phi \frac{E}{S} \quad (7.8)$$

This is how the software calculates the sample temperature.

Note: Strictly speaking, there is a small difference between the temperature within the sample and the measured temperature of the sample crucible. This difference is largely compensated through the right choice of the thermocouple sensitivity, S , in the software.

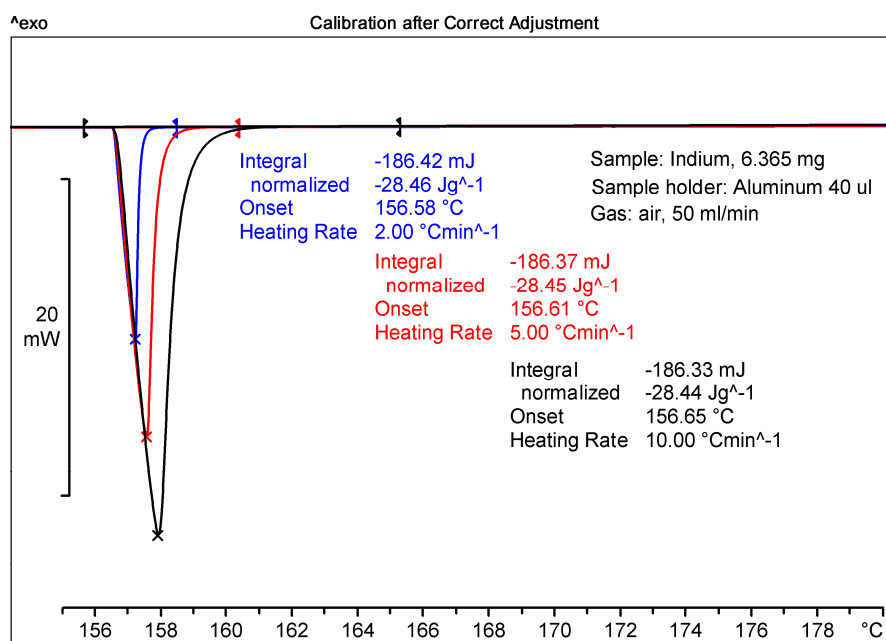


Figure 7.6. DSC curves of the melting of a pure metal (6.225 mg indium) measured at different heating rates. The onset temperatures are independent of the heating rate. The onset is the temperature of the sample at the intersection of the tangent before the effect (the "baseline") with the tangent drawn to the side of the peak.

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.

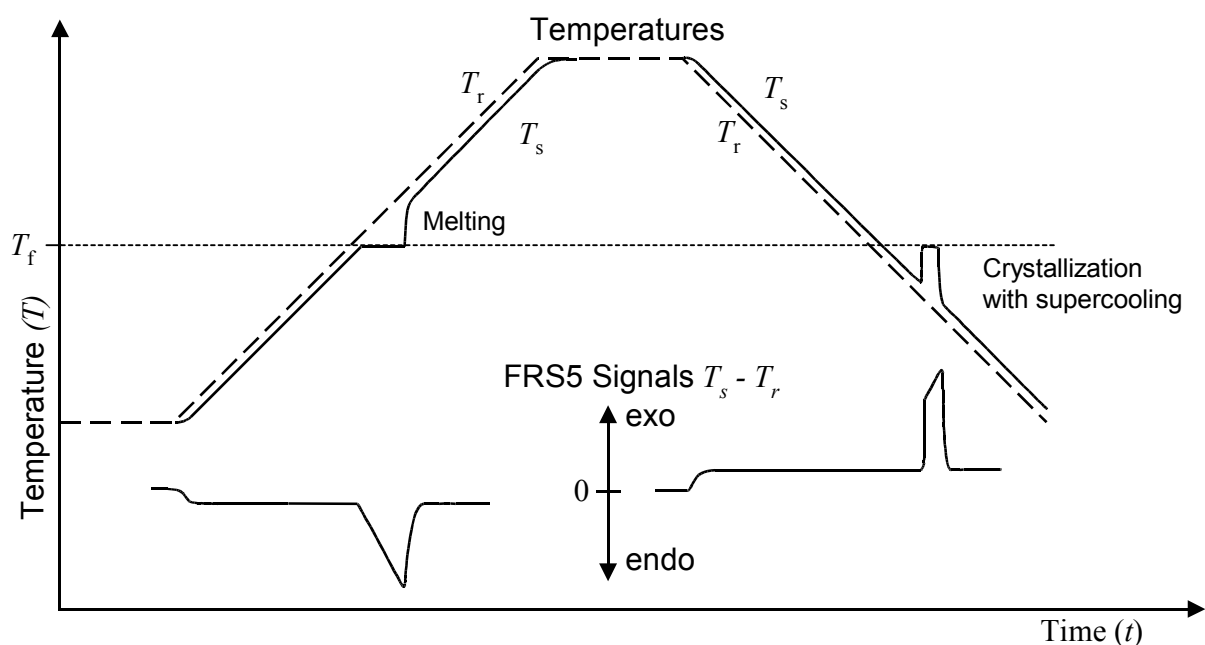


Figure 7.7. Top: The upper diagram shows the course of T_s and T_r on heating a sample with a melting point T_f (left), and on cooling the sample (right). The liquid sample does not crystallize on reaching the melting point but exhibits supercooling. As soon as crystallization begins, the temperature 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.

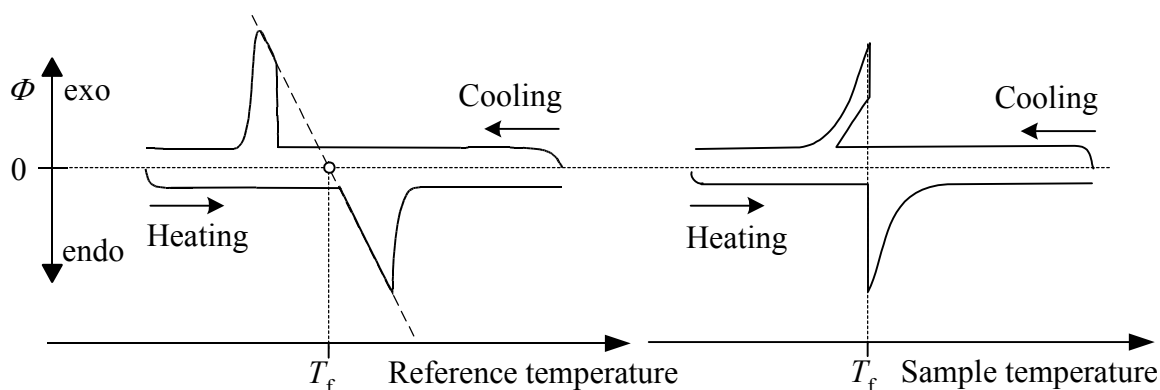


Figure 7.8. Left: The two DSC curves are plotted against the reference temperature. Comparison with Figure 7.7 immediately shows that all sample temperatures on the dashed line must be identical. The slope of this line is $-1/R_{th}$. Right: The DSC curves are plotted against sample temperature. Here 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,

$$\Phi_1 = \frac{T_s - T_c}{R_{th}} \quad (7.1)$$

the heat flow is $-1 \text{ K}/R_{th}$. 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.

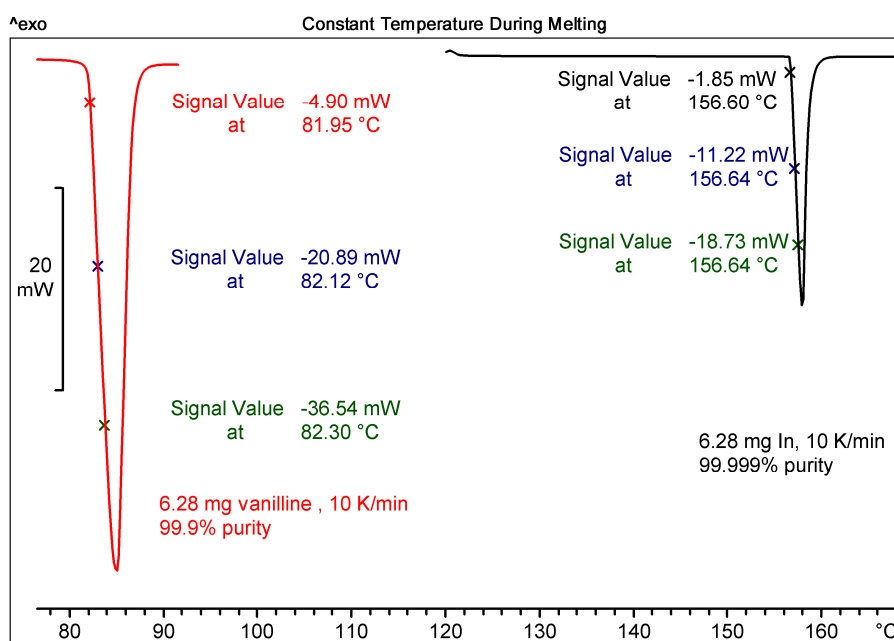


Figure 7.9. The sample temperature of the melting peak of indium remains constant at 156.6 °C (right) while the reference temperature increases from 156.6 to 167.4 °C (not visible from the figure). Only extremely pure non-polymeric materials exhibit a constant (sample) temperature during melting. With 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.

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.

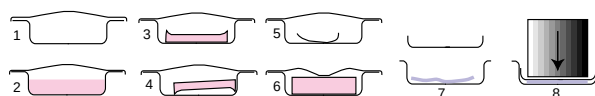


Figure 7.10. (1): Standard 40- μ L aluminum crucible with lid before sealing. (2) to (6): After hermetically sealing through cold welding. (2): Liquid or powder sample of ideal geometry. (3): Punched-out sample with the flat side facing downward. (4): Bad example, with irregular side facing downward. (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.

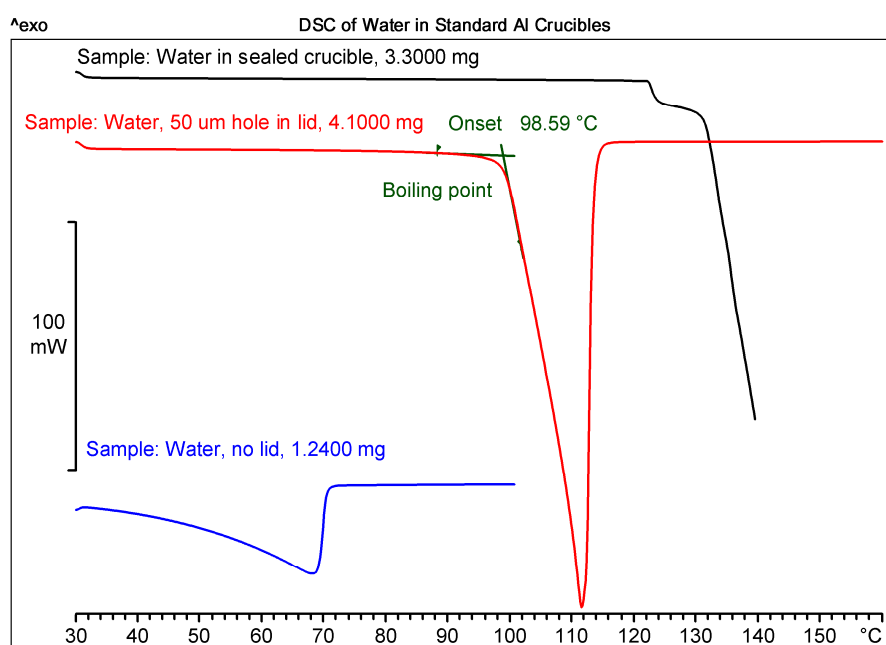


Figure 7.11. DSC curves of water. Above: In a hermetically sealed crucible, there is no boiling point. The effect at about 125° C is due to the crucible bursting. Middle: In a self-generated atmosphere, the boiling point can be measured as the onset. Below: In an open crucible, water evaporates before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

7.4.3 Procedure with Unknown Samples

The temperature range you choose for the first trial measurement is based on any physical-chemical information you have about the particular sample. The temperature range should be sufficiently large to make sure all the effects have been detected. Not too much time is lost at a heating rate of 20 K/min if the range first chosen turns out to be 100 K greater than necessary.

The following information summarizes a number of basic rules when measuring an unknown sample for the first time:

Sample size and temperature range:

Organic substances: 1 to 10 mg in aluminum crucibles with pierced lids. Temperature range 25 to 350 °C, heating rate 20 °C/min, atmosphere N₂ (flow rate about 50 mL/min).

With inorganic substances, a sample mass of 10 to 30 mg is used and a higher final temperature, for example 600 °C.

Mass loss:

It is good practice to weigh the sample and crucible before the measurement. You can then determine a possible loss of mass of the sample by back-weighing after the measurement. Losses up to about 30 µg can be attributed to the evaporation of surface moisture from the crucible, whereas larger losses indicate the loss of volatile substances from the sample.

Examining the measured sample:

- Does it look as if it has melted? Can you identify a melting peak in the DSC curve? If recrystallization is of interest, you can measure a new sample by adding a cooling segment at 10 K/min directly after the melting peak. Do not forget that samples can supercool by 1 to 50 K! Many substances often do not crystallize from the melt but instead form a glass.
- Is it colored? Organic substances turn brown when they decompose.
- Are any gas bubbles visible or are there signs of foam formation? This indicates decomposition accompanied by a significant loss of mass.
- Has a reaction occurred with the material of the crucible? If the crucible is not inert, it might dissolve or be destroyed. A crucible made of a different material is perhaps completely inert.
- Sometimes, chemical analysis of the residue is also very informative.

If overlapping effects occur, you can try to separate them by using higher or lower heating rates, or a self-generated atmosphere. A smaller sample mass often improves separation.

With organic substances, it is often useful to measure a new sample in air or oxygen. At 10 K/min, the exothermic oxidation reaction occurs in the range 150 to 300 °C.

If only weak effects (less than about 2 mW) occur, it often pays to measure a blank curve under the same conditions. The blank curve is then subtracted from the measured sample curve. This usually allows the effects to be more clearly identified.

7.5 Interpretation of DSC Curves

7.5.1 Interpreting Dynamic DSC Curves

The interpretation of measurement effects requires a certain amount of experience in thermal analysis. It is also very helpful to know about any possible reactions that may occur in the sample.

Interpretation is often facilitated by measuring a cooling curve of the sample immediately after the first heating run. The cooling rate that can be used depends on the particular cooling system available. After the cooling run, it is a good idea to heat the sample again, that is, to perform a second heating run. Any differences observed between the first and second heating runs often provide information that aids interpretation.

Another alternative is to shock-cool (quench) the sample after it has been heated to the end temperature for the first time. This is done in order to freeze metastable states that possibly occur. The shock-cooled sample is then measured again to give a second heating run. The automatic sample robot provides an excellent way to shock-cool samples to room temperature. After measurement, the robot places the hot sample on the cold aluminum turntable, which cools it down to room temperature within a few seconds. If you do not have a sample robot, wait until the DSC cell has reached its end temperature and then remove the crucible using tweezers and place it on a cold aluminum plate (possibly with a 2-mm hole to accommodate the center pin of the crucible). Alternatively, the crucible can be dipped in liquid nitrogen for about 10 s.

7.5.1.1 DSC Curves That Show No Thermal Effects

In this case, the sample is inert in the temperature range measured and only the temperature-dependent heat capacity is measured.

An inert sample does not lose mass with the possible exception of about $\leq 30 \mu\text{g}$ surface moisture. When the crucible is opened, the sample looks the same as before the measurement. This can be verified using reflected light microscopy.

If you want to measure c_p values, a suitable blank curve is required. The c_p value obtained should be checked for plausibility - in general, c_p is in the range 0.1 to $5 \text{ J g}^{-1} \text{ K}^{-1}$.

You can check whether other effects occur by extending the temperature range and increasing the sample mass.

7.5.1.2 DSC Curves That Show Thermal Effects

Thermal effects are distinct deviations from the more or less straight-line DSC curve.

They are caused by physical transitions or chemical reactions that occur in the sample.

If two effects overlap, you can try to separate them by using different heating rates (higher or lower) or a smaller sample mass. At the same time, you should take into account that higher heating rates shift chemical reaction peaks to higher temperatures. This also applies to a lesser extent to solid-solid transitions: The onset-temperatures of the melting processes of non-polymeric substances are however independent of the heating rate.

If several effects occur together with a significant loss of mass ($>30 \mu\text{g}$), you would of course like to assign the mass loss to a particular peak. The effect is usually endothermic because of the work of expansion due to gas formation. In this case, heat a new sample step by step across the individual peaks and weigh the crucible before and after each effect (at METTLER TOLEDO, this is called "offline thermogravimetry"). If a TGA instrument is available, you can measure a new sample, if possible, in the same type of crucible used for the DSC measurement.

The shape of the DSC curve of an effect is usually very characteristic and helps you to identify it.

The following sections discuss the most important effects and describe the typical curve shapes obtained.

7.5.1.3 Physical Transitions

In principle, a physical transition can be measured as many times as desired provided that

1. The sample returns to the original state on cooling. This is however not always the case and depends on the sample and the cooling rate. At high cooling rates, many substances solidify from the melt as amorphous glasses, which is why no melting peak is observed in the second heating run. Some metastable crystal modifications only crystallize out in the presence of particular solvents.
2. The sample does not escape from the crucible through evaporation, sublimation, or (chemical) decomposition, or does not undergo a transition. Any sample lost by evaporation cannot crystallize in the sample crucible on cooling because the purge gas has already removed it from the measuring cell.

7.5.1.3.1 Melting, Crystallization and Mesophase Transitions

Evaluation of a melting peak yields the enthalpy of fusion and the melting point or melting range. The low-temperature side of the melting peak of a pure substance is practically a straight line (Figure 7.12a) and the melting point corresponds to the onset temperature. The low-temperature side of melting curves of impure or polymeric samples with concave sides are characterized by their peak temperatures (Figure 7.12b and c). Semicrystalline polymers exhibit particularly broad melting peaks due to the size distribution of the crystallites (Figure 7.12c).

Many organic compounds undergo decomposition on melting. The decomposition reaction can be exothermic or endothermic in nature (Figure 7.12d and e).

An endothermic peak on a DSC heating curve is a melting peak if

- the sample mass does not significantly decrease during the measurement. Some substances, however, exhibit marked sublimation in the region of the melting temperature. The DSC curve is not affected by sublimation or evaporation if hermetically sealed crucibles are used.
- visual inspection after the measurement shows that the sample has melted. Powdered organic substances, in particular, form a pool on melting. On cooling, this solidifies to a glass (no exothermic crystallization peak) or crystallizes (exothermic crystallization peak).

Note: The surface of many metals is covered with a high-melting point oxide layer. The oxide layer remains behind as a rigid envelope which is not deformed when the metal melts. On opening the crucible, the sample still looks the same as it did before it melted. Noble metals form no oxide layer and produce spherical droplets on melting.

- the surface area is in the range 10 to 400 J/g. The enthalpy of fusion of organic non-polymeric substances is usually between 120 and 170 J/g.
- the half-width is significantly less than 10 K. Semicrystalline polymers may in some cases melt over a broader range. The purer and lighter the sample, the narrower the peak. Very small and pure samples give peaks with half-widths of less than 1 K.

Impure samples, mixtures and blends often exhibit several peaks. Substances with eutectic impurities show two peaks (Figure 7.12b). The first is the eutectic peak, whose size increases with increasing impurity, followed by the main melting peak. Sometimes the eutectic is amorphous, in which case the first peak is missing. Liquid-crystalline substances remain anisotropic even after the melting peak. The melt only becomes isotropic after one or more small sharp peaks due to mesophase transitions have occurred (Figure 7.12f).

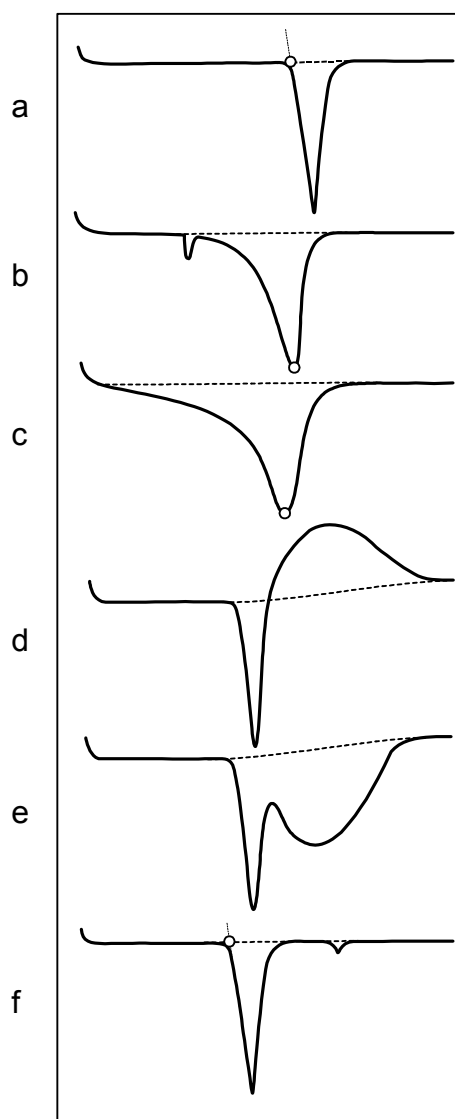


Figure 7.12. Melting.

- a: Non-polymeric pure substance.
- b: Sample with a eutectic impurity.
- c: Semicrystalline plastic.
- d: Melting with decomposition.
- e: Melting with decomposition.
- f: Liquid crystal.

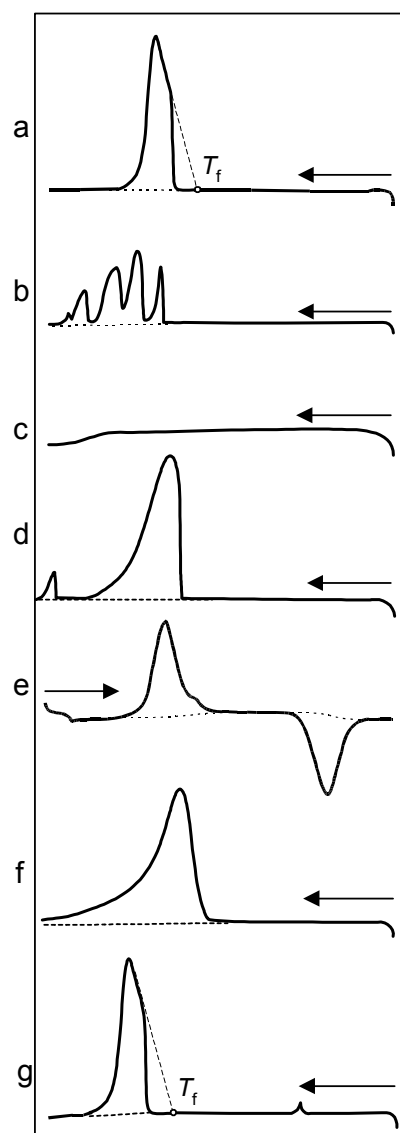


Figure 7.13. Crystallization.

- a: Pure substance (T_f is the melting point).
- b: Separate droplets solidify individually with different degrees of supercooling.
- c: Melt solidifies amorphously.
- d: Sample with eutectic impurity.
- e: Shock-cooled melt crystallizes on heating above the glass transition temperature (cold crystallization).
- f: Semicrystalline plastic.
- g: Liquid crystal.

An exothermic peak on the cooling curve is a crystallization peak if

- the peak area is about the same as that of the melting peak. Since the enthalpy of fusion is temperature dependent, a deviation of up to 20% can however occur on crystallization depending on how much the sample supercools.
- the degree of supercooling (i.e. the difference between the onset temperatures of melting and crystallization) is between 1 and about 50 K. The peak of a substance that crystallizes rapidly after nucleation has an almost vertical side up until the point at which the melting temperature is reached (provided the sample is large enough, Figure 7.13a and g).

If the liquid phase is present as several individual drops, each drop supercools to a different extent and several peaks are observed (Figure 7.13b).

Organic and other compounds that crystallize poorly form a solid glass on cooling (Figure 7.13c). Such amorphous samples can then crystallize on heating to temperatures above the glass transition temperature. This process is known as cold crystallization. On further heating, several possible polymorphic transitions may occur before the solid phase just formed finally melts (Figure 7.13e).

When the melt of sample contaminated with a eutectic impurity is cooled, the main component usually crystallizes out (Figure 7.13d) but can also solidify as a glass (Figure 7.13c). If the eutectic remains amorphous, no eutectic peak is observed.

A polymer melt supercools by about 30 K before it crystallizes (Figure 7.13f). Many polymers solidify to form a glass on rapid cooling (Figure 7.13c).

When a liquid crystal melt is cooled, the mesophase transitions occur first (often without any supercooling!). The subsequent crystallization process exhibits the usual supercooling process (Figure 7.13g).

7.5.1.3.2 Solid-Solid Transitions and Polymorphism

The characteristic feature common to all solid-solid transitions is that a powder sample remains a powder even after the transition.

The **monotropic** solid-solid transition of metastable crystals (marked α' in Figure 7.14) to the stable α -form is frequently observed with organic compounds and is exothermic (Figure 7.14a). As the name implies, monotropic transitions proceed in only one direction (they are irreversible).

Monotropic transitions are generally slow. They are fastest a few degrees K below the melting point of the metastable phase. In spite of this, the peak height is usually less than 0.5 mW and can easily be overlooked next to the melting peak that follows, which is about 10 mW (gray arrow in Figure 7.14b). Often, it is best to wait for the monotropic transition to occur isothermally.

At heating rates above 5 K/min, it is quite possible that the rate is too high to observe the slow transition (Figure 7.14b) and the melting temperature of the metastable form is reached. The monotropic solid-solid transition is then either invisible or it could be misinterpreted as a slight exothermic baseline shift before the melting peak. If a few stable crystals are present that can serve as nucleation points for the crystallization of the liquid phase formed, the melting peak is immediately followed and by the exothermic crystallization peak. This case is referred to as a transition via the liquid phase - on immediate cooling to room temperature the sample would have appeared to have visibly melted. Finally, the melting temperature of the stable modification is reached.

If no α -nuclei are present, no α -crystallization peak and of course no α -melting peak occurs (Figure 7.14c). In contrast, if the entire sample is present as the stable form, only the α -melting peak appears and polymorphic effects are not observed (Figure 7.14d). Depending on the substance, the α' -form melts at a temperature 1 to 40 K lower than the stable modification.

The **enantiotropic** solid-solid transition, which occurs less often, is reversible. The $\alpha \rightarrow \beta$ transition starting from the low temperature form α to the high temperature form β is endothermic. The enantiotropic transition gives rise to peaks of different shape depending on the particle size of the sample because the nucleation rate of each crystal is different. For statistical reasons, finely crystalline samples produce more or less bell-shaped (Gaussian) peaks (Figure 7.15a and c). A small number of large crystals can give rise to peaks with very bizarre shapes (Figure 7.15b and d), especially with the reverse transition $\beta \rightarrow \alpha$.

The half-widths of peaks of enantiotropic transitions are typically about 10 K.

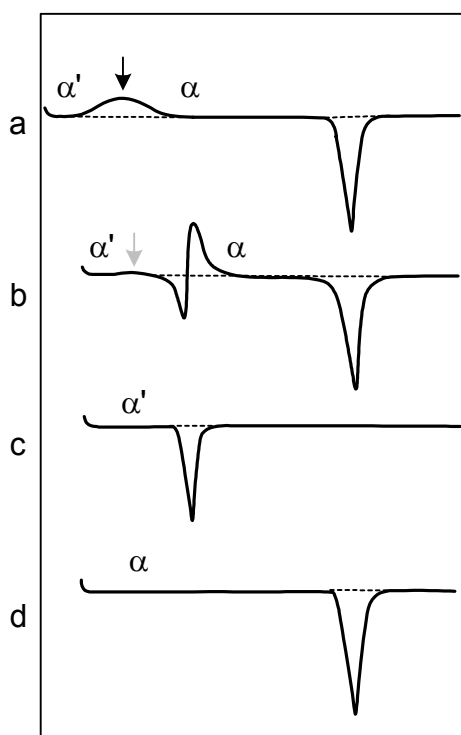


Figure 7.14. Monotropic transitions.

- a: The arrow shows the position of the solid-solid transition; afterward the α -form produced melts.
- b: Solid-solid transition is so slow that the α' -form reaches its melting point, whereupon α crystallizes.
- c: Pure α' -form melts low.
- d: Pure α -form melts high.

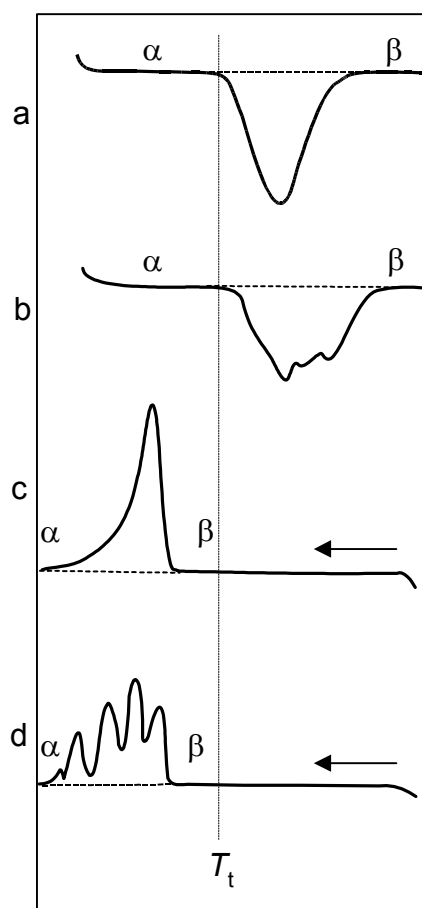


Figure 7.15. Reversible enantiotropic transitions.

- a: Fine powder.
- b: Coarse crystals.
- c: Reverse transition of the fine powder.
- d: Reverse transition of the coarse crystals; at T_t , α , and β are in thermodynamic equilibrium.

7.5.1.3.3 Transitions with Significant Loss of Mass

Transitions of this type can of course only be observed in an open crucible, that is, either without a lid or with a lid with a 1-mm hole to protect the measuring cell against substances that tend to creep out or sputter. The examples shown are the

- evaporation of a liquid sample (Figure 7.11, below and Figure 7.16a),
- drying (desorption of adsorbed moisture or solvent, Figure 7.16b),
- sublimation of solids (Figure 7.16b), and the
- decomposition of hydrates (or solvates) with the elimination of water of crystallization. In an open crucible, the shape of the curve corresponds to that shown in Figure 7.16b, and in a self-generated atmosphere to that in Figure 7.16c.

The peaks have a half-width of ≥ 20 K (except in a self-generated atmosphere); the peak shape is similar to that exhibited by chemical reactions. The decomposition of solvates is known as pseudo-polymorphism (probably because in a hermetically sealed crucible, a new melting point occurs when the sample melts in its own water of crystallization). Pseudo-polymorphism can also be thought of as a chemical reaction.

In a self-generated atmosphere (with a 50- μ m hole in the crucible lid), the evaporation of liquids is strongly impeded. The usually narrow boiling point peak is not observed until the boiling point is reached (Figure 7.11, middle and Figure 7.16d).

The loss of mass common to these reactions causes the baseline to shift in the exothermic direction. This is a direct consequence of the decreased heat capacity of the remaining sample.

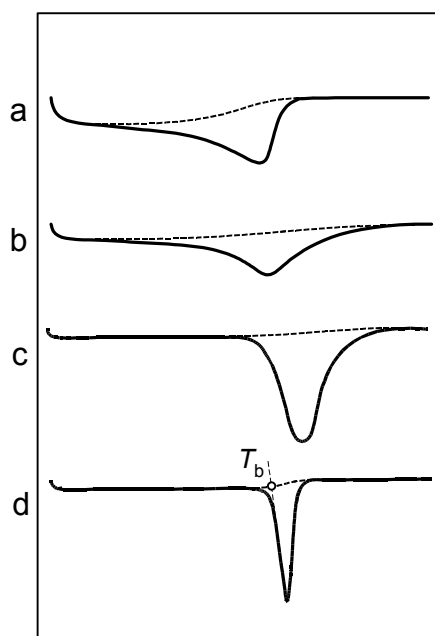


Figure 7.16. Transitions with mass loss.

- a: Evaporation in an open crucible.
- b: Desorption, sublimation.
- c: Dehydration.
- d: Boiling in a crucible with a small hole in its lid T_b is the boiling point.

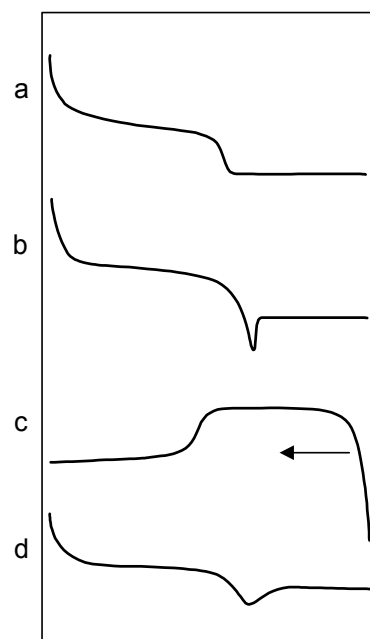


Figure 7.17. Stepwise transitions.

- a: Glass transition.
- b: Glass transition with enthalpy relaxation.
- c: Reverse transition.
- d: Curie transition.

7.5.1.3.4 The Glass Transition

At the glass transition, the specific heat of an amorphous material increases by about 0.1 to 0.5 J/gK. As a result, the DSC curve shows a characteristic shift in the endothermic direction (Figure 7.1, right and Figure 7.17a). Typically,

- the radius of curvature at the onset is significantly greater than at the endset, and
- the curve slopes in the endothermic direction before the transition but is almost horizontal afterward.

If the sample has been stored for a long time below the glass transition temperature, T_g , an endothermic relaxation peak often occurs with an area of 1 to maximum 10 J/g (Figure 7.17b). This peak is not observed on cooling (Figure 7.17c), or when the sample is heated a second time immediately afterward. The glass transition region usually covers a temperature range of 10 to 30 K.

You can identify an effect as a glass transition by checking whether the sample is noticeably soft, almost liquid or rubbery elastic above the T_g . If a TMA or DMA is not available, you can do this by heating a sample isothermally at a temperature of $T_g + 20$ K in a crucible without a lid. After several minutes, open the furnace lid and check whether the sample is soft by pressing it with a spatula or piece of wire. It is, however, difficult to detect the softening of highly filled plastics in this way.

7.5.1.3.5 Lambda Transitions

These second order solid-solid transitions exhibit Λ -shaped c_p temperature functions. The most important of these is the ferromagnetic Curie transition, which was previously used for TGA temperature calibration. The DSC effect is however very weak (Figure 7.17d). To make sure, you can check that there is no ferromagnetism above the Curie temperature using a small magnet.

7.5.1.4 Chemical Reactions

Chemical reactions can generally only be measured in the first heating run. On cooling to the start temperature, the reaction products remain chemically stable, so that on heating a second time no further reaction occurs¹. In some cases, the reaction is incomplete after the first heating run and a weak reaction is observed in the second run (e.g. curing and postcuring of epoxy resins).

The width at half height of a chemical reaction peak is about 10 to 70 K (usually about 50 K at a heating rate of 10 to 20 K/min).

Reactions that take place without significant loss of mass are usually exothermic (about 1 to 20,000 J/g, Figure 7.18a and b). The others tend to be endothermic because the work of expansion predominates.

Ideally, DSC curves obtained from a chemical reaction show just one single smooth peak (Figure 7.18a). In practice, the shape of the peak is often distorted by overlapping reactions, such as the melting of additives (Figure 7.18b), secondary reactions, or decomposition reactions (Figure 7.18c).

Examples of reactions with significant loss of mass are

- thermal decomposition (pyrolysis in an inert gas atmosphere), frequently with gaseous pyrolysis products such as CO, short chain alkanes, H₂O, and N₂,
- depolymerization with more or less quantitative formation of the monomer, and
- polycondensation for example in the curing of phenolic and melamine resins².

Reactions accompanied by a significant increase in mass are nearly always reactions with oxygen and are strongly exothermic. Examples of this are

- the corrosion of metals such as iron, and
- the uptake of oxygen at the beginning of the oxidation of organic compounds. In the course of the reaction, volatile oxidation products such as carboxylic acids, CO₂ and H₂O are formed so that finally a loss of mass occurs. The initial mass increase can best be observed in a TGA curve).

Examples of reactions with no significant change in mass are³

- addition and polyaddition reactions, curing of epoxy resins,
- polymerization, dimerization,
- rearrangements, and
- the oxidation of organic samples (e.g. polyethylene) in hermetically sealed crucibles with just the approximately 10 µg of residual oxygen from the air (Figure 7.18d).

¹ There are a very few exceptions to this rule. One example is the polymerization that occurs on heating sulfur at about 150 °C. This is reversed on cooling to about 130 °C.

² These slightly exothermic reactions are often measured in high-pressure crucibles in order to suppress the endothermic vaporization peak of the volatile side-products.

³ These reactions are often performed in hermetically sealed aluminum crucibles to prevent the release of slightly volatile components.

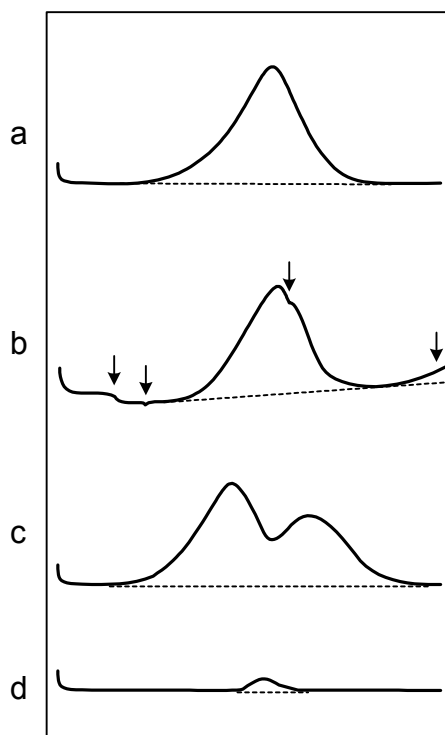


Figure 7.18. Chemical reactions.

- a: Ideal curve shape of an exothermic reaction.
- b: Reaction with interfering physical transitions and the beginning of decomposition.
- c: Chemical reaction with secondary reaction.
- d: Partial oxidation of an organic sample with residual oxygen in a hermetically sealed crucible.

7.5.1.5 Identifying Artifacts

The curve should be first checked for any artifacts in order to eliminate the possibility of false interpretation. Artifacts are effects that are not directly caused by the sample, but have some other origin that does not relate to the sample properties you want to measure. Some examples are shown schematically in Figure 7.19:

- a) Abrupt change of the heat transfer from the sample to the crucible due to
 - irregularly shaped samples that topple over in the crucible or
 - plastic films that have not been pressed down flat on the bottom of the crucible. On heating for the first time, they often twist and warp before they melt. After melting, they make good thermal contact again (Figure 7.20).
- b) Abrupt change of the heat transfer from the crucible to the DSC sensor:
 - 1) Deformation of a hermetically sealed aluminum crucible due to the vapor pressure of the sample.
 - 2) Slight shift of the position of an aluminum crucible on the DSC sensor in a dynamic temperature program due to the different expansion coefficients of aluminum and the DSC sensor (Al ~ 24 ppm/K, DSC sensor ~ 9 ppm/K, see also Figure 7.20). The artifact is about $10 \mu\text{W}$ and is only visible at high ordinate scale expansion (ordinate scale $< 1 \text{ mW}$). This effect does not occur with platinum crucibles (~ 8 ppm/K).
 - 3) The measuring cell suffers a mechanical shock: the crucible jumps around on the sensor and may move horizontally if it does not have a center locating pin.
- c) The inflow of cold air into the measuring cell due to a poorly adjusted furnace lid leads to temperature fluctuations and generates a noisy signal.
- d) Electrical influences:
 - 1) Discharge of static electricity in a metal part of the system or power supply disturbances (spikes).
 - 2) Radio transmitters, mobile phones and other sources of high frequency interference.

- e) Sudden change in room temperature, for example through direct sunlight.
- f) The crucible lid bursts due to an increase in vapor pressure of the sample. Depending on the amount of gas or vapor that escapes, an endothermic peak with a height of 0.1 to 100 mW can occur.
- g) Intermittent blockage (often periodic) of the hole in the crucible lid caused by droplets of sample that condense or foam.
- h) Contamination of the sensor due to residues of sample material from earlier experiments. Effects occur reproducibly at the same temperature and are characteristic of the substances involved. Solution: Cleaning by heating out in air or oxygen. This type of artifact depends to a large extent on the sample material involved.

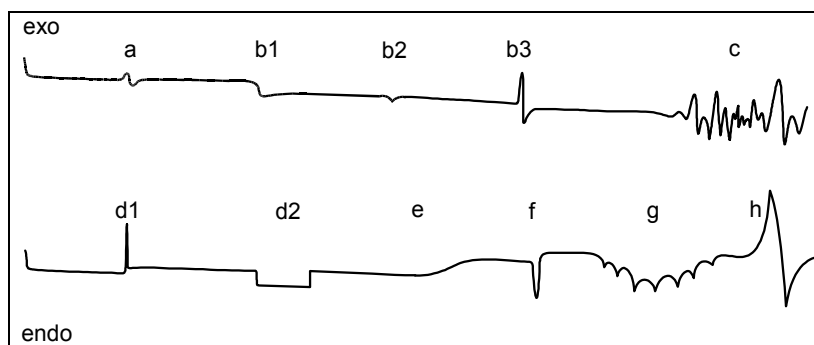


Figure 7.19. DSC artifacts (details are given in the text). Artifacts can be identified by repeating the measurement using a new sample of the same substance and observing whether the effect occurs again at the same place or at a different place on the curve. Exceptions are f and h, which can be very reproducible.

Artifacts can interfere with automatic evaluations (EvalMacro), especially evaluations that use automatic limits.

Isolated artifacts that have been clearly identified as such can be removed from the measured curve using suitable software.

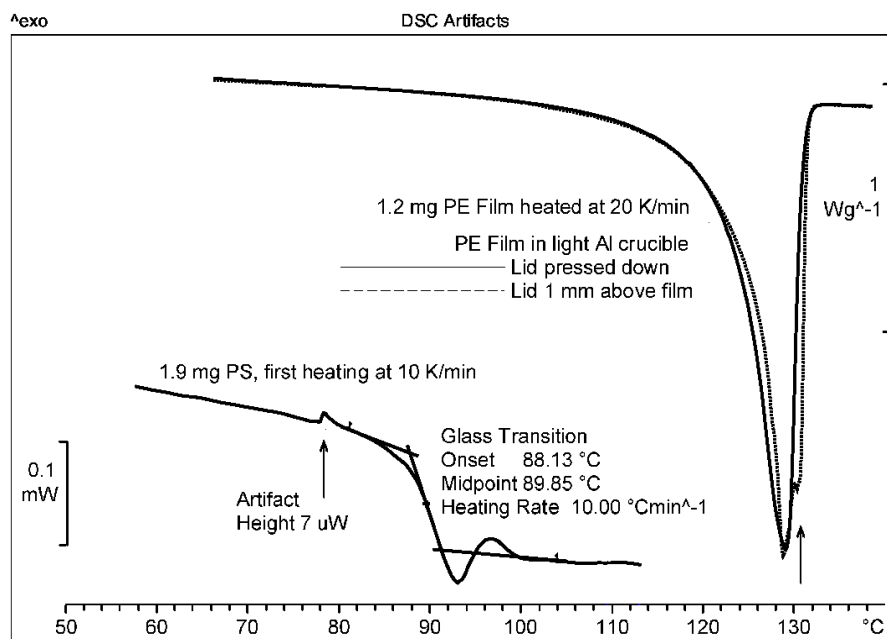


Figure 7.20. Above: The dashed line shows the DSC curve of a PE film that had not been pressed down firmly in the crucible. The artifact (arrow) arises because the film was free to twist and warp within the crucible. The continuous curve shows the "correct" melting curve, obtained from the same PE film after it had been pressed down on the bottom of the crucible using the lid of a light aluminum crucible. Below: DSC heating curve of 1.92 mg polystyrene. The artifact at about 78 °C is caused by the thermal expansion of the aluminum crucible.

7.5.2 Interpreting Isothermal DSC Curves

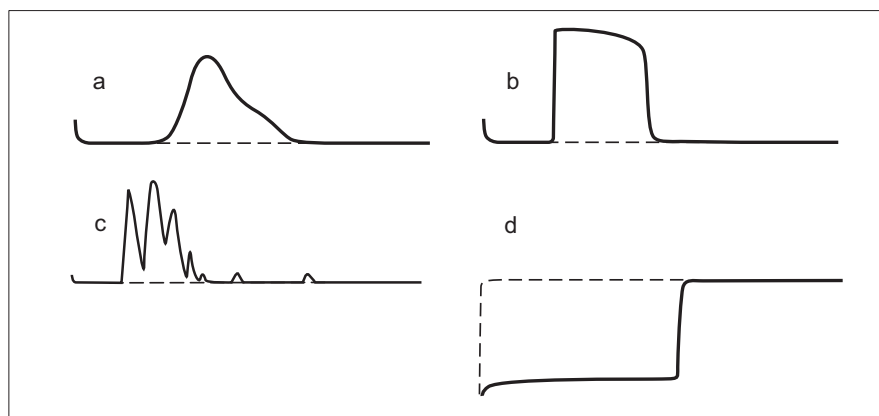


Figure 7.21. Isothermal physical transitions.

- a: Crystallization of a polymer, e.g. polypropylene cooled from the melt, T_{iso} is 130 °C (often with a shoulder).
- b: Crystallization of a pure metal.
- c: Enantiotropic reverse transition of the high temperature to the low temperature modification (the crystallization of a melt consisting of separate drops of a pure substance would look like this).
- d: Evaporation of a solvent about 10 K below the boiling point in a crucible with a 1-mm hole in the lid.

At constant temperature, the crystallization rate of a substance that crystallizes well (b) and the evaporation rate (d) remain practically constant until the end of the process.

Isothermal DSC is used in the following fields:

- The study of crystallization processes including polymorphism.
- Desorption, evaporation and drying.
- Chemical reactions such as autoxidation, polymerization or thermal decomposition.

Isothermal DSC measurement curves are usually easier to interpret than dynamic measurement curves:

An important advantage of isothermal measurements is the fact that an effect can be measured almost free of any interferences (other effects occur at other temperatures).

Changes in the heat capacity of the sample are of course not detected unless quasi-isothermal methods are used such as the isothermal step method [3], or temperature-modulated DSC (ADSC), in which the temperature fluctuates slightly round a mean value [4] or IsoStep® [5]. Because changes in the heat capacity of a sample are not visible in ordinary isothermal curves, baselines are exactly horizontal (except in the initial transition region from dynamic to isothermal).

All isothermal DSC curves approach 0 mW asymptotically at the end of the reaction.

Strictly speaking, only the DSC furnace is isothermal, the sample however “isoperibolic” because it is coupled to the isothermal furnace via the thermal resistance of the DSC sensor. For example, if the thermal resistance is about 0.04 K mW^{-1} , the sample temperature deviates by about 0.4 K from the temperature of the furnace at a heat flow of 10 mW. When the DSC signal reaches zero during the course of the effect studied, the sample temperature equals the furnace temperature.

Isothermal measurements are often performed rather differently to dynamic measurements so we will now summarize the main points.

There are two possible ways by means of which you can raise the temperature of the sample as quickly as possible to the desired temperature for isothermal measurements:

1. Preheat the measuring cell for several minutes at the desired temperature. Insert the sample crucibles using the automatic sample robot. Using this method, the sample reaches the programmed isothermal temperature reproducibly to within 0.1 K in about half a minute. This applies to the light aluminum crucibles and the standard aluminum crucible. Equilibration and thus the transition period take longer with heavier crucibles such as the high-pressure crucible.

If a sample robot is not available, you can introduce the crucible manually even more rapidly (with a bit of practice). This manual method allows you to thermally pretreat the sample. For example, you can shock-cool a sample to a glass in liquid nitrogen and then allow it to crystallize isothermally in the DSC. Alternatively, you can premelt the sample at 200 °C and then allow it to crystallize in the DSC, for example at 130 °C. In the market support laboratory, we use an old DSC20 measuring cell as a very accurate furnace for thermal pretreatment.

2. Raise the temperature of the measuring cell with the sample already inserted to the desired isothermal temperature using a dynamic segment. The advantage of this method is that almost any thermal history can be reproducibly preprogrammed (an advantage with routine measurements). The disadvantage is that it can take several minutes to reach the isothermal temperature and to stabilize (i.e. the transition period is longer). This method is limited by the maximum possible heating and cooling rates of the measuring cell.

If you want to evaluate the measured reaction free of any interference in the transition region from the dynamic to the isothermal transition region, you can correct the measurement curve by deconvolution. A better way is to subtract the curve of an inert sample of similar heat capacity measured using the same method (or a second measurement of the reacted sample).

7.5.2.1 Physical Transitions

Typical examples of physical transitions are:

Isothermal crystallization below the melting point, for example in Figure 7.21a polypropylene at 130 °C, or in Figure 7.22 (above right) indium at 155.9 °C. Compared with dynamic cooling, larger crystallites with few defects are formed.

Isothermal melting in Figure 7.22 above left. Using several isothermal steps, you can try to carefully approach the temperature of thermodynamic equilibrium of the liquid and solid phase (the melting and crystallization rate is 0, i.e. the heat flow is 0).

Isothermal monotropic transition below the melting point of the metastable modification. You can transform the sample completely to the stable form, for example if you want to determine its enthalpy of fusion.

Isothermal enantiotropic reverse transition below the equilibrium temperature. This provides an insight into the bizarre kinetic behavior of the sample (Figure 7.23).

Isothermal evaporation (Figure 7.21d) below the boiling temperature or sublimation below the melting temperature. A volatile component can be completely removed to investigate the residue in a dynamic measurement.

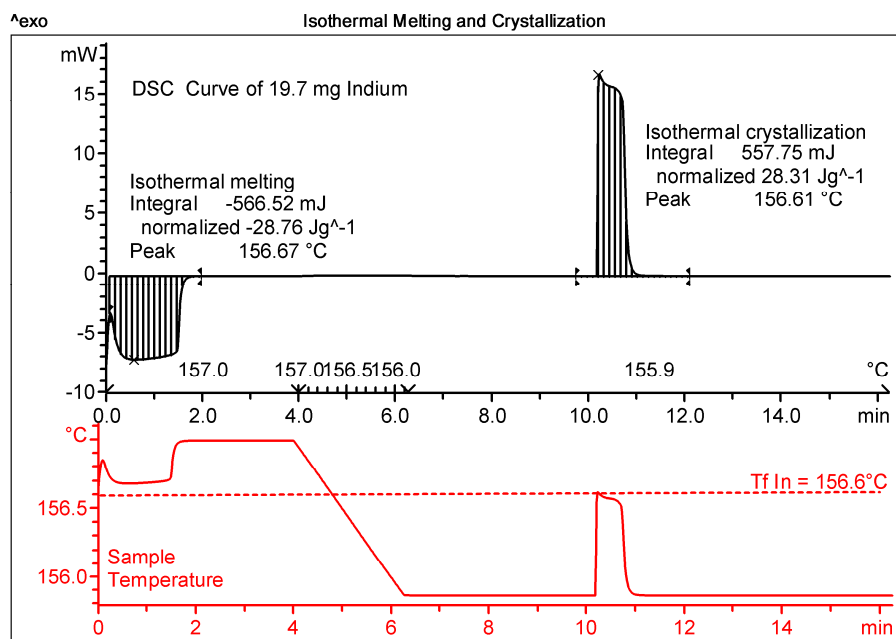


Figure 7.22. Above: The indium sample was inserted into the preheated measuring cell at 157.0 °C. The sample almost immediately begins to melt. It was then cooled to 155.9 °C at 0.5 K/min. Isothermal crystallization begins after about 4 min. Below: The curve displays the sample temperature. Because thermal resistance between the DSC sensor and the indium sample is not exactly reproducible, the measured melting temperature is 0.06 K higher than the solidification temperature.

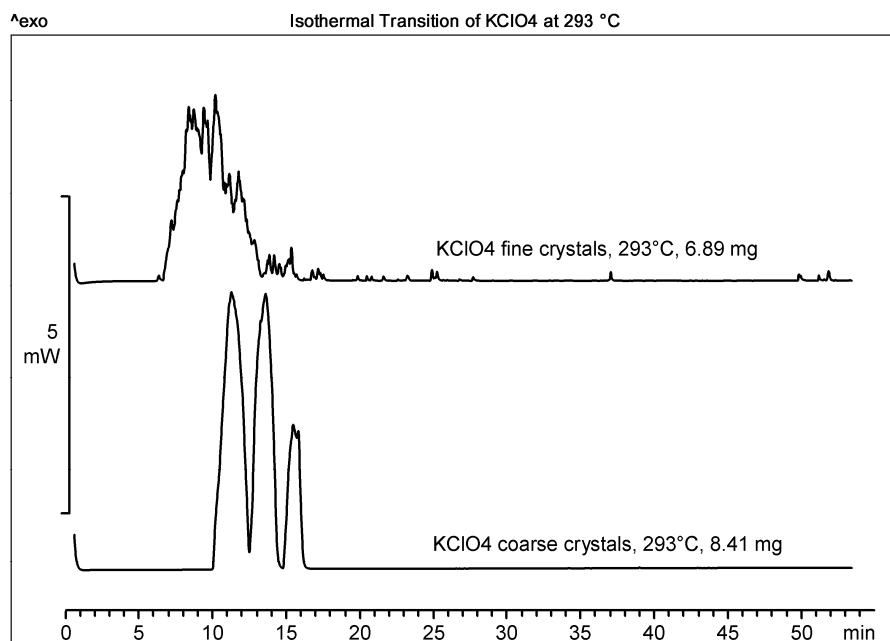


Figure 7.23. The enantiotropic reverse transition of the high-temperature form of potassium perchlorate measured at 7 K below the equilibrium temperature. The kinetics shown by the large number of fine crystals (above) is quite different to the kinetics of the small number of coarse crystals (below). In particular, the finest crystals have an induction period of almost an hour. Samples containing a large number of very fine crystals yield an almost smooth bell-shaped curve because of the large number of individual crystals (statistics).

7.5.2.2 Chemical Reactions

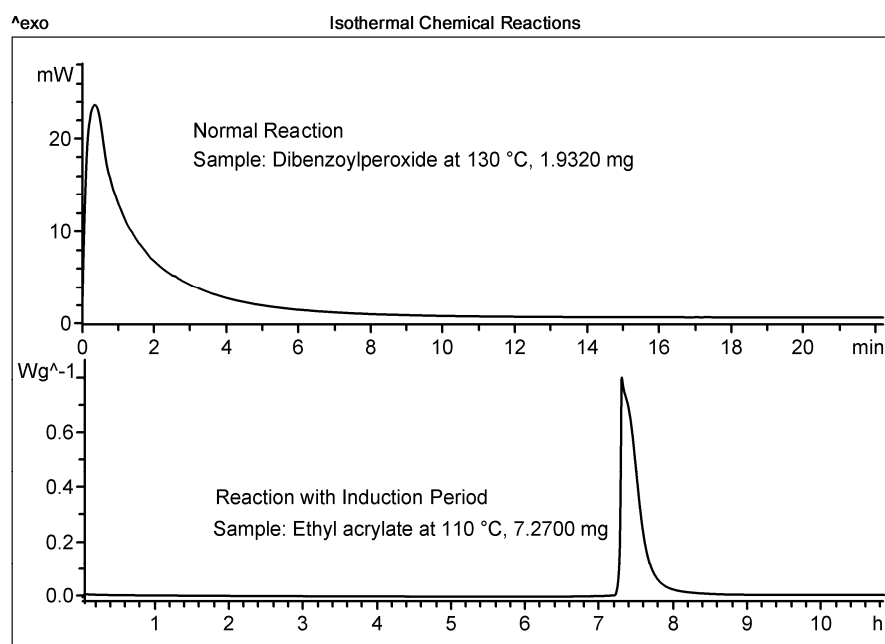


Figure 7.24. Above: The “normal” course of the decomposition reaction of dibenzoyl peroxide dissolved in dibutyl phthalate in an aluminum crucible with a 50- μ m hole in the lid. The rate is highest at the beginning of the reaction when the concentration of the unreacted starting material is greatest. Afterward, the reaction rate decreases asymptotically to zero. Below: An example of a reaction with an induction period of more than seven hours at 110 °C. During the induction period, nothing appears to happen to the ethyl acrylate (in fact, a stabilizer is consumed). After this, the polymerization reaction rapidly reaches the maximum rate.

So-called “normal” chemical reactions begin immediately on reaching the reaction temperature. The reaction rate then steadily decreases as the concentration of starting materials decreases (Figure 7.24, above). Autoaccelerating reactions (autocatalytic or inhibited through the addition of stabilizers) first have an induction period (Figure 7.24, below) in which nothing appears to happen (the DSC signal is certainly less than about 0.1 mW). The reaction rate then increases relatively rapidly to its maximum value after which it decreases in the same way as in a “normal” reaction.

Isothermal measurements are very useful for the detection of autoaccelerating processes that are not so easy to control and that are difficult to recognize using a dynamic temperature program. Preliminary isothermal measurements are usually performed at a temperature about 40 K below the onset of the dynamic measurement.

The isothermal measurement of the OIT (Oxidation Induction Time) is often used to compare the oxidation stability of polyolefins or petroleum oils. The measurement is usually terminated on reaching a threshold value of about 5 mW because only the induction time (i.e. the onset) is of interest. The measurement can also be performed under increased pressure, for example at 3 MPa in a high-pressure DSC, in order to prevent sample material evaporating at the measurement temperature of around 200 °C.

Thermosetting reaction resins are often cured isothermally and the glass temperature determined afterward.

Isothermally measured reaction peaks provide a valuable direct insight into reaction kinetics.

7.5.3 Final Comments on Interpreting DSC Curves

If you are uncertain about the interpretation of the DSC curve, you should consider the use of other thermoanalytical methods. These include for example:

- Thermogravimetric analysis, ideally in combination with DTA or SDTA.
- Thermomechanical and Dynamic Mechanical Analysis.
- Analysis of evolved gaseous substances (EGA, Evolved Gas Analysis) using mass spectrometry (MS) or Fourier transform infrared spectroscopy (FTIR).
- Observing the sample using the hot-stage microscope (TOA, Thermo-Optical Analysis in the FP82 or using the FP84 with simultaneous DSC).
- Other chemical or physical investigations depending on the type of sample. If necessary, this can be done by quickly cooling the sample and performing the analysis each time a thermal effect occurs.

Note: DTA and SDTA curves are interpreted in a similar way to DSC curves. There are of course limitations due the lower sensitivity.

7.6 DSC Evaluations

Most evaluations involve

- the determination of characteristic temperatures and
- the calculation of enthalpy changes (heat conversion). Enthalpy changes correspond to areas, for example, peak areas under the DSC curve calculated by integration with respect to time.

Further evaluations concern the calculation of

- the conversion curve (conversion as a function of temperature or time),
- enthalpy (enthalpy as a function of the temperature or time),
- the specific heat capacity,
- purity, as well as
- kinetic data and predictions of the rates of chemical reactions.

7.6.1 Characteristic Temperatures

The temperature values assigned to DSC effects are usually determined as the points of intersection of lines drawn to a curve (baselines and tangents). Various different standards define how to do this.

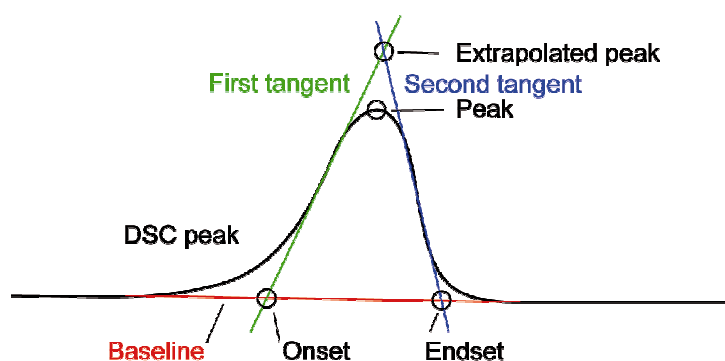


Figure 7.25. Characteristic points of a DSC peak (temperatures with dynamic measurements, times with isothermal measurements). The difference between the peak temperature and the extrapolated peak temperature can sometimes be quite large. The two points of inflection are not drawn.

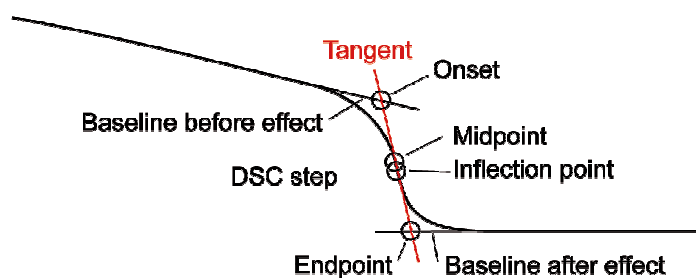


Figure 7.26. Characteristic temperatures of a DSC step, for example due to a glass transition. The difference between the inflection point and the midpoint can be quite large depending on the shape of the curve. The midpoint is defined in different ways: the STAR[®] default evaluation of the glass transition uses the point of intersection of the DSC curve with the bisector of the angle between the two baselines, while ASTM E1356 uses the mean value of the onset and the endpoint.

7.6.1.1 Onset

The onset or extrapolated starting temperature is often evaluated. It is defined as the point of intersection of a baseline before the thermal effect with a tangent. For pure non-polymeric materials, this value corresponds to the melting point.

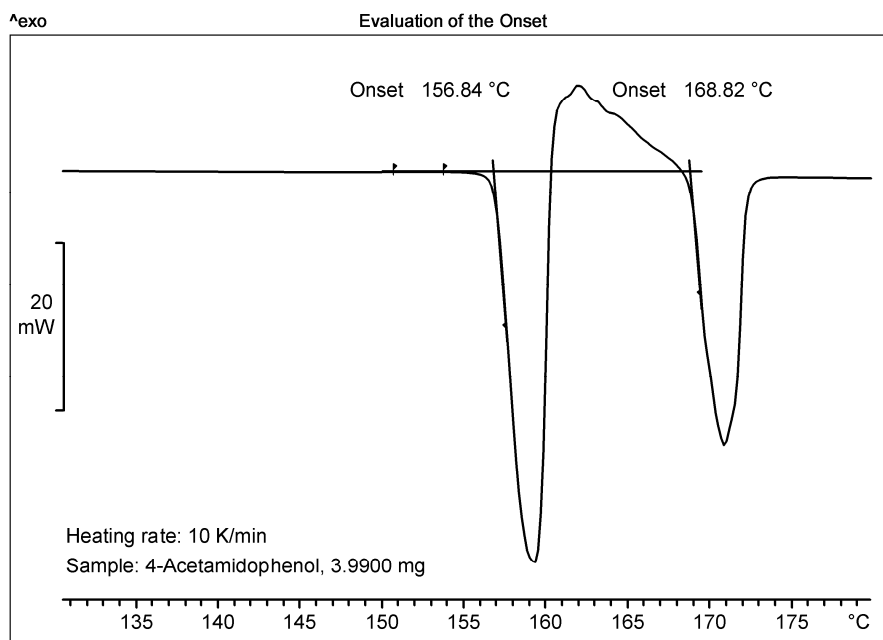


Figure 7.27. The sample is polymorphic and exhibits two DSC melting peaks. To evaluate the two melting temperatures, both onsets have to be determined. The baseline used to determine the second onset is the one used to evaluate the onset of the first peak and not one drawn during the exothermic recrystallization that occurs between the melting peaks.

7.6.1.2 Onset with Threshold Value

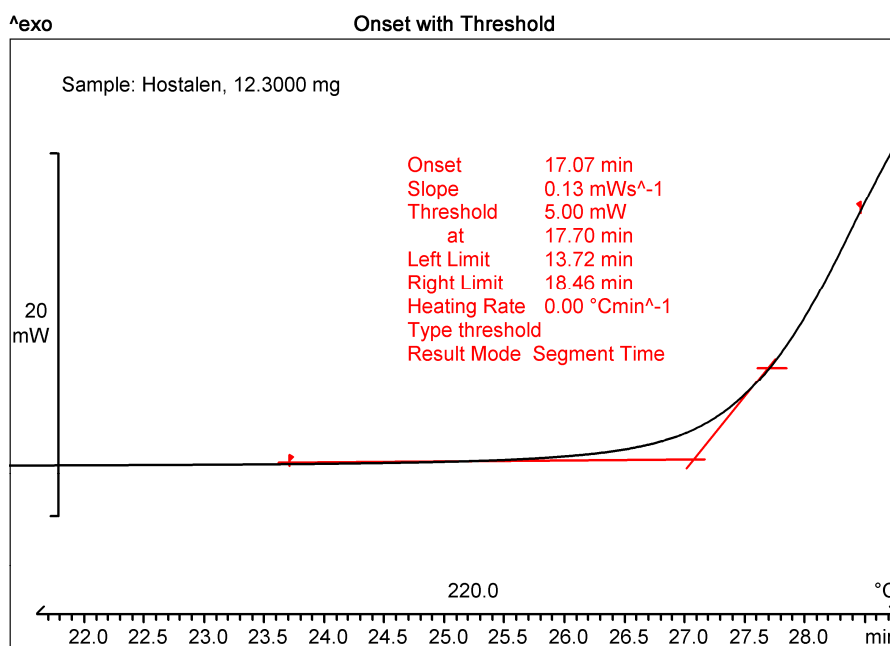


Figure 7.28. The DSC curve of a polyethylene sample measured isothermally at 220 °C in oxygen (the heating and temperature equilibration periods are not shown). After an induction period, the exothermic oxidation reaction begins. There are standards defined for the onset according to which the tangents must be drawn at a certain signal height. In this example, the threshold value chosen was rather large (5 mW). The result obtained (17.07 min) does not agree with the abscissa (about 27 min) because the induction time is measured from the time when the atmosphere is switched to oxygen.

At the onset, the optional results available are

- the slope of the tangent in mW/s, the threshold selected and the time taken to reach the threshold,
- the evaluation limits used,
- the heating rate in the evaluation range,
- the onset type, that is a tangent at the threshold value or at the point of inflection (steepest part), and
- the results mode segment time.

Relative thresholds given in % of the signal size can also be used.

7.6.1.3 Glass Transition

Amorphous materials do not have a melting point but exhibit a glass transition. An introduction to the theory of glass transitions can be found in Chapter 12, The Glass Transition.

At the glass transition, the DSC curve shows a step due to the change of c_p of the sample. In addition, an endothermic relaxation peak can occur with physically aged samples.

The sample is usually measured at a heating rate of 10 K/min. Other heating rates (also cooling rates) can be used. The results are to some extent however influenced by the heating rate used.

Procedure:

1. Select the optional results and standard test method, e.g. Δc_p and ASTM.
2. Set the evaluation range (baseline limits).
3. Choose either the glass transition evaluation or the glass transition with relaxation peak evaluation. The software calculates
 - the two tangential baselines before and after the effect,
 - the bisector of the angle between the two baselines (not shown) and
 - the inflectional tangent through the point of greatest slope of the DSC curve in the evaluation range.

If the tangents do not fit properly, they can be changed using the mouse.

The standard results are

- the onset temperature at the point of intersection of the left baseline with the inflectional tangent, and
- the midpoint at the point of intersection of the angle bisector with the DSC curve (“+” sign on the DSC curve).

Note: If the point of inflection occurs significantly after the intercept of the bisector with the DSC curve (with enthalpy relaxation this is often the case), the onset may be higher than the midpoint!

Optional results:

- Peak: extrapolated relaxation peak temperature (only a glass transition with relaxation).
- Endset: temperature at the point of intersection of the right inflectional tangent of the relaxation peak with the right baseline (only a glass transition with relaxation).
- Endpoint: temperature at the point of intersection of the inflectional tangent with the right baseline.
- Point of inflection: temperature at the point of inflection, which is marked with an “X” on the curve. In addition, the slope is given at the point of inflection.
- Difference in c_p between the onset and the endpoint:

$$\Delta c_p = \left| \frac{\Phi_2 - \Phi_1}{m \beta} \right| \quad (7.9)$$

- Φ_1 and Φ_2 are the DSC signals at the onset and the endpoint, m is the sample mass, β is the heating rate.
- Variation according to DIN53765: Instead of the inflectional tangent, a tangent is drawn iteratively to the DSC curve in such a way that it touches the DSC curve “at half height” between the points of intersection with the baselines. This tangent is not drawn but the midpoint determined in this way is shown and marked with a “Δ”. The c_p difference between the DIN onset and the DIN endpoint is also given.
- Variation according to ASTM D3418/IEC1006: The midpoint lies on the inflectional tangent in the middle between the onset and endpoint (often outside the DSC curve). It is marked with an “◇”. The midpoint therefore corresponds to the mean of the onset and endpoint. In addition, the c_p difference between the tangents at the midpoint is shown (Φ_1 and Φ_2 are the DSC signals of the two tangents at the midpoint). The c_p difference is therefore proportional to the amorphous content of the sample.
- Glass transition according to Richardson: This “fictive” glass temperature is marked with an “□”. In addition, the c_p difference from the distance between the tangents at the “fictive” glass transition temperature is given (Φ_1 and Φ_2 are the DSC signals of the two tangents at the “fictive” glass transition temperature).
- Furthermore, the evaluation limits and the heating rate are also available.

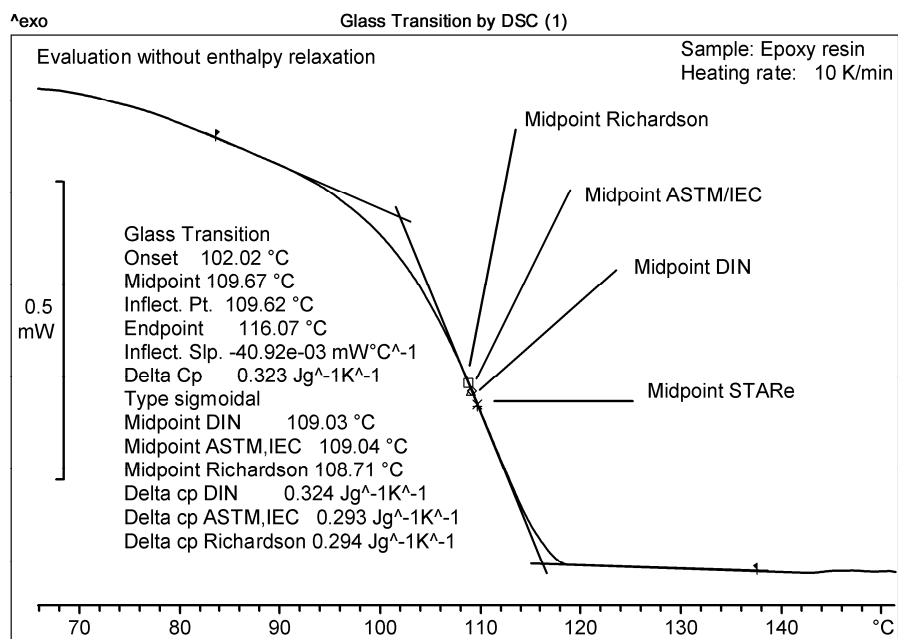


Figure 7.29. If no enthalpy relaxation occurs, the midpoints lie close to one another.

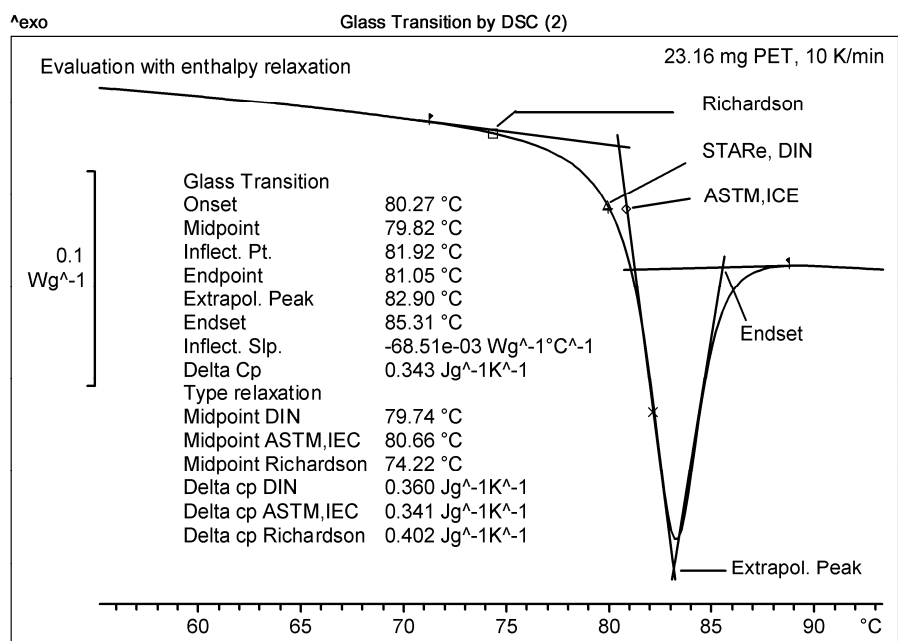


Figure 7.30. If the point of inflection is shifted to higher temperatures by the relaxation peak, large differences between the midpoints occur depending on the different methods. Evaluation with the relaxation peak gives two additional optional results: the extrapolated peak and the endset.

7.6.2 Enthalpy Change by Integration of the DSC Curve

$$\Delta H = \int_{t_1}^{t_2} \frac{dH}{dt} dt \quad (7.10)$$

The DSC curve is the graphical display of the heat flow Φ (or dH/dt) that flows to the sample. The integral with respect to time corresponds to the enthalpy of conversion, ΔH . DSC curves plotted against temperature are also always integrated with respect to time. The area integrated is that between the DSC curve and a baseline.

The following procedure is recommended for integration or peak area determination:

1. Define the type of baseline.
2. Select the desired results: for example, integral normalized to sample mass, onset, peak height (see Figure 7.36).
3. Define the evaluation range (integration and baseline limits).

The first attempt is usually not optimal, in particular the baseline limits and baseline type often have to be redefined. Normally, a baseline begins tangentially to the measured curve before the effect, and rejoins the curve tangentially after the effect. Exceptions to this rule occur, for example, when substances melt with decomposition (Figure 7.33, above right).

7.6.2.1 Baselines

Choosing the right baseline is crucial for the evaluation of a transition or reaction [6].

The interpolated baseline for the determination of transition enthalpy or reaction enthalpy leaves the DSC curve tangentially before the thermal effect and rejoins the curve in the same way after the effect. This is illustrated in Figure 7.31.

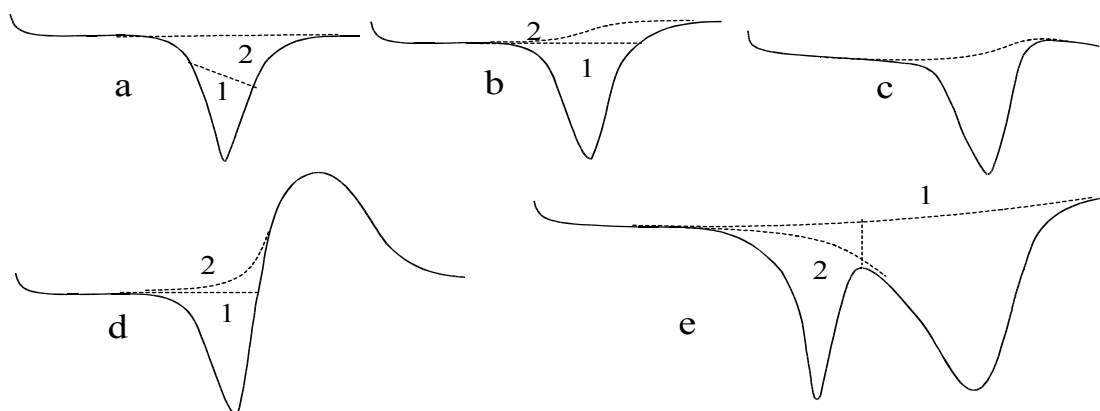


Figure 7.31. DSC baselines. **a**: 1 nonsensical; 2 good (straight line); **b**: 1 unsatisfactory (horizontal straight line); 2 good (integral baseline, possibly **Spline**); **c**: good (tangential integral baseline, possibly **Spline**); **d**: melting with exothermic decomposition, 1 good (straight line to the point of intersection with the DSC curve); 2 rather arbitrary because the DSC curve is the sum of all simultaneously occurring processes; **e**: two overlapping peaks, e.g. the eutectic and melting peak of the main component, 1 good (perpendicular onto the **Spline** baseline across both peaks), 2 possibly also good (peak interpreted as sitting on the second peak, **Spline** baseline); this interpretation makes the first peak smaller at the cost of the second peak.

Baseline type	Description	Typical DSC application
Line	This is a straight line that joins the two evaluation limits on the measured curve. This is the default baseline.	Reactions, without abrupt c_p changes, which exhibit a constant increase in c_p or constant c_p .
Tangential left	This is the extended tangent of the measured curve at the left evaluation limit.	Integration of a melting peak on a curve with subsequent decomposition of the substance.
Tangential right	This is the extended tangent of 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, Melting of plastics, 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). This bow-shaped or S-shaped baseline is based on the tangents left and right.	With overlapping effects.
Integral tangential	This is the baseline calculated in an iterative process in which the integral between the measured curve and a temporary baseline is calculated and normalized between the evaluation limits on the measured curve. 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 type would possibly intersect the DSC curve and lead to large integration errors depending on the limits chosen.
Integral horizontal	This is the baseline calculated in an iterative process in which the integral between the measured curve and a temporary baseline is calculated, and normalized between the evaluation limits on the measured curve. This S-shaped baseline always begins and ends horizontally.	Samples whose heat capacity changes markedly, e.g. through vaporization and decomposition. The Line baseline type would possibly intersect 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 subtraction of a blank curve.	Determination of enthalpy changes including sensible heat.

Table 7.1. List of baseline types.

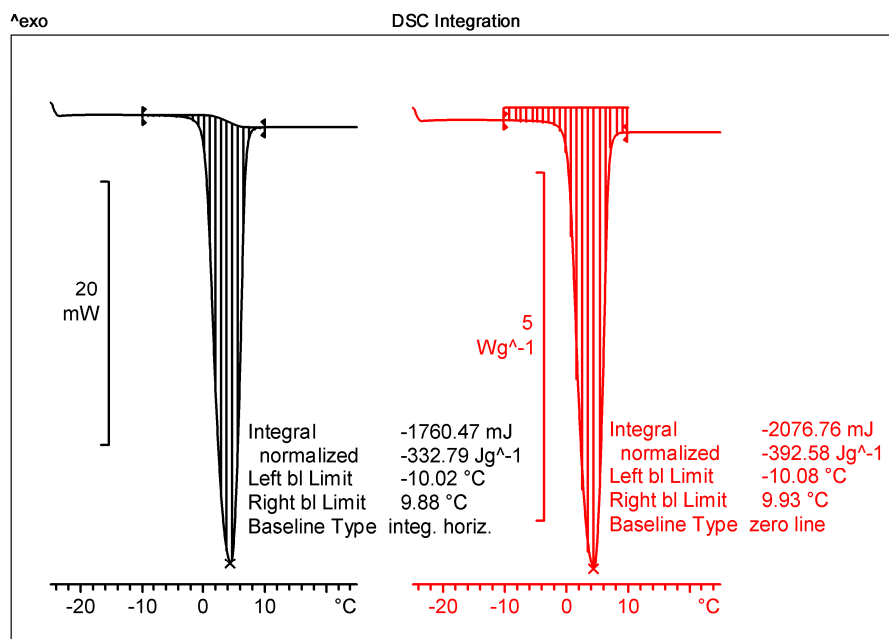


Figure 7.32. The two possibilities for peak integration. Left: Usually, we are concerned with the determination of transition and reaction enthalpies. The baseline defines the boundary that separates the transition or reaction enthalpy from the sensible heat. The example shown is the enthalpy of fusion of ice of 333 J/g. Right: Sometimes the total enthalpy change (sensible heat and latent heat) is of interest. In this case, the zero line (0 mW) is used as the baseline. To transform ice at -10 °C into warm water at +10 °C thus requires 393 J/g. Note: To obtain reliable total enthalpy changes, the DSC curve must be blank-curve corrected.

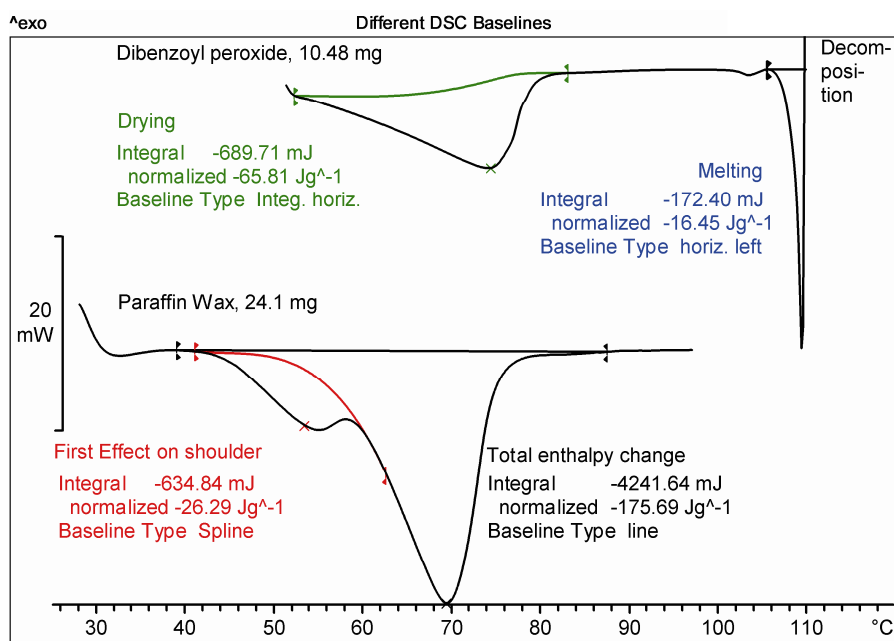


Figure 7.33. DSC baselines. Above left: **Integral horizontal** applied to a drying peak. Above right: **Horizontal left** applied to melting with decomposition (the right evaluation limit is shifted as precisely as possible to the intercept by temporarily zooming). Below left: **Spline** applied to an effect lying on a large peak. Below right: **Line** in a simple case.

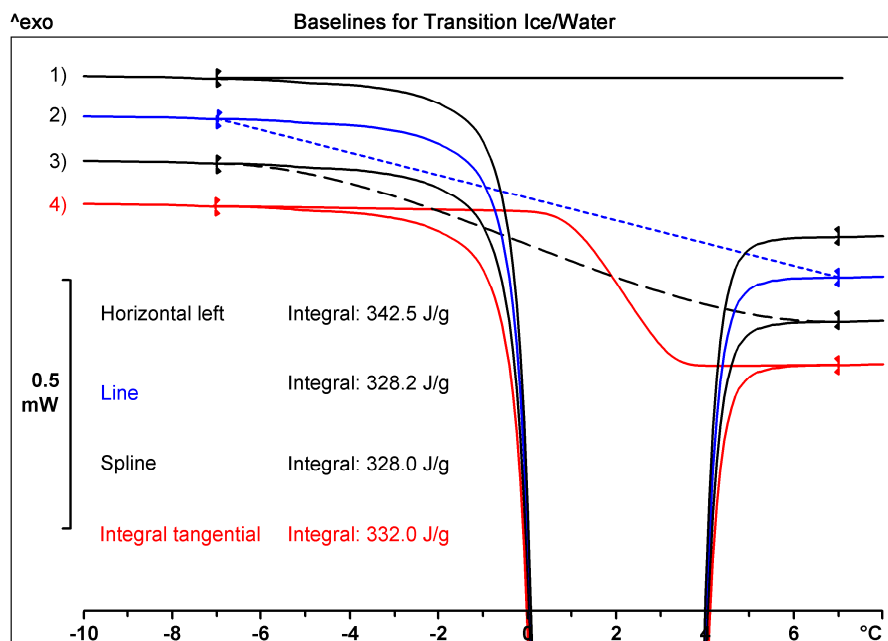


Figure 7.34. The DSC melting peak of ice to water measured at 5 K/min. The diagram shows only the part of the melting peak close to the baseline. The baselines before and after the peak are at different heights because the specific heat capacity of ice and water are very different. The **Horizontal left** baseline (1) yields a peak area that is too large. The straight line (2) is clearly unsuitable (no tangents, intersection with the DSC curve). The **Spline** baseline (3) is an improvement but intersects the DSC curve. An **Integral tangential** (4) or **Integral horizontal** baseline is best. It draws a baseline proportional to the peak area from the level before to the level after the peak.

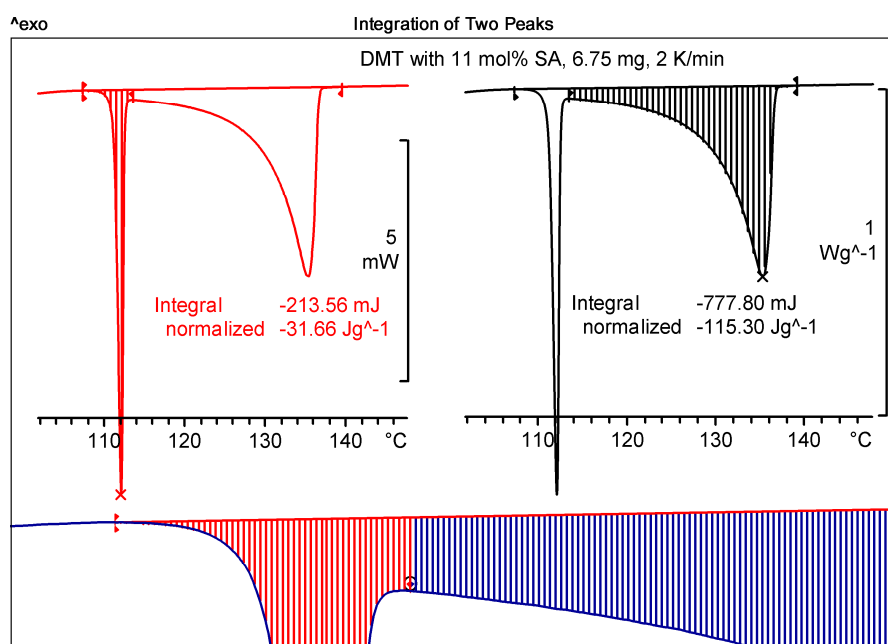


Figure 7.35. Peaks on a common baseline. The heating curve of a mixture of dimethyl terephthalate (DMT) and 11 mol% salicylic acid (SA) shows a eutectic melting peak at 112 $^{\circ}\text{C}$ and melting of the excess DMT crystals between 113 and 137 $^{\circ}\text{C}$. Above left: The diagram shows the integration of the eutectic peak. To do this, the right (upper) integration limit (red flag) was shifted to the left to the end of the eutectic peak. The (optional) shading shows the area integrated. Above right: The second peak is integrated in the same way as the first. The same curve was opened twice in order to explain things more clearly – you can of course perform both integrations on the same curve. Below: The curve shows how the transition region was temporarily zoomed to facilitate setting the integration limits (in the circle).

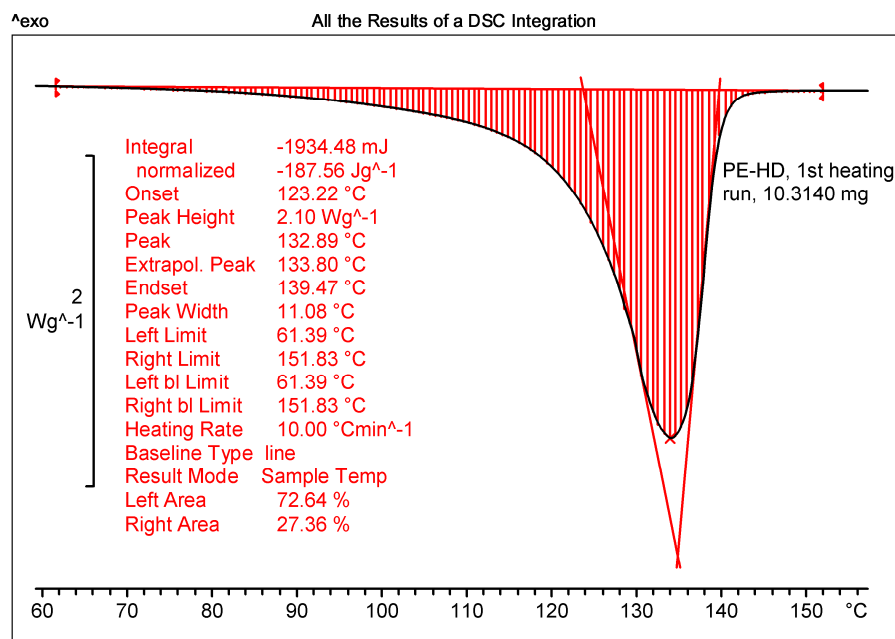


Figure 7.36. The figure shows the complete set of results from peak integration. The onset is the point of intersection of the inflectional tangent with the baseline. It does not have any particular physical importance for semicrystalline polymers because the position of the inflectional tangent depends largely on the thermal history of the sample. The peak height from the baseline is the greatest vertical distance of point on the curve point [marked with a cross] from the corresponding baseline point. It is given in the ordinate units selected, in this case W/g. The peak temperature (cross) should be distinguished from the extrapolated peak temperature (intersection of the onset and endset lines). The endset is the mirror image of the onset. The peak width (at half height) is a measure of the peak shape. Here, the limits set for the baselines and for the integration are identical. Since the heating rate and baseline type can influence the results, they are optionally available. In the sample temperature result mode, all the temperatures given are sample temperatures (for an isothermal measurement, time would make sense). Finally, the areas left and right of the tip of the peak (cross) are a measure of the peak shape.

7.6.2.2 Content Determination

If the component of interest of a mixture exhibits a first order phase transition or if it takes part in a chemical reaction (usually decomposition), the corresponding DSC peak areas are generally proportional to the content, C , of the component. The proportionality constant is the transition or reaction enthalpy, Δh .

$$C = \frac{\Delta h_{\text{measured}}}{\Delta h_{100\%}} \cdot 100\% \quad (7.11)$$

Components that can be measured in this way are for example:

- “Freezable” free water in biological samples using the ice melting peak, $\Delta h_{100\%} = 333 \text{ J/g}$.
- α -quartz in minerals using the solid-solid transition, $\Delta h_{100\%} = 7.5 \text{ J/g}$.
- Peroxide content of a mixture using the decomposition peak. $\Delta h_{100\%}$ can be determined by measuring a sample of known content.
- Moisture using the evaporation peak, $\Delta h_{100\%} = 2400 \text{ J/g}$.
- Degree of cure of thermosets (reacted part), or the non-reacted part using the postcuring peak. $\Delta h_{100\%}$ can be determined by curing a sample to completion in the DSC (if necessary at a lower heating rate to avoid decomposition).

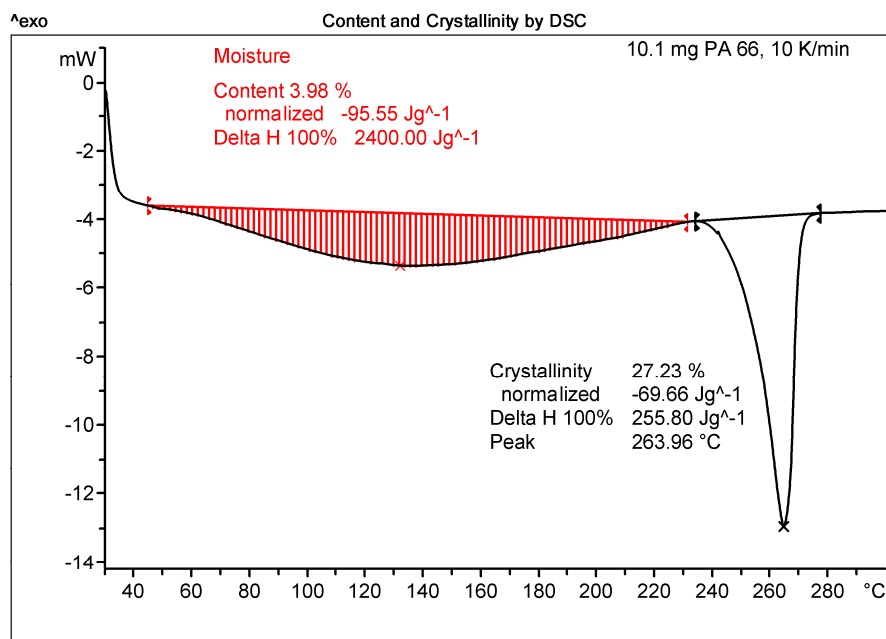


Figure 7.37. In this example, the moisture content, crystallite content, and the degree of crystallinity can be measured in a polyamide sample. Note: The degree of crystallinity referred to the dry sample was 28.4%.

Some important optional results of a content determination shown in Figure 7.37 are the

- specific change in enthalpy in J/g,
- $\Delta h_{100\%}$ used in J/g, and
- peak temperature as a qualitative feature.

7.6.2.3 Determination of the Degree of Crystallinity

The degree of crystallinity, C , that is, the content of the crystalline phase in a semicrystalline material that melts in the temperature range evaluated, is calculated just like any other content (see above). However, $\Delta h_{100\%}$ is not so easy to determine. Normally, “literature values” are used.

Table 7.2. shows literature values for a number of common plastics*.

Plastic	$\Delta h_{100\%} / \text{J g}^{-1}$	Melting peak temperature / $^\circ\text{C}$
Polyethylene low density, PE-LD	293.6	110
Polyethylene high density, PE-HD	293.6	135
Polypropylene, PP	207.1	165
Polyoximethylene, POM	326.2	180
Polyamide 6, PA 6	230.1	225
Polyethylene terephthalate, PET	140.1	255
Polyamide 66, PA 66	255.8	260

Table 7.2. Literature values for common plastics.

* Source: Advanced Thermal Analysis Laboratory, Oak Ridge National Laboratory (ORNL) and The University of Tennessee, Knoxville (UT)
Internet link: <http://athas.prz.edu.pl/Default.aspx?op=db>

Comment

The values of the enthalpies of fusion in the above table apply to 100% crystalline materials in a state of thermal equilibrium. They vary with the melting peak temperature.

7.6.3 Conversion

With samples that undergo a first order phase transition or a chemical reaction, it can generally be assumed that the degree of conversion or the conversion, α , increases proportionally to the peak area.

The conversion up to a certain time or at a certain temperature is equal to the partial area of the peak up to this point Δh_{part} , divided by the total area Δh_{tot} of the peak.

$$\alpha = \frac{\Delta h_{\text{part}}}{\Delta h_{\text{tot}}} \cdot 100\% \quad (7.12)$$

The type of baseline and the evaluation limits are defined as in integration. The result is displayed as a conversion curve and as a table:

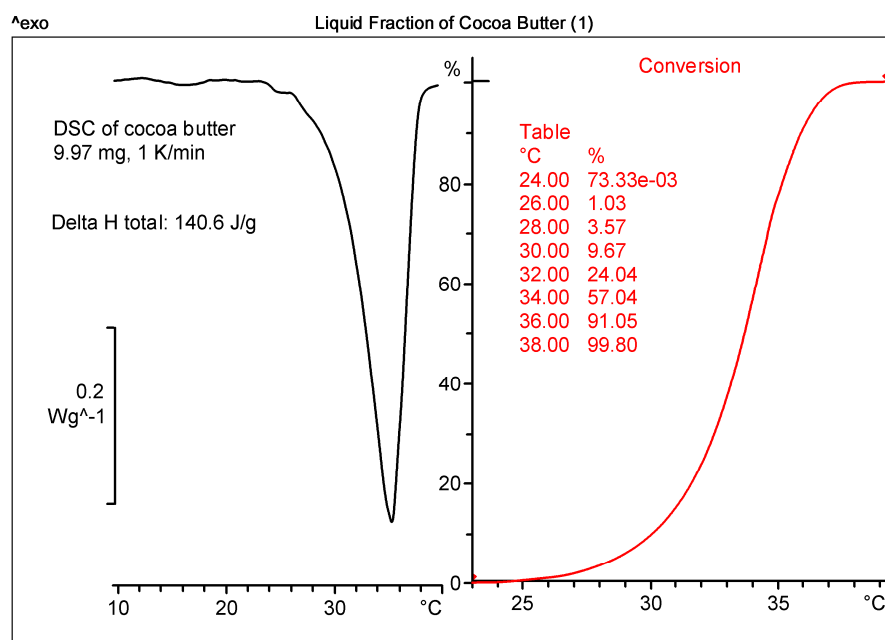


Figure 7.38. The figure shows the DSC melting curve (left) and the evaluation of the conversion as a function of the sample temperature (right). The STAR® software calculates the conversion according to eq 7.12 (shown as a table and a curve in the right diagram). The table is constructed using a starting value of 24 °C and an increment of 2 K. The software allows the two coordinate systems to be displayed separately.

In the case of edible fats, the conversion on melting is known as the “liquid fraction”. For example, Figure 7.38 shows that 91% of the cocoa butter has already melted at 36 °C.

Sometimes the conversion does not begin at 0% because the sample has already reacted to some extent, or in the case of edible fats is already amorphous. To obtain the correct conversion, eq 7.12 has to be modified to

$$\alpha = \frac{\Delta h_{\text{Lit}} - \Delta h_{\text{tot}} + \Delta h_{\text{part}}}{\Delta h_{\text{Lit}}} \cdot 100\% \quad (7.13)$$

In other words, the conversion is normalized with respect to a literature value. This is normally determined beforehand in an experiment using a sample that has not reacted.

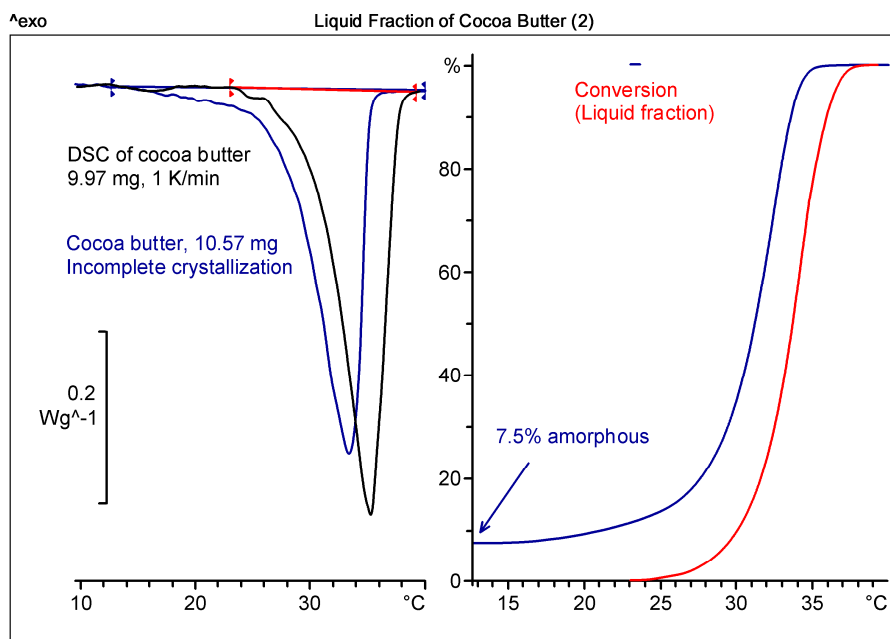


Figure 7.39. The blue DSC curve (left diagram) is the curve of incompletely crystallized cocoa butter. The blue curve of the liquid fraction (right diagram) that begins at 7.5% and ends at 100% is obtained by using a value of 140.6 J/g as the "literature value" for the completely crystalline sample (black DSC curve in the left diagram).

In some cases, one does not want the conversion curve to end at 100%, for example if you know that the reaction is not complete. This is the case for a reaction performed isothermally in which the DSC measurement is terminated to save time. The total enthalpy of conversion can be obtained in a dynamic experiment. The maximum conversion during the isothermal measurement, $\alpha_{\max}$, is then obtained by dividing the enthalpy of reaction of the incomplete reaction by that of the complete reaction.

In this case, eq 7.14 applies:

$$\alpha = \frac{\Delta h_{\text{part}}}{\Delta h_{\text{tot}}} \cdot \alpha_{\max} \quad (7.14)$$

7.6.4 Enthalpy

This evaluation is not only of interest to thermodynamic specialists but also to anyone who wants to determine the heat involved in heating or cooling processes (chemical engineering, injection molding). The enthalpy change from T_1 to T_2 of course corresponds exactly to the quantity of heat converted.

If the enthalpy at the start temperature of the evaluation is known, “absolute enthalpies” can be obtained through addition. If the molar mass of the sample is entered, the molar enthalpy change is obtained.

For the calculation of the enthalpy, a blank curve should always be subtracted. Blank curve subtraction compensates for any asymmetry of the measuring system.

For reliable enthalpy measurements:

- Use the standard aluminum crucible with lids.
After the measurement, check the underside of the sample crucible: it should be flat and not bow-shaped. This would introduce measurement errors and indicate that the pressure had increased during the measurement to an unacceptable level. Remedy: Perform a second measurement using a lower end temperature, or pierce the lid before sealing. If you use a pierced lid, you have to take into account that an additional endothermic effect occurs due to evaporation of part of the sample.
- Select two crucibles of equal mass (50 μg) for the blank and sample measurements. The mass of the reference crucible is not important; the crucible must not however be moved during a measurement series.
- It is easiest to use a method that includes automatic blank curve subtraction.
- If you measure two or three blank curves prior to an enthalpy determination, choose the “best” one for the automatic subtraction. This is usually the third one.
- The sample mass should be large enough to produce a signal of at least 10 mW.

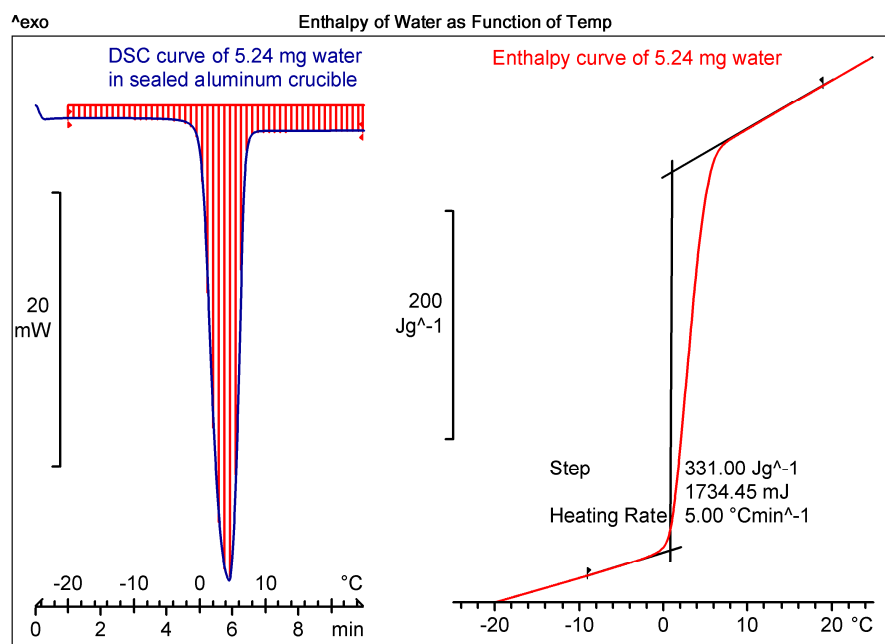


Figure 7.40. Left: The DSC curve of 5.24 mg ice in a hermetically sealed aluminum crucible measured at a heating rate of 5 K/min. The enthalpy evaluation covers the range -20 °C to 25 °C. The step at 0 °C corresponds to the melting of ice. The change in enthalpy function calculated using tangential step has a step height of 331 J g⁻¹. The original sloping tangent is drawn practically vertically using the mouse.

7.6.5 Specific heat capacity

Heat capacity

The heat capacity at constant pressure, C_p , (in contrast to C_v , the heat capacity at constant volume) is the amount of heat, dQ , necessary to raise the temperature of a body by dT (technical definition):

$$C_p = \frac{dQ}{dT}$$

It is expressed in units of Joule per Kelvin.

Since this amount of heat supplied causes a corresponding increase in the enthalpy, H , of the body, we can write the analogous equation (thermodynamic definition):

$$C_p = \frac{dH}{dT}$$

The heat capacity is thus the slope of the enthalpy-temperature function.

Note: Both definitions only apply in the absence of physical transitions and chemical reactions.

The specific heat capacity

The specific heat capacity at constant pressure, c_p , is the amount of heat that must be supplied to raise the temperature of 1 g of a compound by 1 Kelvin. Analogous to the heat capacity, we can write:

$$c_p = \frac{dQ}{dT} \frac{1}{m} \qquad c_p = \frac{dH}{dT} \frac{1}{m}$$

Note: These definitions were only valid in the absence of phase transitions and chemical reactions. Nowadays, this concept has been expanded. In the absence of phase transitions and chemical reactions, c_p is referred to as the baseline c_p . The deviation caused by phase transitions and chemical reactions is called the excess c_p and the sum of both is known as the total specific heat capacity.

The specific heat capacity is temperature dependent and can be measured by DSC. Usually c_p lies in the range 0.1 to 5 J g⁻¹ K⁻¹. During first order physical transitions, c_p is infinitely large (enthalpy change without a temperature change).

Applications: In industry, the specific heat capacity of compounds is used in the calculation of thermal processes. Examples: The amount of heat needed in heating and cooling processes in chemical reactors (process engineering), in spray drying, crystallization and in injection molding. The temperature function of the specific heat capacity of amorphous compounds indicates the glass transition.

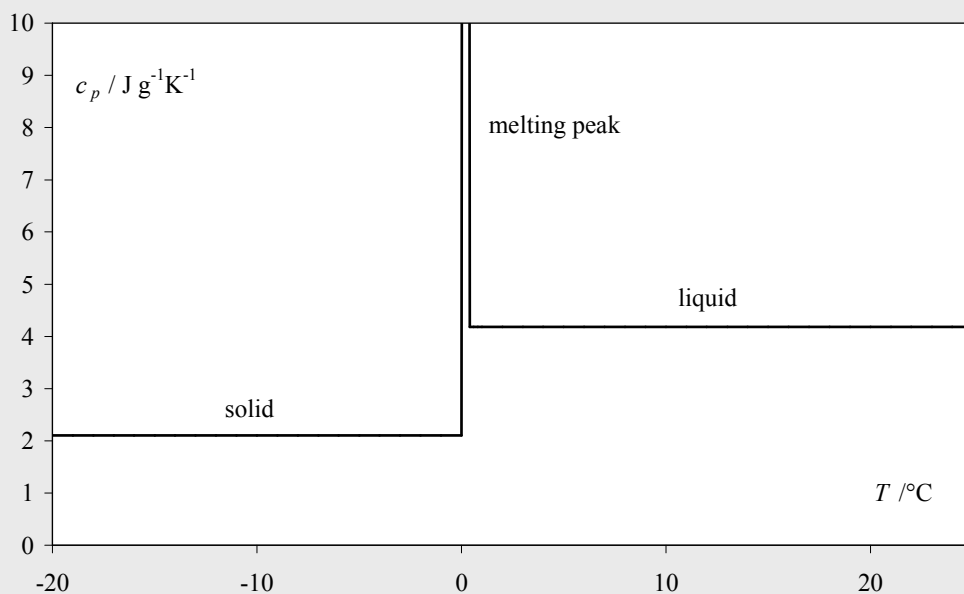


Figure 1. The diagram shows the temperature function of the specific heat capacity of water in the range -20 to +25 °C. The data used for the evaluation are: c_p (ice) 2.10 J/g K, c_p (water) 4.18 J/g K, enthalpy of fusion 333 J/g.

The direct method of determination is derived from the equation that defines the specific heat capacity. The numerator and denominator are differentiated with respect to time. The rate of change of enthalpy, dH/dt , is equal to the DSC heat flow, Φ . The rate of change of temperature, dT/dt , of the sample is the heating rate, β_s :

$$c_p = \frac{dH}{dT} \frac{1}{m} \rightarrow c_p = \frac{dH/dt}{dT/dt} \frac{1}{m} \rightarrow c_p = \frac{\Phi}{\beta_s} \frac{1}{m} \quad (7.15)$$

If no physical transitions or chemical reactions occur, the heating rate of the sample is equal to the heating rate of the temperature program. At the beginning of an endothermic effect, β_s is lower than β . In fact, with first order phase transitions, β_s is practically zero. At the end of the effect, however, β_s becomes greater than β .

$$\text{Since } T_s = T_r + \Delta T, \quad dT_s/dt = T_r/dt + d\Delta T/dt$$

$$\text{So that } \beta_s = \beta + d\Delta T/dt.$$

Here, $d\Delta T/dt$ is the slope of the DSC raw signal.

The specific heat measurement should always be performed using bank curve subtraction. This compensates for any asymmetry of the measurement system.

Recommendations for reliable c_p measurements:

- Use standard aluminum crucibles with lids.
After the measurement, check the underside of the sample crucible: it should be flat and not bow-shaped. The latter would introduce measurement errors and indicate that the pressure had increased during the measurement to an unacceptable level. Remedy: Perform a second measurement using a lower end temperature, or pierce the lid before sealing. If you use a pierced lid, you should take into account that an additional endothermic effect can occur due to part of the sample evaporating.
- Select two crucibles (with lids) of equal mass (50 µg) for the blank and sample measurements. The mass of the reference crucible is not important; the crucible must not however be moved during a measurement series.

- Heating rate: If no physical transitions or chemical reactions occur, 10 or 20 K/min is optimal, otherwise use 5 K/min.
- The temperature range should not be greater than about 200 °C.
- It is easiest to use a method that includes automatic blank curve subtraction.
- If you measure two or three blank curves prior to an heat capacity determination, choose the “best” one for the automatic subtraction. Usually the third (last) one is best.
- The sample mass should be large enough to obtain a signal of at least 5 to 10 mW.
- Liquid samples and flat disks make good thermal contact with the bottom of the crucible. The same applies to powders with a particle size of about 0.1 mm. Very fine powders, however, often contain a lot of air and become poor conductors of heat.

The definition of specific heat capacity originally applied to measurements in the absence of physical transitions and chemical reactions. Nowadays, the meaning has been extended and includes the total heat capacity, the baseline heat capacity and the excess heat capacity. This extends the application of the c_p determination. An example is shown in Figure 7.41.

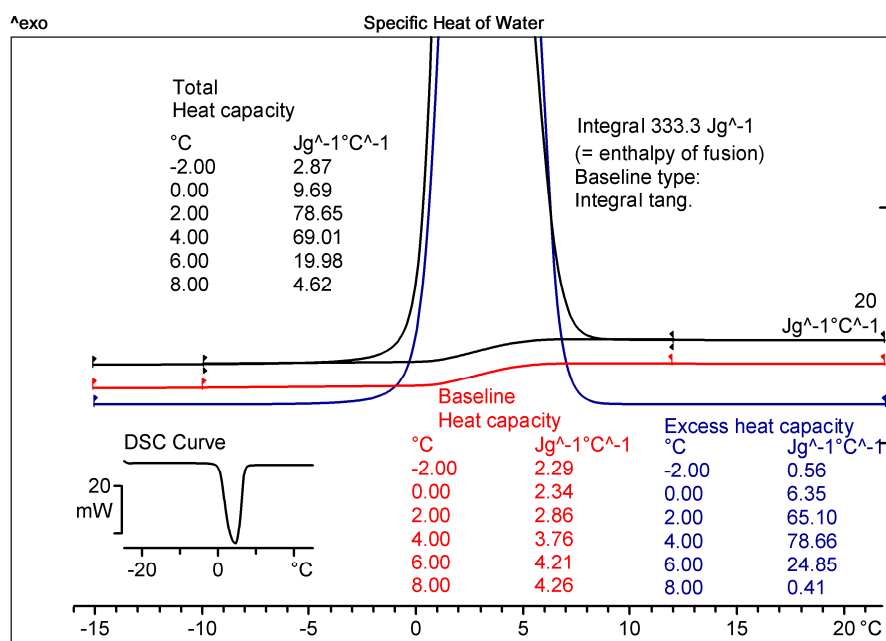


Figure 7.41. The c_p evaluation of the DSC curve from Figure 7.40 yields the total heat capacity (red curve and table). Integration with respect to temperature results in an enthalpy of fusion of 333 J/g. The red curve and table of the baseline heat capacity are obtained by replacing the peak by the tangential integral baseline. The blue curve of the excess-heat capacity is the result of the subtraction of the black curve minus red curve. This curve shows only the enthalpy of the transition.

The excess enthalpy of a c_p temperature function is determined by mathematical integration across the abscissa region.

7.6.5.1 c_p Using Sapphire

The temperature function of the calorimetric sensitivity was not so easy to take into account before the availability of computers. A comparative measurement was therefore frequently used which involved measuring a reference material (sapphire, single crystal alumina $\alpha\text{-Al}_2\text{O}_3$) under the same conditions as the sample. A simple calculation then allowed the unknown specific heat capacity of the sample to be obtained from the known specific heat capacity c_{ps} of $\alpha\text{-Al}_2\text{O}_3$ (eq 7.16).

$$c_p = \frac{\Phi}{\Phi_s} \frac{m_s}{m} c_{ps} \quad (7.16)$$

The same basic principles apply to the sapphire method as for the direct determination method (above). Choose three crucibles that weigh the same (50 μg , for the blank, sapphire and sample), or enter the crucible masses in the software before the experiment.

The method should begin and end with an isothermal segment of 5 min so that any isothermal drift can be compensated. If the temperature range of interest is greater than about 100 $^{\circ}\text{C}$, accuracy can be improved by splitting the range into smaller ranges using additional isothermal segments.

Experience has shown that dry polycrystalline α -aluminum oxide can also be used, for example in our tutorial sample No. 6, instead of the rather expensive 4.8-mm diameter sapphire disks, Order No. ME 17558).

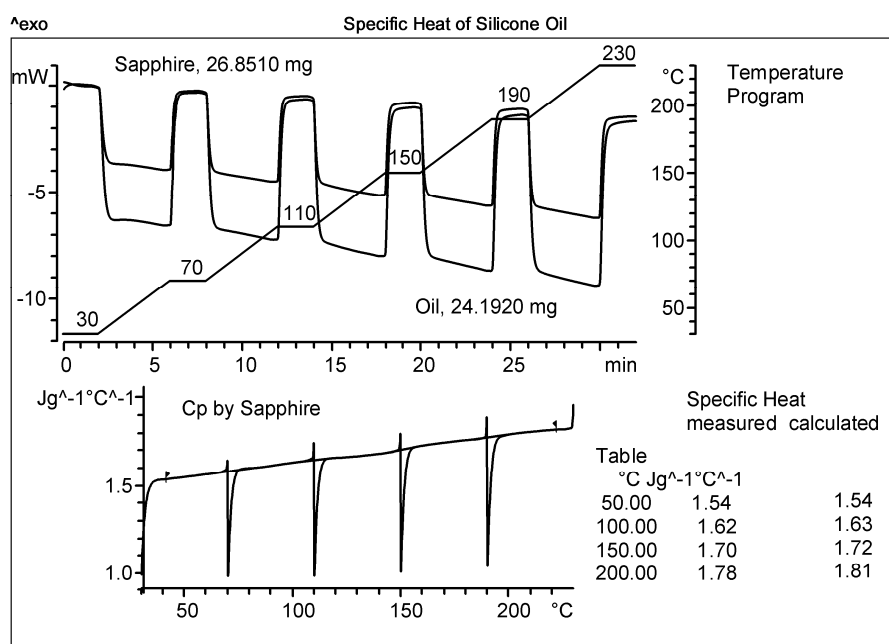


Figure 7.42. Sapphire method for the determination of specific heat. See text for details.

7.6.6 DSC Purity Determination

The theory of DSC purity determination is presented in more detail in Section 13.5 and in reference [7]. We recommend the following general procedure:

1. Check that the substance is suitable for purity analysis
2. Perform the measurement
3. Select the baseline
4. Perform the evaluation
5. Assess the results

Choosing the baseline: The **Horizontal right** baseline (after melting) is often preferred to the otherwise usual connecting line (Line). Horizontal right is the theoretically correct baseline to use because after the eutectic peak small amounts of pure substance continuously melt. If the substance decomposes slightly or exhibits a marked c_p change, it is better to use one of the integral baselines, and with more pronounced decomposition, **Horizontal left**. The linearization correction and the confidence intervals are smallest with the correct baseline.

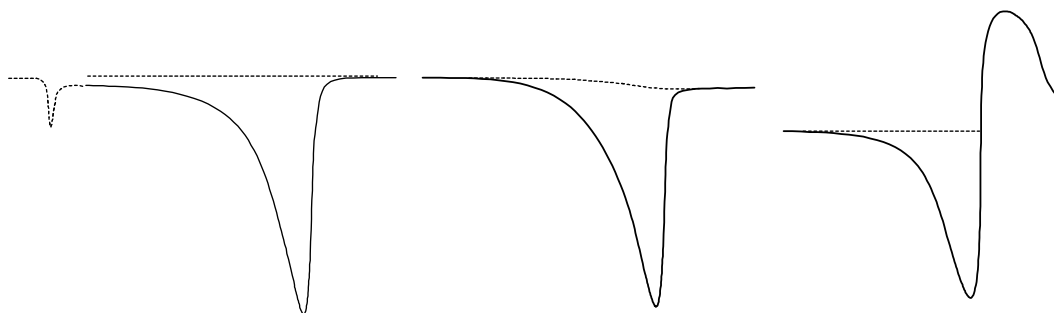


Figure 7.43. Schematic DSC curves of melting substances with recommendations for baselines. Left: Since the eutectic is usually not measured, the **Horizontal right** baseline is a good approximation. Middle: Because of the c_p change at the solid-liquid phase change, the right side of the peak may be shifted in the endothermic direction, so it is best to use the **Integral** or possibly the **Spline** baseline. Right: If melting is followed by marked decomposition, **Horizontal left** is recommended.

Performing the evaluation: Ideally the evaluation range should include sections of the baseline before melting and after the melting peak.

Concerning the purity settings:

The actual calculation of the results should only be done in a carefully selected part of the melting curve, in general between 10 and 50% of the peak height. The lower limit eliminates high concentrations of impurities in the liquid phase at the beginning of melting. The upper limit excludes data that has been recorded well outside equilibrium conditions. In principle, one can change the limits, for example to exclude an artifact.

Another definition of the limits uses the curve range between 10% and 50% of the total peak area. This is advantageous if the eutectic peak lies close to the pure melting peak (of course, only the latter peak is evaluated).

In any case, it is important to make sure that no artifacts occur between the two crosses, the region in which the calculation is performed.

The number of DSC curve points used in the calculation is usually 30. Another parameter is the molar mass of the main component. If this is not known, an estimated value can be used.

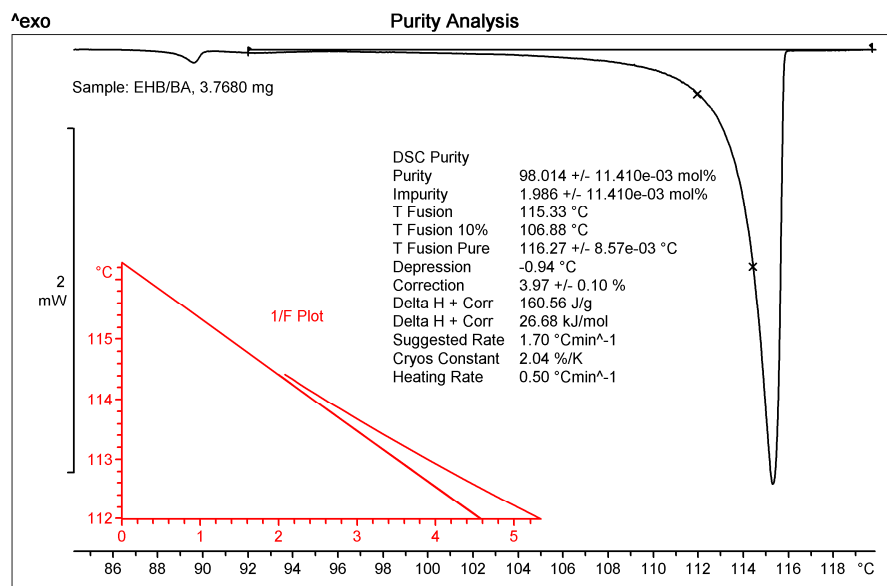


Figure 7.44. Purity analysis of a sample of ethyl hydroxybenzoate (EHB) containing benzoic acid (BA) as an impurity. The baseline is drawn horizontally from the right.

The minimal possible results are

- the purity x_2 in mol%, confidence interval of the purity,
- the clear melting point T_{fus} of the sample, and the
- van't Hoff plot (except using "Short", see Section 13.5.1).

In addition, several optional results are available, namely

- the evaluation limits left/right,
- the type of baseline used,
- the heating rate of the measurement, and the
- molar mass entered.

The detailed optional results include

- the impurity, $x_1 = 1 - x_2$,
- T_{fusion} 10%, corresponding to the liquidus temperature for a melted fraction of 10% (from the linear van't Hoff plot). This temperature corresponds roughly to the "start of melting" in the visual melting point apparatus, that is, the temperature at which the crystals begin to move (at a liquid composition of about 10%). The "melting range" stretches from this "start of melting" to the clear melting point,
- the extrapolated pure melting point T_0 . It characterizes the pure substance, which in some cases is not available,
- the melting point depression ($T_0 - T_{\text{fus}}$) due to the impurity present,
- the linearization correction, c , in % of the peak area. It should be between about -10 to +15% of the enthalpy of fusion,
- the enthalpy of fusion (with correction) in J/g and kJ/mol,
- the recommended heating rate. This is determined empirically from the peak shape, in order to prevent too severe non-equilibrium conditions between the solid and the liquid phases. The more impure the sample, the higher the heating rate can be (in contrast to ASTM E928: 0.3 to 0.7 K/min), and
- the cryoscopic constant: this is the concentration of impurity that would cause a melting point depression of 1 K.

The calculated confidence intervals for 95% probability give an indication of the quality of the fit and hence of the applicability of the van't Hoff equation. They must not, however, be regarded as "error limits" of the results.

Normally, the confidence intervals

- of the purity (and the impurity concentration) are in the range 0.01 to 0.2 mol%, whereby very pure substances often give relatively "bad" confidence intervals,
- of the extrapolated pure melting point are in the range 0.005 to 0.1 K and
- the linearization correction is in the range 0.02 to 5%.

Assessment of the results:

1. Is the calculation range marked by the two crosses, x---x free of artifacts, polymorphism peaks or eutectic peaks?
2. Does the van't Hoff plot look acceptable? Is the linearized curve practically straight (i.e. not S-shaped)?
3. Is the linearization correction between about -10 and +15% of the enthalpy of fusion?
4. Is the confidence interval of the extrapolated pure melting point less than 0.1 K?

Purity Plus: As shown in the theory in Chapter 13, Binary Phase Diagrams and Purity Determination, the simplifications that lead from eq 13.3 to eq 13.4 are only valid for low concentrations of impurity. It would make sense to use the original eq 13.3 for higher impurity concentrations (>2 mol%). In fact, such an evaluation procedure known as "Purity Plus" is available. As expected, it gives the same results for low impurity concentrations as those obtained from eq 13.4. It is interesting to note that the results for more impure samples do not deviate greatly. Purity Plus also allows you to enter the enthalpy of fusion of the pure main component (if it is known), so that this is not subject to measurement errors.

7.6.7 nth Order Kinetics

This kinetics model is based on simple theoretical principles (see information box and [8].) and provides "kinetic data" ($\ln k_0$, E_a and n) that is relatively easy to interpret. Predictions about the course of the reaction under other conditions are of course only true for simple chemical reactions. A further limitation is that it is only valid for reactions that exhibit one peak. These limitations do not apply to model free kinetics.

Kinetics

Chemical reaction kinetics is concerned with the rate of chemical reactions.

Introduction

Thermodynamics provides information about whether and in which direction a chemical reaction proceeds. It does not however tell you anything about the reaction rate, that is, the kinetics of the process.

The kinetics of a reaction is therefore determined by the rate of the actual chemical reaction (reaction kinetics) and by the rate at which starting materials and reaction products are transported in and out of the reaction zone (transport kinetics).

A reaction occurs spontaneously if the free enthalpy of the reaction is less than zero ($\Delta G < 0$). However, even with systems in which this condition is fulfilled, it is often observed that either no reaction or only a very slow reaction occurs. In fact, a system cannot simply change to a state of lower free enthalpy; it has to overcome a certain "reaction barrier". A mixture of 2 mol hydrogen and 1 mol oxygen (detonating gas) remains stable for years at room temperature. In a chemical reaction, two bonds have to be broken and new one made. Effects such as these primarily determine the barriers that oppose a spontaneous chemical reaction. As mentioned earlier (Section 4.8), temperature is a measure of the mean kinetic energy of the molecules of a substance. Since not all molecules have the same kinetic energy, the proportion that has sufficient energy to overcome the energy barrier increases steadily with increasing temperature.

Reactions in which the reactants only have to overcome one energy barrier are called elementary reactions. These are reactions that are assumed to occur in a single step and pass through a single transition state. In most cases, a reaction involves several elementary reactions during which the various intermediate products are created and then decompose. In this case, there are several energy barriers between the starting materials and reaction products. The overall reaction is therefore the sum of several individual reactions, each of which in turn exhibits its own typical time-dependent behavior.

The course of a reaction is determined by the reaction rate. This is defined as the relative change in the number of moles or the concentration of a particular reactant per unit period of time.

The rate of a reaction can therefore be determined by measuring the change in the concentration of a particular reactant. The changes in concentration of the other reactants can then be determined using stoichiometric coefficients. The parameters on which the reaction rate depends are

- the concentration of each reactant,
- the concentration of substances that do not participate in the reaction (e.g. catalysts or inhibitors), and
- the temperature.

To a first approximation, the reaction rate, r , can therefore be written as

$$r = f(c_1, c_2, \dots, c_n, T), \quad (4.3)$$

where c_i describes the concentration of the reactants and T the temperature.

According to Arrhenius, the temperature dependence of the reaction rate constant k has the form

$$k(T) = k_0 e^{-E_a / RT} \quad (4.4)$$

The quantity E_a in the Arrhenius equation is called the Arrhenius activation energy. Its value defines the height of the energy barrier that has to be overcome in the reaction. k_0 is called the pre-exponential factor.

Kinetic modeling in practice

Most chemical reactions consist of several elementary steps so that the overall reaction cannot be described by a rate equation of a particular order. If the different elementary reactions are known, a system of differential equations can be derived for the overall reaction that has to be solved numerically.

In practice, the elementary reactions are hardly ever completely known. It follows that quite often the kinetics of a particular reaction cannot be described using theoretical models.

In these cases, a very general reaction model is used to describe the dependence of the reaction rate $\frac{d\alpha}{dt}$ (the rate of change of the reaction conversion) on the temperature ($k(T)$ according to Arrhenius) and on the conversion α ($f(\alpha)$ according to the nth order):

$$\frac{d\alpha}{dt} = k_0 e^{-E_a/RT} (1-\alpha)^n \quad (4.5)$$

$k(T) \qquad f(\alpha)$

The parameters are determined from the measured data by multiple regression analysis. To do this, either the experimental data from a dynamic thermoanalytical measurement (i.e. measured using a temperature program) or from several isothermal measurements are evaluated.

The values found for the parameters k_0 , E_a and n can then be used to calculate the state of the reaction for any desired temperature. The quality of the prediction can be checked by performing a measurement under the corresponding conditions. The parameters found only yield good predictions for the temperature range in which the measurement has been performed. Extrapolations of up to ± 50 K can practically always be used.

Characteristic for nth order kinetics is that the reaction rate at the beginning of the isothermal reaction is greatest and afterward continuously decreases. It cannot therefore be used to describe autoaccelerating reactions.

Dynamically measured reactions initially show a reaction rate that increases with increasing temperature (Arrhenius). With increasing conversion, the concentration of reactants decreases, which in turn leads to a decrease in the reaction rate. The order of the reaction rate primarily controls this part of the reaction. For a dynamic DSC experiment, this means that at the same values for the activation energy and the pre-exponential factor, the reaction rate order determines the width of the peak in the DSC curve.

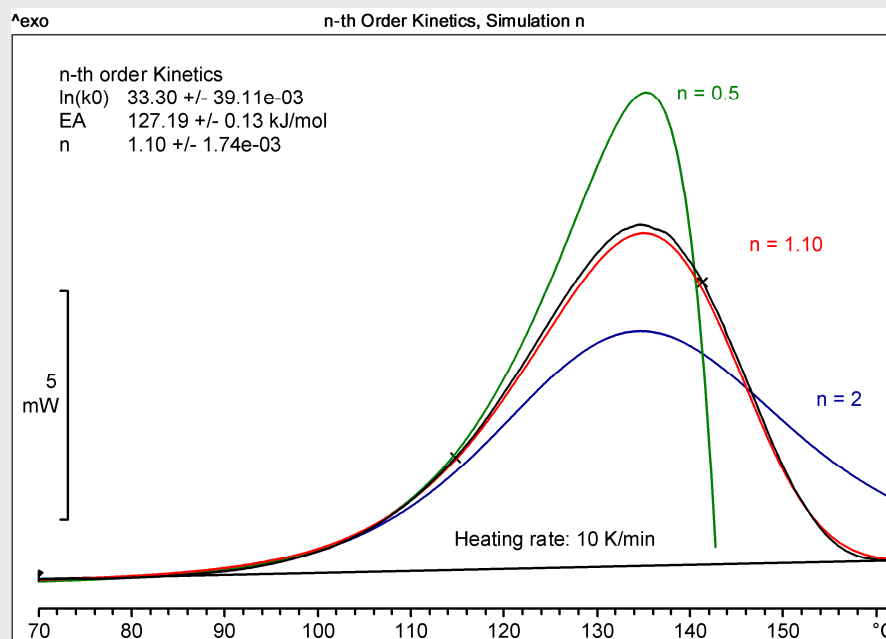


Figure 1. The DSC measurement curve (black) shows the decomposition reaction of dibenzoyl peroxide dissolved in dibutyl phthalate. The green curve is the prediction obtained using the kinetic data shown above left except that the order, n , was entered as 0.5. The red and blue curves are the corresponding simulations obtained using orders of 1.1 and 2. The beginning of the reaction ($<110\text{ }^{\circ}\text{C}$) is practically independent of n and is dictated by the activation energy.

Besides the so-called n th order kinetics, there are innumerable kinetic models for special types of reactions; usually more or less specific assumptions concerning the reaction mechanism are made. In each case, the aim is to determine the parameters used in the models from the experimental data by means of numerical procedures. This is illustrated in Table 1, which summarizes a number of different models for solid reactions.

Reaction model	$f(\alpha)$
power law	$4\alpha^{3/4}$
power law	$3\alpha^{2/3}$
power law	$2\alpha^{1/2}$
power law	$2/3\alpha^{-1/2}$
one-dimensional diffusion	$1/2\alpha^{-1}$
Mampel (first order)	$1 - \alpha$
Avrami-Erofeev	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$
Avrami-Erofeev	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$
Avrami-Erofeev	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$
three-dimensional diffusion	$2(1 - \alpha)^{2/3}(1 - (1 - \alpha)^{1/3})^{-1}$
contracting sphere	$3(1 - \alpha)^{2/3}$
contracting cylinder	$2(1 - \alpha)^{1/2}$
second order	$(1 - \alpha)^2$

Table 1. Different models used for describing solid reactions.

7.6.7.1 Choosing the Baseline and Evaluation Range:

In kinetic evaluations, the baseline is drawn as in other evaluations so that it begins tangentially to the DSC curve before the chemical reaction begins and rejoins the curve tangentially after the reaction has finished. The baseline must not cross the DSC curve in between the evaluation limits because this would lead to areas with the opposite mathematical sign (blue evaluation in Figure 7.45). Often, the “right” baseline gives the smallest confidence interval (i.e. the best fit).

The evaluation limits should be determined manually because the trained eye of the chemist is clearly better than the algorithm for the detection of the evaluation limits (green evaluation in Figure 7.45).

The kinetic results are

- the pre-exponential factor with its confidence interval,
- the activation energy with its confidence interval, and
- the order of the reaction with its confidence interval.

The calculated confidence intervals indicate the quality of fit and hence of the applicability of nth order kinetics. They must not be looked upon as “error limits” of the results. Sometimes small confidence intervals are obtained with reactions whose predictions are significantly wrong!

Besides the usual optional results such as evaluation limits, heating rate and baseline type, the reaction enthalpy in J/g is also available.

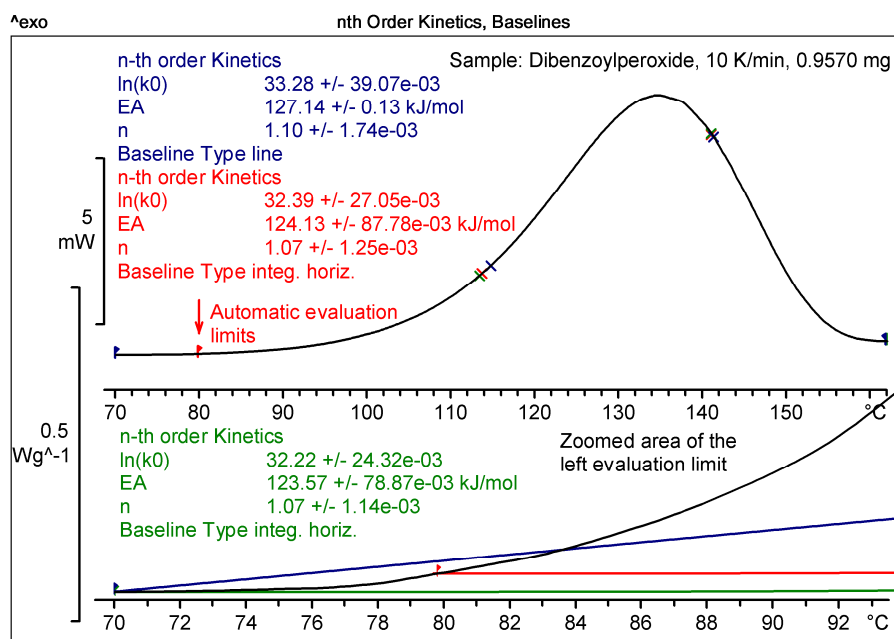


Figure 7.45. The figure shows the evaluation of a section of the DSC curve of the decomposition of dibenzoyl peroxide dissolved in dibutyl phthalate in the range 70 to 162 °C. The initial startup deflection and a possible secondary reaction are not shown. Zooming the curve makes it easier to choose the best evaluation limits. After the kinetics evaluation, you should again zoom the regions around the left and right evaluation limits in order to check whether the baseline is tangential to the curve. This is shown in the lower diagram where part of the upper curve has been zoomed. It is immediately clear that only the green baseline is correctly drawn. In fact, the confidence intervals in the green result block are smallest!

7.6.7.2 Important Evaluation Settings

These include the following:

- The conversion range used for the kinetic calculations: In practice, the middle region of the reaction gives the best fit. The data up to the starting value of 10% conversion and above the end value of 80% conversion is therefore excluded. If you are, however, interested in the kinetics at the beginning of the reaction, you can have this range calculated (start 1%, end 20%, Figure 7.46).
- The number of points: 1000 points are recommended with the fast PCs nowadays available. Possible signal noise no longer influences the results to any extent.

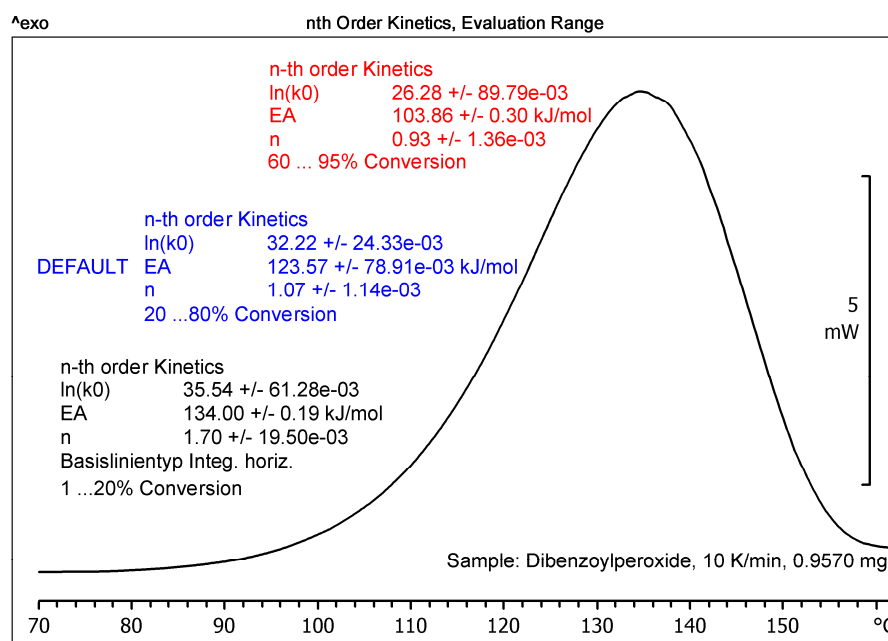


Figure 7.46. Even a simple chemical reaction like the thermal decomposition of dibenzoyl peroxide yields kinetic data that clearly depends on the calculation range. The activation energy decreases with increasing conversion from 134 to 123.6 and then to 103.9 kJ/mol.

7.6.7.3 Applications of Kinetic Data

The calculated data is only an intermediate result. You can use it to

- predict conversion (and the natural logarithm of the rate constants) as a function of time for selected isothermal temperatures (in tabular form and graphically),
- predict the reaction temperature needed to reach a particular conversion in a certain time (in tabular form and graphically), and
- simulate a DSC curve at a selected heating rate. You can also change the kinetic parameters and observe how they influence the shape of the DSC curve.

7.6.7.4 Prediction of Conversion as a Function of Reaction Time

Predictions for the course of isothermal reactions can be obtained much more quickly than by performing the corresponding isothermal measurements. The results give you an overview of the optimum relationship between reaction time and reaction temperature (Figure 7.47).

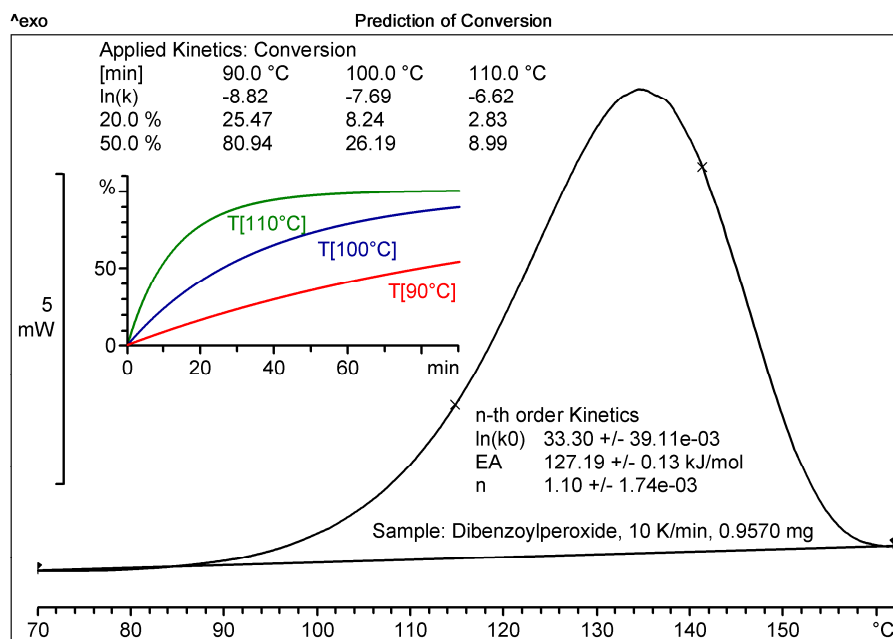


Figure 7.47. Predictions of the conversion for reaction temperatures of 90, 100 and 110 °C (left diagram and table) calculated from the nth order kinetic data. Note: The unit used for the reaction times displayed in the table for 20 and 50% conversion is noted above left [min]. The natural logarithm of the rate constants for 90, 100 and 110 °C are also calculated.

7.6.7.5 Prediction of the Reaction Temperature Needed to Reach a Particular Conversion in a Certain Time

If you are mainly interested in the relationship between reaction time and reaction temperature for several different conversions, then the isoconversion diagram is the best approach (Figure 7.48).

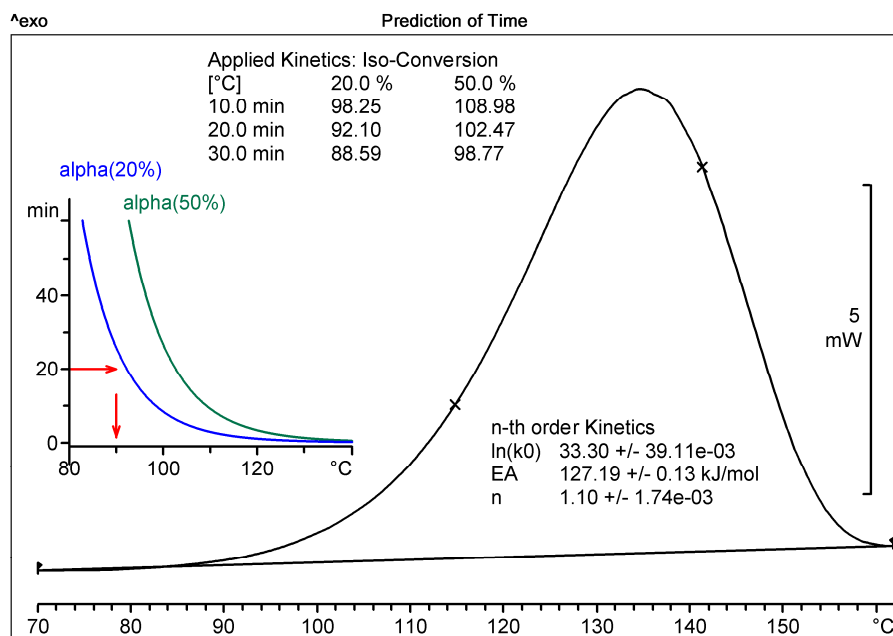


Figure 7.48. Prediction of the reaction time to reach a particular conversion as a function of reaction temperature. What temperature is needed to reach a conversion of 20% in 20 min? Lines of equal conversion are called isoconversion curves.

7.6.7.6 Simulating DSC Curves

A simulated DSC curve that agrees well with the measured curve increases your confidence in the kinetic evaluation. Simulations can also help you plan further measurements at other rates because the temperature range necessary then becomes clear (Figure 7.49).

Finally, you can study the influence of different kinetic parameters on the shape of the curve (Figure 7.50).

Note on the simulation of isothermal DSC curves: The first derivative of the curve predicted for conversion corresponds to the shape of a simulated isothermal DSC curve. Multiplying the derivative by the enthalpy change in mJ (peak area) yields the DSC curve in the correct units.

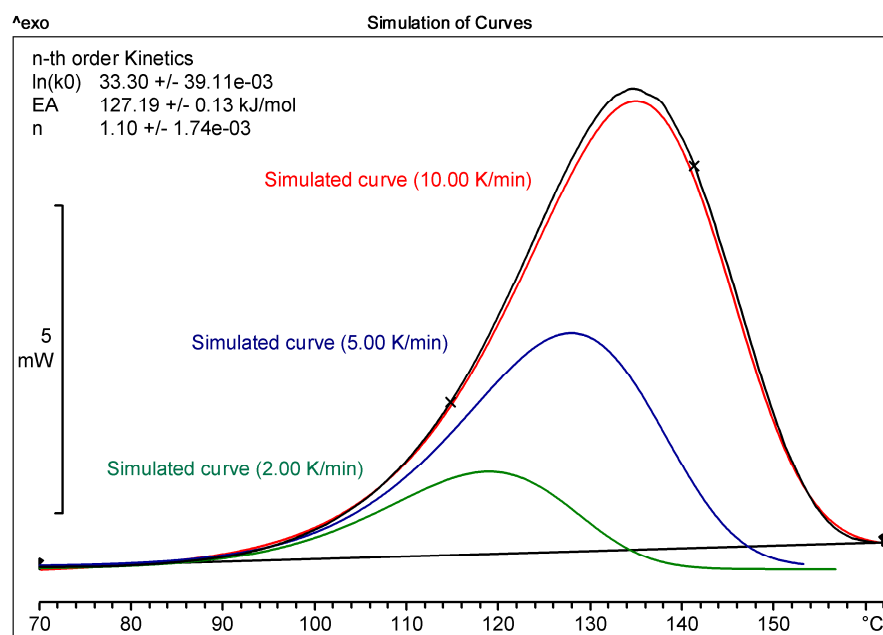


Figure 7.49. The simulated curve for the same heating rate (red) agrees well with the measured curve; as expected, lower heating rates give lower peak temperatures. The peak area appears to become smaller with decreasing heating rates because the abscissa is displayed with respect to temperature; if the curve is displayed with respect to time, the areas are the same.

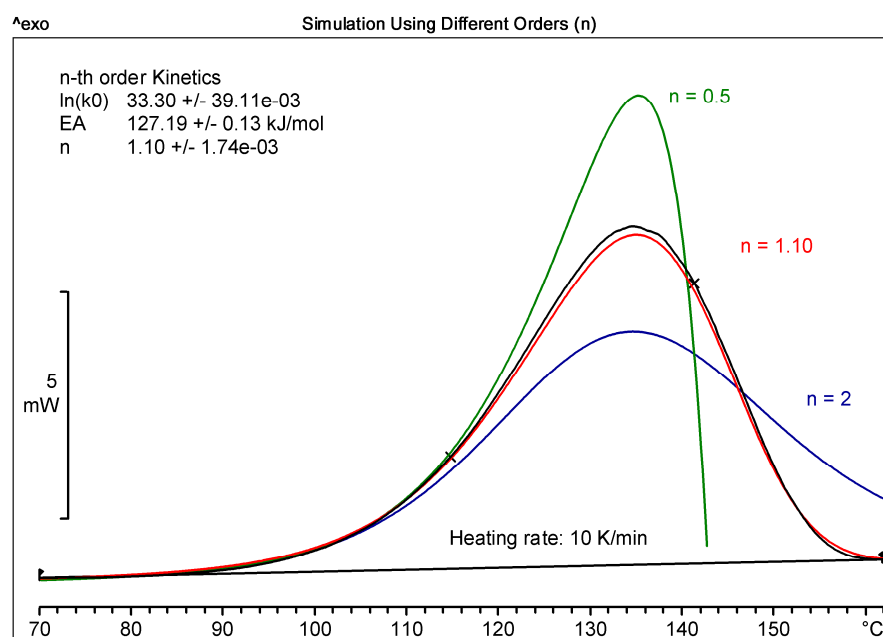


Figure 7.50. The influence of different orders (n) on the DSC curve becomes apparent when different values are entered: the higher the order the longer the reaction time. The order has almost no influence on the beginning of the reaction.

To illustrate the influence of the activation energy on the shape of the DSC curve, one must make sure the rate constants are the same in the region of the peak temperature. This is done by changing the pre-exponential factor:

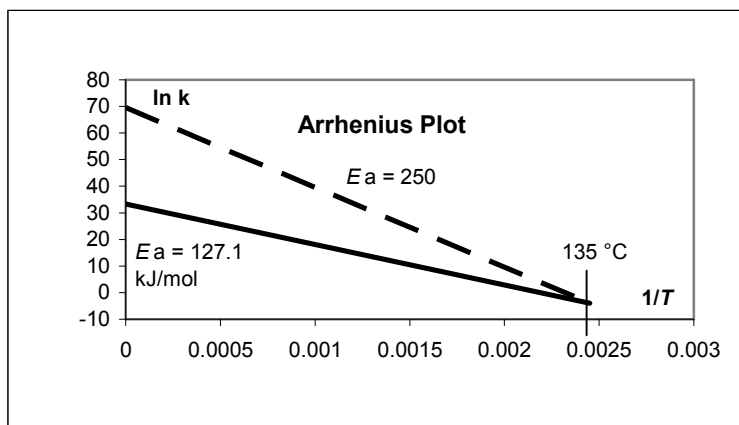


Figure 7.51. The Arrhenius plot immediately shows that for an E_a simulation at $135\text{ }^{\circ}\text{C}$ the ordinate intercept $\ln k_0$ must also be changed so that the rate constant at $135\text{ }^{\circ}\text{C}$ remains the same.

$$\ln k_{\text{new}} = \ln k + \frac{E_{a,\text{new}} - E_a}{RT_{\text{peak}}} \quad \text{Note: } T_{\text{peak}} \text{ is in Kelvin} \quad (7.17)$$

Example (Figure 7.52):

$$\ln k = 33.28,$$

$$E_a = 127.13 \text{ kJ/mol},$$

$$T_{\text{peak}} = 135\text{ }^{\circ}\text{C} = 408 \text{ K},$$

$$E_{a,\text{new}} = 250 \text{ kJ/mol}$$

$$\ln k_{\text{new}} = 33.28 + 122\,870 \text{ J/mol} / (8.31 \text{ J/(mol K)} \cdot 408 \text{ K}) = 33.28 + 36.22 = \underline{69.50}$$

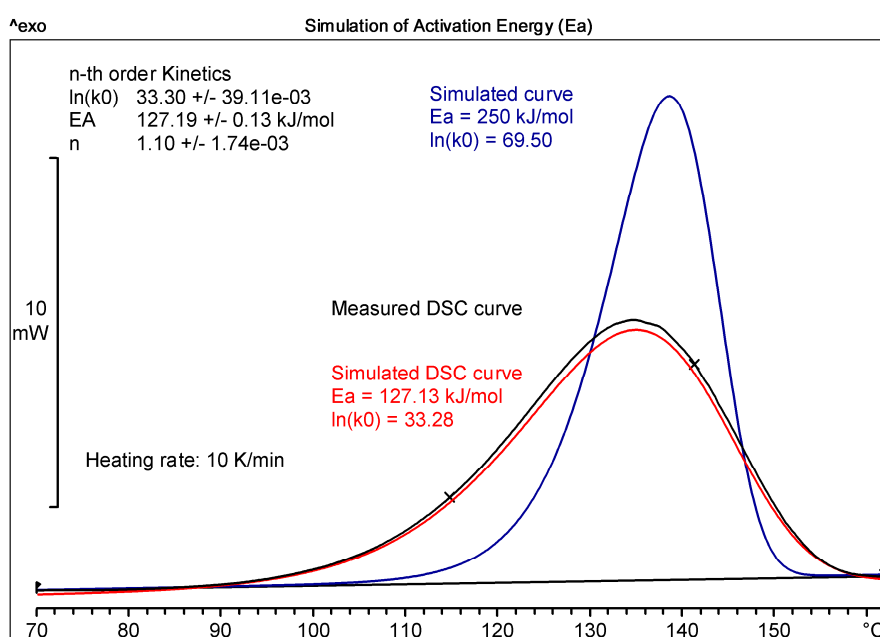


Figure 7.52. As expected, the slope of the DSC curve of a chemical reaction becomes steeper with increasing activation energy (the activation energy is the temperature coefficient of the rate constant).

7.6.7.7 Isothermal Measurements

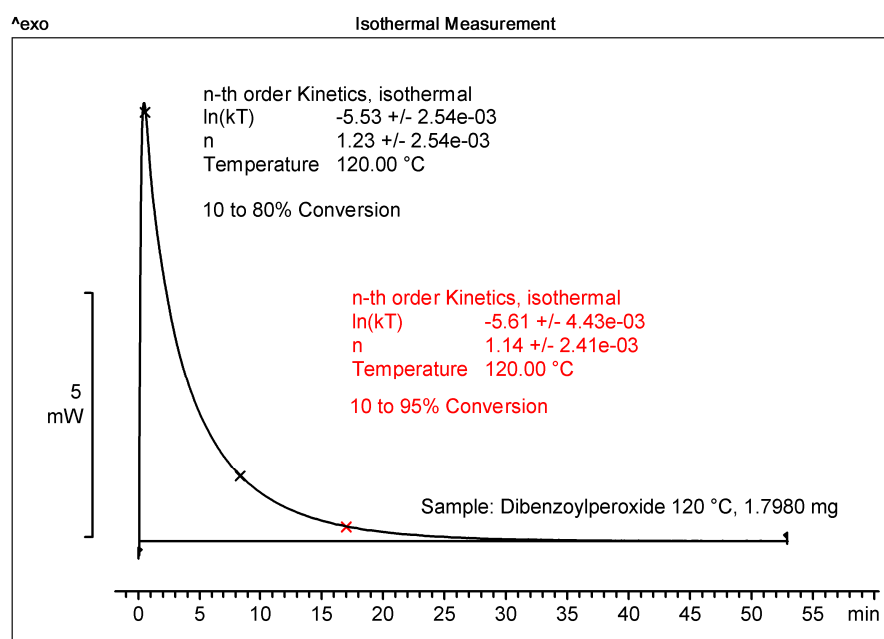


Figure 7.53. The example shows a DSC curve obtained by inserting a cold crucible containing dibenzoyl peroxide into the preheated measuring cell. The curve increases practically vertically at the beginning (temperature equilibration). In general, the curve includes a smaller or a larger piece of the endothermic temperature equilibration curve depending on how quickly the measurement is started. The black result block is evaluated in the range 10 to 80% and the red block from 10 to 95%.

The **isothermal curve** allows you to calculate the reaction order and the rate constants.

If you want to investigate the influence of the calculation range on the kinetic results, you should perform the evaluation in exactly the same range. To do this, remove the endothermic part of the curve at the beginning of the measurement. You can also cut off the right part of the curve as soon as it has asymptotically reached the lowest value (Figure 7.53).

The horizontal from right baseline is practically always used.

To obtain more significant points, you can shift the end of the calculation range from 80 to 95%.

Finally, **two or three isothermal measurements** performed at temperatures differing by 5 to 10 K yield two or three rate constants. $\ln k_0$ and E_a can be calculated from the slope in the Arrhenius plot (Figure 7.54).

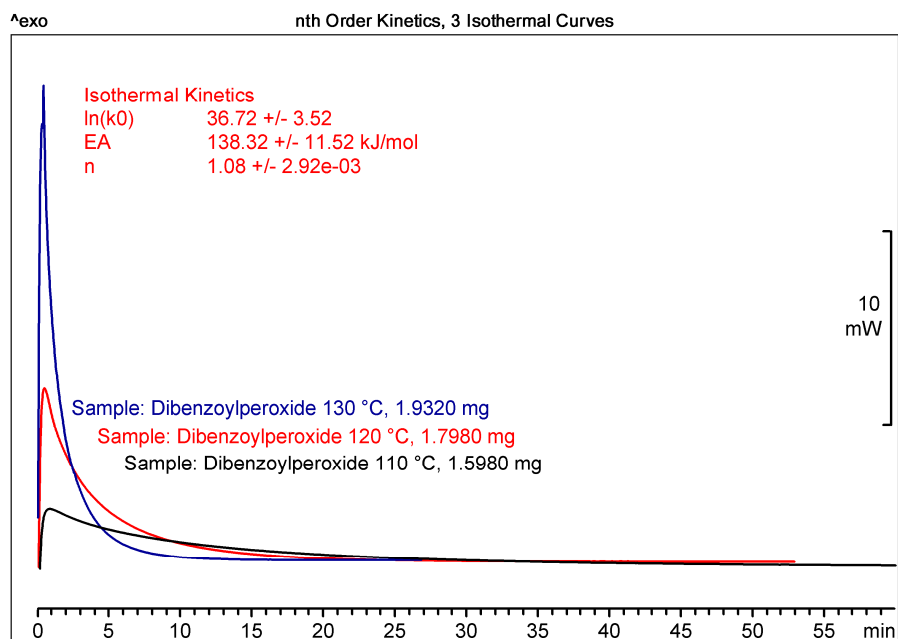


Figure 7.54. The three isothermal DSC curves yield kinetic data that can be used to make predictions and simulate (dynamic) curves, as discussed previously for dynamic curves.

7.6.8 Kinetics According to ASTM E698

The ASTM E698 standard test method originates from the days when computers were not available in laboratories and computing possibilities were limited - each measured curve is reduced to its peak temperature! The evaluation algorithm is model free and accurately described in the standard. According to the standard, $n = 1$ is used for predictions (Figure 7.55).

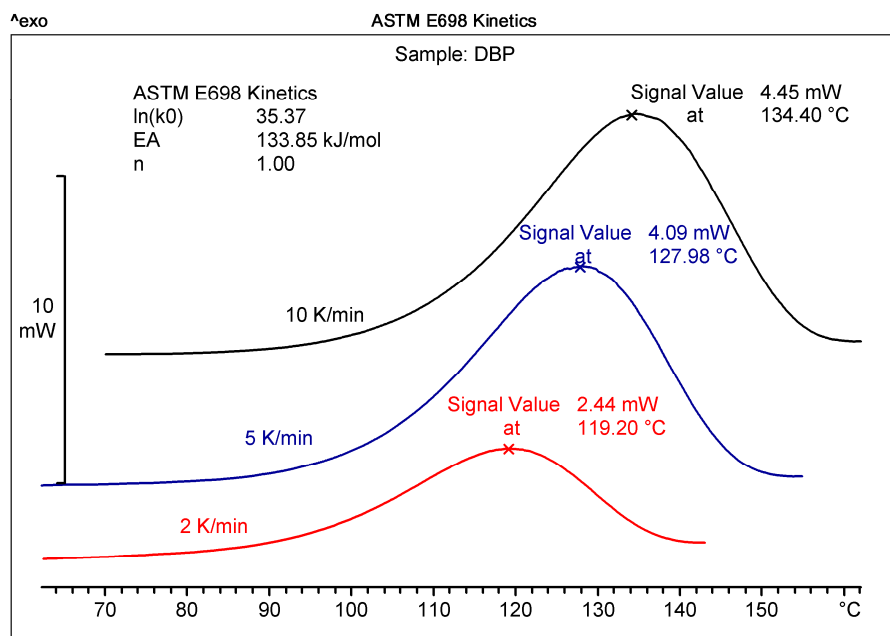


Figure 7.55. Kinetic data for dibenzoyle peroxide (DBP) according to ASTM E698. The order, n , is not a result of the evaluation. For predictions made according to the standard, n is assumed to be 1. The signal values shown at the peak maxima (marked x on the DSC curves) and the corresponding temperatures are optional results.

7.6.9 Kinetics According to ASTM E1641

According to the ASTM E1641 standard test method, the activation energy and the pre-exponential factor for any desired conversion, for example 10%, is calculated model free using an algorithm described in the standard (Figure 7.56).

In this evaluation, the optimum choice of the type of baseline and the evaluation limits is very important especially if you are interested in kinetic data close to 0% or 100% conversion. Wrong partial areas would give wrong temperatures, in contrast to ASTM E698. The kinetic parameters would then also be wrong.

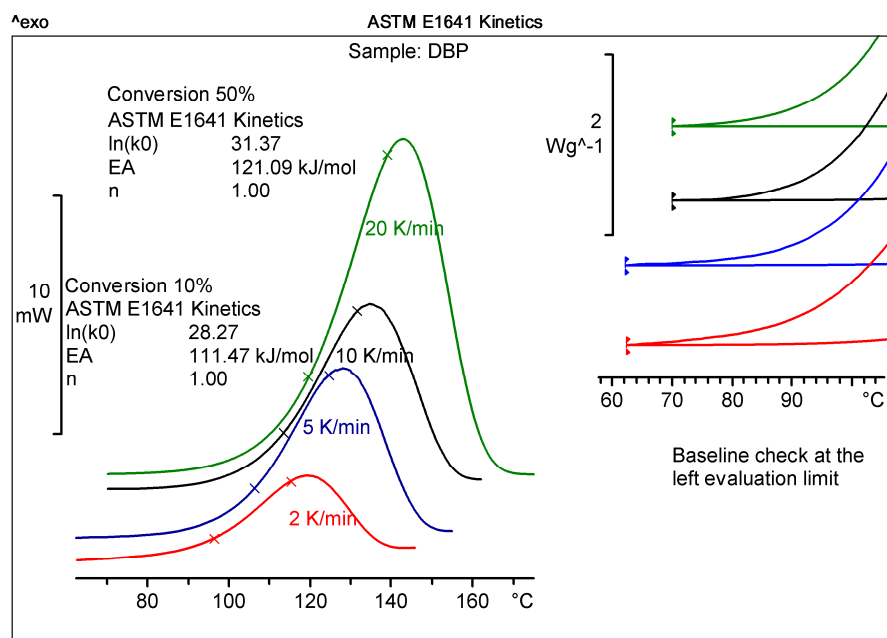


Figure 7.56. Left: Two ASTM E1641 evaluations for conversions of 10% and 50% using four DSC curves of dibenzoyl peroxide (DBP) measured at different heating rates. The corresponding conversion is marked with an x on the DSC curve. Right: The left evaluation limits are checked by viewing the relevant parts of the curves on an expanded scale using the integration software.

The ASTM E1641 evaluation method yields good kinetic parameters. The parameters would also be suitable for predictions. However, you must remember that the standard specifies first order kinetics so the predictions will be very inaccurate for higher conversions. Model free kinetics does not have this disadvantage.

7.6.10 Model Free Kinetics, MFK

Model free kinetics [9] [10] [11] [12] is very good for describing complex chemical reactions in which transport processes play an important role or in which parallel and secondary reactions occur.

The MFK method is based on an evaluation of at least three measurements performed at different heating rates.

Suitable **heating rates** are for example 2, 5 and 10 K/min, whereas heating rates of 9, 10 and 11 K/min are unsuitable because they are too close together. If you want to make predictions for low reaction temperatures, use lower heating rates, for example 0.5, 1 and 2 K/min. Conversely, 5, 10 and 20 K/min are recommended for making predictions for high reaction temperatures in order to reduce extrapolation errors.

As a check, you should compare the reaction enthalpies of the DSC curves (peak integration). The reaction enthalpies should agree to within $\pm 10\%$. An outlier $>20\%$ from the mean value indicates that something is wrong with the measurement.

Conversion curves are then calculated from the DSC curves. The conversion curves must shift to higher temperature at increasing heating rates and must not intersect at any point (Figure 7.57). If the curves do intersect, an error has occurred, for example:

- The evaluation range was wrong (the range must shift to higher temperature with increasing heating rates).
- The baseline type was unsuitable (zoom the evaluation range to make sure the DSC curve meets the baseline asymptotically).
- Erroneous measurements due to inhomogeneous samples (repeat the particular measurement).

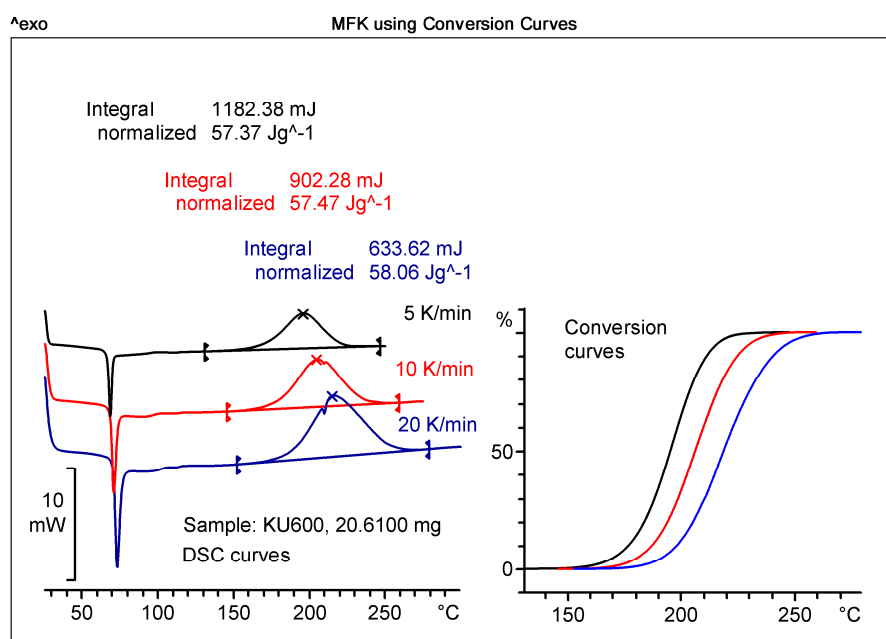


Figure 7.57. The diagram shows the DSC heating curves of an epoxy resin used in coating applications. The reaction peaks were each evaluated with respect to conversion. The normalized integrals were calculated using a **Line** baseline type to check plausibility. The effect observed at about 75 °C is a glass transition. The conversion curves are now evaluated using MFK. This yields the activation energy curve as a function of conversion (Figure 7.58).

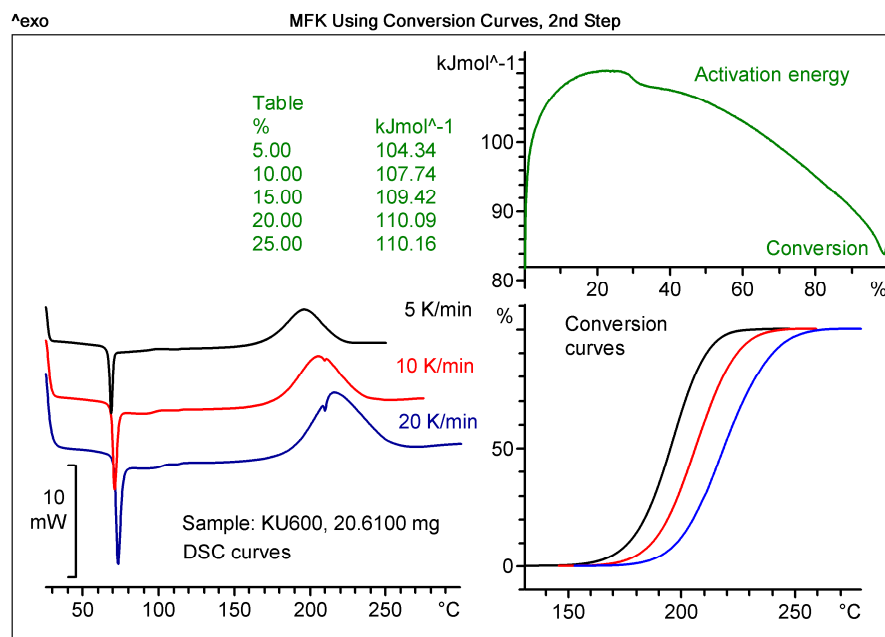


Figure 7.58. The model free kinetics evaluation yields the activation energy curve (above right). Some values are displayed in the table to the left of this. The activation energy is not constant over the course of the reaction, but first increases from 90 kJ/mol to 110 kJ/mol and then later decreases to about 80 kJ/mol. This indicates that the chemical reaction is complex.

Experienced users can interpret the shape of the activation energy curve and derive information about the reaction mechanism. For example, a curve that increases indicates the occurrence of parallel reactions. A decrease in the activation energy can be caused by the reaction changing from kinetic control to diffusion control [11].

7.6.10.1 Applications of Model Free Kinetics

The calculated activation energy function is the first result. It allows you to

- predict the conversion as a function of time for any desired isothermal temperature (presented graphically and as a table),
- predict the reaction temperature needed to reach any desired conversion within a given time (presented graphically and as a table),
- simulate a DSC curve at any desired heating rate.

7.6.10.2 Prediction of Conversion as a Function of Reaction Time

Predictions for the course of isothermal reactions save a lot of time compared with the time it would take you to perform the corresponding isothermal measurements. You quickly get an overview of the relationship between reaction time and reaction temperature.

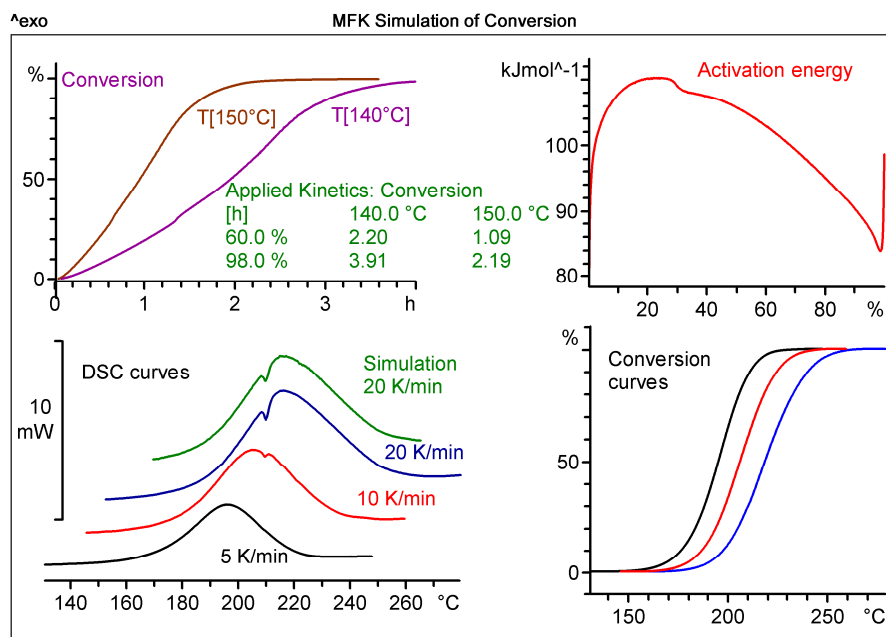


Figure 7.59. Above left: The diagram from Figure 7.58 has now been expanded to include the diagram showing predictions for conversion at two reaction temperatures. The conversion plot for 140 °C shows a clear concave shape in the range up to 2.5 h which cannot be described by nth order kinetics. The small dip on the simulated DSC curve at 20 K/min is only obtained with MFK (green curve, below left).

In the case of this epoxy resin system, the predicted reaction time for a conversion of 98% is more or less the same as the curing time, that is, 4 h at 140 °C or 2 h 10 min at 150 °C.

7.6.10.3 Prediction of the Reaction Temperature to Reach a Desired Conversion in a Certain Time

The reaction temperature-reaction time data pairs for different percent conversions can be used to construct so-called isoconversion curves.

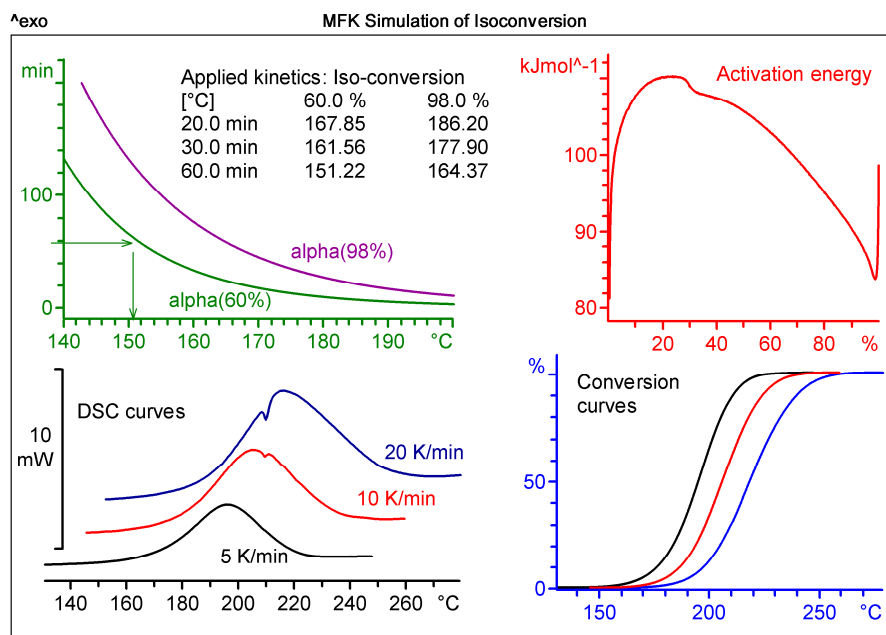


Figure 7.60. Above left: The isoconversion diagram (upper left) for conversions of 60% and 98% was automatically calculated. The table shows the reaction temperatures at which these conversions are reached in 20, 30 or 60 min.

7.6.10.4 Simulation of a DSC Curve

A simulated DSC curve that agrees well with the measurement increases confidence in the kinetic evaluation. Simulations can also help you to plan further measurements at other heating rates because the temperature range necessary becomes clear (see Figure 7.59).

Note on the simulation of isothermal DSC curves: The first derivative of the predicted conversion corresponds to the shape of a simulated isothermal DSC curve. Multiplying the derivative by the enthalpy change in mJ (peak area) yields the DSC curve in the correct units.

7.6.11 Advanced Model Free Kinetics, AMFK

In contrast to MFK, advanced MFK [14] can use isothermal or mixed dynamic and isothermal measured curves.

The evaluation, predictions and the simulations are performed in the same way as classical MFK.

Results from advanced MFK are more reliable when more than three measured curves are used; four to five curves are optimal.

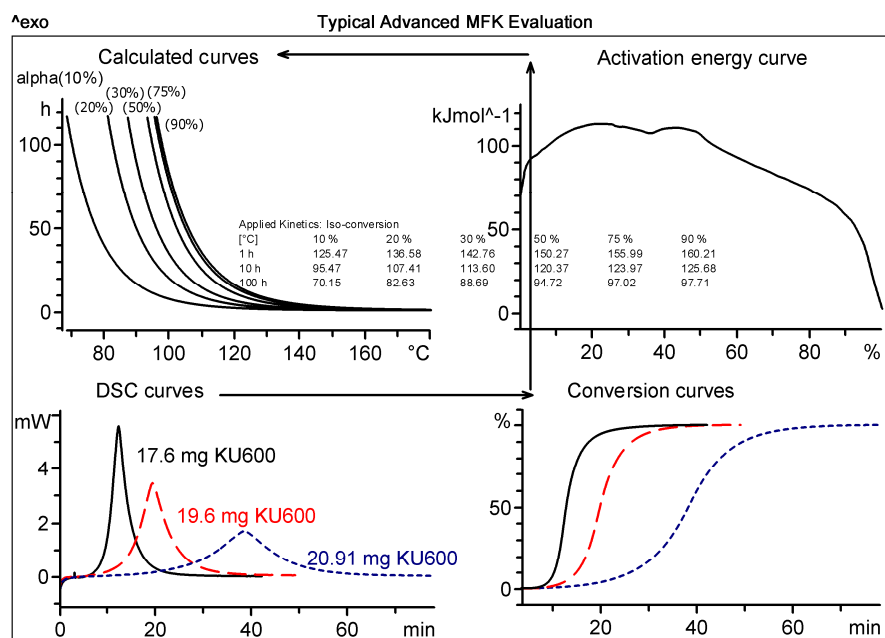


Figure 7.61. The KU600 epoxy powder was measured dynamically and isothermally in order to remain below the temperature at which decomposition occurs (i.e. it was dynamically heated at different heating rates to various isothermal end temperatures). The mixed conversion curves are therefore displayed with respect to time. Above right: the activation energy curve. Above left: isoconversion predictions.

7.6.12 Deconvolution

Deconvolution is a mathematical process that improves the resolution (separation of close-lying effects) on a curve. The deconvoluted signal, S , is calculated from the measured signal, S_{measured} :

$$S = S_{\text{measured}} + \tau \frac{dS}{dt} \quad (7.18)$$

where τ is the signal time constant. Deconvolution is usually performed in a narrow temperature range in which the temperature dependence of the time constant can be neglected.

Previously, deconvolution often improved peak separation because the time constant of older DSC instruments was relatively large. The time constant is however nowadays less than 2 s due to the introduction of the FRS5 DSC sensor and the use of smaller samples and smaller crucibles. This has made deconvolution almost unnecessary.

Deconvolution can also be used to determine the current signal time constant (Figure 7.62).

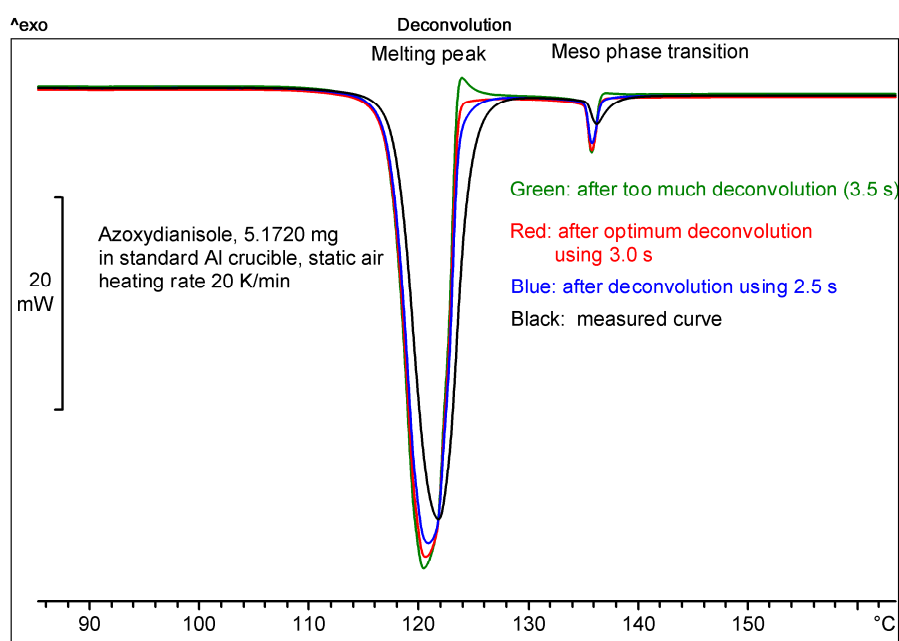


Figure 7.62. DSC measurements performed in a standard aluminum crucible with relatively large sample amounts give sharper peaks after optimal deconvolution. Excessive deconvolution leads to overshooting. The time constant here is 3 s (optimum curve shape).

7.7 Some Special DSC Measurements

7.7.1 The Determination of OIT (Oxidation Induction Time):

Very many organic compounds are attacked by oxygen and undergo an oxidation reaction even at low temperatures. Under isothermal conditions, some classes of substances exhibit a period of induction, OIT, during which no reaction with oxygen seems to occur. In fact, however, an “oxygen stabilizer” is steadily consumed. After this, oxygen attack occurs at an increasing rate (autoxidation). The classes of substance involved include

- polyolefins (mainly polyethylene and polypropylene),
- lubricating greases and oils, and
- edible fats and oils.

Clearly, for practical reasons, a DSC measurement cannot last for weeks. The solution is to increase the temperature. According to some standards, the oxygen pressure is also increased (high-pressure DSC).

The measurement can be performed in two ways: The sample is inserted directly into the measuring cell which is under oxygen and has already been heated to the desired isothermal temperature. The measurement is then immediately started (called the fast method). Alternatively, the sample is inserted at room temperature and is heated to the desired isothermal temperature in a nitrogen atmosphere. After temperature equilibration, the gas is switched to oxygen and the induction period is measured from this time onward (Figure 7.63).

Lubricating greases and polyolefins are in direct contact with copper in some applications (electrical cables) or alloys that contain copper (bronze bearings). Since copper is a redox catalyst, oxidation occurs much more quickly. To prevent this, additives are added that suppress the effect of copper. Such products are referred to as being “stabilized against copper”. The degree of copper stabilization is measured by comparing the induction period of a sample in the aluminum crucible with that in the copper crucible. Non-copper stabilized PP has OITs of 38 min (Al), and 2 min (Cu) at 200 °C, while a copper stabilized product gives practically the same values, for example 40 min (Al), and 36 min (Cu).

Choosing the Isothermal Temperature:

To achieve reproducible measurements, the OIT should be at least 5 min. If it is less, the temperature should be lowered by 10 K. Furthermore, the cleanliness of the aluminum crucible and the samples is very important. Because the measurement is very temperature dependent, precise temperature adjustment is essential.

If the OIT is more than 1 h, the measurement temperature should be increased by 10 K.

Sample preparation:

To obtain reproducible results, the mass of the sample should always be about the same.

The crucible is either open (no lid) or partially closed with a lid pierced with five 1-mm holes to prevent oxidation products from creeping out.

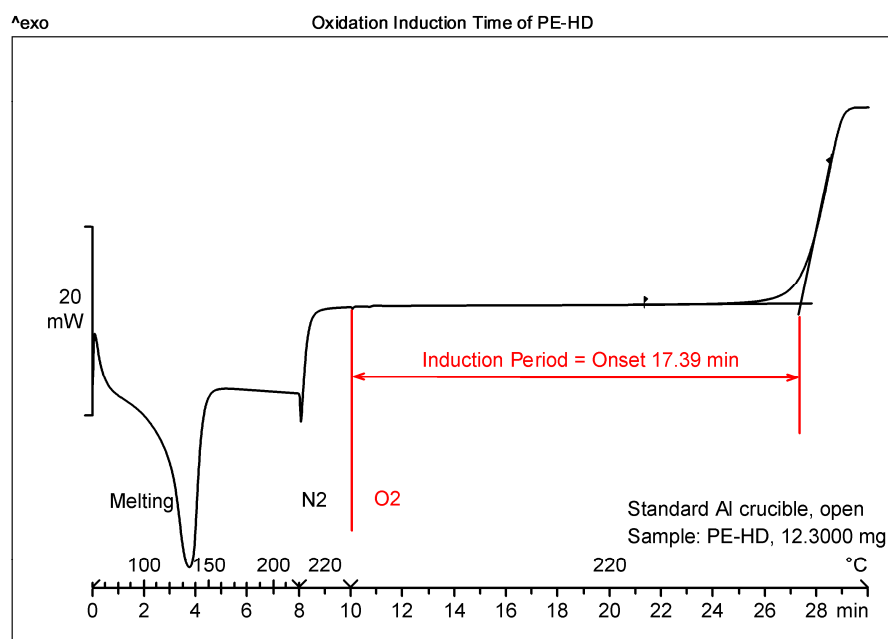


Figure 7.63. The determination of the oxidation induction time of polyethylene. The sample is heated to 220 °C in nitrogen. After 2 min at 220 °C, the gas flow (50 mL/min) is switched to oxygen and measurement of the induction time begins. This gives an OIT of 17.4 min.

Other organic compounds are of course attacked by oxygen but do not exhibit autoxidation. This means that they cannot be measured isothermally in this way because the reaction proceeds at a practically constant rate. In such cases, the sample is heated rather slowly (2 or 5 K/min) in oxygen and the onset temperature of the oxidation peak is evaluated.

7.7.2 DSC Measurements under Pressure

Changes in pressure influence all physical transitions and chemical reactions that are accompanied by a volume change.

For example, the boiling point increases markedly with increasing pressure. If a side-product such as water is formed in a chemical reaction, its evaporation peak will mask the exothermic reaction peak at normal pressure. At increased pressure, the evaporation peak appears 50 to 100 K higher and does not interfere with the evaluation.

Heterogeneous reactions are accelerated by the higher gas concentrations resulting from increasing pressure, or they can be measured at lower temperature. This is made use of in the determination of oxidation stability under pressure (ASTM D6186 and E1858). Besides this, the tendency of volatile additives to vaporize is greatly reduced.

If overlapping chemical reactions occur at normal pressure, one of the reactions may be much more strongly influenced by an increase in pressure than the other. The result is that the two reactions are separated under increased pressure. Example: the thermal decomposition temperature of organic substances increases with increasing pressure of an inert gas.

The solubility of gases, liquids and solids increases with increasing pressure. For example, dissolved CO₂ can significantly lower the glass transition temperature of polymers.

The gastight construction combined with the defined gas outlet means that with proper precautions trained personnel can use poisonous and flammable gases, for example to hydrogenate unsaturated compounds with hydrogen. There are nevertheless still risks attached to this type of work and METTLER TOLEDO accepts no responsibility whatsoever for injury to persons or damage to equipment and facilities.

The HP DSC is based on the same technology as a METTLER TOLEDO standard DSC. Its pressure range is up to 10 MPa, and the temperature range up to 700 °C [2].

7.7.3 Safety Investigations

Here we are concerned with the determination of possible exothermic reactions of a substance or a reaction mixture that is subjected to a temperature program. The temperature range is normally from room temperature to about 300 or 400 °C. Samples that are particularly heat sensitive are precooled to -50 °C in order to detect reactions below room temperature. The heating rate is about 5 K/min. For safety reasons, the initial trial experiments are performed using very small amounts of sample (2 to 5 mg).

Evaporation or vaporization of sample components can be prevented by using high-pressure crucibles. To avoid undesired catalytic effects, disposable crucibles in the form of gold plated steel crucibles or glass crucibles are available. If necessary, metal turnings or other potential catalysts can be added in small amounts.

Based on the exothermic reaction enthalpy, a trained person can decide whether the substance or the reaction mixture can be processed in a reaction calorimeter (100-g scale) or even directly in the pilot plant (kg-scale). One of the problems connected with this so-called scale-up is that with larger amounts of material, the cooling capacity decreases rapidly (cooling area per volume). The risk of a runaway through accumulation of heat increases. The worst-case situation of a failed cooling system are adiabatic conditions in which the entire enthalpy of reaction is available to heat the reaction mixture (see information box: Chemical Reactions).

Chemical Reactions

Chemical reactions are practically always involved when changes to compounds take place. We cannot attempt to discuss in detail the many different types of reactions that occur but will restrict ourselves to a few important terms and topics important in thermal analysis.

In general, in a chemical reaction the starting materials or **reactants** react to form the **reaction products**. A **catalyst** accelerates the reaction, an **inhibitor** slows it down.

One distinguishes between **homogeneous** and **heterogeneous** reactions. In **homogeneous reactions**, the reactants are present in the same phase, for example in the liquid phase. In **heterogeneous reactions**, the reactants are in different phases (e.g. solid and gaseous phases). Typical thermoanalytical examples are the curing of an epoxy resin (a homogeneous reaction: resin and hardener are liquid at the reaction temperature and soluble in each other) or the investigation of the oxidation stability of polyethylene (a heterogeneous reaction: liquid polyethylene and gaseous oxygen).

Autocatalytic reactions, in which the reaction is accelerated by a reaction product (catalyzed), initially take place very slowly at constant temperature. As soon as a sufficient quantity of catalytically effective product has formed, the reaction rate continuously increases. Such reactions are also called self-accelerating or **autoaccelerating reactions** and exhibit a so-called induction period (IP) in which nothing appears to happen. In contrast, the reaction rate of normal isothermal reactions is greatest at the beginning.

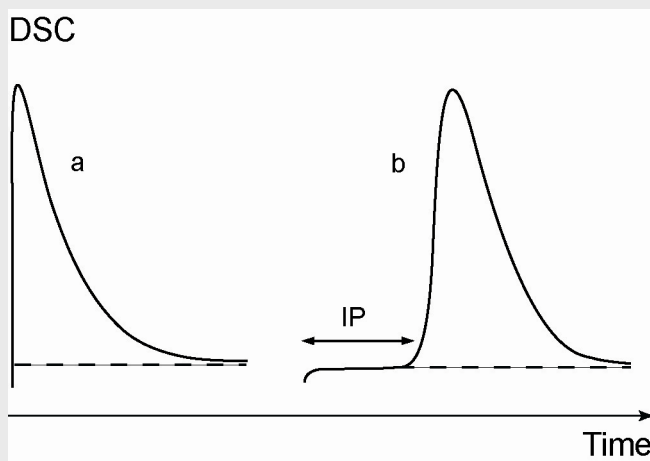


Figure 1. Comparison of a normal (a) and an autocatalyzed reaction (b).

There are also reactions in which a component undergoes a **phase transition**. This leads to a change in the transport conditions within the reaction zone. This can accelerate (or slow down) the reaction. An example of this is the accelerated decomposition of many organic substances on melting (Fig. 2 melting with decomposition). In contrast, the rate of curing of an epoxy resins decreases on reaching the glass transition temperature (see polymers).

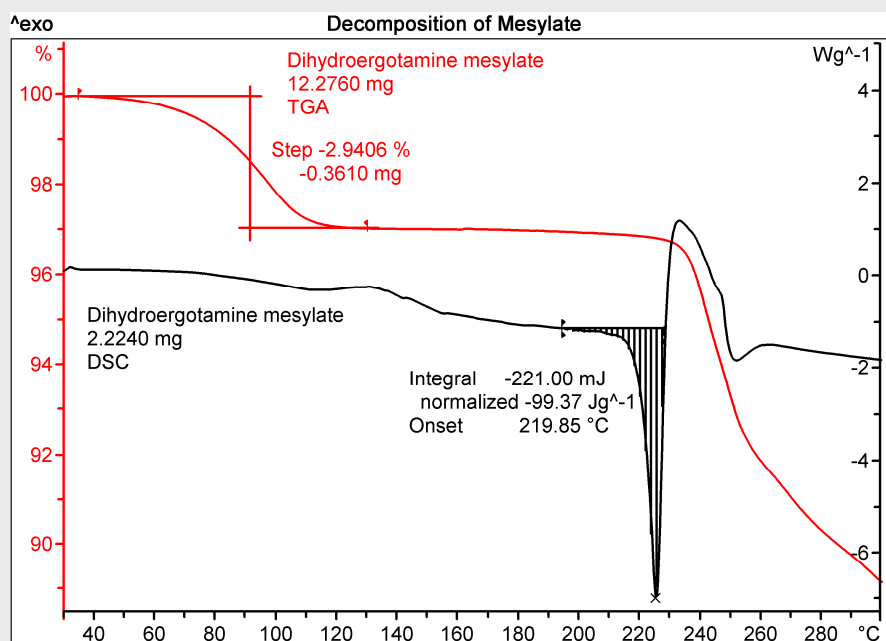


Figure 2. Melting with decomposition.

Finally, undesired **side reactions** can occur. For example, in the esterification of glycerin with phosphoric acid, a small amount of glycerin is dehydrated to acrolein in a **side** reaction. This can then polymerize in a strongly exothermic **secondary** reaction. The heat generated by the reaction is considerable, about 700 J/g.

The **heat of reaction** (or **reaction enthalpy**) is an important characteristic quantity in chemical engineering because it allows the heating or cooling requirements and the hazard potential of the reaction to be estimated.

An **exothermic reaction** generates heat. If the heat is not immediately dissipated, it heats the reaction mass and accelerates the reaction. In the extreme case, this leads to uncontrolled or **runaway** reactions. Strongly exothermic reactions are therefore extremely dangerous and must be carefully investigated beforehand. DSC is ideal for this because the technique requires only a few milligrams of sample. Any runaway reactions that do occur cause only limited damage. The good thermal coupling of the reaction mass with the temperature-controlled DSC furnace ensures that runaway reactions usually do not occur. The possibility of a runaway reaction taking place can be significantly reduced by diluting the sample with an inert material such as α -aluminum oxide. The diluent absorbs heat generated by the reaction and improves the dissipation of heat to the crucible.

In contrast to the very good temperature control of a small sample in the DSC, a large quantity of a reaction mixture behaves practically **adiabatically** (no heat exchange) because of the limited cooling possibilities.

The reaction enthalpy, ΔH , and the mean specific heat capacity, c_p , of the reaction mixture allows the maximum (adiabatic) temperature increase, ΔT , to be calculated (Table 1).

$$\Delta T = \Delta H / c_p \quad (4.1)$$

Exothermic reaction enthalpy in J/g	Adiabatic temperature increase in °C	Hazard potential
0 ... 50	<50	low
50 ... 500	<500	large
500 to about 25,000	>500	very large

Table 1. Classification of exothermic reactions.

The so-called adiabatic explosion time t_{ad} (time to a reaction runaway) can be estimated if the activation energy, E_a , and the rate constants k at T_0 are known:

$$t_{\text{ad}} = \frac{c_p \cdot R \cdot T_0^2}{\Delta H \cdot k \cdot E_a}. \quad (4.2)$$

Here, c_p is the specific heat capacity, T_0 the starting temperature in K, ΔH the reaction enthalpy and R the gas constant.

For example, if

$$\Delta H = 5000 \text{ J/g},$$

$$c_p = 2 \text{ J g}^{-1} \text{ K}^{-1},$$

$$R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1},$$

$$k = 10^{-5} \text{ s}^{-1}, T_0 = 400 \text{ K and } E_a = 100\,000 \text{ J/mol},$$

a value of 530 s is obtained for t_{ad} .

The term **decomposition temperature** is frequently used. Chemical compounds are in fact stable in a certain range of temperature, that is, they do not decompose on their own or at the most very slowly. Since the decomposition rate continuously increases with increasing temperature, there is really no actual decomposition temperature. For example an organic compound decomposes at a rate of 1% per year at 80 °C, 3% per year at 90 °C, and 10% per year at 100 °C. At 160 °C it can withstand a short time without noticeable decomposition (less than 1% per hour).

However, for comparison purposes, the onset temperature of DSC or TGA measurements at a heating rate of 10 K/min is often used as the “decomposition temperature”.

Other applications have to do with various aspects of **storage lifetime** and the maximum **shelf life** of a chemical at a given temperature without an unacceptable degree of decomposition (e.g. <1%). Since direct measurements would usually take far too long, use is made of kinetic predictions based on measurements at higher temperatures.

7.8 DSC Application Overview

In general, evaluations are concerned with abscissa information (time or temperature) and ordinate information (heat flow, amount of heat and derived quantities) as shown in Table 7.3.

Effect, property of interest	Evaluation
Specific heat capacity as function of temperature	Specific heat capacity, ADSC
Enthalpy-temperature function ¹	Enthalpy
Enthalpy changes, enthalpy of conversion	Integration
Enthalpy of fusion, crystallinity	Integration, crystallinity
Melting behavior (liquid content, liquid fraction)	Integration (partial areas) ² , Conversion ³
Melting point ⁴ , solidus and liquidus point, ⁴	Onset, Purity, Integration
Melting point of semicrystalline plastics	Peak, Integration
Melting point of the pure substance	Purity
Purity of non-crystalline non-polymers	Purity
Crystallization behavior, supercooling	Onset, Integration, Conversion
Solid–Solid transition, polymorphism	Integration, Onset, Conversion
Vaporization, sublimation, desorption	Integration, Conversion
Boiling point ⁹	Peak, Onset or Integration
Glass transition, amorphous softening	Glass transition
Curie temperature, temperature of a lambda transition	Peak, Integration possibly Step tangential
Thermal decomposition, pyrolysis, depolymerization,	Integration, Onset, Kinetics
Temperature stability	Onset, Integration, Kinetics with predictions
Chemical reaction, e.g. polymerization	Integration, Kinetics
Reaction enthalpy	Integration
Reaction kinetics investigations and applied kinetics (predictions)	Kinetics
Safety investigation of chemical reactions	Integration, Kinetics
Oxidative degradation, oxidation stability, OIT	Onset
Content determination ¹⁰	Content (proportional to area)
Comparison of different lots ⁷ , Comparison of competitive products ⁷ , Comparison “good / bad” ⁷	Integration (partial areas) ³ , Peak height and width ⁸ , Onset, Peak, Endset, First derivative ⁵ , Curve subtraction ⁶ , depending on the effect other specific evaluations

Table 7.3. Different DSC evaluation possibilities.

- ¹ Not only for thermodynamic specialists, but also for the determination of heating or cooling capacity in thermal processes (chemical engineering, injection molding processes)
- ² Fractional area before the peak maximum to that afterward (“shape factor” for complex melting behavior, for example with edible oils)
- ³ Partial area as a function of temperature in relation to the total area. Especially for complex melting behavior, such as with edible oils.
- ⁴ With very pure samples ($\geq 99.9\%$), the onset is the best evaluation method. With less pure samples, the purity should be analyzed. If the program is not available, the peak temperature can be used, of course only at low heating rates (≤ 2 K/min).
- ⁵ Differences in the curve shape are clearer in the first derivative.
- ⁶ The curve of the delivery batch in question minus that of the recognized good quality shows all the differences. Problematical because sample preparation and sample mass influence the width of the effect.

- ⁷ In curve comparisons, if possible identify individual effects and relate these to the problem involved. Examples:
- Check brittle and normal plastic batches for the glass transition or copolymer melting peak.
 - Investigate brown-colored and white chemical samples for the melting peak (purity) and beginning of decomposition (possibly influenced by impurities).
 - Investigate sticky and non-sticky batches of a powdery, organic compound for amorphous parts (smaller or missing melting peak), mass loss (moisture, solvent) as well as polymorphism (occurrence of lower melting modifications).
- A purely qualitative comparison of curves based on non-interpretable bumps on the DSC curve is less meaningful, can sometimes be used as a “fingerprint”.
- ⁸ The peak height is an optional result of the integration. The peak width at half height is used to assess how rapidly an effect occurs.
- ⁹ In the standard aluminum crucible with a 50- μm hole in the lid, at low heating rate (about 2 K/min) and with low sample weight (about 2 mg), the peak temperature corresponds to the boiling point.
- ¹⁰ Examples: freezable water in biological samples using the ice-melting peak, α -quartz in minerals above the solid-solid transition, peroxide content of a mixture above the decomposition peak, moisture using the evaporation peak.

7.9 Calibration and Adjustment

Definitions and basic principles on this topic can be found in Chapter 6, General Measurement Methodology.

The most important DSC quantities that have to be calibrated are

- the temperature T ,
- the heating rate dependence of the temperature (τ_{lag}), and
- the heat flow Φ .

7.9.1 One-point calibration versus multi-point calibration

One-point calibrations and adjustments are based on measurements using a single reference substance. For example, calibration measurements with indium are sufficient if high accuracy ($T \pm 0.3^\circ\text{C}$, $\Phi \pm 2\%$) is only required in the relatively small temperature range of about $\pm 50\text{ K}$ around the melting point of the reference substance - in the case of indium, between about 100 to 200 $^\circ\text{C}$.

For larger temperature ranges, we recommend multi-point adjustments using two or three reference substances whose melting points are uniformly spread over the temperature range of interest. The highest temperature accuracy over a wide range is achieved by using four or more reference substances [9].

Measurements in the non-adjusted temperature range

They are of course possible but less accurate, (extrapolation is less accurate than interpolation).

7.9.2 One-point calibrations and adjustments

Many users do not need the highest level of measurement quality and do not want to invest a lot of time in performing detailed measurement checks. These users trust a calibration using one reference substance and for example perform the In-Check once a month.

Note: The one-point adjustment shifts the scale in the entire temperature range by the corresponding amount.

7.9.2.1 Calibration with Indium

A sample of indium in a standard aluminum crucible is heated in air from 120 to 180 $^\circ\text{C}$ at 10 K/min. At the end of the measurement, the melting peak is evaluated with respect to normalized peak area and onset temperature.

The STAR[®] software “In-Check” program automatically performs the measurement and evaluation. If the temperature deviates by more than 0.3 K from the reference value (or the normalized peak area by more than 2%), the user is requested to perform an adjustment.

Procedure:

1. Check the DSC sensor visually for dust or residues from previous samples. Possibly purge the measuring cell or carefully dab the two crucible holders with a moist cotton-tipped swab.
2. Heat the measuring cell briefly to 400 °C to remove moisture from the system.
3. Accurately weigh out an indium sample of about 6 mg to an accuracy of 10 µg. Careful users prepare two In crucibles and compare the results. These crucibles are stored dust-free and can be used for about 20 calibration measurements.
4. Perform the calibration measurement three times. Sometimes the first measurement is an outlier.
5. If the onset temperature and the specific enthalpy change are within the permissible limits, the instrument can be used perfectly normally in the temperature range 100 °C to 200 °C for measurements.
6. If the deviation exceeds the permissible limits of error, the instrument parameters must be adjusted. A calibration measurement is performed afterward as a check.

7.9.3 Multi-Point Calibrations and Adjustments

Multi-point calibrations and adjustments provide better accuracy than the one-point method especially over a wide temperature range. For most practical purposes, two well-chosen reference substances are sufficient. For the highest possible accuracy, three to five calibration points uniformly spread over the temperature range of interest are sufficient.

The measured melting peaks are used to determine all parameters of interest. This elegant method is called **Total Calibration** by METTLER TOLEDO because the temperature, the rate dependence (τ_{lag}) and the heat flow are measured simultaneously. The reference substances undergo melting at three different rates.

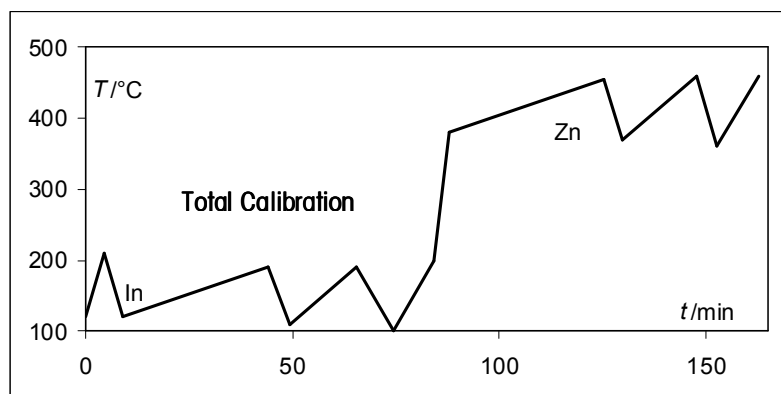


Figure 7.64. The figure shows the temperature program used for DSC Total Calibration using indium and zinc. After the In sample has melted for the first time, it is cooled until it solidifies and then melted at three different heating rates, e.g. 2, 5 and 10 K/min. An analogous temperature program is applied to the Zn sample. Finally, the 6 melting peaks are automatically evaluated.

Usually, during the Total Calibration, two reference substances contained in the crucible are repeatedly melted at different heating rates. When using such multi-samples, it is very important to separate the individual substances. This can be achieved by packing one or both reference materials in a very small piece of aluminum foil. There should only be one layer of foil against the bottom of the crucible. Several layers would have a thermal insulation effect and the τ_{lag} determination would be wrong. The foil must not be pressed too strongly against the sample because a low melting alloy could be formed. The same applies to the Zn sample if it is pressed too strongly against the bottom of the crucible.

7.9.3.1 Other Measurement Combinations

Other crucible combinations can also be defined through adjustment besides the standard aluminum crucibles in air (the standard adjustment). The initial values calculated with the less accurately known conversion factors in the database are overwritten. In the case of the DSC, it is mainly the temperature function of the calorimetric sensitivity. This is best determined using two to four reference substances with single calibrations that cover the temperature range of interest. A calibration of this type is also available for the τ_{ag} determination.

7.9.3.2 Single Calibrations

This type of calibration results in the most accurate adjustments. As many single samples as desired are measured one after the other using a suitable temperature program.

7.9.3.3 Multiple Temperature Calibration

This is a quick method to measure up to about three different reference substances. These are present in the crucible but not touching one another. Usually they are metal reference substances because, in contrast to organic compounds, metals do not decompose at higher temperatures. Separation is achieved by packing 2 of the 3 reference materials in a very small piece of aluminum foil. Only one layer of foil should be in contact with the bottom of the crucible.

Number of reference substances ¹	1	2 or 3	4 or more
Temperature function: $f(T) = A + BT + CT^2$	Only A is adjusted: the previous function is shifted parallel	A and B are adjusted: The slope changes	A , B and C are adjusted: Slope and curvature change
Time needed	½ h	2 to 4 h	5 h and more
Temperature range with very good accuracy ²	100 °C	200 to 300 °C	>400 °C

Table 7.4. Reference substances.

¹ It is assumed that the melting points of the reference substances are about 100 K apart. This is especially important with the 4-point adjustment. If the melting points lie close to one another, measurements could lie outside the temperature range covered by the adjustment and be inaccurate due to the changed curvature.

² Temperature accuracy ± 0.5 K, calorimetric accuracy $\pm 2\%$
The table shows that one-point adjustment is optimal from the point of view of time. The 2-point adjustment has the best cost/benefit ratio especially when based on the Total Calibration method.

Note: The calibration and adjustment procedures have proven themselves in practice. If official methods or other procedures have to be followed, the procedure will have to be changed accordingly.

7.10 Appendix: Assessing the Performance of a DSC Measuring Cell using Simple Measurements

7.10.1 Determination of Important Parameters from the Indium Melting Peak

Measure the indium melting peak: To minimize thermal resistance, use a sample of about 6 mg indium that has been pressed flat. Melt the sample twice using the following temperature program: Start temperature 120 °C, End temperature 180 °C, Heating rate 10 K/min. Use the second melting peak for the evaluations.

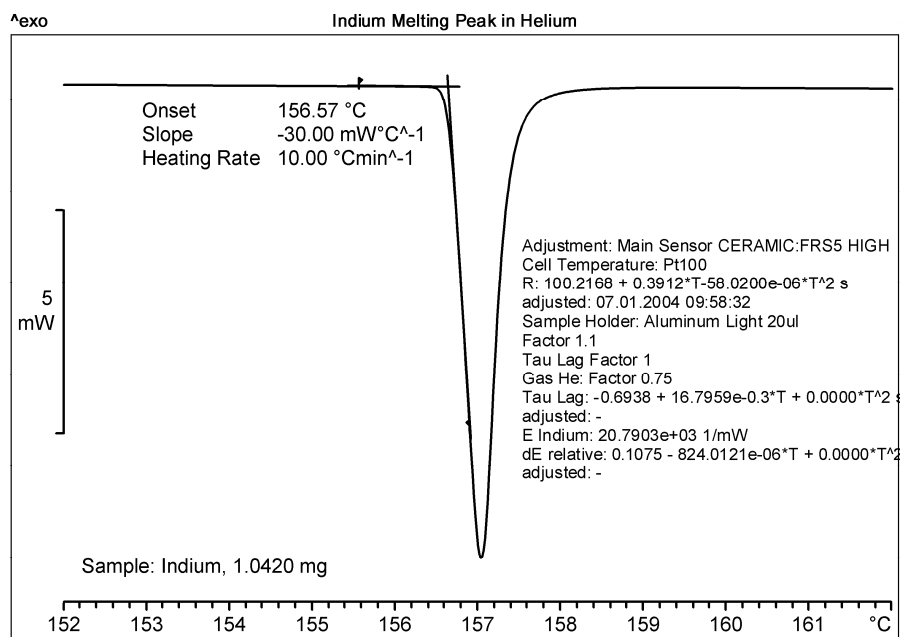


Figure 7.65. Indium peak measured at 10 K/min. The calibration data are displayed in the diagram.

According to Ohm's law, the **thermal resistance** R_{th} of the measurement setup is given by $R_{th} = \Delta T / \Phi$ and therefore corresponds to the reciprocal value of the slope of the melting curve (Φ plotted against T_r).

Example: The slope (Onset with Slope evaluation) is 19.8 mW/K. R_{th} is thus 0.050 K/mW.

The **signal time constant**, τ , can be determined from the decaying DSC signal, or from a deconvolution experiment (see Figure 7.62). In Figure 7.62, the time constant is 2.8 s. It also can be estimated from a TAWN resolution experiment.

The **heat capacity** C : The signal time constant, τ , is the product of the thermal resistance R_{th} and the sum of the heat capacities, C , of the sample, the crucibles and the part of the DSC sensor directly below the crucible: $\tau = R_{th} C$. From this, it follows that: $C = \tau / R_{th}$, that is 2.8 s / 0.050 K mW⁻¹, which gives 56 mJ/K.

The standard aluminum crucible with a mass of 50 mg accounts for almost 50 mJ/K of this ($c_{p, Al} \sim 1 \text{ J g}^{-1} \text{ K}^{-1}$). Clearly then, lighter crucibles result in shorter time constants.

7.10.2 The Resolution of a DSC Measurement

The resolution or separation of physical transitions that occur over a small temperature interval is an important performance feature of a DSC instrument.

An instrument with a good resolution gives tall and narrow melting peaks. In other words, the peak width, t_{peak} , should be small and the height of the peak, Φ_{max} , should be large.

Simple mathematical considerations indicate which properties influence the shape of a melting peak:

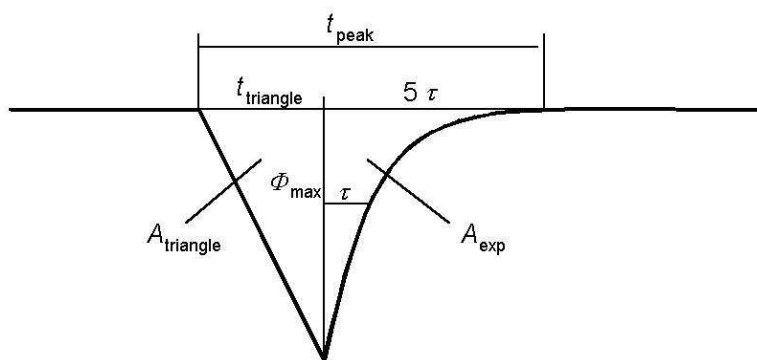


Figure 7.66. The schematic DSC fusion peak of a pure sample consists of two parts, namely the surface area of the triangle, A_{triangle} , and the area under the exponential curve, A_{exp} . The two areas added together yield the peak area ΔH . The width of the exponential tail is taken to be 5τ because an exponential curve decays to below 1% of the original height within 5 time constants (i.e. after 5 time constants, to a good approximation the signal reaches the baseline).

Symbols used:

t_{peak}	peak width,	t_{triangle}	base of the triangle in s,
T_{triangle}	base of the triangle in K,	A_{triangle}	area of the triangle,
A_{exp}	area of the exponential part,	Φ_{max}	height of the peak,
τ	time constant,	R_{th}	thermal resistance of the DSC sensor.

The area of the triangle is given by:

$$A_{\text{triangle}} = t_{\text{triangle}} \Phi_{\text{max}} / 2.$$

From Ohm's law $\Phi = \Delta T / R_{\text{th}}$, we obtain:

$$\Phi_{\text{max}} = T_{\text{triangle}} / R_{\text{th}}.$$

Substituting $T_{\text{triangle}} = t_{\text{triangle}} \beta$ yields:

$$\Phi_{\text{max}} = t_{\text{triangle}} \beta / R_{\text{th}}$$

thus

$$A_{\text{triangle}} = t_{\text{triangle}}^2 \beta / 2 R_{\text{th}}.$$

The area under the exponential curve is:

$$A_{\text{exp}} = \tau \Phi_{\text{max}} = \tau t_{\text{triangle}} \beta / R_{\text{th}}$$

The two areas added together correspond to the peak area ΔH :

$$\Delta H = t_{\text{triangle}}^2 \beta / 2 R_{\text{th}} + \tau t_{\text{triangle}} \beta / R_{\text{th}}$$

This quadratic equation is resolved for t_{triangle} :

$$t_{\text{triangle}} = \sqrt{\tau^2 + \frac{2 \Delta H R_{\text{th}}}{\beta}} - \tau$$

To obtain the total peak width t_{peak} , we add the width of the exponential tail of 5τ .

$$t_{\text{peak}} = \sqrt{\tau^2 + \frac{2\Delta H R_{\text{th}}}{\beta}} + 4\tau \quad (7.19)$$

If we multiply t_{peak} by the applied heating rate, we obtain the peak width in degrees. For $\tau = 2\text{ s}$, $\Delta H = 170\text{ mJ}$ (corresponding to 6 mg In), $R_{\text{th}} = 0.04\text{ K/mW}$ and $\beta = 10\text{ K/min}$, the result is 17 s or 2.9 K .

In this case, the DSC therefore separates two peaks completely if they are at least 17 s or 2.9 K apart when a heating rate of 10 K/min is used.

Summary: Apart from the sample properties, the resolution of a DSC depends solely on R_{th} , τ and β [15].

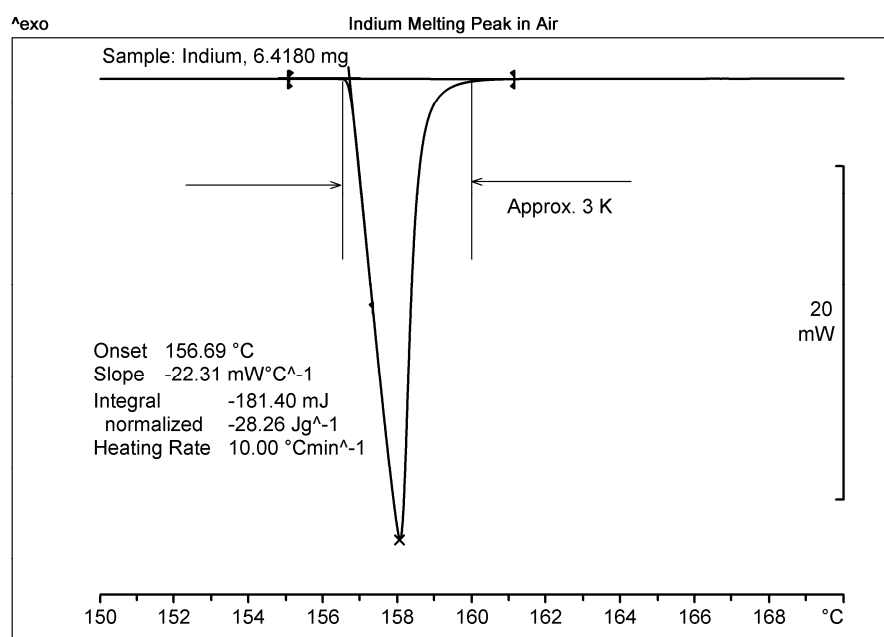


Figure 7.67. The diagram shows the DSC curve of 6.11 mg indium in a light Al crucible heated at 10 K/min . The width of the measured peak is 3 K . This agrees well with the calculated value of 2.8 K .

An empirical approach is the so-called “**TAWN Resolution Test**” [16] using the liquid crystal 4,4'-azoxydianisole as a test substance. In this test, a sample of 5.0 mg is heated at 20 K/min . A fusion peak occurs at approx. 118 °C and a mesophase transition at approx. 135 °C .

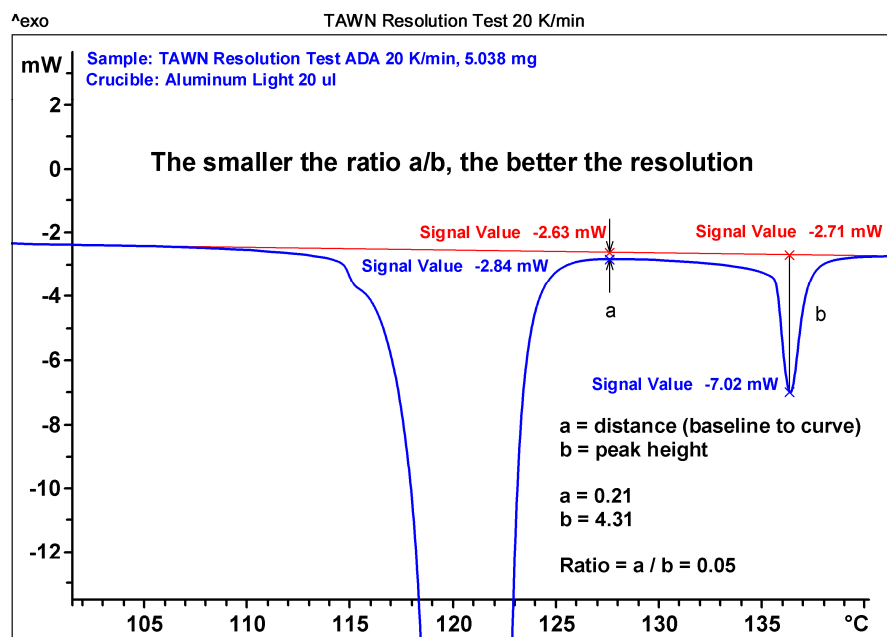


Figure 7.68. The TAWN resolution test performed in a METTLER TOLEDO DSC822°. The smaller the distance, a , between the DSC melting curve and the linear baseline drawn between the effects, the better the resolution.

TAWN draws a straight baseline from 100 to 150 °C and measures the minimum distance, a , to the DSC curve between the peaks.

The resolution is given by the ratio of the minimum distance, a , to the height, b , of the small peak:

$$\text{TAWN Resolution} = \frac{a}{b} = \frac{0.22 \text{ mW}}{4.33 \text{ mW}} = 0.05 \quad (\text{a low value means good resolution})$$

7.10.3 The “Sensitivity” of a DSC

The signal-to-noise level determines the ultimate **detection limit**. Two definitions of noise are currently used: the peak-to-peak (pp) and the root-mean-square (rms) noise. For further details, see Section 4.4.

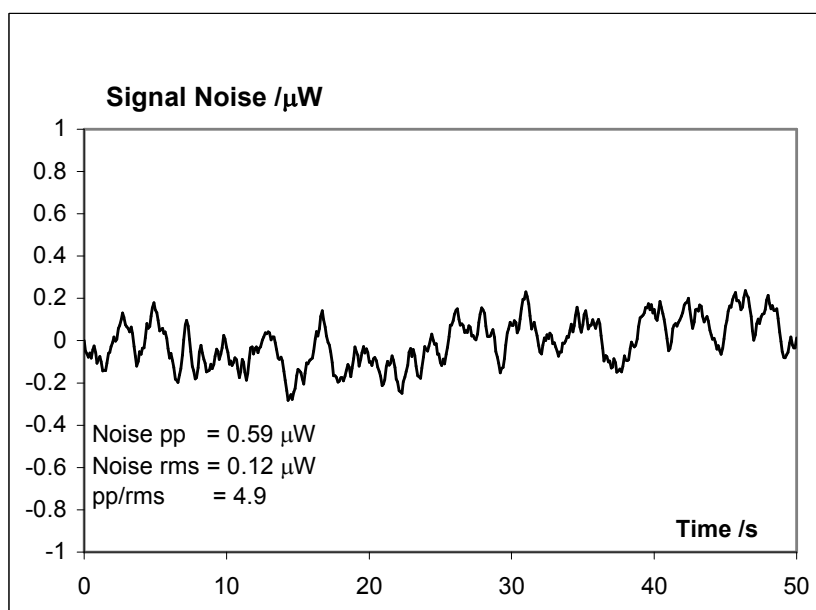


Figure 7.69. Calculation of peak-to-peak (pp) and root-mean-square (RMS) values from random noise.

It would be easy to obtain a low noise level by using smoothing procedures. This would however cut off weak but real sample effects, so that a low noise level does not necessarily mean high sensitivity.

In the “**TAWN Sensitivity Test**” [16], a sample with a known weak effect is measured and the peak height divided by the noise_{pp}. This signal-to-noise ratio characterizes the sensitivity of a DSC.

Sample: 4,4'-azoxydianisole; mass 0.25 mg ($\pm$ 0.02 mg); heating rate 0.1 K/min; sampling interval 0.1 s.

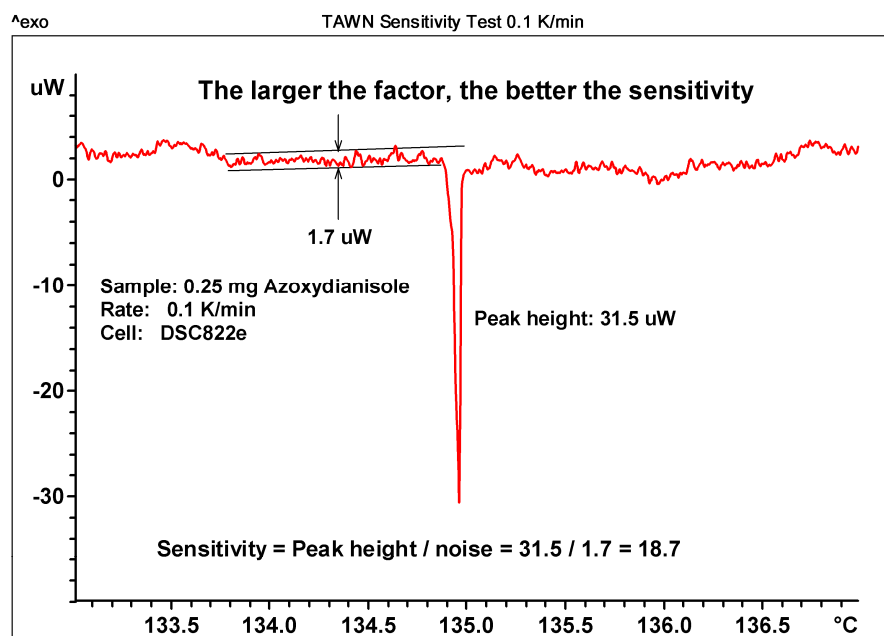


Figure 7.70. The DSC curve of 0.25 mg 4,4'-azoxydianisole measured in a METTLER TOLEDO DSC822^e at a heating rate of 0.1 K/min using a sampling interval of 0.1 s.

The two properties used for the calculation of the TAWN sensitivity are the noise_{pp}, d , and the peak height, c , of the mesophase transition.

$$\text{TAWN Sensitivity} = \frac{c}{d} = \frac{31.5 \mu\text{W}}{1.7 \mu\text{W}} = 18.7$$

The larger this ratio, the better the “sensitivity” or signal-to-noise ratio of the instrument.

Note: The TAWN test enables you to compare different DSC instruments. The sample preparation and the purity of the 4,4'-azoxydianisole are of course important.

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UserCom: Many of the application examples in this chapter have been taken from UserCom, the METTLER TOLEDO technical customer journal that is published twice a year. Back issues of UserCom can be downloaded as PDFs from the Internet at www.mt.com/ta-usercoms .

8 Differential Thermal Analysis

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In differential thermal analysis (DTA), the sample and an inert reference substance are heated linearly. The temperature difference that occurs between the sample and reference is the measurement signal.

8.1 The DTA Measurement Principle

In 1887, the French chemist Henri Louis LeChatelier described a method in which the sample temperature within a clay sample was measured while it was subjected to a temperature program. Le Chatelier displayed the sample temperature graphically to determine deviations from the applied temperature program. The temperature deviations are caused by exothermic or endothermic processes that occur in the sample.

In 1899, the British scientist William C. Roberts-Austen devised the first classical DTA arrangement. The sample crucible and a reference crucible of the same type were arranged symmetrically in a single heat source and subjected to a common temperature program. The temperature difference between sample and reference was measured by two thermocouples coupled back to back in the sample and in an inert reference substance. This arrangement yielded the first DTA curve.

The DTA signal is plotted as the temperature difference or the thermoelectric voltage as a function of the sample temperature.

There are three basic designs (Figure 8.1):

- Block furnace: Thermocouples are inserted in the sample and in the reference material which are heated in a single furnace. This design is simple to set up but has serious disadvantages: the thermocouple must be cleaned (or replaced) before it is inserted in the sample for the next measurement. Since the thermal resistance is created by the sample itself, the baseline shifts markedly when the sample melts. This classical DTA design allows the thermal effect to be detected but the conversion enthalpy cannot be quantitatively determined because the measured temperature difference depends on the thermal resistance of the sample. Ideally, the thermal resistance between the thermocouple and the sample should be as small as possible.
- Boersma DTA introduced in 1955 by the Dutchman S. L. Boersma: This design also uses a single furnace but there are thermal resistances between the furnace and the crucible holders: This setup measures the temperature difference between the two crucible holders. The main advantages are that
 - the thermocouple does not come into direct contact with the sample, and
 - the reproducibility of the DTA curve compared to that obtained using the classical block furnace is greatly improved. A new measurement is performed by simply inserting a crucible with the new sample.
- SDTA (Single DTA): This technique measures the difference between the sample temperature and the reference temperature calculated from the temperature program. The advantages of this design with just one crucible are
 - lower thermal inertia and hence faster response due to the small sensor mass,
 - better symmetry because the sample crucible is at the center of the furnace, and
 - higher temperature accuracy due to the smaller furnace.

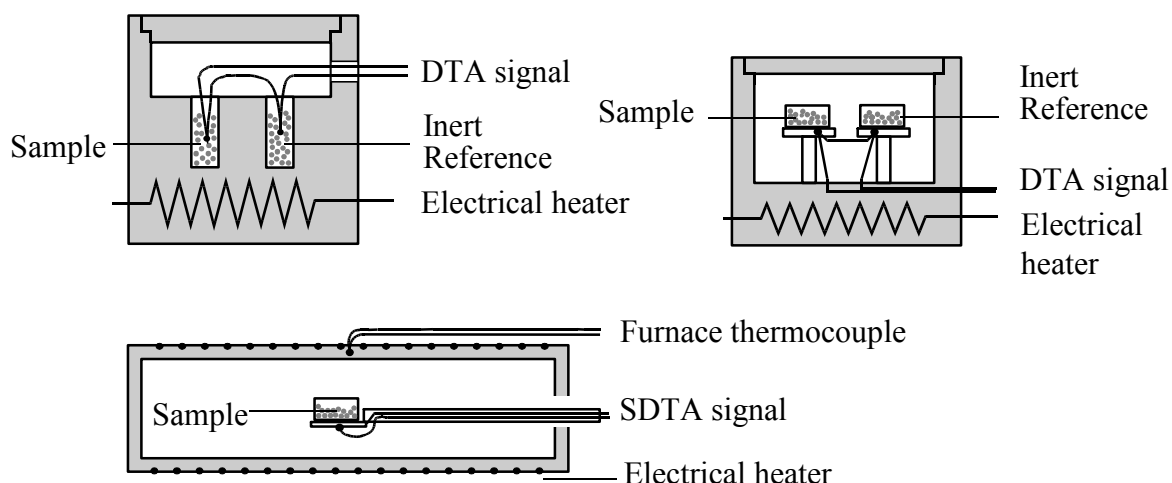


Figure 8.1. Above left: DTA measuring cell with block furnace; the thermocouples are in direct contact with the sample and the reference material. Above right: Boersma type DTA measuring cell with discrete thermal resistances between furnace and crucible holder; sample and inert reference material are contained in separate crucibles. Below: SDTA measuring cell setup in the METTLER TOLEDO horizontal furnace.

DTA is used mostly for simultaneous TGA, TMA, and DMA measurements. The additional information facilitates interpretation and measures the sample temperature more accurately.

8.2 Typical DTA Curves

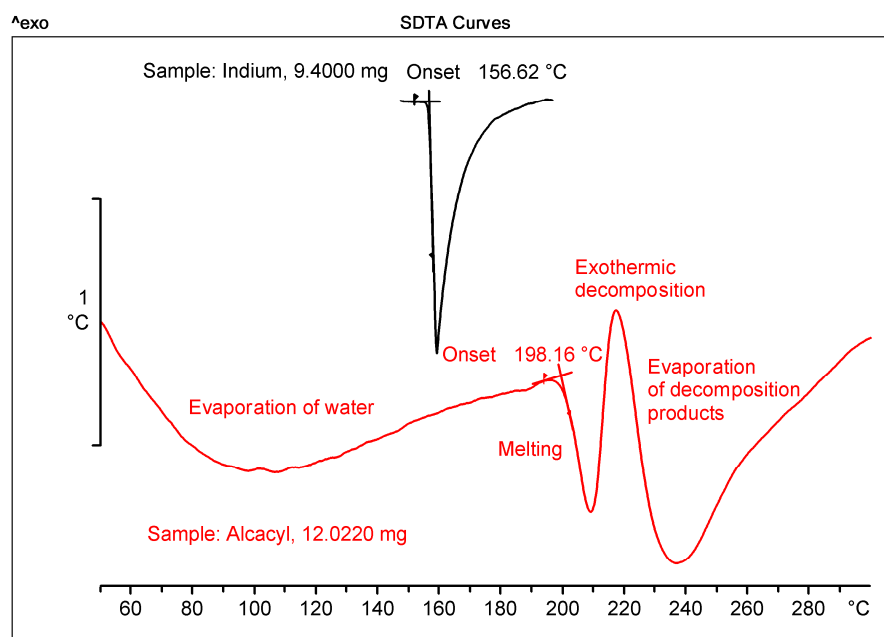


Figure 8.2. Above: The upper curve shows a simple melting curve. The onset temperature corresponds to the melting point. Below: The SDTA curve of an analgesic containing 48% of the active substance (calcium salt of acetyl salicylic acid). The binder contains moisture. This evaporates up to about 180 °C and gives rise to a broad endothermic peak. At 198.2 °C, the active substance begins to melt. The exothermic decomposition reaction is much faster in the liquid phase and produces an exothermic peak at 220 °C. The endothermic peak that follows is due to the vaporization of volatile decomposition products.

8.3 The Calculation of the DSC Curve from SDTA

SDTA curves show that the areas of melting peaks are proportional to the sample mass used and are therefore proportional to the amount of heat exchanged. On this basis, it is thus possible to calculate a DSC curve from the qualitative SDTA curve using a calibration curve. The calibration curve is obtained by means of so-called calibration factors, k , which are plotted against the corresponding temperatures.

If the enthalpy of fusion, Δh_{lit} , of the reference substance used is known, the calibration factor, k , of the enthalpy of melting to the peak area, A_{peak} , can be calculated according to the equation

$$k = \frac{m \Delta h_{\text{lit}}}{A_{\text{peak}}} \quad (8.1)$$

where m is the sample mass.

The unit of k is $\text{mW}^\circ\text{C}^{-1}$. Measurements have shown that k is almost independent of the purge gas flow rate. k is determined by the heat transfer and therefore depends on the temperature and type of purge gas.

The calibration factor, k , can be determined in the temperature range 50 °C to 1100 °C using indium, zinc, aluminum and gold standards. The data determined using platinum crucibles in a nitrogen atmosphere is presented in Table 8.1. Alloy formation and consequent destruction of the crucible is prevented by spreading about 5 mg $\alpha\text{-Al}_2\text{O}_3$ powder over the bottom of the crucible and placing the metal samples directly on the layer of powder. Indium and zinc, and aluminum and gold are placed together in separate crucibles but so that they do not touch each other.

Substance	$T_f / ^\circ\text{C}$	$\Delta h_{\text{lit}} / \text{J g}^{-1}$	m / mg	$A_{\text{peak}} / ^\circ\text{C s}$	$k / \text{mW}^\circ\text{C}^{-1}$
Indium	156.6	28.4	12.54	98.7	5.09
Zinc	419.5	107.5	18.45	227.2	8.73
Aluminum	660.3	397.0	3.79	98.7	15.25
Gold	1064.2	63.7	11.13	21.5	32.9

Table 8.1. Data for converting a DTA curve to a DSC curve.

A third order polynomial fit of the function $k(T)$ can be calculated from the plot of the four measurement points against temperature. Multiplication of the SDTA curve by the fitted k curve yields a curve with an ordinate in heat flow units that corresponds to a DSC curve (Figure 8.2).

DSC curves calculated from SDTA curves in this way are noisier and have a longer time constant than “true” DSC curves. The blank curve reproducibility is also not so good. In spite of this, enthalpy changes can be measured with good accuracy (using standard Al or small Pt crucibles).

The importance of this method is that correct reaction enthalpies are obtained in addition to changes in mass. This is done by normalizing the calculated DSC curve to the current sample mass.

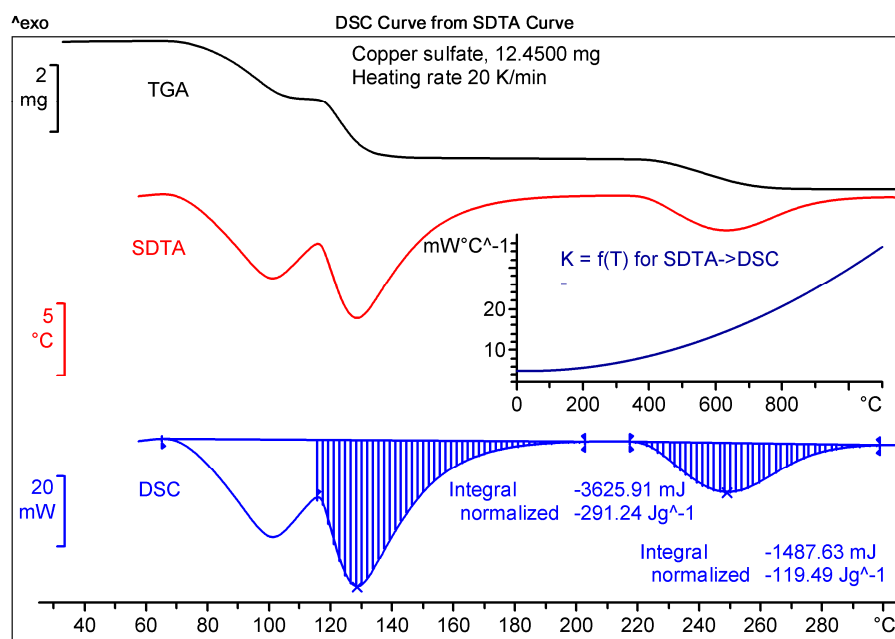


Figure 8.3. The figure shows TGA and SDTA measurements of copper sulfate pentahydrate. The SDTA curve is multiplied by the k curve to obtain the DSC curve. This can be integrated just like a directly measured DSC curve to obtain enthalpy changes.

8.4 The SDTA Evaluations in the STAR^e Software

SDTA curves are mainly evaluated for the onset and peak temperature. DSC evaluations can be used when SDTA curves are converted to DSC curves (see Section 7.6).

References and Further Reading

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9 Thermogravimetric Analysis

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9.1 Introduction

Thermogravimetric analysis (TGA) is an experimental technique in which the weight or strictly speaking the mass (see information box) of a sample is measured as a function of sample temperature or as a function of the time in isothermal experiments. The instrument used to perform such measurements is called a thermogravimetric analyzer, TGA.

Note on mass and weight

In everyday usage, weight is used as a synonym for mass. The mass (m) of an object is, however, a fundamental measure of the amount of matter in an object. In contrast, the weight (w) of an object is its mass (m) times the acceleration of gravity (g) and is therefore a force. For measurements made on the earth's surface, the distinction between mass and weight is not generally useful. A TGA instrument measures a force which is converted to a mass. In this text, mass will be used when we are talking about the sample, and weight when we mean the TGA balance signal.

The results of a TGA measurement are usually displayed as a TGA curve in which mass is plotted against temperature or time. Another useful and complementary presentation is to use the first derivative of the TGA curve with respect to temperature or time. This shows the rate at which the mass changes and is known as the differential thermogravimetric or DTG curve.

Mass changes occur when the sample loses material in one of several different ways or reacts with the surrounding atmosphere. This produces steps in the TGA curve or peaks in the DTG curve. A number of different effects can cause a sample to lose, or even gain, mass and so produce steps in the TGA curve. These include the following:

- Evaporation of volatile constituents; drying; desorption and adsorption of gases, moisture and other volatile substances; loss of water of crystallization.
- Oxidation of metals in air or oxygen.
- Oxidative decomposition of organic substances in air or oxygen.
- Thermal decomposition in an inert atmosphere with the formation of gaseous products. With organic compounds, this process is known as pyrolysis.
- Heterogeneous chemical reactions in which a starting material is taken up from the atmosphere, for example reduction reactions with a purge gas containing hydrogen. Furthermore, reactions in which a product is evolved, for example decarboxylation or condensation reactions.
- Ferromagnetic materials. The magnetic properties of some materials change with temperature (Curie transition). If the sample is measured in an inhomogeneous magnetic field, the change in magnetic attraction at the transition generates a TGA signal. The magnetic field is produced by placing a permanent magnet below the furnace close to the sample.

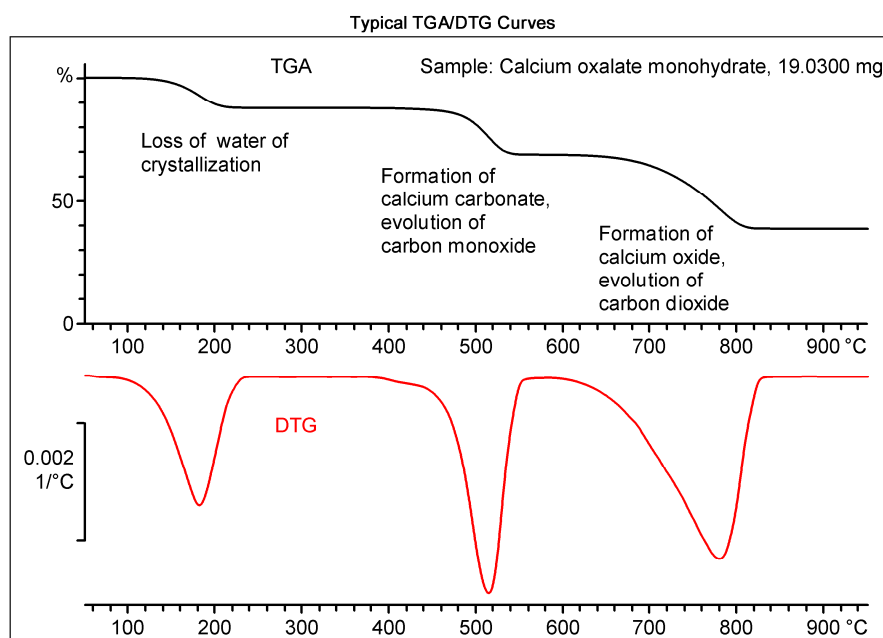


Figure 9.1. Stepwise decomposition of calcium oxalate monohydrate: sample mass 19 mg, heating rate 30 K/min, nitrogen atmosphere. The TGA curve has been normalized (divided by the sample mass) and therefore begins at 100%. The temperature range of the three mass loss steps is particularly clear in the first derivative or DTG curve.

9.2 Design and Measuring Principle

Three different thermobalance designs are shown schematically in Figure 9.2. Nowadays, mainly compensation balances are used. With this type of balance the position of the sample in the furnace remains exactly the same even when the mass changes. At the same time, however, one can distinguish between simple moving coil measuring systems and more sophisticated weighing cells (parallel-guided). In the horizontal arrangement, simple moving coil systems have the disadvantage that samples that move horizontally during heating (e.g. during melting) generate an apparent change in mass. METTLER TOLEDO use a parallel-guided system that overcomes this potential problem.

Constructional measures have to be incorporated between the balance and the furnace to protect the balance in the balance chamber against the effects of heat radiation and the ingress of corrosive decomposition products. In most cases the balance housing is purged with a protective gas.

Depending on the resolution they provide, balances are classed as semimicro- (10 µg), micro- (1 µg) or ultramicro- (0.1 µg) balances. Besides resolution, the (continuously measurable) maximum capacity of the balance is also an important factor. This is particularly the case when measuring inhomogeneous materials where a few milligrams are often hardly representative and a larger sample mass is desirable.

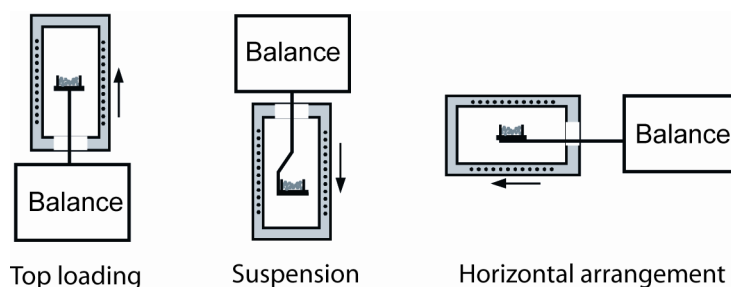


Figure 9.2. Thermobalance designs showing the top loading, suspension and horizontal arrangements. The arrow shows the direction in which the furnace is moved for sample loading.

9.2.1 Buoyancy Correction

Due to the change in density of a gas as the temperature changes, buoyancy corrections must be made in TGA measurements. Without corrections every sample will appear to show an increase in mass during a heating experiment. TGA measurements are usually corrected for the effect of buoyancy by performing a blank measurement. A blank measurement uses the same temperature program and crucible used for the sample but without a sample. The resulting blank curve is then subtracted from the sample measurement curve. Buoyancy correction is essential for tests such as ash content where the residue at the end of the test needs to be determined accurately, and where very small mass losses are expected.

When a body with a volume V is immersed in a medium (in this case a gas), it experiences an upthrust or buoyancy force, F , which corresponds to the mass of the medium displaced,

$$F = V \cdot \rho \cdot g \quad (9.1)$$

where ρ is the density of the gas and g is the acceleration of gravity, 9.81 kg/ms². Since a thermobalance is on the one hand a force compensating balance, but the signal is displayed in units of mass, the buoyancy in terms of mass, m , is given by the equation

$$m = V \cdot \rho \quad (9.2)$$

The pressure in a thermobalance is usually constant because it is open to the atmosphere at the outlet.

The buoyancy effect in the thermobalance is however not constant because gas density is temperature dependent. This means that even a sample whose mass does not change shows an apparent increase in mass with increasing temperature. The total volume of the parts enclosed by the furnace atmosphere is responsible for this change in buoyancy. This includes the sample, crucible and the parts of the crucible holder within the furnace volume. In recent METTLER TOLEDO TGA instruments, the volume is typically between 200 µl and 400 µl.

The temperature dependence of density at constant pressure is given by the equation

$$\rho = \rho_0 \frac{T_0}{T} \quad (9.3)$$

where ρ_0 is the density of the gas at the reference temperature, T_0 , of 25 °C (298 K) and T is the temperature in Kelvin.

Gas	Density [mg/mL] at 25 °C	Density [mg/mL] at 500 °C	Density [mg/mL] at 1000 °C
Dry air	1.184	0.457	0.269
Nitrogen	1.146	0.441	0.268
Oxygen	1.308	0.504	0.306
Argon	1.634	0.630	0.383
Helium	0.164	0.063	0.038
Carbon dioxide	1.811	0.698	0.424

Table 9.1. Density of several gases at 25, 500 and 1000 °C at a standard pressure of 101.3 kPa. From this data, it follows that a body with a volume of 1 mL experiences a buoyancy effect in air of 1.184 mg at 25 °C or 0.269 mg at 1000 °C. This means that the body becomes 0.879 mg heavier on warming.

As mentioned above, the buoyancy effect is corrected by subtracting a blank curve from the measurement curve. The small change in buoyancy due to the change in volume of the sample during the thermal effect is however not compensated.

9.2.2 Simultaneous TGA/SDTA

Modern thermobalances are often equipped so that they can record the DTA signal (see Chapter 8, Differential Thermal Analysis) at the same time as the actual thermogravimetric measurement. In METTLER TOLEDO TGAs, the DTA signal is measured without the need of a special crucible holder. This is possible because the temperature of an inert reference sample (necessary for the DTA measurement) is available from the blank curve. This method is therefore referred to as **Single Differential Thermal Analysis (SDTA)**.

In addition to showing the energetic nature of events involving mass loss, the DTA signal can also show thermal effects that are not accompanied by a change in mass, for example melting, crystallization, or a glass transition. The evaluation is usually restricted to the determination of onset and peak temperatures. Processes involving a loss of mass usually give rise to endothermic DTA effects because of the work of expansion. There are exceptions however. If combustible gases are formed at sufficiently high temperature (spontaneous ignition, possible catalytic effects on the surface of the platinum crucible) and sufficient oxygen is available, then the enthalpy of combustion is greater and the net effect is exothermic (see Figure 9.3).

If the SDTA signal is calibrated and adjusted using the melting peaks of reference substances, the SDTA curve (in °C) can be converted to a DSC curve (in mW). Enthalpy changes can then be quantitatively determined (see Chapter 8, Differential Thermal Analysis). This occurs automatically in the TGA/DSC 1.

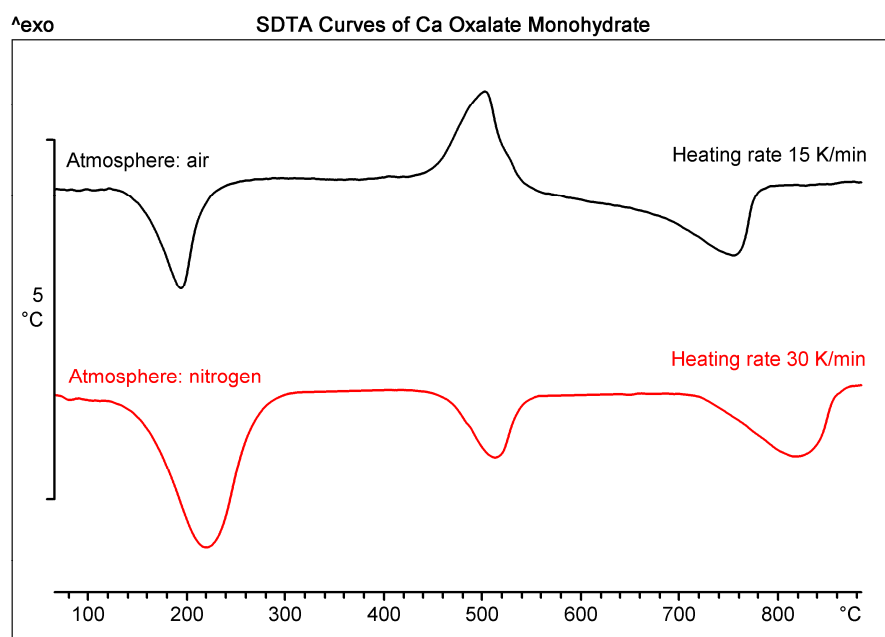


Figure 9.3. SDTA curves of calcium oxalate monohydrate measured in air (upper curve) and N_2 (lower curve). The second effect at 500 °C corresponds to the elimination of carbon monoxide, a process that is endothermic in an inert atmosphere. If oxygen is present, the CO immediately burns to CO_2 , which produces an exothermic effect (above).

9.3 Sample Preparation

A number of factors should be considered when preparing a sample for TGA experiments:

- The sample should be representative of the material being analyzed.
- The mass of the sample should be sufficient to achieve the precision required for the test.
- The sample should be changed as little as possible by the sample preparation process.
- The sample should not be contaminated by the sample preparation process.

The morphology of the sample influences the diffusion rate of reaction products and in turn the course of the reaction. At the same time it also affects heat transfer within the sample.

The mass used in the experiment also influences the rate of mass loss due to the same diffusion and heat transfer processes.

It is therefore important in quality control measurements to use a consistent and reproducible sample preparation technique. Using consistent sample masses is very important in producing comparable TGA data.

In Figure 9.4, the decomposition of finely ground copper sulfate pentahydrate is compared with the decomposition of more coarse crystals. The reaction is faster in the powdered sample because the gaseous reaction products reach the surface of the individual powder grains more rapidly. This example illustrates the importance of sample preparation in thermogravimetric measurements.

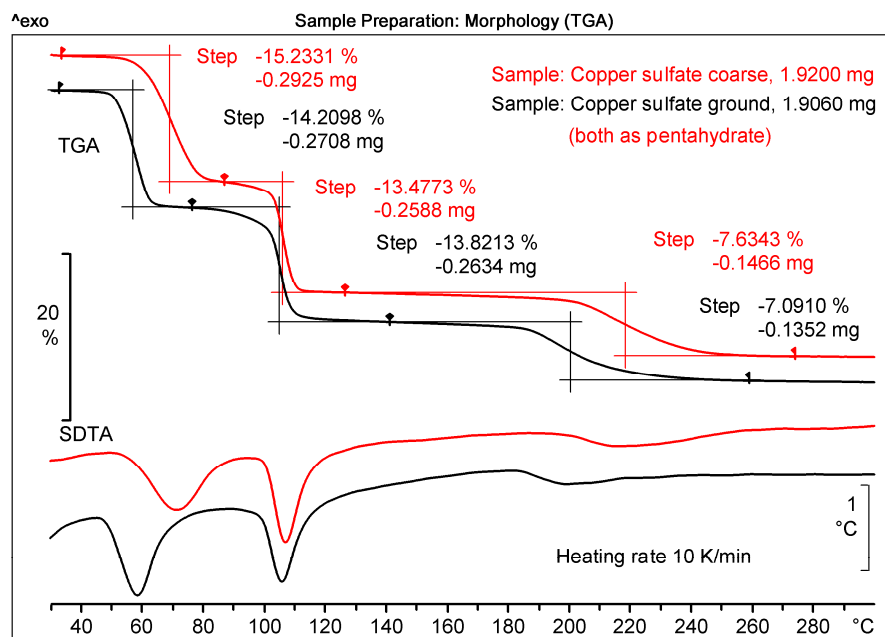


Figure 9.4. TGA and SDTA curves showing the elimination of water of crystallization from copper sulfate pentahydrate. The red curves were measured with rather coarse crystals, the black curves with finely ground crystals. The first and third steps in the curve of the finely ground crystals are shifted more than 10 K to lower temperature. The heating rate was 10 K/min. The curves are offset for comparison.

9.4 Performing Measurements

Thermogravimetric measurements are influenced by various factors such as:

- Method parameters: heating rate, atmosphere (air, nitrogen, argon; pressure).
- Sample preparation: sample size, homogeneity and morphology of the sample: coarse crystals, fine powder.
- Choice of crucible (see Section 6.3).
- Instrumental influences such as buoyancy and gas flow effects. These can be reduced or eliminated by performing blank curve subtraction.
- Changes in the physical properties of the sample during the measurement. For example, a change in emissivity (which affects the heat transfer within the sample and from the furnace to the sample), or the volume (which leads to a change in buoyancy).
- The sample may spit or move and artifacts caused by such events can be minimized by grinding the sample or covering with a platinum mesh.

9.4.1 Influence of the Heating Rate

The systematic deviation between the true sample temperature and the measured temperature, which is heating-rate dependent, can be determined and corrected through temperature calibration and adjustment. This is usually done using pure metals with good thermal conductivity. Real samples (e.g. polymers) can of course exhibit quite different thermal conductivity behavior. For this reason, the measured sample temperature will still be expected to show a slight dependence on the heating rate, even in an instrument that has been properly adjusted. The effect is very small with the onset temperature, but is more pronounced with the peak temperature.

If the sample undergoes chemical reactions, the temperature region in which the reaction occurs is very much dependent on the heating rate. In general, higher heating rates cause reactions to shift to higher temperatures. The choice of the heating rate is particularly important if secondary reactions occur with starting temperatures that differ only slightly from each other. If unsuitable heating rates are used, the reactions may overlap and remain undetected. It is, however, often possible to separate different reactions by choosing favorable heating rates (in general lower, sometimes higher).

A quite different approach for separating overlapping reactions is based on the use of DTG to automatically control the heating rate: the faster the change in mass, the slower the heating rate. This idea was first published by Hans Georg Wiedemann as long ago as 1958. Nowadays, software is available that automatically controls the heating rate in this way (MaxRes) [1].

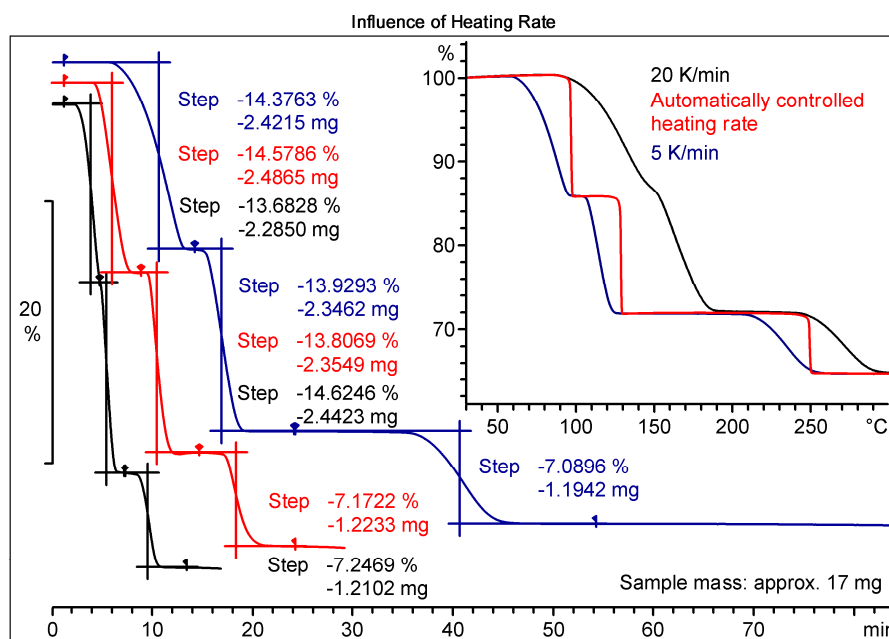


Figure 9.5. Influence of the heating rate on the resolution of partial reactions. In the inserted diagram on the right, the blue and black TGA curves were measured conventionally at 5 K/min and 20 K/min, while the red curve was recorded using the automatically controlled heating rate (MaxRes). In this presentation of mass against temperature, the steps in the MaxRes curve appear practically vertical because at low heating rates, the reaction takes place almost isothermally. In contrast, in the mass against time presentation (large diagram), the shape of the three curves looks similar. On closer inspection, the better separation obtained using sample controlled heating rates (MaxRes) – becomes apparent – especially in the first two steps.

9.4.2 Influence of Crucible

During the TGA measurement, crucibles must of course be “open” to the atmosphere. It can be important, however, to seal the sample hermetically before the actual measurement is performed in order to prevent it from coming into contact with air. The lid of the crucible is then pierced immediately before the start of the measurement (e.g. in the sample changer).

Reactions in the gas phase proceed more rapidly in completely open crucibles than in a so-called self-generated atmosphere. In a sealed crucible with a very small hole in the lid, or in a crucible with a lid without a hole placed loosely over the sample, the mass loss is shifted to higher temperature.

The material of which the crucible is made must not influence the reaction of the sample. In general, alumina (aluminum oxide) crucibles are used for TGA measurements. These have the advantage that they can be heated to over 1600 °C without problems. Sapphire crucibles are even more resistant and are especially suitable for the measurement of metals with high melting points such as iron that partially dissolve and penetrate ordinary alumina crucibles at high temperatures.

Platinum crucibles have the advantage of good thermal conductivity, which improves SDTA performance. Above 1000 °C, platinum crucibles can however stick irreversibly to the crucible holder, which is also made of platinum. This problem can be avoided by placing a thin sapphire disk on the crucible holder to prevent the two platinum surfaces touching each other. And finally, platinum is not always inert. It has a catalytic effect and can for example promote combustion reactions.

Metal samples in platinum crucibles

Damage to platinum crucibles due to alloy formation with metal samples can be prevented by covering the bottom of the crucible with a very thin layer of α -aluminum oxide powder before inserting the metal sample.

9.4.3 Furnace Atmosphere

Clearly, the mass of a sample in a closed system remains constant and cannot be a function of temperature or time. Thermogravimetric measurements are therefore only possible if the sample is free to exchange material with its immediate surroundings. An important requirement is therefore that the gas atmosphere surrounding the sample can be adapted to the experimental requirements. To achieve this, several gas inlet and outlets are available to the user.

First a protective gas is required to protect the balance against any corrosive gases that may possibly be evolved. Typically, dry inert gases such as nitrogen or argon and flow rates of 30 mL/min are used. Besides the protective gas, a purge gas and/or reactive gas can be led into the furnace chamber via separate lines. The purge gas removes the gaseous reaction products from the furnace chamber. If helium is used as purge gas, heat transfer from the wall of the furnace to the sample improves, especially at temperatures below about 700 °C. Reactive gases can be delivered to the sample to observe the interaction of the reactive gas with the sample. Examples of reactive gases are air or oxygen (oxidation) or hydrogen (catalysis, reduction) diluted with argon (usually 4% hydrogen with 96% argon) to prevent the possibility of explosion. Typically, flow rates of 30 mL/min are used for reactive and purge gases.

9.4.3.1 Residual Oxygen in an Inert Atmosphere

Very often the question arises as to amount of residual oxygen in the system. This can very easily be determined by measuring the combustion of activated carbon at 700 °C in the thermobalance.

Example: After purging for about 20 min at a flow rate $\Delta V/\Delta t$ of total 100 mL/min (the sum of the protective, purge and reactive gas flow rates measured at 25 °C, all for example N₂) the loss of mass stabilizes at a combustion rate, $\Delta m/\Delta t$, of 10 $\mu\text{g}/\text{min}$. Under these conditions, practically every oxygen molecule still present reacts with the activated carbon to form carbon dioxide (at temperatures ≥ 1000 °C, CO would increasingly be formed).



The combustion of 1 mole of carbon (12 g) requires 1 mole, or 22.4 L oxygen (measured at 25 °C). This means that a combustion rate of 12 $\mu\text{g}/\text{min}$ corresponds to an oxygen consumption of 22.4 $\mu\text{L}/\text{min}$.

From this, the residual oxygen content, c_r , can be obtained through comparison with the total purge gas rate, $\Delta V/\Delta t$:

$$c_r = \frac{\Delta m/\Delta t}{12 \mu\text{g}/\text{min}} \frac{22.4 \mu\text{L}/\text{min}}{\Delta V/\Delta t} = 1.87 \mu\text{L}/\mu\text{g} \frac{\Delta m/\Delta t}{\Delta V/\Delta t} \quad (9.5)$$

if $\Delta m/\Delta t$ is 5 $\mu\text{g}/\text{min}$ and $\Delta V/\Delta t$ is 100 mL/min, it follows that

$$c_r = (1.87 \mu\text{L}/\mu\text{g} \times 5 \mu\text{g}/\text{min} / 100\,000 \mu\text{L}/\text{min}) = 0.00009 = 90 \text{ ppm}$$

Alternatively, instead of the ppm calculation, it may be easier to just observe the combustion rate. A routine check might require the mass loss to be less than, say, 10 $\mu\text{g}/\text{min}$.

Sources of residual oxygen	Precautions
Oxygen content of the purge gas. Leaks in the gas supply tubing and other fittings and connections.	Use an inert gas containing less than 10 ppm oxygen. Oxygen can diffuse through plastic tubing! Use either very short sections of plastic tubing (less than 50 cm) or metal tubing with a minimum number of connections and joints. Carefully check all joints for leaks.

Sources of residual oxygen	Precautions
Outgassing of constructional components (oxygen adsorbed on parts of the measuring cell) and dead volume.	Switch on the flow of protective gas to the microbalance several hours before measurement. Purge vacuum connection as well. Only open the furnace briefly to insert the sample. Active replacement of air through slight evacuation to about 1 kPa. Then flood with the desired purge gas (if necessary twice).
Ingress of atmospheric oxygen due to leaks.	A possible cause of leakage is the furnace seal which could be damaged or dirty.
Ingress of atmospheric oxygen due to back diffusion at the purge gas outlet.	Attach a long thin tube to the outlet (this functions as a diffusion baffle)

Table 9.2. Sources of residual oxygen and precautions.

9.4.3.2 Overpressure

For safety reasons, thermogravimetric measurements above atmospheric pressure are usually avoided. In recent METTLER TOLEDO TGA instruments, the force holding the furnace chamber together limits the possible overpressure to about 10 kPa. Even if the gas outlet valve is unintentionally closed, the slight build-up of overpressure is periodically released at the furnace O-ring (this would at the same time create periodic artifacts on the TGA signal).

9.4.3.3 Reduced Pressure

Mass losses through vaporization or evaporation often occur at the same time as a decomposition reaction and are therefore difficult to distinguish from one another. The separation of the effects can often be improved by reducing the pressure in the measuring cell. A typical example is shown in Figure 9.6. The measurement at normal (atmospheric) pressure shows that mass is lost from about 320 °C onward and that the process possibly occurs in two steps. When the measurement is performed under reduced pressure at 1.5 kPa (15 mbar), the separation of the two steps is greatly improved.

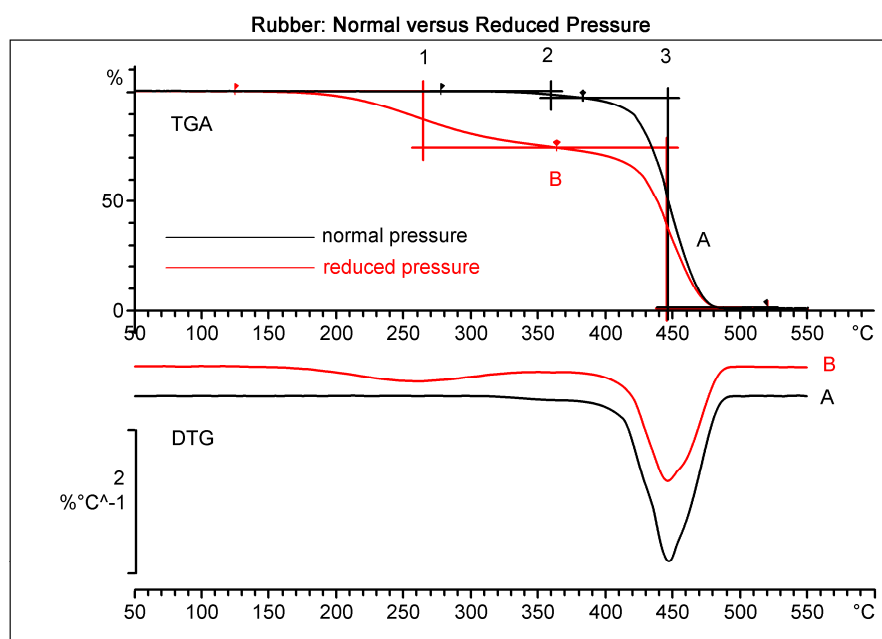


Figure 9.6. Effect of pressure on the decomposition of an elastomer: sample A is measured at normal (atmospheric) pressure, and B under reduced pressure, 1.5 kPa (15 mbar, B). Under reduced pressure, the vaporization of the volatile components (additives, 1) is clearly separated from the decomposition of the elastomer (2, 3). At normal pressure, the step height evaluated (on an expanded scale) from the stable region of the baseline at 270 °C to the next DTG maximum at 380 °C does not correspond to the true additive content.

Even at reduced pressure, a purge gas is still needed to protect the microbalance against the condensation of possibly corrosive decomposition products.

In vacuum operation, the vacuum pump is normally in continuous operation because the reaction products, air from possible leakage, and the purge gas have to be removed in order to achieve a constant vacuum. To obtain realistic values for the pressure in furnace chamber, the pressure meter should be installed close to the furnace chamber and not in the vacuum line leading to the vacuum pump. The working pressure is typically in the range 0.1 to 10 kPa.

The use of reduced pressure may require recalibration of the temperature scale if high temperature accuracy is required.

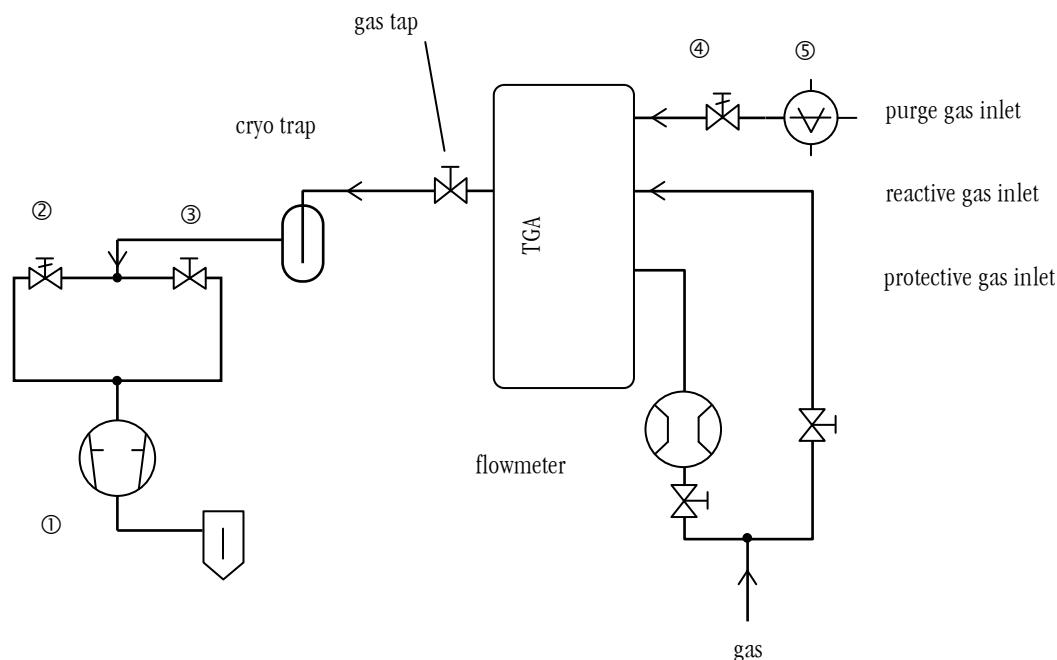


Figure 9.7. Schematic diagram of a TGA for operation under reduced pressure or vacuum. The protective gas protects the microbalance against decomposition products from the sample. The needle valve of the flowmeter is completely open so that the flow is measured at normal pressure. The vacuum meter (5) measures the pressure at the purge gas connection (which is closed). The tube at the furnace outlet is connected to the control valves (2, 3) before the vacuum pump (1).

9.4.4 Special Points in Connection with the Automatic Sample Robot

When the automatic sample robot is used, the samples on the sample turntable waiting for measurement must be protected against loss of volatile components such as moisture or the uptake of water or oxygen from the surrounding air. Ideally, the crucible should only be opened just before it is actually measured.

This can be done in a number of ways:

1. The sample is protected against direct contact with the surrounding atmosphere by placing an **aluminum lid** on top of the crucible. The lid is then removed and held by the gripper of the sample robot during the measurement. In this case, alumina or other high-temperature crucibles can be used.
2. The aluminum crucible (40 or 100 μL) is sealed (cold-welded) with a **perforable aluminum lid** and then automatically pierced immediately before insertion into the measuring cell (three different needle diameters are available: 0.1, 0.7 and 1.0 mm). The maximum temperature is limited to 640 $^{\circ}\text{C}$ to prevent melting of the crucible.

9.4.5 Inhomogeneous Samples and Samples with Very Small Changes in Mass

If the volatile content of the material is very low, or if the material is inhomogeneous, then clearly a large sample must be used.

An idea of the sample mass required to detect small changes in mass can be obtained by considering the following imaginary experiment:

You want to determine an ash residue of 1% with an accuracy of about 1%. If the reproducibility of the blank curve is about 10 µg, then an ash residue of about 1 mg is required to obtain 1% accuracy. It follows that the quantity of sample required is 100 mg.

9.5 Interpreting TGA Curves

In addition to the TGA curve, a number of other curves are used for interpretation purposes:

- The first derivative (DTG curve, rate of change of mass).
- The SDTA curve (shows exothermic or endothermic events similar to DSC); SDTA curves can be interpreted in much the same way as DSC curves.
- EGA, evolved gas analysis, online FTIR or MS measurements of evolved gases.

The visual control of the sample after the measurement – if possible using a reflected light microscope – can yield qualitative information about the residue (ash-like, glassy, white or colored powder, soot particles).

The effects described in the following sections show the typical shape of TGA curves. The curves have been blank curve corrected.

9.5.1 Chemical Reactions

The width of the mass loss step of a chemical reaction can be about 100 K (from 1% to 99% conversion). Usually the step develops quite slowly from the initially horizontal TGA curve. The point of inflection is at about 60% conversion. The radius of curvature at the end of the reaction is significantly smaller at the beginning (Figure 9.8a).

If the reaction occurs stoichiometrically, the molar mass of the eliminated molecule can be calculated. For example: The molar mass of aspartame (Figure 9.10) is 312 g/mol, the step of 10.4% at 180 °C therefore corresponds to 32 g/mol. The possibilities are O₂, S or CH₃OH. However, since aspartame is not a peroxide and does not contain sulfur, methanol is the most likely decomposition product.

Oxidation reactions, for example the rusting of metals, lead to an increase in mass (Figure 9.8b and Figure 9.9).

Diffusion-controlled reactions occur at an almost constant rate (i.e. the slope of the TGA curve is almost constant, Figure 9.8c). Here the transport of reactants or products is the limiting factor.

The decomposition process often occurs in several steps (Figure 9.8d).

Explosive materials sometimes decompose so rapidly that the recoil disturbs the TGA signal (Figure 9.8e). This problem can be overcome by using smaller sample quantities or diluting the sample with an inert material.

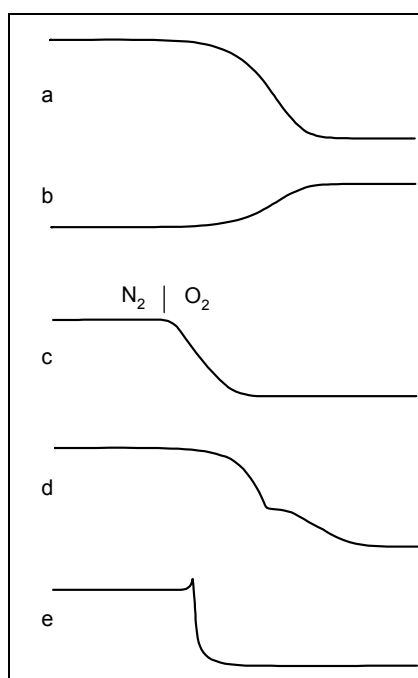


Figure 9.8. TGA curves of different chemical reactions.

- a: Thermal decomposition with the formation of volatile reaction products.
- b: Corrosion, oxidation of metals (formation of non-volatile oxides).
- c: Combustion of carbon black on switching from N_2 to O_2 .
- d: Multi-step decomposition.
- e: Explosive decomposition with recoil effect.

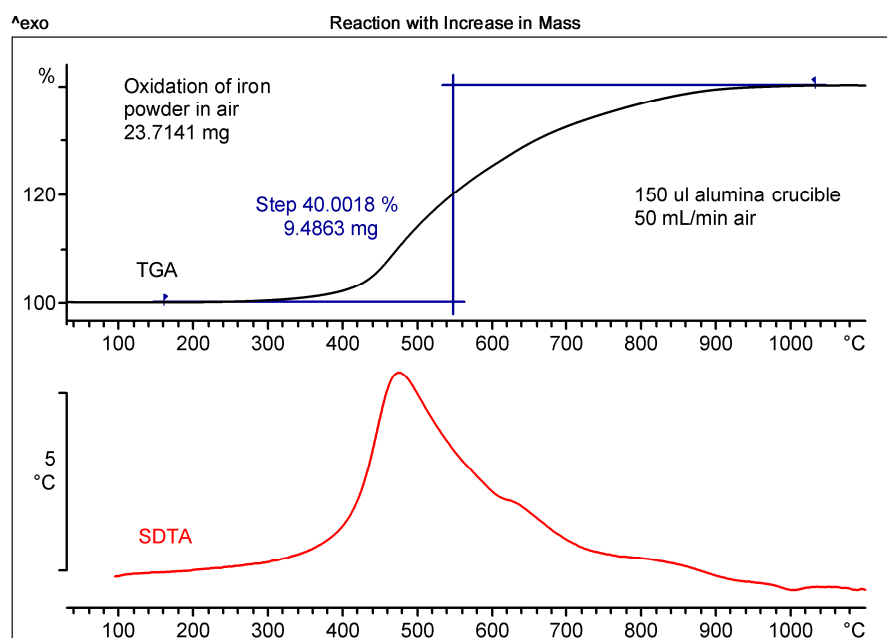


Figure 9.9. Example of a chemical reaction with an increase in mass. The iron powder takes up 40% oxygen in air with the formation of Fe_3O_4 and Fe_2O_3 . The SDTA curve below confirms that the reaction is strongly exothermic. Heating rate 20 K/min, Al_2O_3 crucible 150 μ L. This reaction has an exceptionally wide temperature range of 600 K for 1 to 99% conversion.

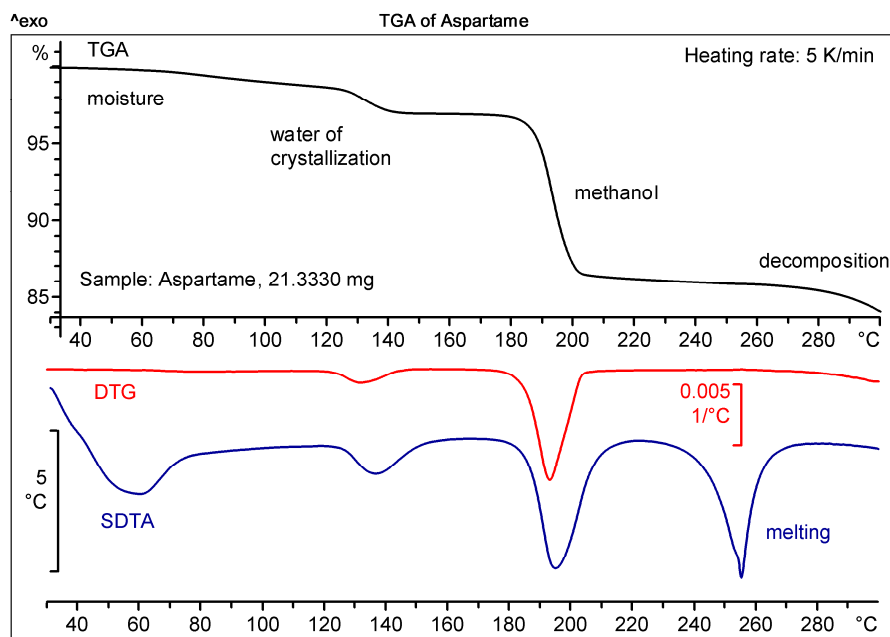


Figure 9.10. The decomposition of the artificial sweetener aspartame appears to be relatively complex. First, the water of crystallization is lost at 130 °C. This is followed by the elimination of methanol at 180 °C and the formation of a piperazine ring. This reaction takes place in an extremely narrow temperature range of just 20 K for 1 to 99% conversion. The SDTA curve shows that the piperazine derivative melts at 250 °C.

9.5.2 Gravimetric Effects on Melting

In general, one does not expect to observe a gravimetric effect on melting. The change in buoyancy due to the small change of sample density on melting is usually less than 1 µg. Even so, the point at which the sample melts can often be seen in the TGA curve. This is due to effects such as increasing vapor pressure or the more rapid decomposition in the liquid phase (Figure 9.11 and Figure 9.12). In some cases, however, the melting process can immediately be followed by a loss of trapped solvent. Simultaneous TGA/SDTA instruments are useful for identifying such events.

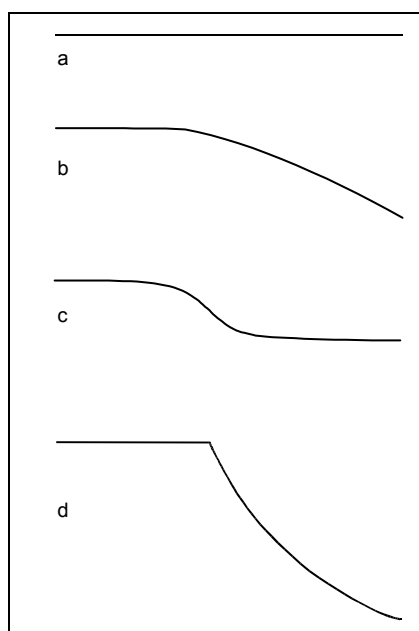


Figure 9.11. Thermogravimetric effects on melting.

- a: Sample with low vapor pressure (no TGA effect).
- b: Volatile melt (the liquid sample evaporates).
- c: Moisture escapes on melting.
- d: Sample melts and decomposes.

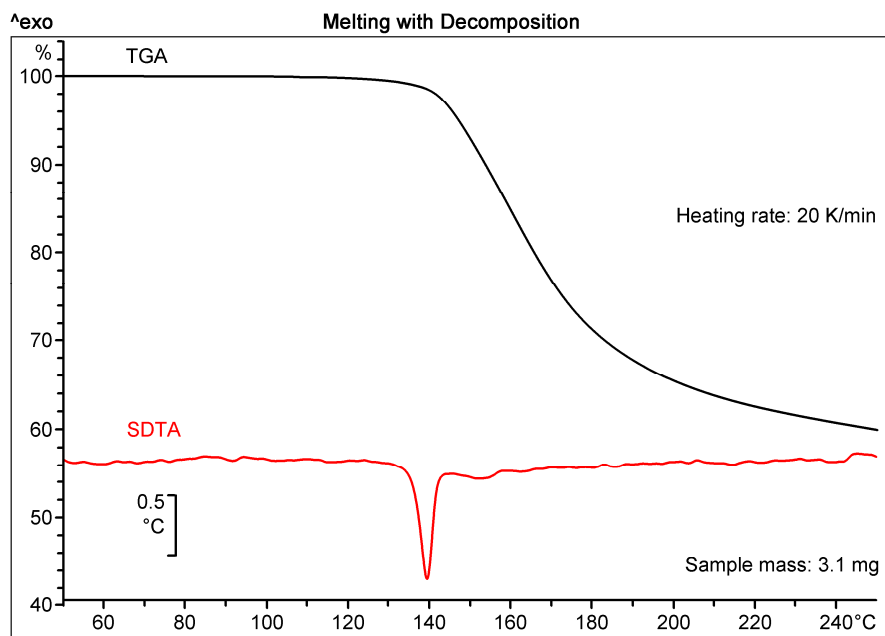


Figure 9.12. Acetylsalicylic acid melts at 140 °C and begins to decompose. The decomposition product acetic acid would be expected to result in a mass loss of 33.3%. The measured loss of mass is clearly greater. This is due to the simultaneous vaporization of other substances.

9.5.3 Other Gravimetric Effects

These include drying steps, which typically occur at the beginning of the temperature program and have a width of about 100 K (Figure 9.13a). The desorption of other substances such as solvent residues or monomers occurs in much the same way. Organic compounds that consist of relatively small molecules show a tendency to sublime, that is, they pass directly from the solid phase into the gas phase.

Liquids evaporate in a completely open crucible over a wide temperature range below their boiling point. If the crucible is sealed but the lid has a small hole, a so-called self-generated atmosphere is established in which the vapor molecules remain in equilibrium with the liquid phase right up until the boiling point is reached. Within a short time, the liquid evaporates completely and produces a sharp TGA step whose onset temperature corresponds to the boiling point (Figure 9.13b).

Ferromagnetic materials become paramagnetic above their Curie temperature. In an inhomogeneous magnetic field this transition causes a gravimetric signal. The magnetic field is produced by placing a permanent magnet at a cool place close to the furnace. Its magnetic field exerts an attractive force on the ferromagnetic sample and a different mass is recorded. When the Curie temperature is exceeded, the force is no longer exerted and there is a sudden change in apparent mass (Figure 9.13d and Figure 9.14).

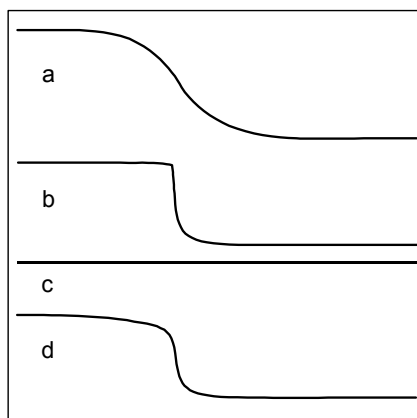


Figure 9.13. Other thermogravimetric effects.

- a: Drying, desorption, sublimation.
- b: Boiling in a crucible with a small hole in the lid.
- c: Ferromagnetic Curie transition without a magnet: no TGA effect.
- d: The same sample with a permanent magnet below the furnace.

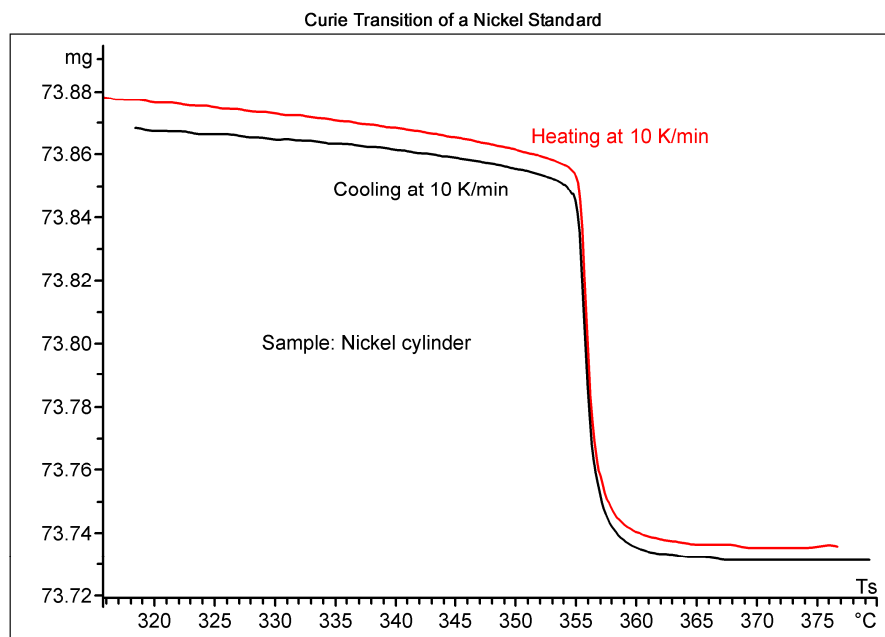


Figure 9.14. A permanent magnet placed below the furnace of the thermobalance attracts a ferromagnetic material (causing an apparent increase in mass). When the Curie temperature of the sample is exceeded, the force is no longer exerted and there is a sudden change in apparent mass. The abscissa shows the sample temperature, T_s .

9.5.4 Identifying Artifacts

Artifacts are effects observed on the measurement curve that are not directly caused by the sample, that is, effects that have nothing to do with the sample properties you want to measure.

The main types of TGA artifacts include the following:

- Buoyancy effects caused by the density of the surrounding gas decreasing on heating. Typically this results in an apparent mass gain of 50 to 200 μg . Since buoyancy effects are reproducible, the curves can be corrected by performing automatic blank curve subtraction. This also applies to buoyancy effects due to gas switching, a technique often used in TGA.
- Fluctuations of the purge gas flow rate can also affect the measurement curve. The flow rate should therefore be kept as constant as possible and not be changed during a measurement.
- Sudden loss of mass arising from ejection of part of the sample. This often occurs when a sample decomposes with the formation of gas. This can be prevented by covering the sample with coarse grain Al_2O_3 , or using a crucible lid with a hole.
- Apparent mass gain caused by samples that foam and make contact with the furnace wall. This problem can be overcome by using smaller samples.
- Artifacts can be identified by making repeat measurements, and performing blank experiments.

9.5.5 Final Comments on the Interpretation of TGA Curves

If the interpretation of a TGA effect is uncertain, other measurement techniques can be used to gain additional information. These include for example:

- Analysis of evolved gaseous compounds (EGA).
- DSC measurements.
- Observation of the sample under the hot-stage microscope.

9.6 TGA Evaluations

Most TGA evaluations involve the determination of step heights of TGA effects. Since several effects occur one after the other and often partly overlap, the question is how do we choose the limits for evaluating the step. Here, the first derivative or DTG curve is very useful. In the DTG curve, the mass loss steps appear as more or less distinct peaks. The METTLER TOLEDO **STAR**^e evaluation software provides methods for evaluating the steps in the TGA curves. These yield the absolute and percentage change in sample mass (the step height) of the different effects.

9.6.1 Horizontal or Tangential Step Evaluation

Normally the steps are interpreted as a change in mass before and after the effect, so that the corresponding “baseline” is horizontal. The sum of all the steps plus the residue at the end of the last step is equal to the original sample mass or 100% (assuming the blank curve correction was properly performed and that no oxidation of the sample has occurred).

The automatic step separation feature is particularly easy to use (Figure 9.15).

The steps can also be defined manually; usually the two evaluation limits for each TGA step are set using the DTG curve (Figure 9.16).

The residue is usually only of interest after the last step.

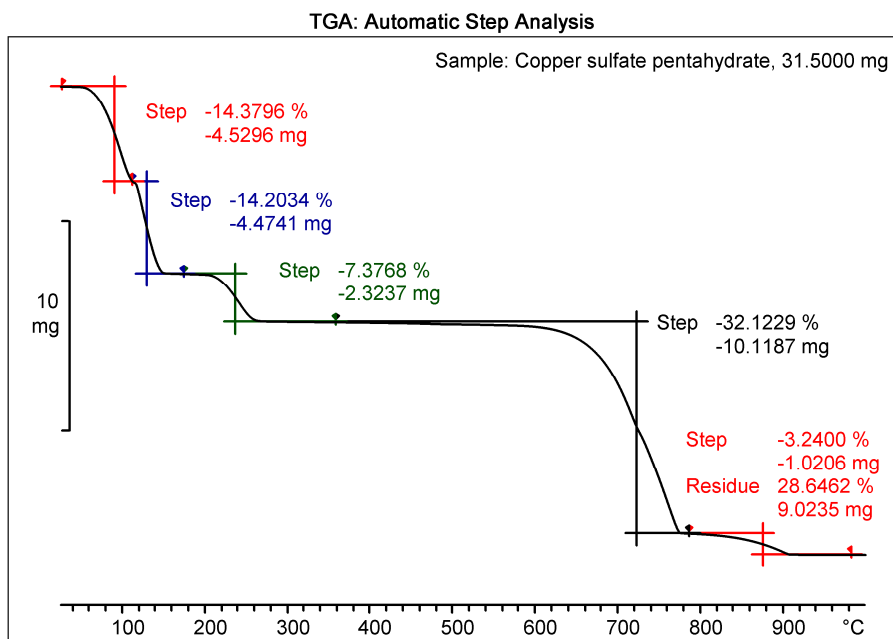


Figure 9.15. Perfect automatic step separation in a TGA curve of copper sulfate pentahydrate at 10 K/min. The individual steps correspond to the elimination of 2 H₂O, 2 H₂O, 1 H₂O, SO₃, 0.5 O₂. The residue consists of Cu₂O.

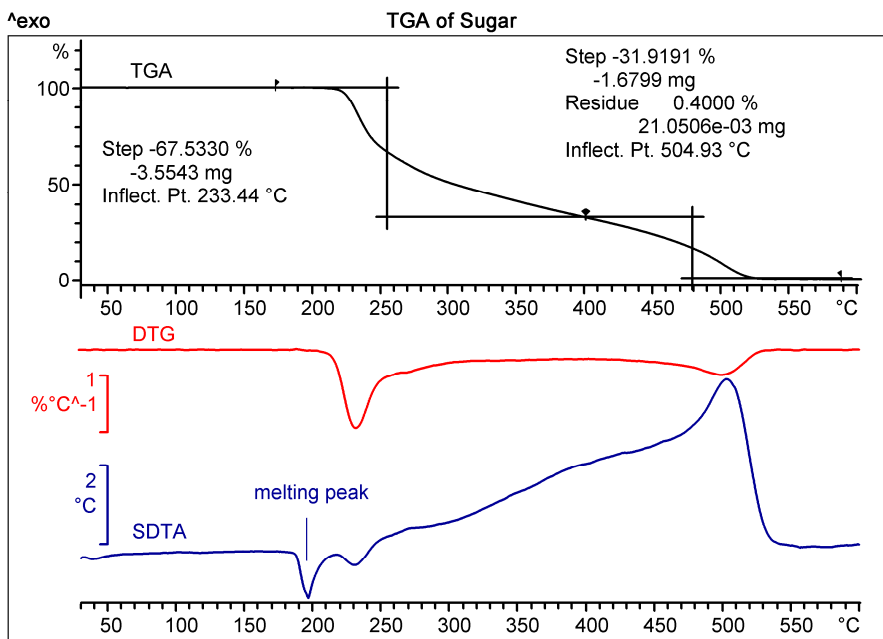


Figure 9.16. The decomposition of sugar at 10 K/min in air occurs in two consecutive steps, the second directly following the first. In the evaluation, a value of 405 °C was used for the end of the first step and the beginning of the second step. The simultaneously measured SDTA curve shows the endothermic melting peak followed by the endothermic caramelization, at which stage the exothermic decomposition/combustion occurs. An almost white residue of 0.4% remains at the end of the measurement. This corresponds to the ash content.

Sometimes relatively sharp decomposition steps of other components occur during broad vaporization or decomposition processes. In such cases, the step evaluation with “tangential” baseline is used (Figure 9.17).

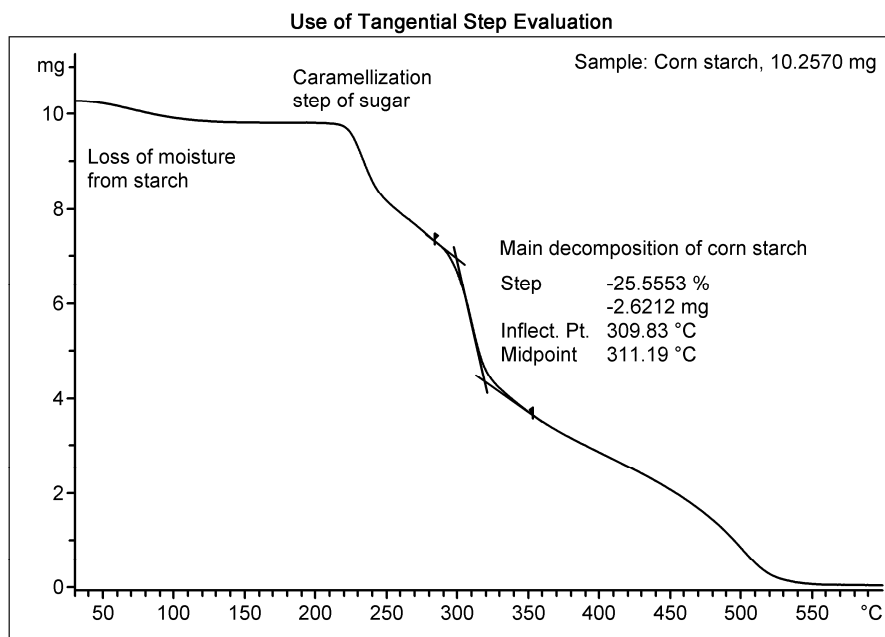


Figure 9.17. TGA curve of a 1:1 mixture of maize-corn starch and crystalline sugar: heating rate 10 K/min, purge gas air at 50 mL/min. The main decomposition step of corn starch occurs at about 310 °C (midpoint). In a mixture with crystalline sugar, this “starch” step occurs in a region in which the mass of the sugar continuously decreases. The step obtained using a “horizontal” evaluation would be too large. This error can be avoided using a “tangential” baseline evaluation. The measured step of 25.5% refers to the initial total mass of the mixture at the beginning of the measurement (see Section 9.6.3).

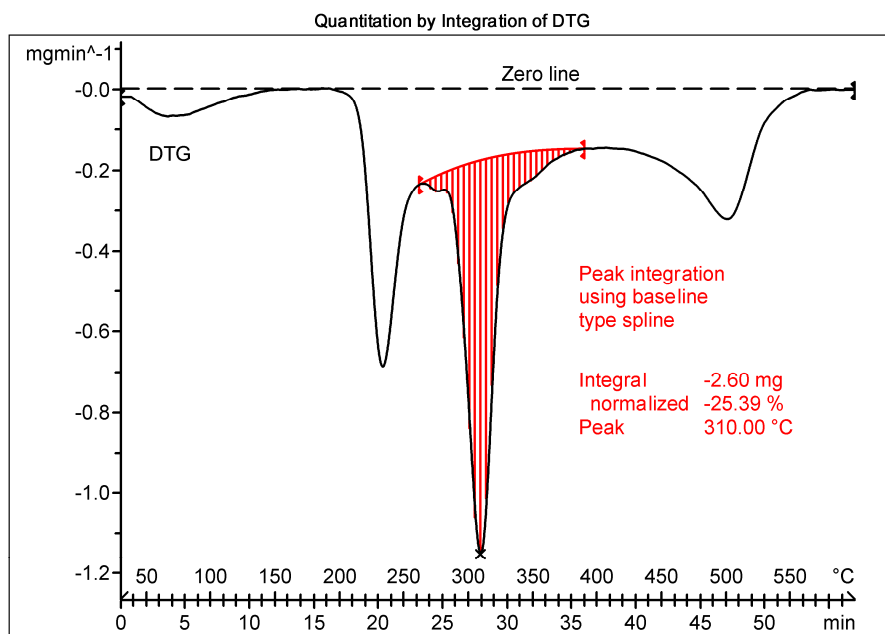


Figure 9.18. Instead of using a step evaluation, a mass loss can be quantified by integrating the DTG peak that corresponds to the TGA step. This is illustrated here using the example described in Figure 9.17. This method is useful for evaluating a relatively sharp decomposition step on the background of a broad step. It has the advantage that different baseline types can be used for the evaluation. In this example, the “spline” baseline of the DTG curve simulates the decomposition of the sugar.

Optional results that can be obtained from the step evaluation are

- the residue at the end of a step,
- the left and right evaluation limits,
- tangential onset and endset,
- point of inflection and midpoint at 50% of the step height,
- the heating rate,
- the “type” namely horizontal or tangential, and
- the result mode (sample temperature, segment time or abscissa units).

From the step heights, you can determine the content or check the stoichiometry of reactions using pure starting materials.

9.6.2 Determination of Content

Content determination is easiest when the constituent you want to determine disappears completely during the measurement (e.g. moisture or other volatile substances, residue-free decomposition reactions as well as certain depolymerization reactions, or the combustion of carbon black). In this case, the percentage content, G , can be calculated from the mass loss, Δm , and the initial sample mass, m_0 , as follows:

$$G [\%] = \frac{\Delta m}{m_0} \cdot 100\% \quad (9.6)$$

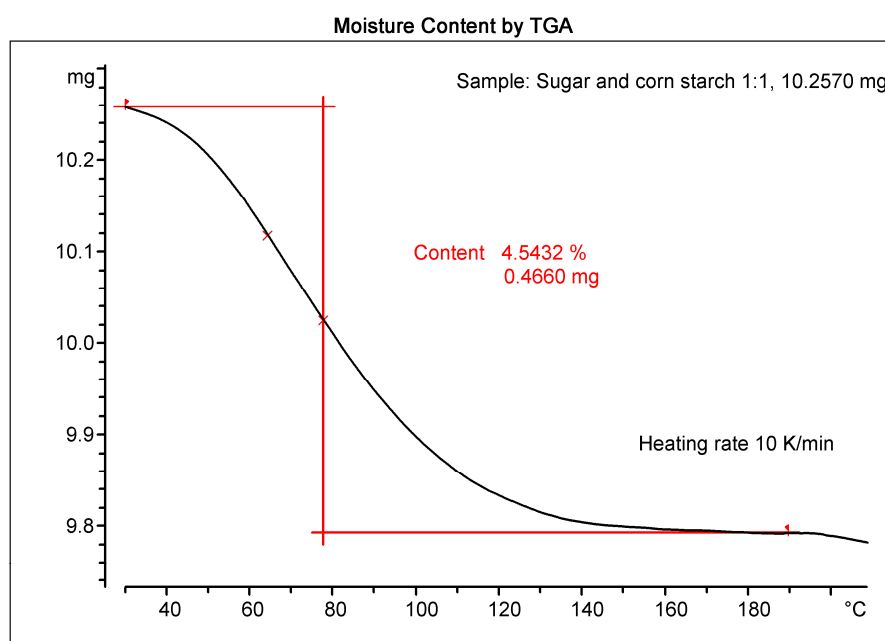


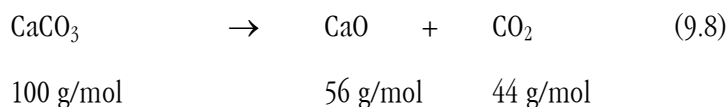
Figure 9.19. The moisture content of the starch-sugar mixture used in Figure 9.17. The sample mass is 10.257 mg, the mass loss is 0.4660 mg, and the content 4.54%.

In the case of stoichiometric reactions where there is only partial mass loss (e.g. dehydration, decarboxylation), G can be calculated using the equation

$$G [\%] = \frac{\Delta m}{m_0} \cdot \frac{M}{n \cdot M_{\text{gas}}} \cdot 100\% \quad (9.7)$$

where M_{gas} and M are the molar masses of the eliminated gases and original constituent of interest in the sample material, and n is the number of moles of gas eliminated for each mole of sample material.

Example: Determination of the calcium carbonate content of a sample of limestone.



One CO_2 molecule is eliminated for every CaCO_3 molecule. This means that n is 1, M is 100 g/mol, and M_{gas} is 44 g/mol. The sample mass, m_0 , is 10.136 mg, the measured weight loss, Δm , is 4.2439 mg. Entering these numbers in eq 9.7 gives a CaCO_3 content of 95.16%.

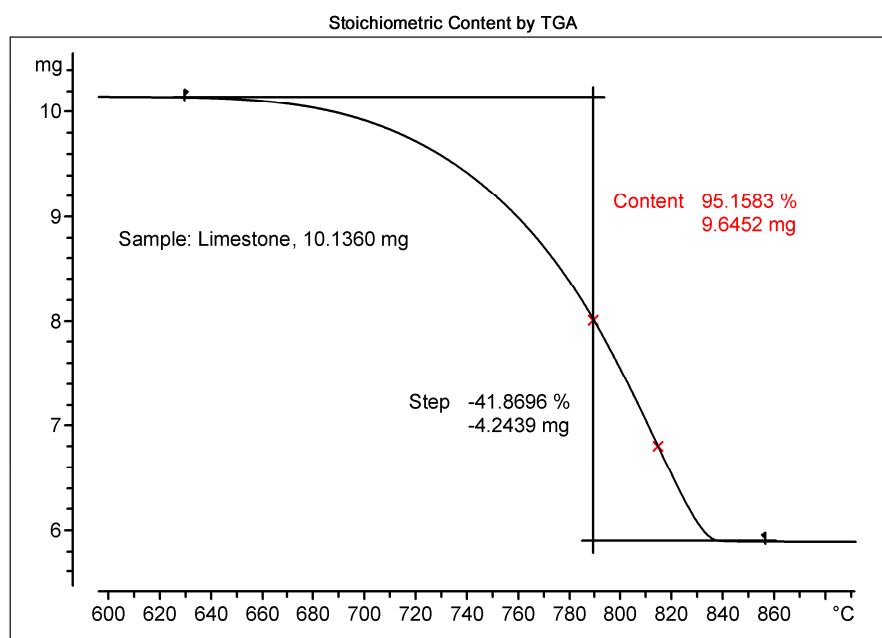


Figure 9.20. Section of the TGA curve of limestone used for stoichiometric content determination; heating rate 20 K/min. The CO_2 elimination resulted in a mass loss of 41.87 mg, which corresponds to an original CaCO_3 content of 95.16%. The residue is mainly CaO .

9.6.3 Empirical Content

Non-stoichiometric or complex reactions require a reference sample of known purity (content) whose TGA curve is measured beforehand under the same conditions. The empirical “reference step” R_{emp} is calculated as follows:

$$R_{\text{emp}} = \frac{\Delta m_r}{m G_0} \quad (9.9)$$

where Δm is the measured mass loss step in %, m the sample mass used and G_0 is the purity (or content) of the reference sample in %.

The reference step is needed for the evaluation of the empirical content determination:

$$G [\%] = \frac{\Delta m}{m_0 R_{\text{emp}}} \cdot 100\% \quad (9.10)$$

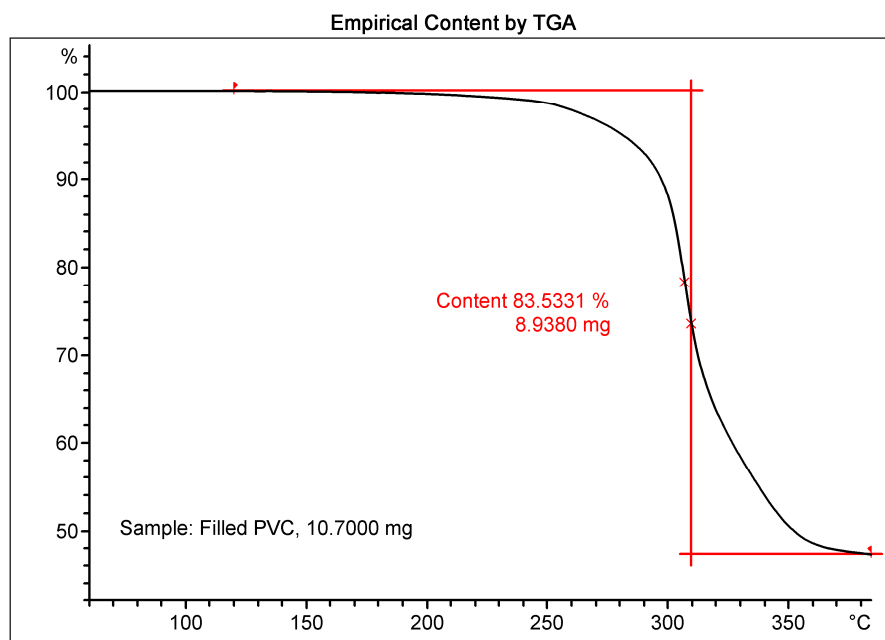


Figure 9.21. Pyrolysis reaction of PVC containing a filler in nitrogen. A mass loss of 52.79% occurs. Divided by the reference step of the pure PVC, this gives a PVC content of 83.5%.

PVC eliminates HCl in the temperature range shown in Figure 9.21. Stoichiometrically this would result in mass loss of 58.3%. In fact a mass loss of 63.2% was determined in the range 120 to 385 °C. The value of R_{emp} is then 63.2%/100% or 0.632 (the content of unfilled PVC reference sample was assumed to be 100%).

9.6.4 Reaction Conversion, α

On the assumption that a mass loss step can be attributed to a single chemical reaction, the reaction conversion, α , can be calculated as a function of temperature:

If the loss of mass of a sample is calculated in relation to the total mass loss step, one obtains the reaction conversion, α , relating to the temperature T :

$$\alpha(T) = \frac{\Delta m_T}{\Delta m_{\text{tot}}} \quad (9.11)$$

where Δm_T is the mass loss at the temperature T and Δm_{tot} is the step height.

The conversion calculated in this way can be calculated and displayed over the entire mass loss step. It is in fact a normalized presentation of this TGA step, which begins at 0 and ends at 1 (or 100%).

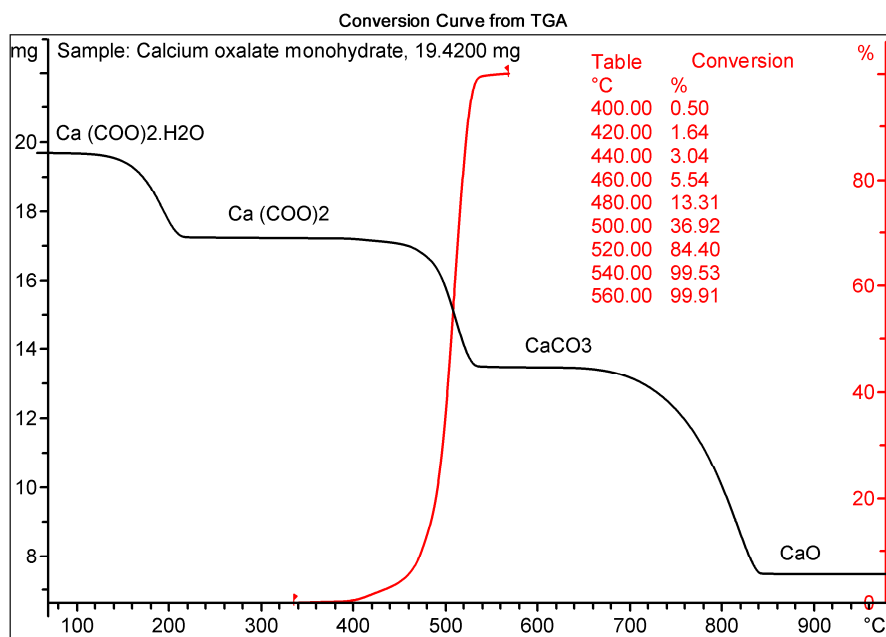


Figure 9.22. At a heating rate of 20 K/min, calcium oxalate eliminates CO and forms calcium carbonate between 350 and 600 °C. The red curve displays the reaction conversion.

From such conversion curves, it is possible to gain information on the reaction kinetics of the system observed using kinetic models or also with model free kinetics (similar to with DSC, see Section 7.6).

9.7 Typical Application: Rubber Analysis

The aim of rubber analysis is to quantitatively determine the main constituents of technical elastomer systems. In general, it is possible to distinguish between the following main components:

- Volatile substances such as moisture, plasticizers and other additives.
- The actual elastomers involved.
- Carbon black.
- Inorganic fillers and ash.

Using an optimum choice of measuring conditions (atmosphere, heating rate) it is in fact possible to determine all the components. In a nitrogen atmosphere, the volatile constituents (plasticizers) vaporize up until about 300 °C and elastomers and other organic compounds undergo pyrolysis up to about 600 °C. At 600 °C, the gas is switched from nitrogen to air or oxygen leading to the combustion of the carbon black. The inorganic fillers (typically zinc oxide, calcium carbonate or calcium oxide) and the ash of the elastomers are left behind as a residue. The results of such a rubber analysis are shown in Figure 9.23.

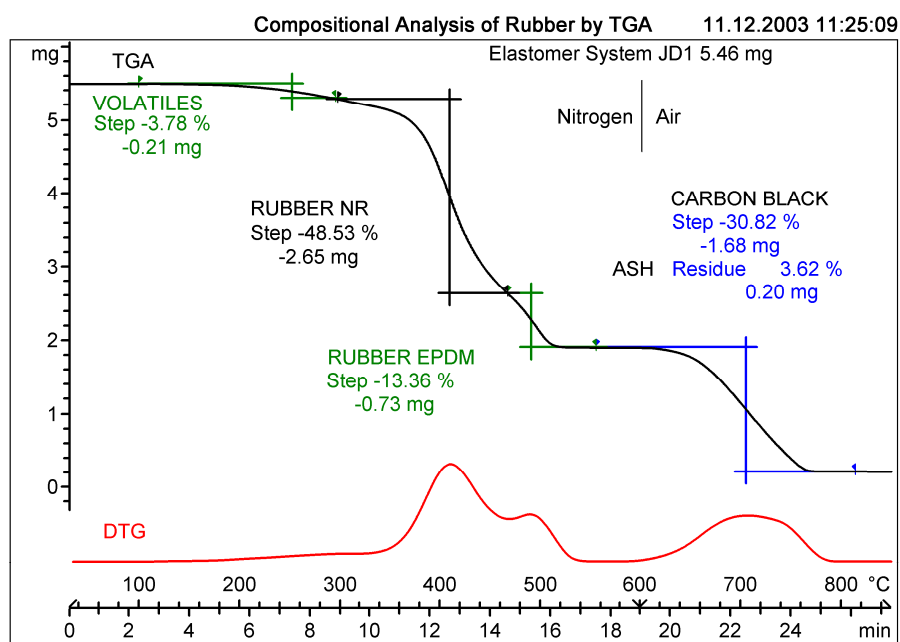


Figure 9.23. Compositional analysis of an elastomer system by TGA showing typical results; heating rate 30 K/min.

Besides the quantitative information obtained from the mass loss steps, certain qualitative results can also be obtained from the DTG curve. For example the measured peak temperatures are characteristic of certain types of elastomers; some examples are summarized in Table 9.3.

Elastomer	DTG peak temperature, measured at 10 K/min
NR, natural rubber	373 °C
SBR, styrene butadiene	445 °C
BR, polybutadiene	460 °C
EPDM, ethylene-propylene terpolymer	461 °C

Table 9.3. DTG Peak temperatures under pyrolysis conditions, measured at 10 K/min.

9.8 Application Overview

Effect, property of interest	Evaluation used
Composition	Step evaluation, residue
Thermal stability, decomposition	Step evaluation
Stoichiometry of reactions	Content
Kinetics of reactions	Conversion, kinetics
Adsorption / Desorption processes	Step evaluation
Vaporization behavior	Step evaluation, SDTA, integration
Influence of reactive gases	Step evaluation
Moisture	Step evaluation
Oxidation stability	Onset, limits
EGA	DOS file import, Mathematics

Table 9.4. Overview of applications.

9.9 Stoichiometric Considerations

With a pure compound of known composition and molar mass, M , the mol mass M_{gas} of the eliminated gaseous elimination product of a step using the equation below, where n is the number of gas molecules for each original molecule.

$$n M_{\text{gas}} = \frac{\Delta m}{m_0} M \quad (9.12)$$

Example: The second mass loss step of calcium oxalate monohydrate is 19.2%, and M is 146 g/mol. This means that $n M_{\text{gas}} = 0.192$ times 146 g/mol, which equals 28.03 g/mol. Since with this oxalate it is not possible to form a gas with a mol mass of 14 or 56 g/mol, n must be 1 and the eliminated compound is therefore carbon monoxide.

9.10 Calibration and Adjustment

A thermobalance measures the sample mass as a function of sample temperature. It follows that the user must make sure that the mass and temperature values measured are in fact correct. This is done through frequent checking using a suitable reference sample (determining the deviation of a measured value with respect to the known true value). If the deviation is too large, the instrument must be adjusted (the instrument parameters are changed in such a way as to eliminate the deviation).

The balance is calibrated with reference masses. METTLER TOLEDO TGAs are automatically calibrated and adjusted with built in reference masses when switched on and during longer periods of waiting.

The temperature may be calibrated using a method based on Curie point transitions of certain ferromagnetic materials (e.g. Ni, Fe, Isatherm, etc.). This is done by placing a permanent magnet close to the reference sample (outside the furnace). The sample experiences a magnetic force of attraction and a higher mass is recorded. The sample is then heated in the normal way. At the so-called Curie temperature the sample loses its ferromagnetic properties and is no longer attracted by the magnet, resulting in a sudden loss in apparent mass. This transition occurs over a relatively narrow temperature range and produces a step in the TGA curve step. The temperature is recorded at the point of inflection or endset of the step and compared with the Curie temperature of the reference material. The accuracy of the Curie points is limited to about ± 5 °C due to physical reasons (hysteresis, heating/cooling rate dependence, magnetic field dependence) and is not as accurate as the use of melting point standards.

The temperature can be calibrated more accurately using the DTA or SDTA signal and melting point standards. Very pure samples of In, Zn, Al, Au and Pd are often used for this purpose. The onset temperatures of the melting peak are used for calibration and adjustment. A number of typical SDTA melting peaks are shown in Figure 9.24 (lower curves).

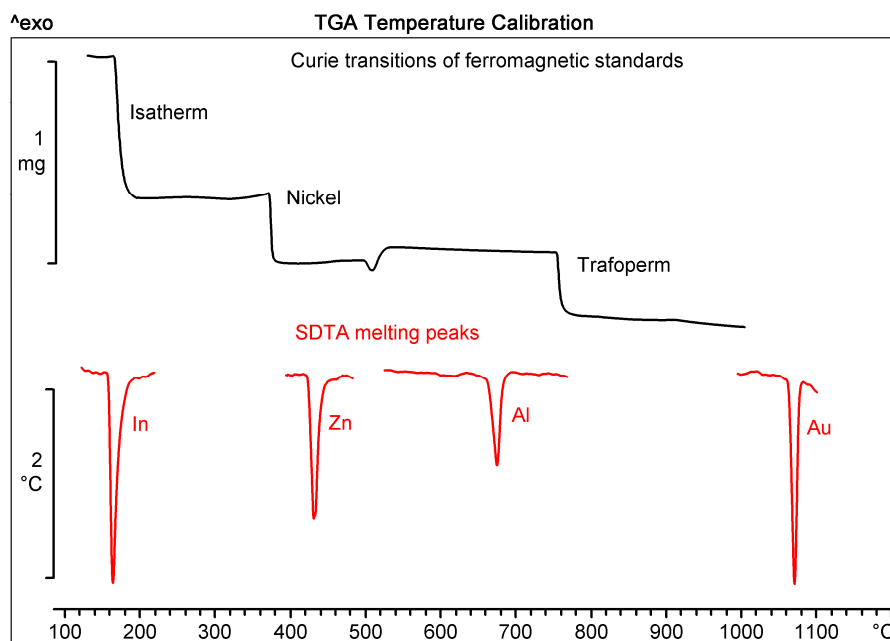


Figure 9.24. Temperature calibration by measuring ferromagnetic materials in a magnetic field (above) and using the SDTA signal of pure metal melting point standards (below).

References and Further Reading

- [1] METTLER TOLEDO Data Sheet: "MaxRes".
- [2] Peter Haines, Principles of Thermal Analysis and Calorimetry, Royal Society of Chemistry, 2002.
- [3] Paul Gabbott, Principles and Applications of Thermal Analysis, Blackwell Publishing, 2008.
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- [6] METTLER TOLEDO Collected Applications Handbook: "Elastomers".

UserCom: Many of the application examples in this chapter have been taken from UserCom, the METTLER TOLEDO technical customer journal that is published twice a year. Back issues of UserCom can be downloaded as PDFs from the Internet at www.mt.com/ta-usercoms.

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10.1 Introduction

Thermomechanical analysis (TMA) can be defined as the measurement of the dimensional changes of a sample as a function of temperature while it is subjected to defined mechanical stress or load. The instrument used for such measurements is called a thermomechanical analyzer, TMA.

In the dilatometric mode (dilatometry), the applied load is very small. The technique is used to measure the coefficient of thermal expansion of the sample.

Depending on the mode used, TMA allows you to determine

- thermal effects (softening, penetration, changes in the coefficient of thermal expansion, swelling in solvents, shrinkage),
- temperatures that characterize the thermal effect,
- deformation step heights (extent of deformation), and
- coefficients of thermal expansion.

In the Dynamic Load TMA or DLTMA mode, the Young's modulus of a sample can be measured, providing its shape is suitable.

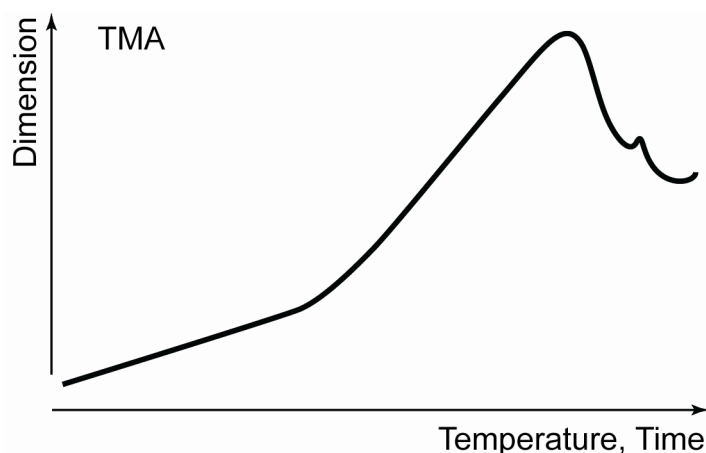


Figure 10.1. A typical TMA curve shows a dimension (e.g. thickness) of a test specimen as a function of temperature. The normalized presentation in percent (length divided by the original length) is more practical for comparison purposes than the absolute thickness in μm .

10.2 The Design and Measurement Principles of a TMA

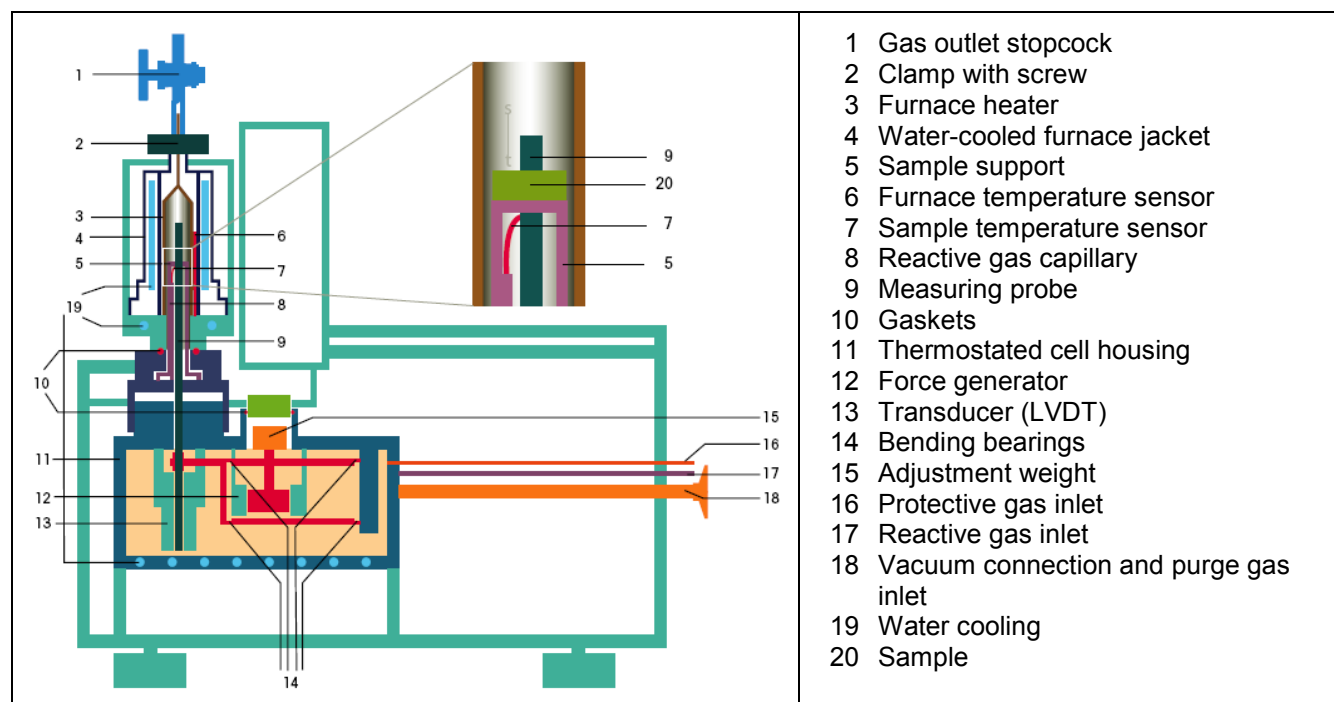


Figure 10.2. Schematic diagram of a thermomechanical analyzer. The probe is parallel-guided and can be moved vertically by means of frictionless bearings. The desired load on the probe is produced by the force generator. A displacement sensor measures the position of the probe with nanometer resolution. The sample chamber can be purged with an inert gas. The quartz glass measuring probe (enlarged diagram) rests either directly on the test specimen or on a quartz disk placed on it. The thermocouple for measuring the sample temperature is located directly below the test specimen.

The TMA sample support and probe are made of quartz glass. This has a very low coefficient of linear thermal expansion in the temperature range up to 1100 °C. Quartz glass must not be heated to more than 1100 °C because it crystallizes above this temperature. Aluminum oxide ceramic material can be used for measurements at higher temperatures. The measuring probe moves freely vertically on bearings and precisely follows the dimensional changes of the test specimen.

The displacement sensor is an LVDT (linear variable differential transformer). The ferromagnetic core inside the coil system is connected to the measuring probe and generates an electrical signal proportional to the displacement. An electromagnetic linear motor counteracts the weight of the moving parts and ensures that the probe transfers the desired force to the test specimen. The force used is typically in the range 0 to 1 N.

TMA measurements are often performed under zero flow conditions in air. A protective gas such as air or nitrogen should be used to protect the LVDT and the linear motor from the effects of any corrosive decomposition products. The LVDT must also be protected against temperature changes. This is achieved through the use of reflector baffles and thermostating.

A modern TMA usually has two thermocouples. One measures the furnace temperature and controls the temperature program. The other is situated in the sample support directly below the test specimen and measures its temperature and SDTA signal (see Chapter 8, Differential Thermal Analysis, DTA).

10.2.1 The Measurement Modes

The optimum measurement mode depends on the shape of the sample, on the properties of the sample and on the information required.

Compression or dilatometric mode

The parallel-sided test specimen is covered with a quartz glass disk to distribute the compressive stress uniformly over it. For example, a force of 1 N acting on a test specimen measuring 3 mm by 3 mm results in a compressive stress of 0.11 N/mm^2 or 0.11 MPa.

In a dilatometric measurement, a force of 0.01 N acting on a cylindrical test specimen of 5 mm diameter results in a very low compressive force of just 0.0005 N/mm^2 .

Penetration mode

The aim of such measurements is to determine the temperature at which the sample begins to soften or deform under load. A ball-point probe is often used for such so-called penetration measurements. Initially the ball-point probe is only in contact with a very small area of the test specimen. If it softens on warming, the probe penetrates more and more into it and the contact area increases (spherical indentation). This effect leads to a decrease in the compressive force in the sample during the measurement.

Alternatively, a probe with a surface area of 1 mm^2 can be used. Care must be taken to make sure that the area of contact is exactly parallel to the surface of the test specimen. If the specimen is uneven or slopes, the probe initially touches only a fraction of its surface area, which results in a high local compressive force. The probe then sinks relatively rapidly into the soft material while at the same time the contact surface area increases (similar to with the ball-point probe).

Three-point bending

This geometry is ideal for very stiff samples such as fiber-reinforced plastics or metals that would not show any measurable deformation in the compression mode. The optimum thickness of the test specimen depends on the modulus but is between 0.1 and about 2 mm for a width 2 to 5 mm. The separation of the quartz glass supports is 6 to 12 mm.

Tensile modes

The film attachment device allows the shrinkage or extension behavior of a plastic film or a metal foil of 2 to 4 mm width to be investigated. The test specimen is installed in the instrument using two clips.

The fiber attachment device is used to perform extension measurements on fibers, threads and wires of 0.01 to about 0.5 mm thickness. These are fixed in place with copper clips that are mounted in the fiber attachment device.

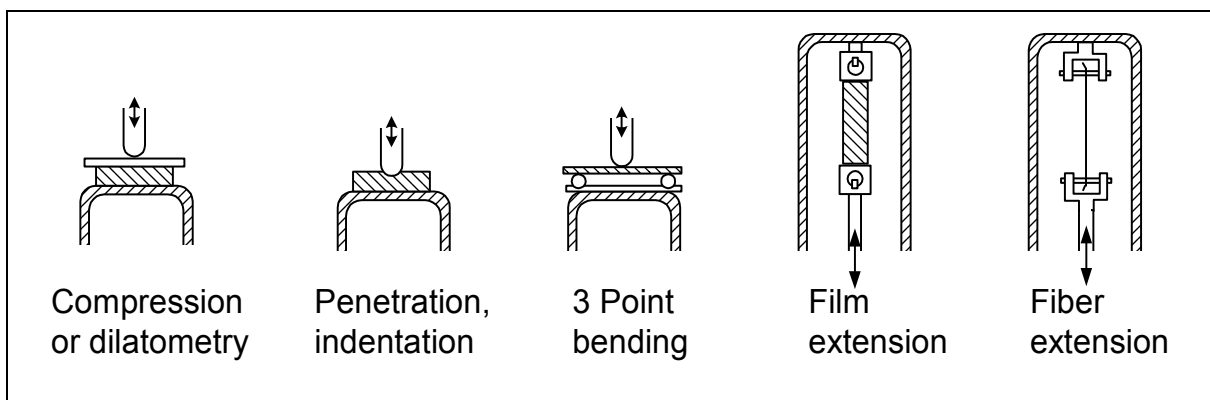


Figure 10.3. The most frequently used TMA measurement modes: compression or dilatometry, penetration, bending, film and fiber extension. In the first three modes, the probe presses onto the test specimen from above – usually with a ball-point tip of 3 mm diameter. In tension, the probe exerts a downward force.

10.2.2 Dilatometry versus Penetrometry

Whether a measurement is primarily dilatometric or is in fact a TMA deformation measurement depends on the applied force and on the stiffness of the sample. For example, a quartz crystal exhibits a dilatometric curve with no sign of sample deformation even with a measuring force of 1 N. In contrast, if an organic material, such as a piece of chocolate, is mounted between quartz glass disks and measured through the melting region using a force of 0.01 N, the expansion can only be observed in the solid state. On melting, the stiffness decreases to such a degree that the liquid is squeezed out even with the lowest force; in other words, it undergoes deformation. Metals often require a much greater force (e.g. 0.5 N) to squeeze out the melt because the surface oxide layer must also be deformed.

In a purely dilatometric measurement, the mechanical stress, σ , acting on the test specimen should not be greater than one thousandth of its modulus. The modulus can of course decrease during the measurement due to increasing temperature. The initial dilatometric measurement then changes to a deformation measurement (Figure 10.4).

Examples: $E_{\text{quartz}} = 200 \text{ GPa}, \quad \sigma_{\text{max}} = 200 \text{ N/mm}^2;$
 $E_{\text{rubber}} = 2 \text{ MPa}, \quad \sigma_{\text{max}} = 0.002 \text{ N/mm}^2$

10.2.3 Dynamic Load Thermomechanical Analysis, DLTMA

In DLTMA measurements, the force applied to the sample alternates periodically. In practice, a period of about 12 s is often used. Other periods (mostly longer), can however also be programmed for specific purposes.

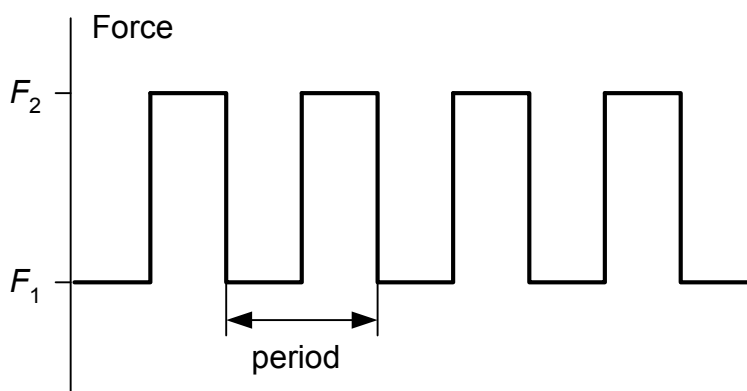


Figure 10.4. The force applied to the sample alternates between F_1 and F_2 . Each force is constant for 6 s over the total period of 12 s.

To determine the Young's modulus, the mechanical stress must be the same throughout the test specimen. This means the ball-point probe cannot be used directly. Furthermore, the measured signal must be significantly greater than the signal resulting from the finite stiffness of the TMA instrument. Before evaluating the modulus, a blank curve of an "infinitely stiff" sample is subtracted from the measurement curve. This blank curve correction is not necessary if only the change in modulus is of interest, for example at the glass transition.

The E modulus is equal to the ratio of the mechanical stress to the relative expansion.

For compression, the following equation therefore applies:

$$E = \frac{\Delta F / A}{\Delta L / L_0} \quad (10.1)$$

and for three-point bending:

$$E = \frac{\Delta F l^3}{4 \Delta L a^3 b} \quad (10.2)$$

ΔF Difference of the two forces with DLTMA

A Cross-sectional area of the test specimen

L_0 Original thickness

ΔL Deformation due to the changing load

l Separation of the supports

a Thickness of the test specimen

b Width of the test specimen

Completely elastic samples such as a steel spring deform without delay under changing load. In contrast, viscoelastic materials such as polymers exhibit significant time dependence in the temperature range of the glass transition due to relaxation processes (Figure 10.5).

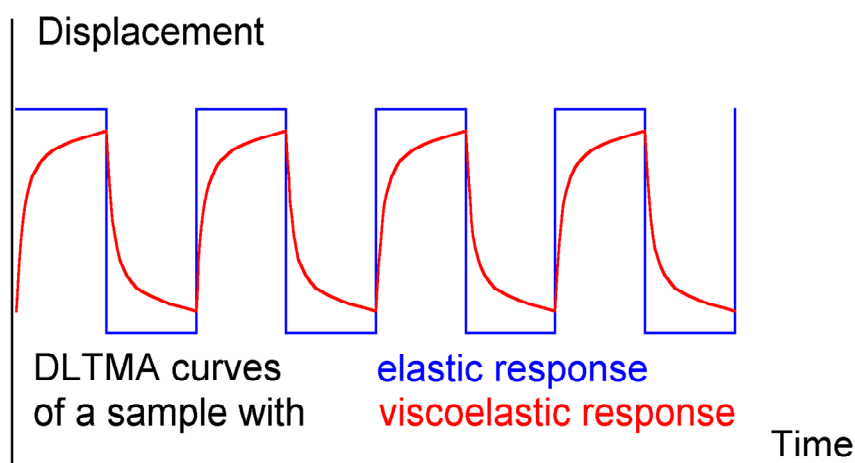


Figure 10.5. Isothermal DLTMA curves of a completely elastic steel spring (blue) and a viscoelastic PVC sample (red).

If one of the forces exerted is very small (e.g. 0.01 N), a section of the dilatometric curve is recorded during the period of low force, and a section of the TMA deformation curve during the high force period (Figure 10.6).

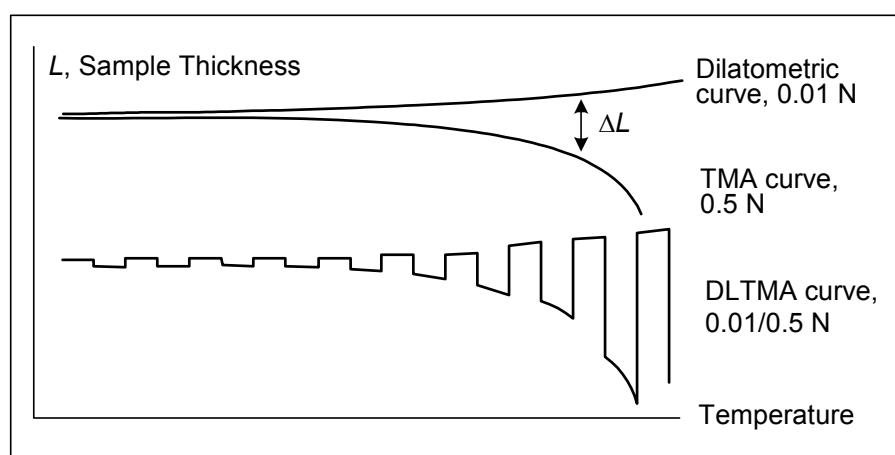


Figure 10.6. The dilatometric curve (measured with negligible compressive stress) increases with increasing temperature due to the thermal expansion of the sample. The TMA curve measured with a significant compressive force shows that the ball-point probe sinks into the test specimen as it softens. Effectively, DLTMA measures both curves in a stepwise manner. The signal delay in the region of the glass transition is not shown here.

10.3 Sample Preparation

The size and shape of the test specimen should be optimized depending on the analytical information required. The determination of the coefficient of thermal expansion requires a thick specimen, especially if the expansion coefficient is less than 10 ppm/K. This is the case with mineral glass, ceramics or certain metals. A test specimen that is 4 to 6 mm thick and 2 to 3 mm wide is ideal.

In contrast, the softening behavior of paint films can be performed on very thin samples (just a few μm).

Ideally, TMA measurements should be performed on parallel-sided test specimens. If they are not flat, they can shift during measurement and produce step-like artifacts (Figure 10.13). The surface of a test specimen should be smooth so that it is not just measured on a few individual surface bumps (grind and polish the sample). It should also be free of dust and particles. The sample properties should not change during sample preparation. In particular, with plastics the temperature should not be allowed to rise above 40 °C during mechanical treatment. A water-cooled diamond saw is ideal for this purpose. It also provides the desired plane-parallel test specimen. The test specimens must of course be dried after processing and allowed to dry in air for a few hours prior to measurement.

The force exerted by the probe can be uniformly distributed over the test specimen by covering it with a quartz glass disk. An additional disk under the specimen protects the sample support from contamination through melting or from samples that decompose.

Films can be cut to size using a punch or a knife. The width of the films should be the same over their entire length. If the modulus is to be determined, the thickness must be measured with an accuracy of $\pm 1\%$ using a suitable instrument. The TMA with the ball-point probe and a force of about 0.1 N is an ideal instrument for measuring the thickness of test specimens. They are mounted in the TMA using suitable clamps. Care must be taken to ensure that the clamps do not damage soft films at the point of attachment.

Fibers can be mounted in the TMA using copper clips. Since direct measurement of the thickness of a fiber is often difficult, it is usually better to weigh a long section of fiber (say 1 m) and then calculate the cross-sectional area or the diameter using the density.

In the textile industry, the thickness of fibers is given in terms of linear density. The SI unit is the tex. Usually, however, dtex (decitex) is used, corresponding to the mass (in g) of 10,000 m of fiber.

The diameter d (in mm) can be determined from the linear density d_l (in dtex) using the following equation:

$$d = \sqrt{\frac{4 d_l}{10^4 \pi \rho}} \quad (10.3)$$

where ρ is the density of the fiber material (in g/cm³)

For example, 0.337 m of a silk thread weighs 12.8 mg. The linear density, d_l , is given by

$$d_l = 10 \cdot 12.8 / 0.337 = 380 \text{ dtex.}$$

If the density is 1 g/cm³, the diameter of the thread is 0.22 mm.

For comparison purposes, the force can be normalized for different fibers to their linear density, for example 0.1 mN/dtex. The force, F , is then 0.038 N.

Conditioning

- Humidity:
Samples are affected by the relative humidity during storage prior to measurement. If the relative humidity is high, drying effects (usually shrinkage) can occur at the beginning of the TMA curve. Solution: Store the test specimen in a desiccator, insert it quickly, and start the measurement immediately.
- Thermomechanical history:
Mechanical processing of a test specimen can cause undesirable changes to its properties. Internal stresses may be generated or dissipated. Often, a first measurement up to a moderate end temperature can be performed to eliminate the thermal history. The second heating run is then the actual measurement.
- Predeformation:
In extension experiments involving soft samples, the force used for mounting the specimen influences the TMA curve.

Sample mass

The mass of the test specimen is usually not determined and is not needed to calculate the results. For comparative measurements, it is best to use test specimens of the same shape and mass. The temperature gradients that inevitably occur in the specimen are then more reproducible. Large test specimens exhibit significant temperature gradients. The factors that contribute to this are the relatively low surface to volume ratio, the poor thermal conductivity (plastics) and high heating rate. This causes thermal effects to be broadened and delayed.

10.4 Temperature Program

Heat transfer is not so good compared with DSC (poor heat conductance through solids; test specimens are often much larger). Heating rates in the range 1 to 5 K/min are used to prevent excessively large temperature gradients. Higher rates of 10 to 20 K/min can be used for trial measurements.

In general, heating is stopped well before the sample decomposition temperature is reached in order to prevent contamination of the sample support and the measuring probe with molten or foaming decomposition products. To make sure, it is best to perform a trial experiment on a very small test specimen or make a TGA measurement.

10.5 Interpretation of TMA Curves

10.5.1 TMA Effects of Phase Transitions

Melting behavior is usually investigated by placing the test specimen between 2 quartz glass disks and using a force of 0.5 N and a heating rate of 5 K/min. The smaller the amount of material between the quartz glass disks the better. The melting time is shorter because less heat has to be transferred. The liquid phase formed is squeezed out more rapidly because the melt is only pressed out when the entire sample has melted. When a small test specimen is used, the onset or the point of inflection corresponds to the melting point (Figure 10.7).

Flat samples, such as plastic films or surface coatings, can also be measured directly with the ball-point probe. When melting occurs, the probe penetrates through the entire coating.

Semicrystalline polymers are only slowly squeezed out from between the quartz glass disks on melting because the melt is very viscous. Three-dimensional network materials (crosslinked PE, PE-X) such as elastomers are not squeezed out at all even under high compressive stress (Figure 10.7).

When molten samples are cooled, there is of course no TMA effect if the melt has been completely squeezed out. In contrast, crosslinked PE crystallizes with volume contraction.

Amorphous polymers with a tendency to crystallize exhibit so-called cold crystallization when slowly warmed (Figure 10.7 and Figure 10.11).

Solid-solid transitions (polymorphism) can be detected because the changes in the crystal lattice are accompanied by dimensional changes (very dependent on orientation). With non-polar materials it is best to measure a single crystal using the 1-mm² probe (Figure 10.7). Figure 10.9 shows the polymorphic behavior of a plastic.

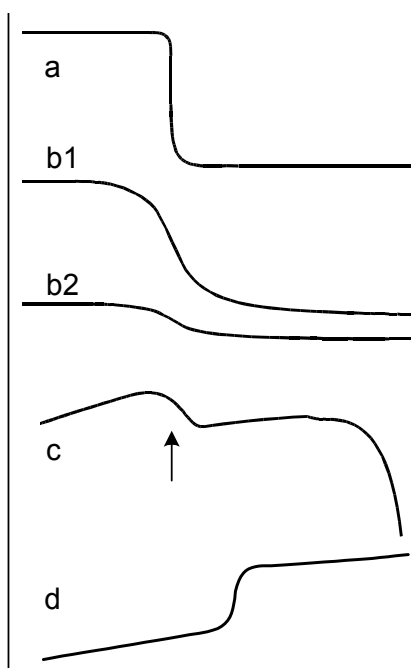


Figure 10.7. TMA curves of different transitions.

- a: Melting with or without decomposition.
- b1: Melting of semicrystalline polymers with a broad melting range.
- b2: Crosslinked PE-X does not melt.
- c: Cold crystallization (arrow) can be measured due to the volume change. Afterward, the sample melts.
- d: Polymorphism: solid-solid transition.

10.5.2 TMA at the Glass Transition

One of the TMA measurements most frequently performed is the determination of the glass transition temperature. The thermal expansion coefficient increases at the glass transition resulting in a marked increase in the slope of the dilatometric curve (Figure 10.8). The first heating run of a new test specimen often exhibits typical anomalies at the glass transition. These can be caused by volume and stress relaxation, drying effects or the penetration of a foreign body (dust particle) into the material (Figure 10.8).

In a penetrometric measurement, the ball-point probe rests directly on the test specimen and penetrates increasingly into the material (Figure 10.8) at the glass transition. The influence of probe force on the TMA curve is shown in Figure 10.10.

The probe cannot penetrate highly filled composites (e.g. carbon-fiber reinforced materials) to any extent. Such materials should be measured with the bending accessory using a force of 0.5 N (Figure 10.8). The glass transition is often even clearer with DLTMA because of the change in modulus (Figure 10.20).

If a sample material is very soft at the glass transition, DLTMA can also be used with success in the compression mode (Figure 10.11).

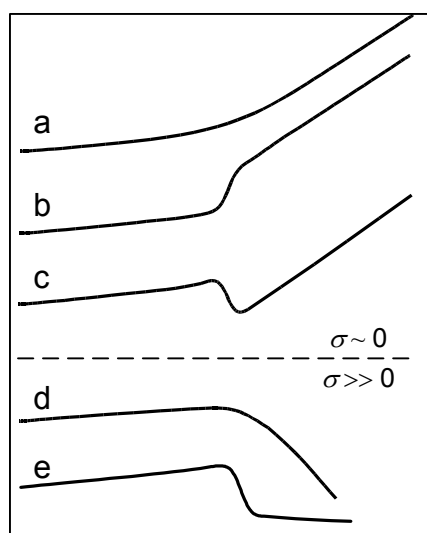


Figure 10.8. TMA glass transition (a, b, and c are dilatometric using a very low compressive force, σ).

- a: Ideal glass transition due to the increase in the thermal expansion coefficient.
- b: Sample with internal (compressive) stress in the Z-direction (vertical) relaxes at the glass transition with an increase in thickness (example: compressed plate); so-called volume relaxation is also observed like this in the first heating run.
- c: Sample with internal (compressive) stresses in the X- or Y-direction (horizontal) relaxes at the glass transition, or a foreign body (also the measuring probe) penetrates into the sample as it softens.
- d: Softening of an amorphous sample, for example an unfilled plastic (penetration measurement).
- e: A bending measurement allows the T_g of highly filled polymers to be determined, even if they hardly show any effects in other measurement modes.

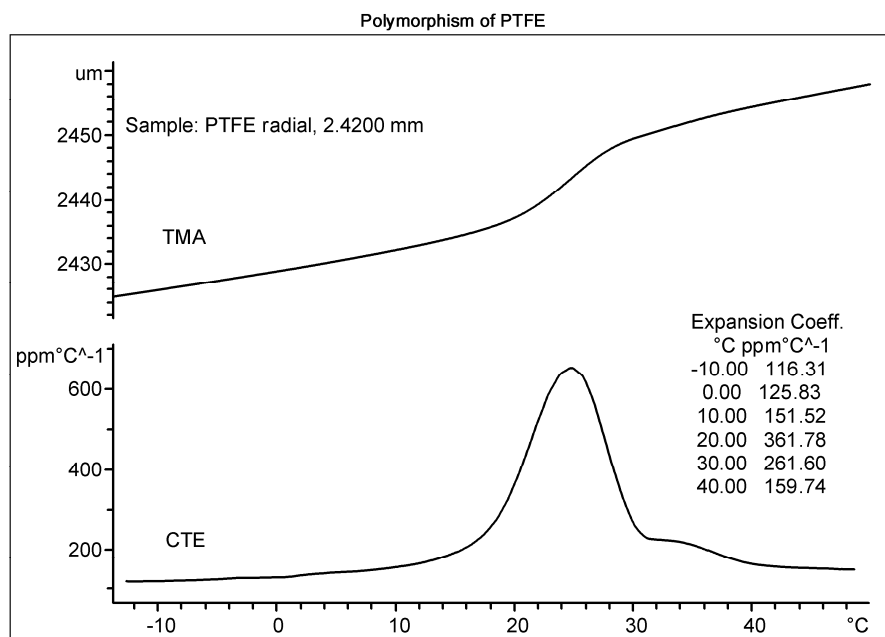


Figure 10.9. Above: The thermal expansion of PTFE in the radial direction. The solid-solid transition at about 25 °C causes an additional expansion. Measurement conditions: heating rate 5 K/min, force 0.05 N; a quartz glass disk between the test specimen and the ball-point probe distributes the force uniformly. Below: The coefficient of thermal expansion.

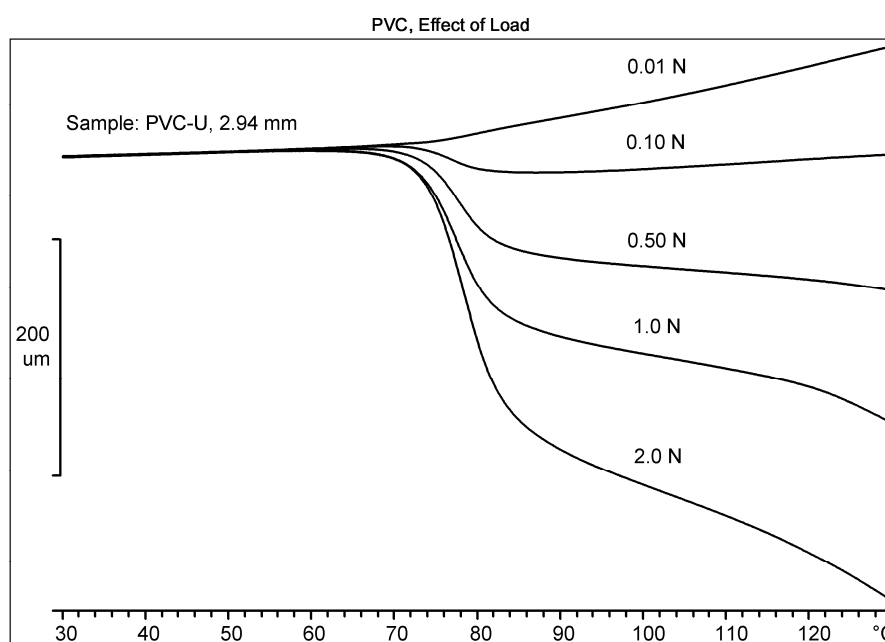


Figure 10.10. The figure shows the change from dilatometric to a penetrometric TMA measurement using PVC-U as an example. Heating rate 5 K/min, 3-mm ball-point probe placed directly on the cylindrical sample: diameter 5 mm, thickness 2.94 mm. The onset values are practically independent of the applied force. With a force of just 0.01 N, the measurement is dilatometric (increased expansion above the glass transition). With higher forces, the measurement is penetrometric and the sample exhibits viscous flow from about 120 °C onward after softening.

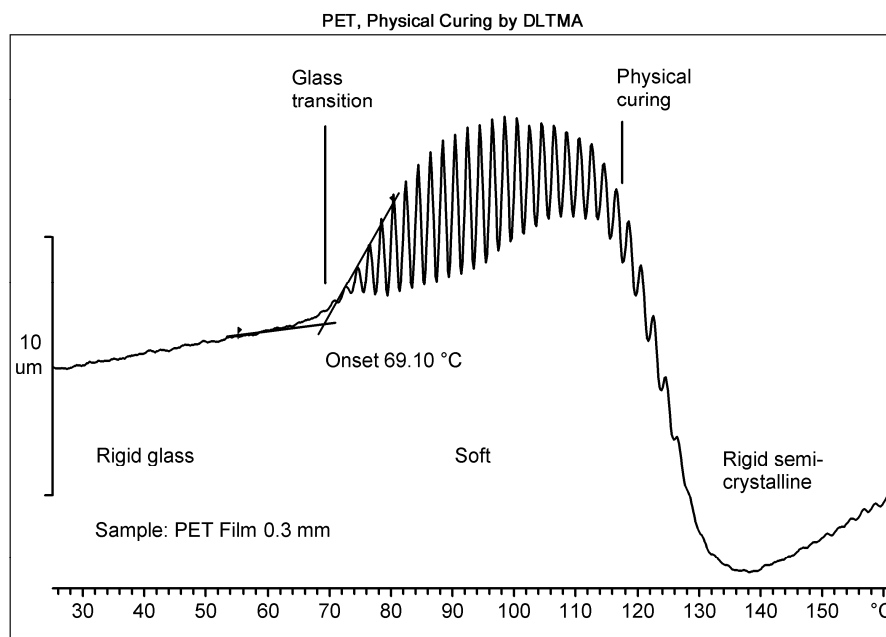


Figure 10.11. The DLTMA curve of polyethylene terephthalate shows the glass transition at 70 °C (increasing amplitude and decreasing modulus) and the cold crystallization at about 120 °C (increasing modulus, decreasing thickness due to increasing density). F_1 is 0.01 N, F_2 is 0.19 N, β is 10 K/min. 3-mm ball-point probe on the 0.3-mm thick PET film. Pretreatment: heating to 90 °C and cooling under dynamic load.

10.5.3 Chemical Reactions

TMA is mainly used to measure surface reactions, for example the thermal or oxidative decomposition of surface coatings. If decomposition is complete, the step height corresponds to the thickness of the coating (Figure 10.12). Ash, inorganic fillers and fibers possibly remain behind. The decomposition of organic samples is sometimes accompanied by foaming. Additives are also available that blow polymers to foam as they soften. In such cases, the curve of the volume increase is of interest. Samples like this are best measured in a crucible with a lid on top that is free to move. After expansion, the foam often collapses.

Laminates delaminate when the matrix resin decomposes and form gaseous decomposition products that force the layers apart.

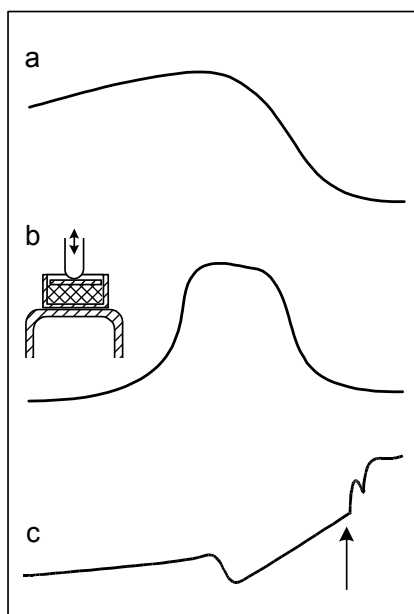


Figure 10.12. Effects due to chemical reactions or decomposition products.

- a: Decomposition of organic samples, e.g. surface coatings.
- b: On warming, the sample forms a voluminous foam that afterward collapses.
- c: Delamination (arrow).

10.5.4 Artifacts

The main artifacts in thermomechanical analysis occur in the following situations:

- If the compressive force is low, mechanical vibrations can cause the probe to “dance” on relatively hard samples or on the quartz glass disk covering the sample. This is observed as a large signal noise or spikes (0.5 μm). Solution: Install the TMA on a stone table equipped with shock absorbers in order to eliminate the possibility of vibrations and, if possible, increase the measuring force.
- Test specimens whose surfaces are not plane-parallel (e.g. slightly wedge-shaped) often produce step-like artifacts caused by the probe sliding down the specimen. Solution: Use test specimens with plane-parallel surfaces.

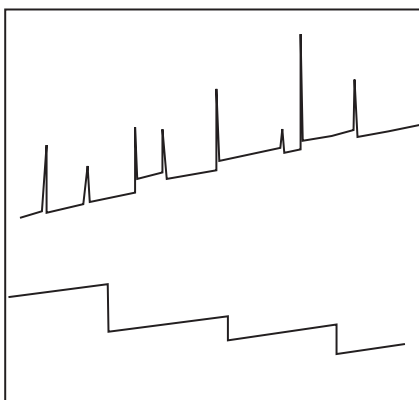


Figure 10.13. Above: Artifact caused by the probe “dancing” on the surface of the test specimen. Below: Artifact caused by the probe sliding down the wedge-shaped specimen.

10.6 TMA Evaluations

Basic evaluations of TMA curves are described in Chapter 5, General Thermal Analysis Evaluations. For example, the onset is an evaluation frequently used to characterize an effect with regard to temperature.

10.6.1 Glass Transition

If the slope of a TMA curve changes due to the glass transition of the sample, the evaluation is of the “onset” type (Figure 10.14). The results are as follows:

- The glass transition onset temperature.
- The thermal expansion coefficient, α , at the onset temperature.

If the curve in a penetration measurement is S-shaped (Figure 10.14), or as in the first derivative of a dilatometric measurement (Figure 10.15, lower curve), the following results - just as with DSC - are obtained:

- The glass transition onset temperature.
- The midpoint temperature (intersection of the curve with the bisector of the two baselines).
- The temperature at the point of inflection.
- The temperature at the endpoint (intersection of the inflectional tangent with the second baseline).
- The slope at the endpoint in current coordinate units.
- The step height Delta l (the difference in signal from onset to endpoint).

It should be noted that the result obtained from the first derivative does not correspond exactly to the onset temperature on the TMA curve.

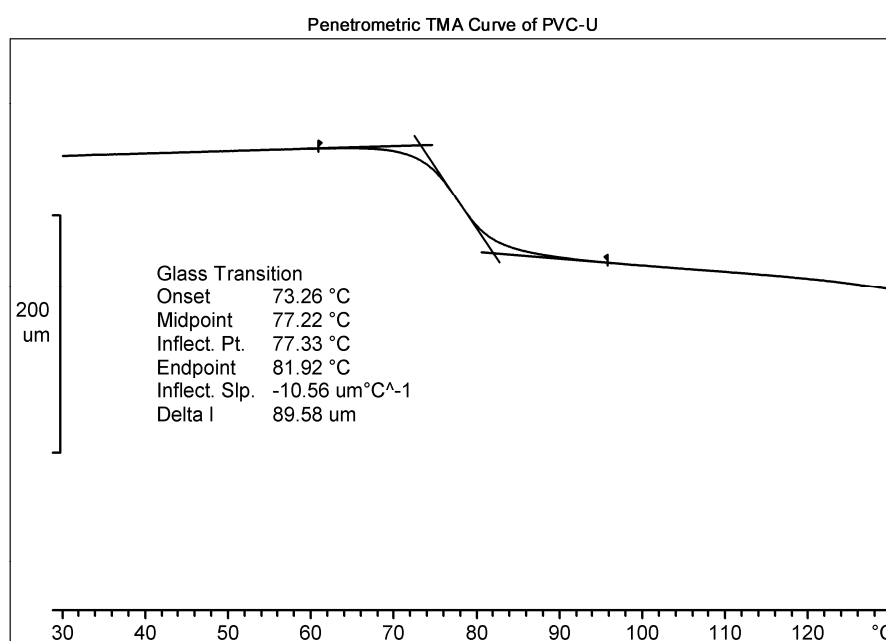


Figure 10.14. The TMA curve of a 3-mm thick PVC-U sample is S-shaped due to penetration of the probe. The curve was measured using a 3-mm ball-point probe, a force of 0.5 N and a heating rate of 5 K/min. The probe penetrates 91.3 μm between the onset and the endpoint.

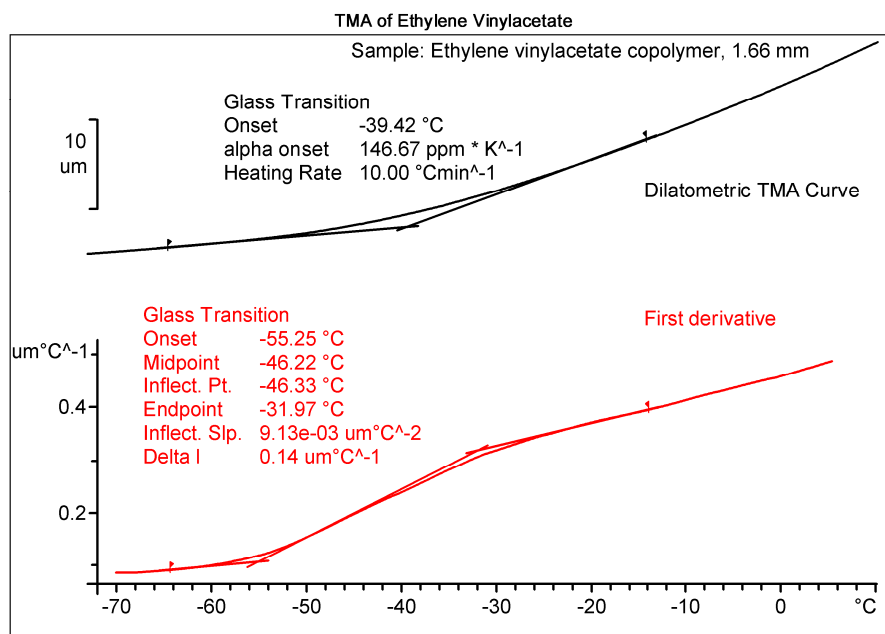


Figure 10.15. Above: Dilatometric TMA curve of a 1.66-mm thick E/VAC copolymer film between quartz glass disks measured with a force of 0.02 N and a heating rate of 10 K/min. At the glass transition, the slope of the curve increases. The evaluation is of the onset type. Below: The first derivative is S-shaped as expected. The evaluation automatically adapts to the shape of the curve: tangents (baselines) appear at the beginning and end of the evaluation range and the inflectional tangent.

10.6.2 Coefficient of Thermal Expansion

Two different coefficients of thermal expansion - the instantaneous value at a particular temperature and the mean value over a particular temperature range are defined in this section. (See the information box, Figure 10.16 and Figure 10.17). The coefficient of thermal expansion (CTE) is also known as the thermal expansion coefficient or just simply the expansion coefficient.

The Expansion Coefficient

Most materials expand on heating.

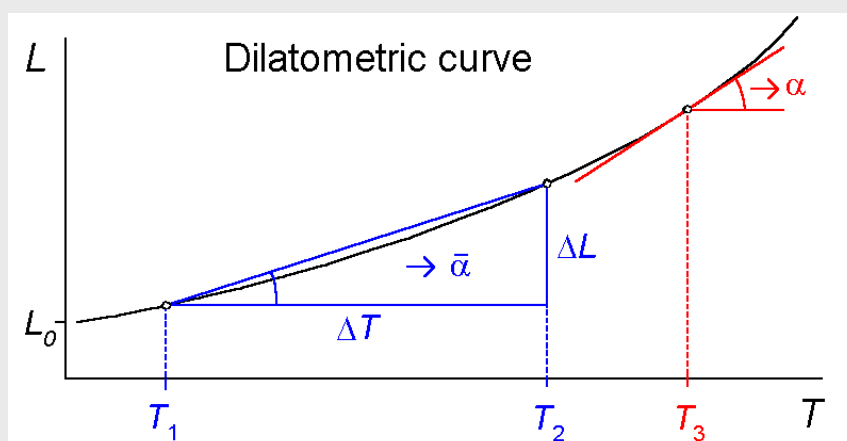


Figure 1. The diagram shows the length of a sample as a function of temperature. L_0 is the length at room temperature. The mean coefficient of linear thermal expansion, $\bar{\alpha}$, in the temperature range ΔT from T_1 to T_2 is equal to the slope of the triangle divided by the original length L_0 . The instantaneous coefficient of expansion, α , is equal to the slope at the temperature of interest, T_3 , divided by the original length, L_0 .

The linear coefficient of thermal expansion, α , is defined as follows:

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

where

dL is the change in length of the sample caused by a change in temperature of dT ,

L_0 is the initial length at the temperature T_0 , usually room temperature 25 °C, and

α is the instantaneous expansion coefficient according to this definition.

The usual unit is 10^{-6}K^{-1} ; the units $\frac{\mu\text{m}}{\text{m}\cdot\text{K}}$ and ppm/K are the same.

The mean coefficient of thermal expansion, $\bar{\alpha}$, is a measure of the expansion of the sample in the temperature range T_1 to T_2 .

$$\bar{\alpha}_{T_1 T_2} = \frac{L_2 - L_1}{T_2 - T_1} \frac{1}{L_0} = \frac{\Delta L}{\Delta T} \frac{1}{L_0}$$

where

L_0 is the length of the sample at T_0 , usually room temperature (reference length),

L_1 is the length of the sample at the lower temperature, T_1 , and

L_2 is the length of the sample at the upper temperature, T_2 .

In general, older dilatometers needed very long samples due to their limited displacement resolution. Such instruments therefore only measured mean coefficients of thermal expansion with isothermal steps at T_1 and T_2 . The evaluation software of modern TMA instruments allows both the instantaneous and the mean coefficient of linear thermal expansion to be calculated from dynamic measurements (without isothermal steps).

Material	$\alpha / 10^{-6}\text{K}^{-1}$
Invar (36% Ni, 64% Fe, cold formed)	0.1
Quartz glass	0.5
Glass, Pyrex	3
Aluminum oxide ceramic, polycrystalline	7
Platinum	8
Iron	12
Copper	16.6
Aluminum	24
Zinc	35
Sodium chloride	40
PVC-U	70
PE-HD	150
Natural rubber, vulcanized	220

Table 1. Coefficients of linear expansion of different materials at room temperature.

Analogous to the linear expansion coefficient, the volumetric expansion coefficient γ is defined as:

$$\gamma = \frac{dV}{dT} \frac{1}{V_0}$$

where

V_0 is the volume of the sample at the temperature T_0 , and

dV is the infinitesimally small change in volume due to the infinitesimally small change in temperature, dT

The volumetric expansion coefficient of isotropic materials can be calculated to a good approximation from the linear coefficient of expansion according to the equation

$$\gamma = 3 \alpha$$

For anisotropic materials, a good approximation is

$$\gamma = \alpha_x + \alpha_y + \alpha_z$$

The coefficients can be

- determined as individual values,
- presented as a table, and
- displayed as a curve.

Some notes concerning the evaluation:

- The initial length, L_0 , for the calculation of the expansion coefficient is the length (thickness) at the start of the measurement.
- Correction for the quartz glass expansion: The section of the measuring probe that corresponds to the sample length, L_0 , expands downward during heating. This expansion is compensated using a polynomial fit based on the expansion data of quartz glass.

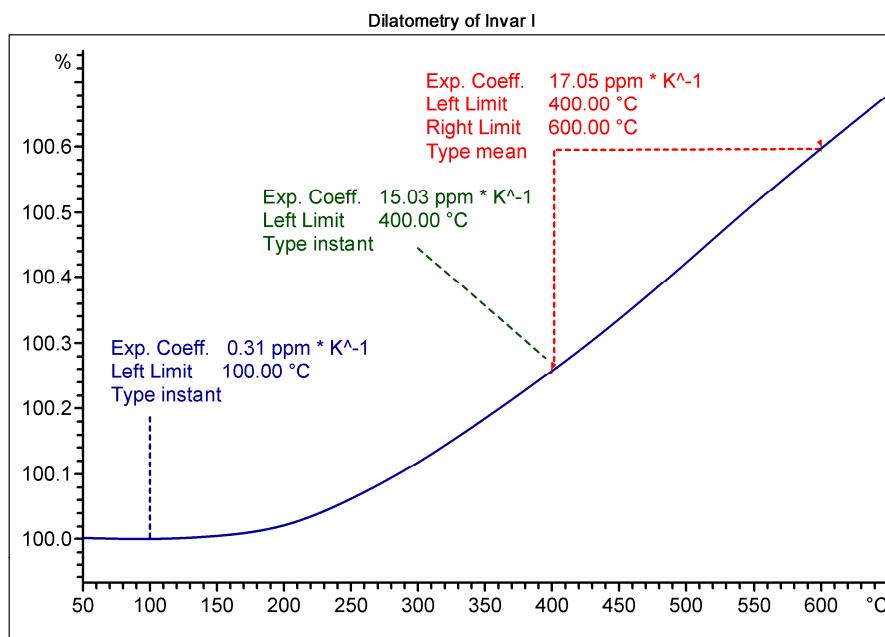


Figure 10.16. The instantaneous expansion of Invar at 100 °C and 400 °C is evaluated from the dilatometric TMA curve. For comparison, the mean thermal expansion coefficient between 400 and 600 °C. Invar is an iron-nickel alloy that is dimensionally stable around room temperature. Above 200 °C, the thermal expansion coefficient increases to typical values for metals of the iron group. Sample thickness: 2.5 mm, heating rate: 10 K/min.

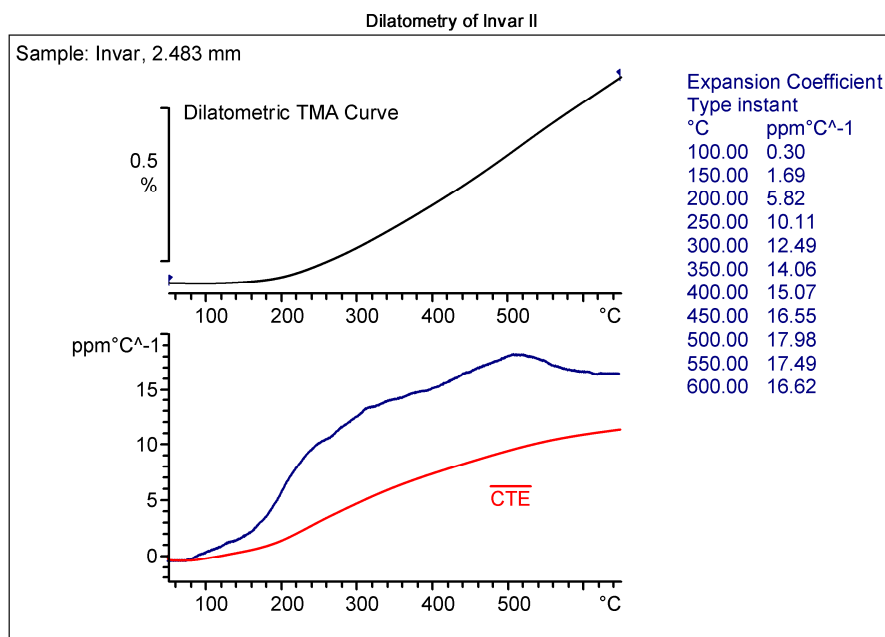


Figure 10.17. The upper diagram shows a normalized presentation of the TMA curve from Figure 10.16. The local coefficient of expansion is displayed as a curve (CTE, coefficient of thermal expansion) and as a table. For comparison, the mean coefficient of expansion between 50 °C and the particular temperature is shown in the lower curve.

Anisotropic materials such as wood, single crystals and composites exhibit direction-dependent properties. A printed circuit board (Figure 10.18) for example expands at 50 °C in the Z-direction (thickness) about three times more than in the X- and Y-directions, which are reinforced with glass fibers.

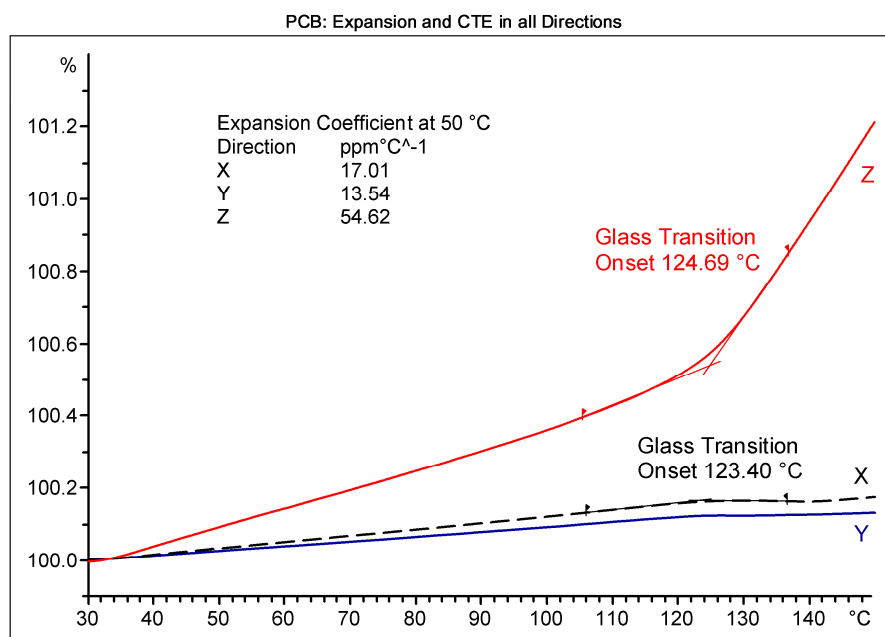


Figure 10.18. Expansion of a composite (printed circuit board, glass-fiber reinforced epoxy resin). Z: perpendicular to the glass fibers; X and Y in the same plane as the fibers. TMA measurement with a force of 0.02 N at 5 K/min, initial length L_0 4 mm. At the glass transition temperature, the coefficient of expansion of the resin matrix in the Z-direction changes markedly from about 125 °C onward. This is why this curve was used to evaluate the glass transition temperature.

10.6.3 Conversion

If part of or all the sample disappears during the measurement, a step-like TMA curve is produced. An example of this is a lacquer film that disappears due to melting or decomposition (Figure 10.19). In contrast, the length (thickness) can also increase, for example, rubber can swell in a solvent.

The conversion, α , is the change of thickness ΔL (length) with respect to the entire change in thickness.

$$\Delta L_{\text{tot}}: \alpha = \Delta L / \Delta L_{\text{tot}} \quad (10.4)$$

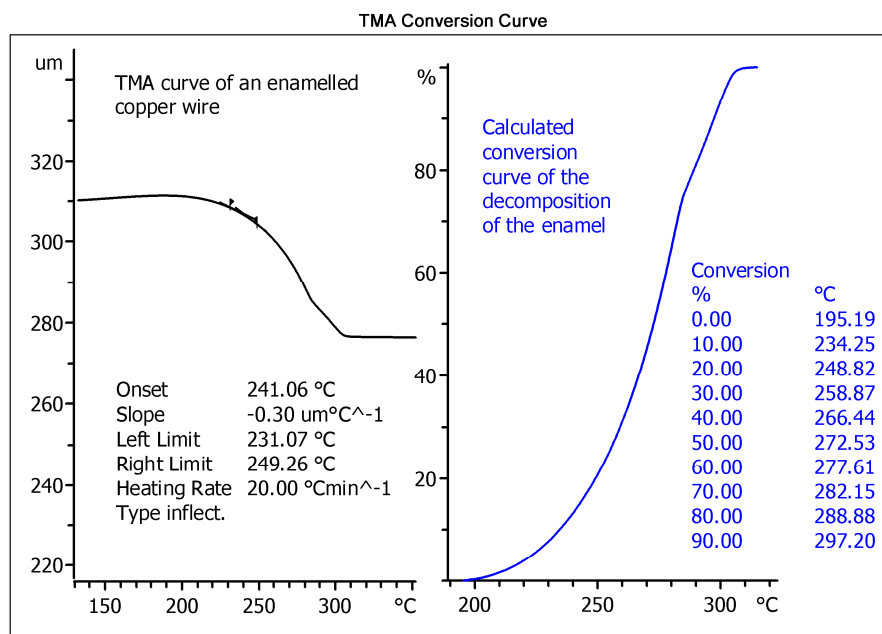


Figure 10.19. Left: The TMA curve of an enamelled insulated copper wire measured using the flat 1-mm² probe. The curve records the reduction in thickness of the organic insulation layer. The relatively high heating rate of 20 K/min was possible for the measurements because the sample is very small. Right: The corresponding conversion curve is presented as a table with equidistant ordinate points. Under these measurement conditions, a 50% reduction in thickness is reached at 272 °C. An insulation layer with higher temperature stability would yield a conversion curve that is shifted more to the right.

10.6.4 Young's Modulus

The Young's modulus (elastic modulus) can be determined from DLTMA curves if care is taken to ensure that the mechanical stress is the same throughout the test specimen during the measurement. Furthermore, the change in the measured signal must be significantly greater than the signal due to the finite stiffness of the TMA instrument. Before evaluating the modulus, the blank curve with an "infinitely stiff" sample is subtracted from the measured curve.

- Very soft samples such as foam rubber and soft elastomers can be measured in compression mode (modulus range 0.1 to about 5 MPa).
- Three-point bending allows a modulus range of 1 to about 200,000 MPa to be covered depending on the thickness and width of the test specimen. The modulus values are of course not so accurate because of the small specimens. In particular, the thickness of the test specimen must be constant and accurately measured because it affects the result to the power of three.
- The film and fiber attachment device enables measurements in another modulus range of about 1 to 1000 MPa to be made if favorable sample dimensions are used.

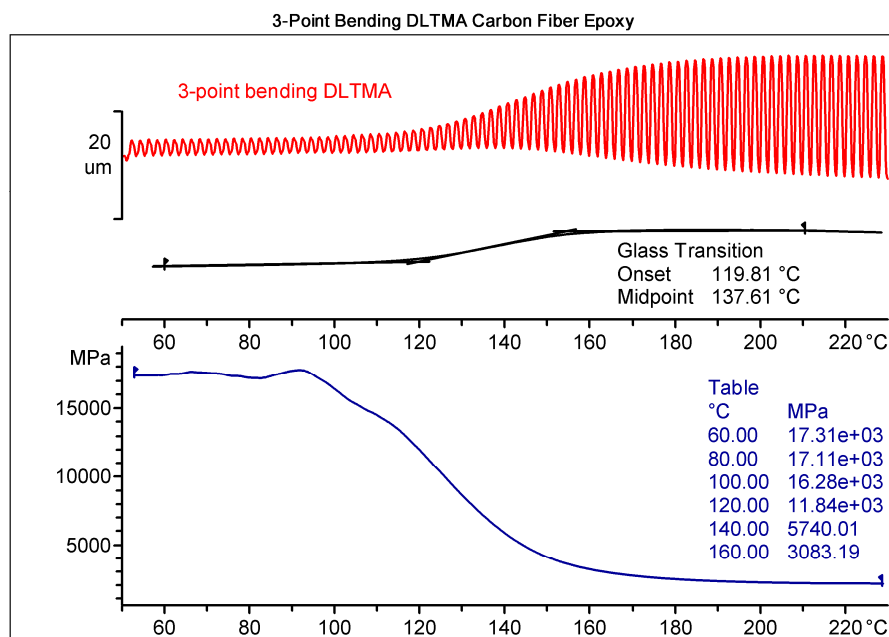


Figure 10.20. Above: DLTMA with three-point bending. Test specimen: Carbon-fiber reinforced epoxy resin. Distance between the supports 8 mm, sample width 3 mm, sample thickness 0.8 mm, period 12 s, F_1 0.02 N, F_2 0.5 N, heating rate 10 K/min. Below: Young's modulus is shown graphically and as a table.

In principle, Fourier analysis can be used to calculate the phase relationship between the stress and the strain. This allows the complex modulus to be separated into the storage modulus and the loss modulus. These calculations are however inaccurate for several reasons, especially in the bending mode. It is therefore better to use dynamic mechanical analysis, DMA for this.

Simultaneous measurement of the Young's modulus and the SDTA curve

The Young's modulus of a resin changes during curing. The exothermic chemical reaction can be simultaneously followed by recording the SDTA curve. If the starting material is not sufficiently stiff to be measured directly in a bending experiment, a thin piece of steel sheet can be used to support the resin layer. The modulus is of course incorrect due to the use of the steel support. The changes are however correctly measured.

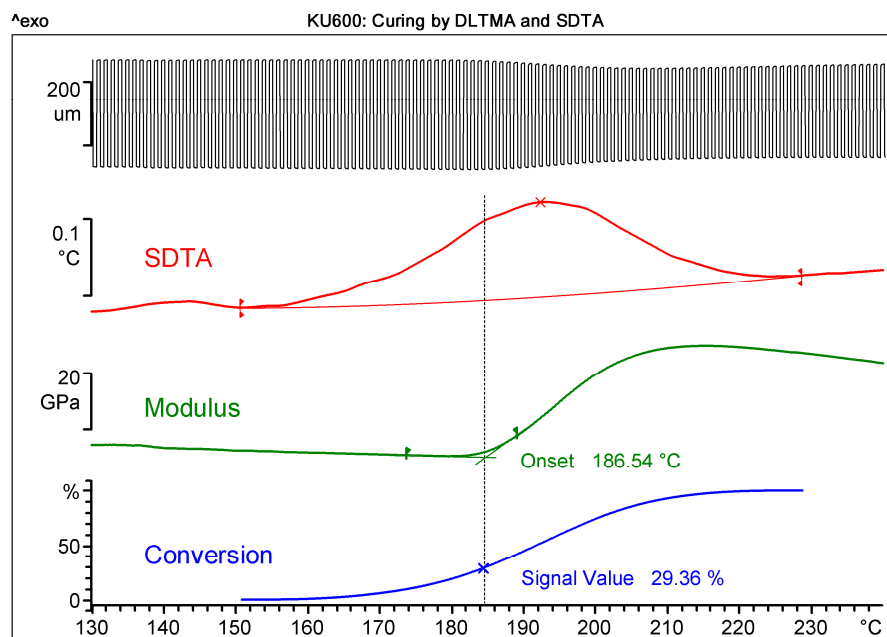


Figure 10.21. The curing of a KU600 epoxy resin is recorded using DLTMA and the simultaneously measured SDTA curve. Sample preparation: The viscous reaction mixture was applied to the surface of a 4-mm wide and 0.1 mm-thick steel sheet at room temperature and measured by three-point bending. The resin vitrifies (sudden increase in the modulus) at about 185 °C. For comparison, the SDTA curve and the conversion curve calculated from this show the course of the exothermic curing reaction. The numbers obtained for the modulus are arbitrary because the thickness of the layer is not perfectly uniform and because of the stiffness of the steel sheet used as the support.

10.7 Application overview for TMA

Effect, property of interest	Evaluation used	Figure
Coefficient of expansion	Mean expansion Instantaneous expansion	10.16, 10.17, 10.18
Young's modulus, DLTMA	Young's modulus	10.20, 10.21
Melting point	Onset	10.7
Solid-solid transition, polymorphism	Onset	10.7, 10.9
Glass transition, softening	Glass transition, Onset	10.7, 10.10, 10.11, 10.14, 10.15
Thermal decomposition, Pyrolysis, depolymerization, Delamination	Onset, Step, Conversion	10.12, 10.19
Polymerization, curing	Young's modulus, Conversion / SDTA	10.21
Increase in thickness due to foam formation or swelling	Step, Conversion	10.12
Thickness of a coating that melts or decomposes during the measurement	Step	10.19
Temperature stability	Onset	10.12
Oxidative decomposition, oxidation stability, OIT ¹⁾	Onset	
Comparison of competitive products, "good / bad"	Onset, Step, Young's modulus, Coefficient of expansion	

¹⁾ The oxidation reaction is exothermic and can therefore easily be followed from the SDTA signal.

10.8 Calibration and Adjustment of a TMA/SDTA

Definitions and information on calibration and adjustment can be found in Chapter 6, General Measurement Methodology.

10.8.1 What Needs to Be Calibrated in TMA?

- The thermocouple for the furnace temperature, T_c , and the thermocouple for the sample support temperature, T_{sh} . T_c is used for temperature control. T_{sh} is used to determine the sample temperature, T_s .
- The heating rate dependence of the temperature, expressed by the time constant τ_{lag} .
 τ_{lag} between the furnace temperature and the “reference temperature”, T_r , is used to calculate the temperature increase applied to the furnace temperature. The reference temperature corresponds to the temperature of a sample with no thermal effects and no heat capacity.
The time constant between the sample support temperature and the sample temperature is used to determine the exact sample temperature.
- The displacement sensor, LVDT is adjusted using accurate gauges.
- The linear motor, which generates the desired force, is adjusted using a calibration mass.

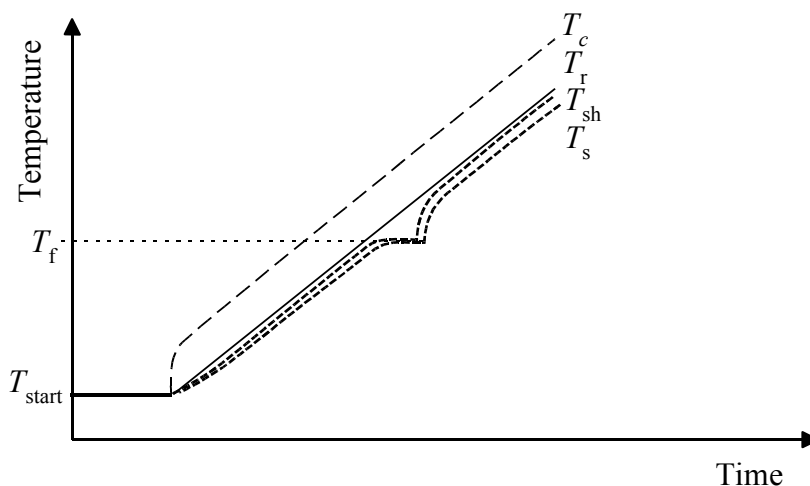


Figure 10.22. The temperatures in a TMA/SDTA:
 T_c : Furnace temperature, measured by a thermocouple.
 T_r : Reference temperature, program temperature.
 T_{sh} : Sample support temperature, also measured by a thermocouple.
 T_s : Sample temperature.
 T_f : Melting temperature of the sample.

The horizontal distance between the lines T_c and T_r corresponds to the furnace time constant, τ_{lag} ; the vertical separation is the temperature increase applied to the furnace temperature. The horizontal distance between the lines T_{sh} and T_s corresponds to the time constant of the sample support.

The adjustment requires repeated measurements of melting point reference substances at several heating rates followed by evaluation of the SDTA melting peak. The sample is cooled each time to a sufficiently low temperature for it to crystallize.

Calibration with indium and zinc is recommended for the important temperature range from about 100 °C to about 500 °C. This is done by measuring three melting peaks at heating rates of 5, 10 and 20 K/min and automatically evaluating the onset temperatures. For other temperature ranges, it may be necessary to use other reference substances (e.g. octane and indium for a low temperature TMA).

The In-Zn check is used to routinely check the temperature of a TMA. In this, small samples of each metal (0.2 to 0.5 mg) are placed as far as possible apart between two quartz glass disks. This sandwich is subjected to a force of 0.1 N and heated from 50 to 500 °C at 10 K/min. The melting of the samples appears on the TMA curve as small, practically vertical steps whose inflection temperatures can be evaluated.

References and Further Reading

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UserCom: Many of the application examples in this chapter have been taken from UserCom, the METTLER TOLEDO technical customer journal that is published twice a year. Back issues of UserCom can be downloaded as PDFs from the Internet at www.mt.com/ta-usercoms .

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11.1 Introduction

Dynamic mechanical analysis yields information about the mechanical properties of viscoelastic materials as a function of time, temperature and frequency. The sample is subjected to a periodic (sinusoidal) mechanical stress. This causes it to undergo deformation with the same period. The instrument used to perform such measurements is called a dynamic mechanical analyzer, DMA. A DMA instrument measures

- the force amplitude,
- the displacement amplitude, and
- the phase difference between the force and displacement signal.

The result of a dynamic mechanical analysis is the complex modulus of the sample. The stress applied to the sample during the measurement must be within the linear range as defined by Hooke's Law. Definitions of the different moduli can be found in the information box.

The Stress-Strain diagram

A stress-strain diagram is obtained by subjecting a material to a force that slowly increases (i.e. quasi-static conditions). The applied force and the dimensional change are continuously measured. In this example, the tensile stress (force per area) is then plotted against the tensile strain (ΔL divided by the original length L_0).

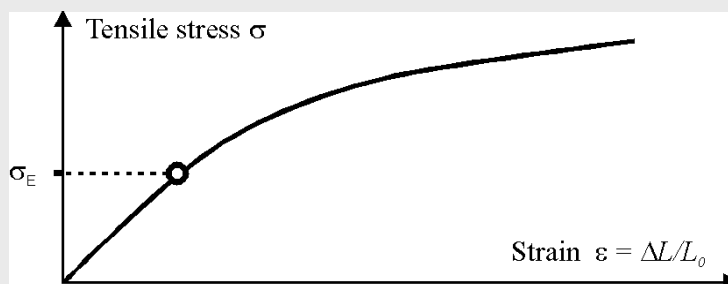


Figure 1. Schematic stress-strain diagram of a solid material. σ_E is the elastic limit (end of the linear region).

The linear part of the curve below the elastic limit, σ_E , is the so-called Hooke's region. In this region, where the deformation is small, the material behaves purely elastically and there is no permanent deformation after removal of the stress. Within the elastic limit, stress and strain are directly proportional to each other, that is, stress/strain is a constant. This is known as **Hooke's law**. The ratio of stress to strain is called the elastic modulus; in the case of tensile stress the ratio is called the **Young's modulus**.

Above the elastic limit, structural changes cause permanent deformation that does not disappear on removal of the force that produced it. This is known as inelastic behavior.

The linear range of metals is often greater than that of plastics. Highly stretched synthetic fibers exhibit a linear range similar to that of metals.

Compressive stress, tensile stress, shear stress

A static force or load applied to a solid or a very viscous liquid produces a mechanical stress σ . The compressive stress is calculated by dividing the vertical force F acting on the surface by the area A :

$$\sigma = F/A$$

The unit is N m^{-2} known as the Pascal, Pa, so that 1 MPa equals 1 N/mm^2 .

A negative compressive stress is known as **tensile stress**. A body is compressed in the direction of the compressive stress, whereas in tensile stress it is stretched.

A completely different type of stress occurs in **shear**, in which shear forces act tangentially on two opposite surfaces of the body. This generates a shear stress, τ .

$$\tau = F/A$$

The **shear stress** deforms the body (here a rectangular block) obliquely as shown in the diagram below. The unit is the Pascal.

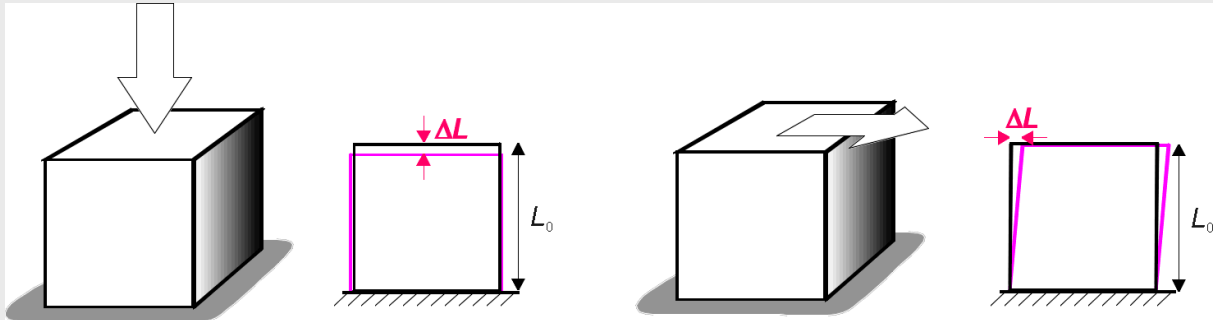


Figure 1. Left, compressive stress: The force acts vertically on a surface of the rectangular block (the counter force is exerted by the support or base) and presses it together by an amount ΔL . Right, shear stress: The force acts tangentially to the surface of the block (the counter force is exerted by the support or base) and shifts it by an amount ΔL .

The elastic modulus

The elastic modulus, E , is a measure of the dimensional stability under mechanical stress. It is equal to the slope of the stress-strain diagram in the linear or Hooke's region. If there is no linear region, the slope $d\sigma/d\varepsilon$ at the lowest stress is used. Since the expansion, ε , is dimensionless, the unit of E is Pascal.

$$E = \left. \frac{d\sigma}{d\varepsilon} \right|_{\sigma \approx 0}$$

The shear modulus (and torsional modulus)

The shear modulus, G , like the elastic modulus, is equal to the slope in the linear region of the shear stress-strain diagram. The strain, γ , is equal to the shear angle. At small angles it corresponds to ΔL divided by L_0 . ΔL and L_0 are defined in Figure 2, right.

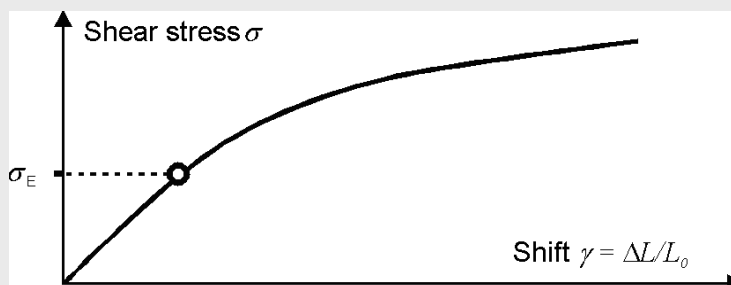


Figure 2. Schematic shear stress shift diagram of a solid material. The shear modulus is equal to the slope in the linear region. σ_E is the elastic limit.

If there is no linear region, the slope, $d\tau/d\gamma$, at the lowest shear stress is used. The unit of G is the Pa.

$$G = \left. \frac{d\tau}{d\gamma} \right|_{\tau \approx 0}$$

G and E of isotropic materials are related by the following equation:

$$G = \frac{E}{2(1 + \mu)}$$

Here, μ is **Poisson's number**, a material constant, whose value lies between 0 and maximum 0.5. This means that E is 2 to 3 times greater than G . In the case of anisotropic materials such as fiber reinforced polymers, E can be 10 or 100 times greater than G in the direction of the fibers.

Material	E at 25 °C /GPa	G at 25 °C /GPa	μ 25 °C
PVC	2.5	1	0.25
aluminum	70	26	0.34
steel	210	81	0.29
iridium	530	210	0.26

The oscillating stress applied to the sample produces a corresponding oscillating strain. Unless the sample is perfectly elastic, the measured strain lags behind the applied stress. This is called the phase difference or the **phase angle**, δ . The ratio of peak stress (stress amplitude) to peak strain (strain amplitude) gives the **complex modulus**, M^* , which consists of an in-phase component M' (or **storage modulus**) and a 90° out-of-phase component, M'' (or **loss modulus**). The ratio of the loss and storage moduli (M''/M') is a useful quantity known as the **loss factor** (or damping factor), **$\tan \delta$** . A high $\tan \delta$ value indicates that a material has a high non-elastic strain component while a low value indicates that the material is more elastic. It is a measure of the energy dissipated as heat during each deformation cycle.

Thus, in general, one distinguishes between three different types of sample behavior:

- Purely elastic: The applied stress (or force) and the strain (deformation) are in phase. The phase angle, δ , is 0. A purely elastic sample oscillates without loss of energy.
- Purely viscous: The phase angle, δ , is $\pi/2$ (90°). In a purely viscous sample, the deformational energy is converted into heat.
- Viscoelastic: The deformation of the viscoelastic sample follows with a certain delay with respect to the applied stress (or force). The phase angle δ is therefore between 0 and $\pi/2$ (90°). The larger the phase angle, the stronger the oscillation is damped.

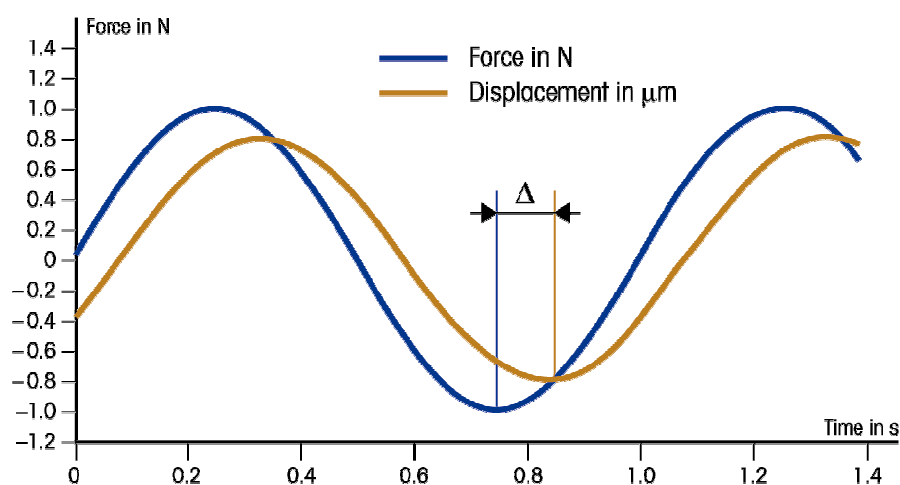


Figure 11.1. Force and displacement at a frequency, f , of 1 Hz for a viscoelastic sample. The sinusoidal deformation of the sample is the reaction to the sinusoidal stress. The deformation follows the force with a time delay of Δ , which can also be expressed as the angle δ , where $\delta = 2\pi f\Delta$.

DMA measurements allow many different mechanical sample properties to be determined. These include

- viscoelastic material properties, for example moduli and the loss factor, $\tan \delta$,
- temperatures that characterize the viscoelastic behavior of the sample,
- damping,
- the glass transition temperature (DMA is the most sensitive method),
- the curing behavior of resins, and
- the frequency-dependent mechanical behavior of materials.

11.2 Measurement Principle and Design

11.2.1 The Measurement Principle

The periodically changing force $F(t)$ is described by the following equation:

$$F(t) = F_A \sin \omega t \quad (11.1)$$

F_A is the amplitude of the force, ω the angular frequency ($= 2\pi f$), f is the frequency of oscillation.

The resulting deformation $L(t)$ is given by:

$$L(t) = L_A \sin(\omega t + \delta) \quad (11.2)$$

where δ is the phase shift of the deformation with respect to the force.

11.2.2 Stiffness and Modulus

The ratio of force and displacement is also referred to as stiffness. The stiffness is a quantity that depends on the sample geometry and the modulus of the sample.

The modulus is of physical importance because it is a material property. It is calculated from the force normalized to the area, A , on which it acts and the deformation normalized to the original sample length L_0 . These quantities are referred to as the

- mechanical stress (force per area) or stress, σ and the
- relative deformation or strain, ε .

In dynamic mechanical analysis, the force amplitude F_A and the displacement amplitude L_A are used to calculate the complex modulus, M^* .

11.2.3 The Geometry Factor

For practical reasons the two quantities are normalized in the so-called geometry factor, g .

This is illustrated using the elastic modulus, E , from a tension or compression experiment:

$$E^* = \frac{\sigma}{\varepsilon}, \quad \sigma = \frac{F_A}{A}, \quad \varepsilon = \frac{L_A}{L_0}, \text{ it follows that}$$

$$E^* = \frac{\sigma}{\varepsilon} = \frac{F_A}{A} \frac{L_0}{L_A} = \frac{F_A}{L_A} \frac{L_0}{A} \text{ and } g = \frac{L_0}{A} \quad (11.3)$$

F_A/L_A is the stiffness. The final equation for the determination of the elastic modulus is therefore:

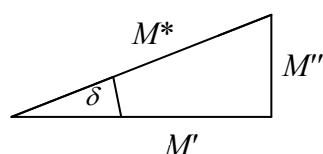
$$E^* = \frac{F_A}{L_A} g \quad (11.4)$$

The geometry-dependent modulus is obtained by multiplying the stiffness by the geometry factor.

Formulas for calculating the geometry factor for other measurement modes such as shear or bending are given in Table 11.2).

11.2.4 Storage Modulus and Loss Modulus

The diagram shows the geometrical relationship between the three moduli and the loss angle, δ :



M^* : complex modulus
 M' : storage modulus
 M'' : loss modulus
 δ : loss angle

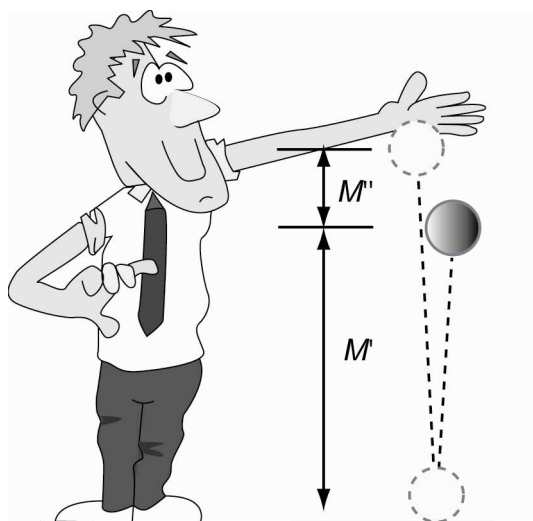


Figure 11.2. A ball falls onto a hard surface and does not rebound to the original height because of loss of energy.

The storage modulus M' is proportional to the mechanical energy stored in the sample during the stress period.

In contrast, the loss modulus M'' describes the energy dissipated (lost as heat) during a stress cycle in the material. A high loss modulus indicates viscous behavior and hence marked damping properties.

Finally, the loss factor, $\tan \delta$, corresponds to the ratio of the elastic to the viscous properties. A high value therefore indicates high degree of energy dissipation and thus a high degree of non-elastic deformation. The loss factor has the advantage that it is not affected by the geometry factor. It can therefore also be accurately measured even with unfavorable geometry.

The reciprocal values of the moduli are known as compliances.

Stress	$\sigma(t)$	$= \sigma_A \sin \omega t = F_A/A \sin \omega t$
Strain	$\varepsilon(t)$	$= \varepsilon_A \sin(\omega t + \delta) = L_A/L_0 \sin(\omega t + \delta)$
Modulus	$M^*(\omega)$	$= \sigma(t)/\varepsilon(t) = M' \sin \omega t + M'' \cos \omega t$
Value of the modulus	$ M^* $	$= \sigma_A/\varepsilon_A$
Storage modulus	$M'(\omega)$	$= \sigma_A/\varepsilon_A \cos \delta$
Loss modulus	$M''(\omega)$	$= \sigma_A/\varepsilon_A \sin \delta$
Loss factor	$\tan \delta$	$= M''(\omega)/M'(\omega)$

Table 11.1. Summary of definitions.

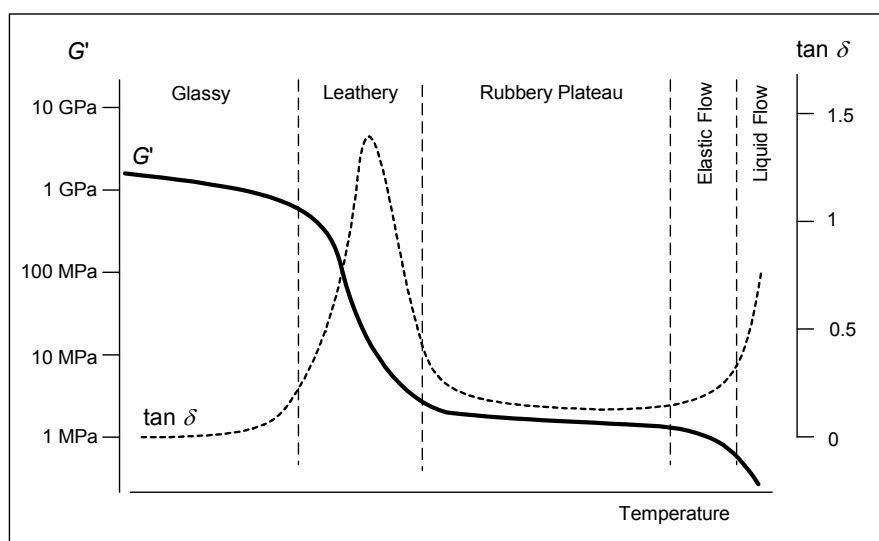


Figure 11.3. DMA curves of a typical thermoplastic. In the glassy state, the storage modulus is of the order of a several GPa. The loss factor is small. The mechanical properties of the material changed markedly in the region of the glass transition: the storage modulus decreases typically by several orders and the loss factor shows a distinct maximum. There then follows a region in which the material is rubbery soft. At higher temperatures, the thermoplastic becomes softer and begins to flow. This is apparent in a further decrease of the storage modulus, whereas $\tan \delta$ shows a marked increase.

11.2.5 The Frequency Temperature Equivalence Principle

The following principle is valid for homogeneous isotropic viscoelastic materials that behave linearly when a mechanical stress is applied, that is, the elastic modulus is independent of the force or displacement amplitude.

If such a material is subjected to a constant load, the material deforms in the course of time because the molecules slowly rearrange in order to minimize the stress.

If an oscillating stress is applied, the strain decreases with increasing frequency because less time is available for molecular rearrangement. The material is therefore stiffer at higher frequencies than at lower frequencies. This means that its modulus increases with increasing frequency.

With increasing temperature, the molecules are able to rearrange more rapidly, which is why the displacement amplitude increases. This is the same as a decreasing modulus.

A modulus measured at room temperature at a certain frequency is equivalent to a measurement at higher temperature at a higher frequency.

This means that frequency and temperature influence the material properties in a complementary way.

This can be used to obtain information about the modulus at frequencies that are experimentally not directly accessible. For example, information on the damping behavior of a rubber blend at several kHz and room temperature is not possible to obtain from a direct measurement because the maximum frequency of the DMA is not sufficiently high. This is where the temperature-frequency-equivalence principle is of great help. Thanks to this, the loss factor can be extrapolated to several kHz and room temperature using measurements performed at low temperatures and frequencies within the measurement range. This is known as the WLF relationship or the Vogel-Fulcher relationship (see the master curve technique described in Section 11.6).

Since low frequencies correspond to long times (and vice versa), one refers to the temperature-frequency equivalence as the time-temperature superposition (TTS).

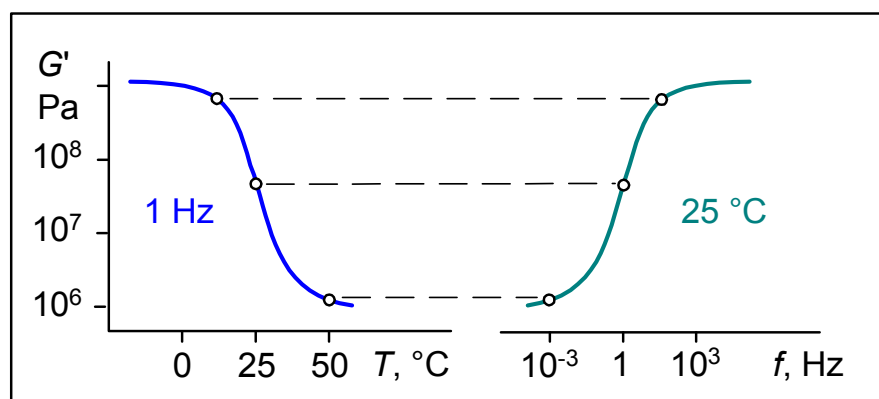


Figure 11.4. Left: Schematic curve of the storage modulus of a polymer at 1 Hz in the region of the glass transition as a function of the temperature. Right: Schematic curve of the frequency dependence of the storage modulus of the same polymer, measured at room temperature. In the logarithmic frequency presentation, the two curves appear as mirror images.

The upper line shows the same moduli at low temperature and high frequency; the middle line connects the identical measurement values under identical measurement conditions; the lower line shows the same moduli at high temperature and low frequency.

11.2.6 Important Applications of Dynamic Mechanical Analysis

DMA can be used to

- detect thermal effects due to a change in the modulus or the damping behavior,
- distinguish between frequency-dependent and frequency-independent effects,
- measure temperatures that characterize a thermal effect,
- measure the loss angles or the mechanical loss factor,
- measure the modulus or its component storage and loss modulus, and
- determine the frequency- and the temperature-dependence of these quantities.

11.2.7 Design of a DMA Instrument

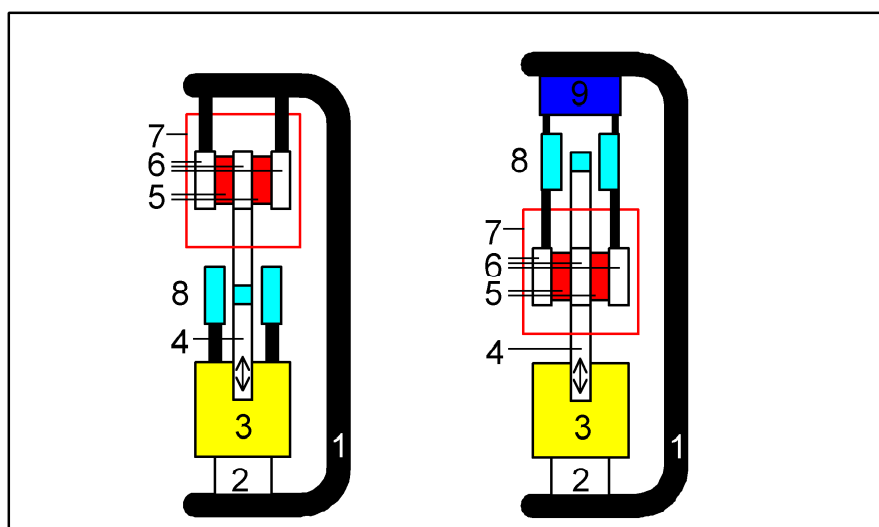


Figure 11.5. Left: A conventional DMA. Right: The operating principle of the METTLER TOLEDO DMA/SDTA861°.

1: stand, 2: device for setting the height, 3: drive motor, 4: drive shaft, 5: shear samples, 6: shear sample holder, 7: furnace, 8: displacement sensor (LVDT), 9: force sensor (only in the DMA/SDTA861°).

The main components of a DMA instrument are shown schematically in Figure 11.5:

1. The stand is very robust and stiff and exhibits negligible deformation under the action of the forces produced by the drive motor.
2. The device for setting the height is used to center the drive motor.
3. The drive motor moves the drive shaft at the desired frequency and force or displacement amplitude.
4. The drive shaft transmits the oscillation to the sample and the displacement sensor.
5. The sample is shown here mounted on both sides of the shear clamp. The temperature is measured very close to the sample using a separate thermocouple.
6. The sample holder is the sandwich-like shear sample holder.
7. The furnace for subjecting samples to the desired temperature program.
8. The displacement sensor measures the amplitude and the phase of the sinusoidal deformation. The amplitude is usually in the range 0.1 to 1000 μm .
9. The force sensor measures the amplitude and the phase of the sinusoidal force.

In instruments that do not have a force sensor, an attempt is made to determine the force and phase position from the electrical alternating current transmitted to the drive motor.

In conventional DMA instruments, deformation of the drive shaft and the stand reduces the stiffness of the instrument. This makes it impossible to measure very stiff samples.

11.2.8 The Measurement Modes

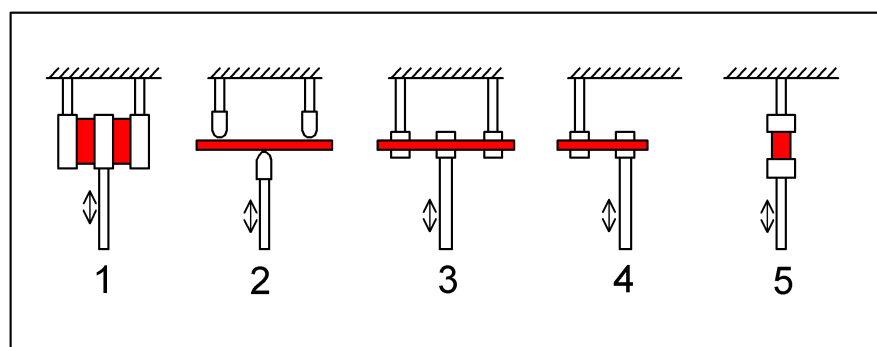


Figure 11.6. The most important DMA measurement modes. 1: shear, 2: three-point bending, 3: dual cantilever, 4: single cantilever, 5: tension or compression.

Each measurement mode has its specific range of applications and its limitations. These are briefly discussed below:

1. The shear mode is the only mode that allows you to determine the shear modulus, G . It is ideal for soft samples in the modulus range 0.1 kPa to 5 GPa.
2. In the three-point bending mode, the sample has to be pre-stressed so that it remains in contact with the three supports during the measurement. A sample that becomes soft can undergo considerable deformation due to this pre-stressing. This mode is ideal for samples of high modulus, for example fiber-reinforced polymers, metals, and ceramic materials. Modulus range: 100 kPa to 1000 GPa.
3. In the dual cantilever mode, the sample is clamped securely at three positions and is not so free to expand on warming. The sample can buckle and suffer additional stress on cooling. Furthermore, due to clamping effects, it is not easy to determine the effective free sample length. A length correction takes into account that the effective mechanical stressed sample length is greater than the free clamped length. These effects lead to incorrect modulus values. The modulus range is 10 kPa to 100 GPa.
4. The single cantilever avoids the problem of restricted thermal expansion or contraction of the dual cantilever mode. Here again, it is not easy to determine the free sample length. The modulus range is 10 kPa to 100 GPa.
5. In the tension mode, the sample has to be pre-stressed to prevent it buckling. The tension mode is ideal for films, fibers and samples in the shape of thin rods. The modulus range is 1 kPa to 200 GPa.
6. In the compression mode, sample pre-stressing is also necessary to ensure that the sample is always in contact with the clamping plates. The modulus range is 0.1 kPa to 1 GPa.

Table 11.2 shows the moduli calculated for different measurement modes at a measured stiffness of 0.1 kN/mm based on typical sample dimensions. The modulus range can be increased by orders of magnitude by varying the dimensions, especially the sample thickness in bending modes and in tension experiments. Further orders of magnitude are of course accessible because a stiffness range of 0.001 to 10 kN/mm is available and not just 0.1 kN/mm.

Note: A stiffness of 0.1 kN/mm corresponds for example to a force amplitude of 2 N with a displacement amplitude of 20 μm .

DMA measurement mode	Formula to calculate the geometry factor	Typical sample dimensions in mm, or mm ²			Elastic modulus in MPa for a stiffness of 0.1 kN/mm
		Thickness <i>b</i>	Width <i>w</i>	Length <i>l</i>	
Shear	$g = \frac{b}{2wl}$	1	5	5	0.01 ¹⁾
3-point bending	$g = \frac{l^3}{4wb^3}$	1	10	60	2200
Dual cantilever	$g = \frac{l^3}{16wb^3}$	1	10	60	540
Single cantilever	$g = \frac{l^3}{wb^3}$	1	10	30	270
Tension	$g = \frac{l}{wb}$	0.01	5	20	40
Compression	$g = \frac{l}{wb}$	10	10	20	0.02

Table 11.2. Comparison of measurement modes: The last column shows that the shear and compression measurement modes cover very low moduli. The 3-point bending mode is optimal for samples of very high modulus. The modes that require pre-stressing are marked blue.

¹⁾ The elastic modulus here is calculated from the shear modulus (see information box at the beginning of the chapter).

11.3 Sample Preparation

The shape of the sample must be prepared so that it is suitable for the measurement mode you want to use:

- For shear: quadratic or round test specimens with a thickness of 0.5 to 1 mm.
- For bending: flat parallel-sided test bars with a thickness of 0.1 to about 3 mm, a width of about 2 to 4 mm and a length of about 90 mm (50 mm for the single cantilever).
- For tension: films cut with uniform width and a thickness of 0.005 to about 0.5 mm.
- For compression: cube- or cylinder-shaped plane-parallel test specimens.

Test specimens for DMA measurements must be plane-parallel in order to avoid serious measurement errors. The surfaces should be smooth, so that the force does not act on just a few individual surface irregularities (grind and possibly polish).

The properties of the sample should not change during preparation of the test sample. In particular, plastics must not heat up to more than about 40 °C during mechanical processing. We recommend the use of a water-cooled diamond saw. This also produces the desired plane-parallel test specimen. The test specimens must however be dried after processing and allowed to dry in the air for a few hours before the measurement.

Films can be punched out or cut out with a knife. Soft flat materials cut out using a sharp die give good plane-parallel test specimens. Ideally, the die is mounted in a stand-mounted drill.

Conditioning

- Humidity:
Test specimens can change during storage before measurement due to atmospheric humidity (possibly store them in a desiccator). Since water behaves as a plasticizer for some polymers, the glass transition may possibly shift to lower temperatures.
- Thermomechanical history:
Mechanical processing of the test specimen can cause an undesired change to its properties. Internal stresses can also be created or eliminated. In certain cases, a first heating run up to a moderate end temperature can be used to eliminate the thermal history. The actual material properties are then measured in a second heating run.

11.4 Performing Measurements

11.4.1 Force- or Displacement-Controlled Measurements

A DMA measurement is performed at either a preset force amplitude or a preset displacement amplitude. In the first case, this is referred to as a force-controlled experiment and in the second case a displacement-controlled experiment. The DMA/SDTA861^e allows the measurement to be automatically switched from force-controlled to displacement-controlled during an experiment. This ensures that the deformation of softening samples remains within preset limits.

An unfavorable choice of the displacement or force amplitude can have a negative effect on measurement accuracy. Amplitudes of more than 1 μm (0.5 to 50 μm) and 50 mN to 5 N are optimal providing the displacement amplitude does not exceed 1% of the corresponding sample dimension.

11.4.2 Frequent Causes of Error

- Clamping error: With the exception of the 3-point bending and compression modes, errors frequently occur if the test specimen is clamped unevenly, too strongly or too weakly. The latter is particularly the case in measurements performed below room temperature.
- Errors due to mechanical friction: In the single cantilever mode, the expansion of a test specimen can shift the core of the LVDT to such an extent that it touches the coil housing. In measurements below 0 °C, icing problems can cause a bridge to form between the movable and fixed parts.
- Errors due to amplitudes that are too small. Test specimens that are too stiff can give displacement amplitudes that are too small; specimens that are too soft give force amplitudes that are too small.

11.4.3 Measurements using a Dynamic Temperature Program

The test specimens used in DMA are large compared with those used in DSC or TGA. Consequently, only low heating or cooling rates of 1 to 3 K/min can be used if accurate measurements are to be obtained. Rates of up to 10 K/min can be used for trial measurements.

To avoid unforeseen decomposition (with corresponding cleaning afterward), it pays to determine the beginning of decomposition of an unknown sample beforehand using TGA or TMA.

There are different types of oscillation:

- Constant frequency, e.g. 10 Hz.
- Multi-frequency, 4 frequencies simultaneously, e.g. 10, 20, 50 and 100 Hz.
- Multi-frequency, frequencies are activated sequentially, e.g. 300, 100, 30, 10, 3 and 1 Hz.

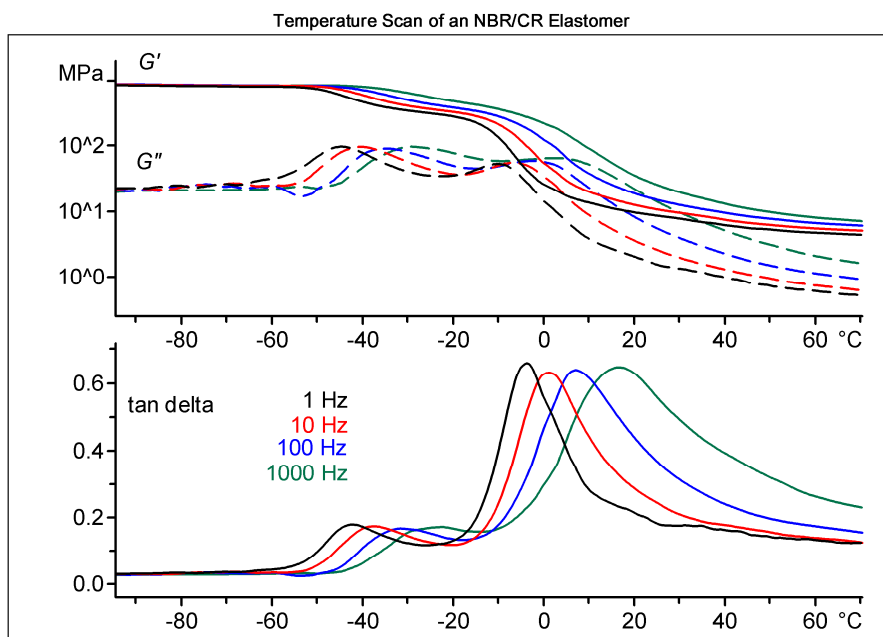


Figure 11.7. DMA measurement of a NBR/CR elastomer at a heating rate of 2 K/min.

11.4.4 Isothermal Measurements at Different Frequencies

These are performed if there is special interest in frequency-dependent thermomechanical behavior at a particular temperature. Example: 500, 50, 5, 0.5 Hz (in logarithmic steps) or at 100, 90, 80...20, 10 Hz (with linear increments). Each frequency yields a set of results (moduli and $\tan \delta$). The results are more accurate than with the temperature-programmed measurement because the sample is in thermal equilibrium.

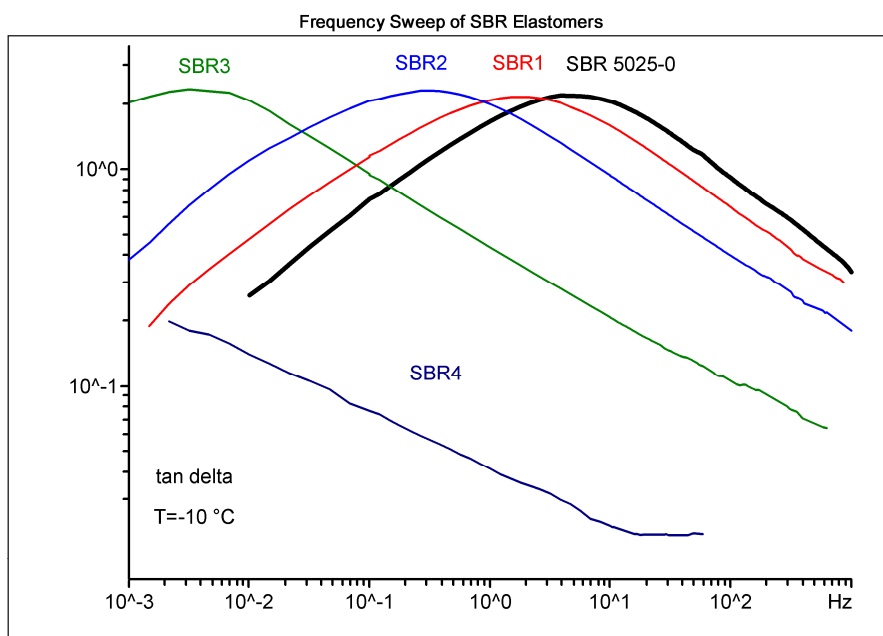


Figure 11.8. DMA frequency sweeps of different vulcanized SBR elastomers [1].

11.4.5 Isothermal Measurements with Increasing Amplitude

To obtain an accurate measurement of the modulus over a wide temperature range, the stress applied to the sample must lie within the linear range as given by Hooke's law. Trial experiments are first performed to determine the measurement parameters. These can be measurements with increasing deformation or increasing force. In the linear range, the modulus is independent of the amplitude. The limit of linearity is reached when the modulus decreases noticeably with increasing amplitude. It is better to determine the linearity limit in a measurement in which the displacement amplitude is increased under control. The results should be plotted in double logarithmic presentation.

A further application is the investigation of the interaction between the matrix and fillers. In this case, $\tan \delta$ is evaluated.

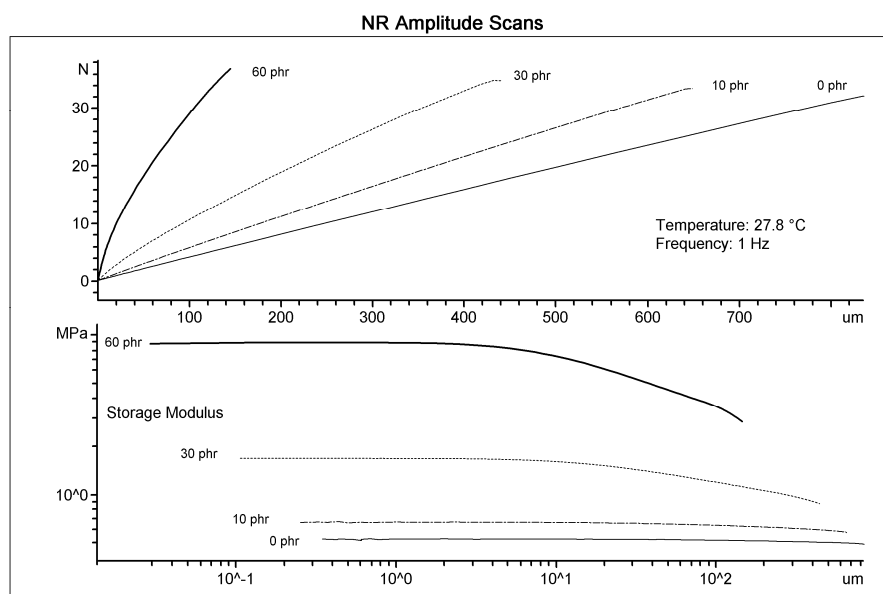


Figure 11.9. DMA measurement of NR test specimens with increasing displacement amplitude.

11.5 Interpretation of DMA Curves

11.5.1 Interpreting the Temperature Dependence of DMA Curves

11.5.1.1 The Presentation of DMA Curves

Since moduli can change by several orders of magnitude, a linear presentation cannot satisfactorily display the information contained in the measurement data (Figure 11.10). For example, a step of 1 GPa to 10 MPa cannot be distinguished from a step of 1 GPa to 1 MPa. In the logarithmic presentation, however, such differences can easily be seen (Figure 11.11).

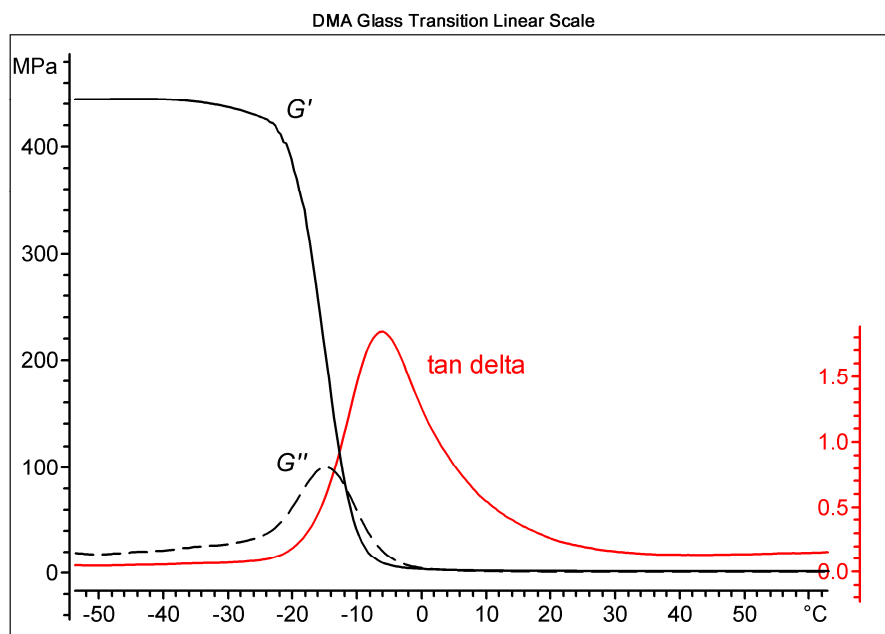


Figure 11.10. A linear presentation of the modulus overemphasizes the region with high values. The point of inflection of the storage modulus G' corresponds approximately to the maximum of the loss modulus. The latter is often taken to be the glass transition temperature, T_g , at the frequency concerned. Because $\tan \delta = G''/G'$, the maximum of $\tan \delta$ is at higher temperature. At the point of intersection of G' and G'' , $\tan \delta = 1$. Sample SBR, 1 Hz, 2 K/min.

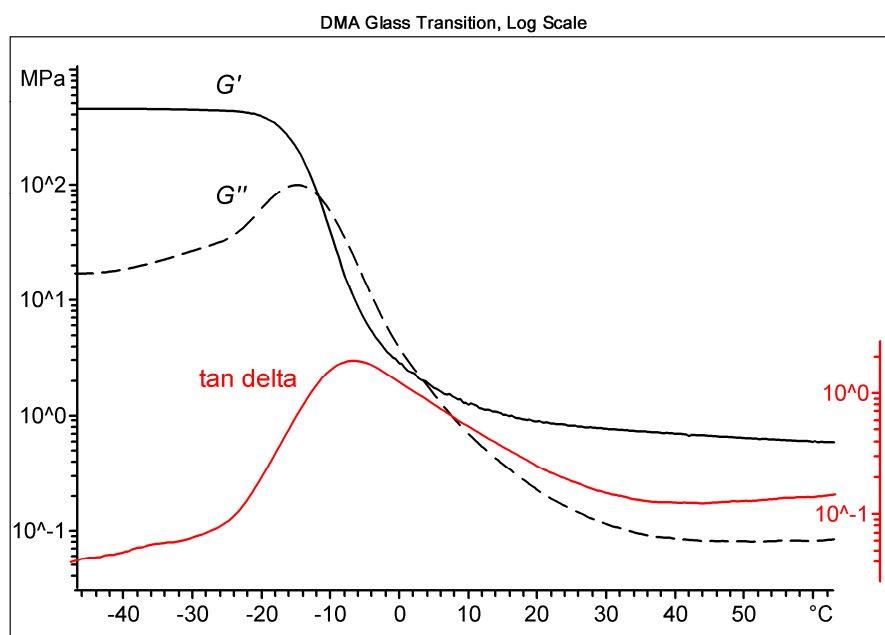


Figure 11.11. The same measurement data as in Figure 11.10 but displayed in the usual logarithmic presentation. Compared with the linear presentation, the low-value region now appears scale-expanded. In this presentation, T_g corresponds to the onset of the decrease of G' . The loss factor in the rubbery elastic region is clearly larger than in the glassy state. The ordinate of the loss factor is displayed on the right in the diagram.

11.5.1.2 Interpreting DMA Curves Measured with a Dynamic Temperature Program

In general, the storage modulus of commonly used materials decreases with increasing temperature. The storage modulus of metals used for constructional purposes such as steel or aluminum alloys hardly changes up to temperatures of 400 °C (Figure 11.12). Stepwise changes are caused by relaxation transitions (e.g. the glass transition) or phase transitions (e.g. melting and crystallization). Peaks in the loss modulus and the loss factor, $\tan \delta$, correspond to steps in the storage modulus.

Amorphous materials go through a glass transition on heating or cooling. The modulus changes by one to four decades. The same occurs when the crystallites of semicrystalline polymers melt. Such phase transitions do not of course exhibit the large frequency dependence of relaxation transitions.

Commonly used thermoplastics such as polyvinylchloride and polystyrene have an elastic modulus of about 3 GPa at room temperature. Their glass transition temperatures lie between room temperature and about 200 °C. At about 100 K above the glass transition, the polymers flow and can be plastically deformed (Figure 11.12).

Elastomers such as natural rubber, NR, exhibit a glass transition below room temperature but do not flow because of chemical crosslinking (Figure 11.12). This low degree of crosslinking occurs during vulcanization of the originally thermoplastic rubber.

Thermosets such as epoxy resins are three-dimensionally crosslinked macromolecules. Their glass transition region is significantly above room temperature. They do not flow when the temperature is increased because of their three-dimensional crosslinking. The starting materials of thermosets consist of several different components, which are often referred to as the “resin” and the “hardener”. When thermoplastic starting materials harden or cure, a three-dimensional network is produced and the glass transition temperature increases by 50 to 300 K (Figure 11.16).

If the macromolecules are aligned due to processing, they are referred to as oriented polymers. They are then anisotropic, that is, their properties depend strongly on their orientation. This also applies to fiber-reinforced polymers.

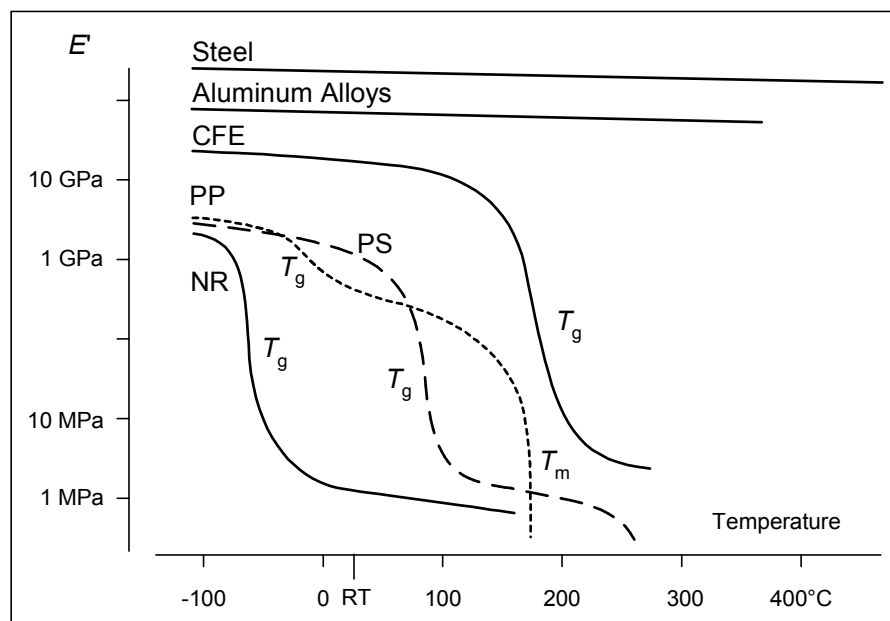


Figure 11.12. The storage part of the elastic modulus, E' , of various materials as a function of temperature. The E' of steel decreases only slightly (210 GPa at room temperature, 177 GPa at 400 °C). In contrast the storage modulus (proportional to stiffness) of organic materials is lost almost completely in one or more steps. T_g is the glass transition temperature and T_m the melting temperature. CFE is a carbon-fiber-reinforced epoxy resin, PP: polypropylene, PS polystyrene, NR natural rubber.

With amorphous and semicrystalline materials, several relaxation transitions are observed. For historical reasons; the transition at the highest temperature is known as α -relaxation or the glass transition. It is assigned to cooperative molecular movement over a range of several nanometers, while the weaker secondary relaxation or β -relaxation is due to the movement of short segments.

Relaxation processes are frequency dependent in contrast to melting processes, crystallization and chemical reactions, and can therefore easily be identified. The glass transition shifts by 5 to 10 K per frequency decade. β -Relaxation is even more frequency dependent with values of at least 10 K/decade (Figure 11.13).

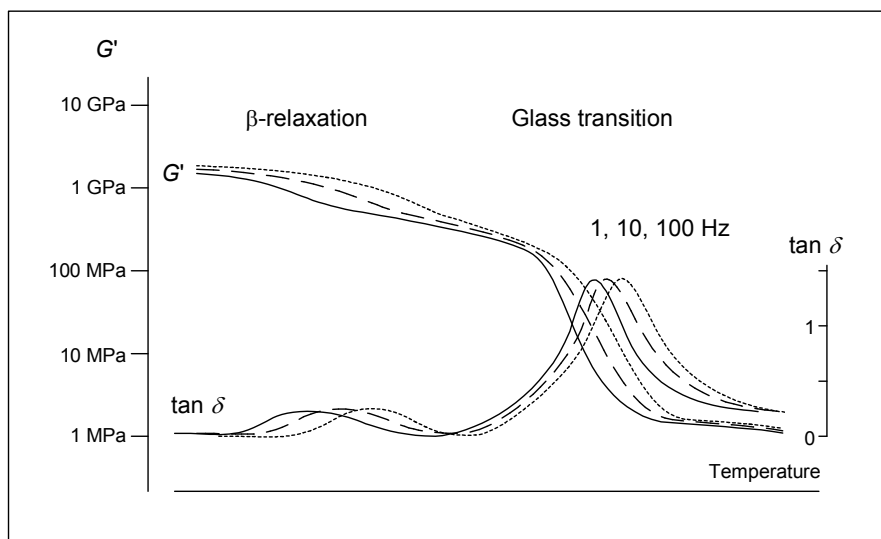


Figure 11.13. Shear modulus, G' , and loss factor measured at three frequencies differing by a decade. The β -relaxation shifts more strongly than the glass transition. Usually the loss factor only exceeds a value of 1 at the glass transition.

Incompatible mixtures of amorphous polymers and block copolymers show the two glass transitions of the individual components, whereas compatible mixtures and random copolymers exhibit only one glass transition. This lies between the glass transitions of the individual components (Figure 11.14). The relative contents of such samples can be estimated from the curves of the pure polymers.

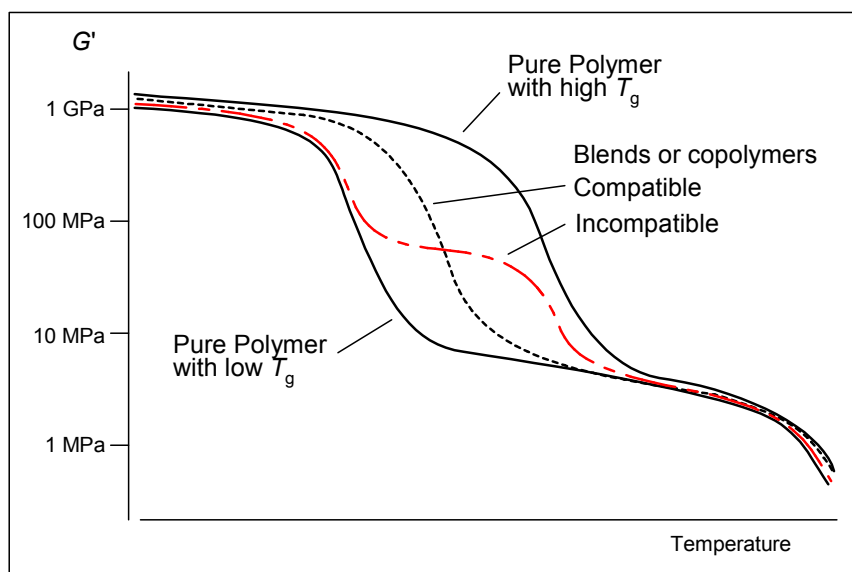


Figure 11.14. Compatible and incompatible polymer mixtures or copolymers compared with the basic pure homopolymers.

The properties of semicrystalline thermoplastics depend on the crystallinity. Some plastics, for example polyethylene terephthalate, remain amorphous after shock-cooling from the melt, and then crystallize when heated to above their T_g (Figure 11.15).

In the case of thermosets, the main interest lies in the behavior of the thermoplastic starting materials, the increase of the modulus on gelation, and the glass transition of the fully cured thermoset (Figure 11.16). Such measurements may cover a modulus range of more than four decades and can only be performed in the shear mode.

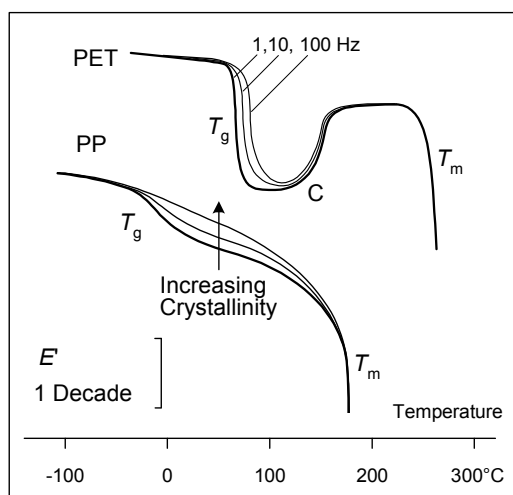


Figure 11.15. Above: Amorphous polyethylene terephthalate softens at the glass transition and crystallizes at the point C. The modulus then increases slightly because crystallites with a greater degree of perfection are formed. Finally the crystallites melt. Only the glass transition shifts with increasing frequency. Below: The modulus of a semicrystalline thermoplastic such as polypropylene increases with increasing crystallinity. The change at the glass transition becomes smaller with highly crystalline materials.

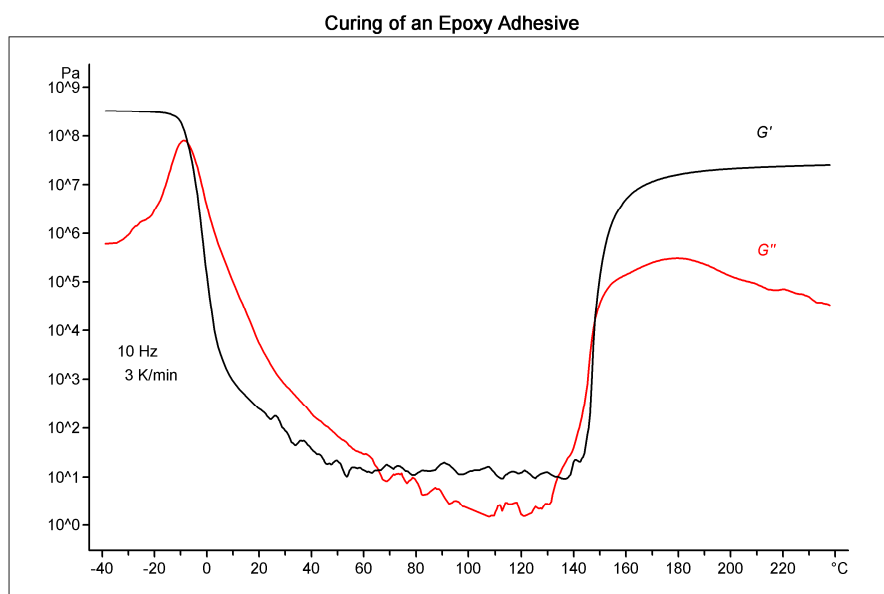


Figure 11.16. Shear modulus, G' , and loss modulus, G'' , of a two-component epoxy resin system liquid at room temperature, consisting of DGEBA, diglycidylether of bisphenol A and DDM, diaminodiphenylmethane. Heating and cooling rates 3 K/min, frequency 10 Hz, sample geometry: diameter 11 mm, thickness 2 mm.

At the starting temperature of -50 °C, the two-component epoxy resin mixture in Figure 11.16 is a hard glass. It changes to the liquid state above 0 °C. The storage modulus, G' , decreases by 7 decades. During the curing reaction, gelation occurs at 140 °C.

11.5.1.3 Final Comments

DMA measurements give an insight into temperature- and frequency-dependent molecular movement, and provide the engineer with information on material properties regarding stiffness, damping behavior and the range of temperature in which materials can be used. DMA measurements show especially well how the glass transition depends on factors such as relative humidity/moisture or the degree of cure.

Before an unknown sample is measured by DMA, it is a good idea to perform a DSC measurement at 20 K/min over a relatively large temperature range. The information from the DSC curve can be used to choose a reasonable temperature range for the DMA measurements to prevent the sample from completely melting or decomposing in the DMA. A second measurement of the same sample can then be performed, if need be with new sample geometry.

In general, DSC measurements aid the interpretation of DMA curves (and vice versa). DSC and DMA measurements provide different information and complement each other in an ideal way; one technique cannot however replace the other.

11.5.2 Interpretation of the Frequency Dependence of DMA Curves

This part deals with the frequency dependence of the mechanical properties and quantities of stable samples. Because this field is so large, only the basic principles and general rules that explain the behavior of materials are discussed.

In practice, materials are subjected to stresses at many different frequencies. It is therefore extremely important to have a detailed understanding of the effect of frequency on mechanical properties. In addition, it means that materials need to have different properties under different conditions. For example, an adhesive should behave elastically without breaking when it suffers a blow (high frequencies), but should at the same time be able to “accommodate” stress arising from temperature fluctuations (low frequencies) like a liquid.

11.5.2.1 Complex Modulus and Compliance

11.5.2.1.1 The Ideal Elastic Solid

In the shear mode, DMA measures the shear modulus, G^* , and the shear compliance, J^* . An ideal elastic material stores the entire mechanical energy involved in the deformation. When the shear stress is removed, the energy is liberated. The modulus is independent of the frequency; stress and deformation (strain) are in phase. In this case, $G^* = G'$, whereby G' is known as the storage modulus. A spring provides a good example to illustrate this behavior (Figure 11.17, left).

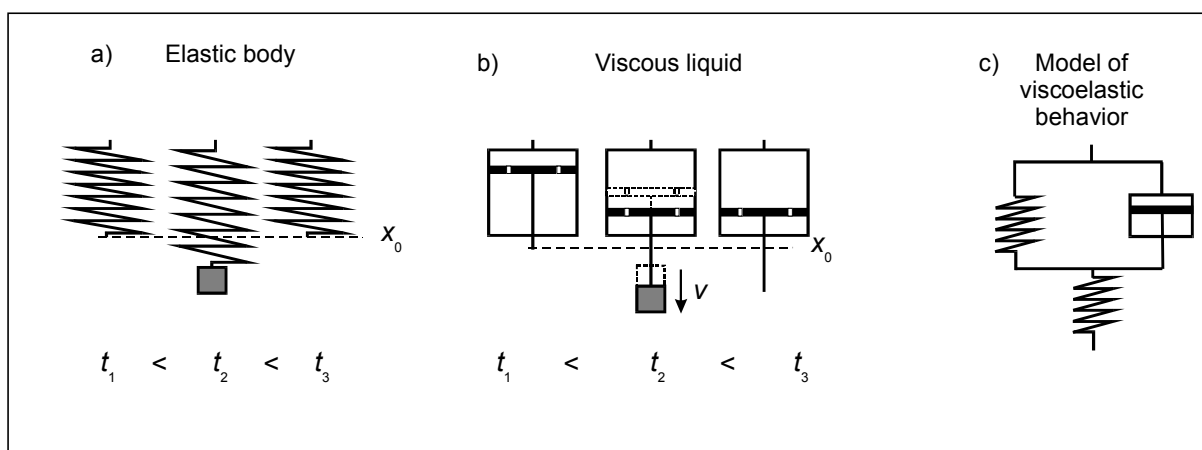


Figure 11.17. Models illustrating the mechanical behavior of materials. t_1 , t_2 and t_3 are the times before, during and after the load was applied, x_0 is the initial length and v is a constant speed.

11.5.2.1.2 The Ideal Viscous Liquid

In an ideal liquid, the stress and the strain are phase-shifted by 90°. Since the molecules are free to move, no mechanical energy is stored in the material – the energy is completely converted to heat. The corresponding model is the damping device shown (see Figure 11.17, middle). Typically, a liquid is described by the frequency-independent viscosity, η_0 . In the case of the shear modulus, $G^*(\omega) = i G''(\omega)$. The imaginary number $i = \sqrt{-1}$ is a mathematical expression that represents the fact that mechanical energy is dissipated, that is, converted to heat. G'' is the loss modulus where $G'' = \omega \eta_0$. In a liquid, the loss modulus therefore increases linearly with frequency $f = \omega/2\pi$.

11.5.2.1.3 Viscoelastic Materials

In real materials, the reaction to an external stress is accompanied by molecular rearrangements that take place over a wide frequency range. Examples of this are lattice vibrations in solids at about 10^{14} Hz and cooperative rearrangements at the glass transition at about 10^{-2} Hz. Molecular rearrangements are the reason for the different relaxation processes. At higher temperatures, the frequency of the molecular rearrangements increases.

The properties of real materials lie between those of an ideal solid and an ideal liquid. Since they have both elastic and viscous properties, the materials are said to be viscoelastic. Their behavior is described mathematically by the complex, frequency-dependent modulus:

$$G^*(\omega) = G'(\omega) + i G''(\omega) \quad (11.5)$$

where G' is the elastic part of the modulus and G'' the energy dissipation part (viscous component). Technical models that illustrate viscoelastic behavior are combinations of springs and damping devices (see Figure 11.17, right).

11.5.2.1.4 The Complex Compliance

The G^* modulus describes the relaxation of the mechanical stress for a given strain. In everyday language, a material with a larger storage modulus is said to be “harder”.

The DMA experiment can also be performed in such a way that the stress is given and the resulting strain measured. One then talks of strain retardation. In this case, the compliance, J^* , is determined. This is also complex and frequency dependent and is given by:

$$J^*(\omega) = J'(\omega) - i J''(\omega) \quad (11.6)$$

where J' and J'' are the storage and loss compliances. In simple terms, one can say that a “softer” material has a greater (storage) compliance.

The relationship between the modulus and the compliance is given by the equation:

$$J^*(\omega) = 1 / G^*(\omega) \quad (11.7)$$

This allows the following two equations to be derived:

$$J' = G' / (G'^2 + G''^2) \text{ and}$$

$$J'' = G'' / (G'^2 + G''^2).$$

The relationship between modulus, compliance and loss factor in a relaxation transition is illustrated in Figure 11.18.

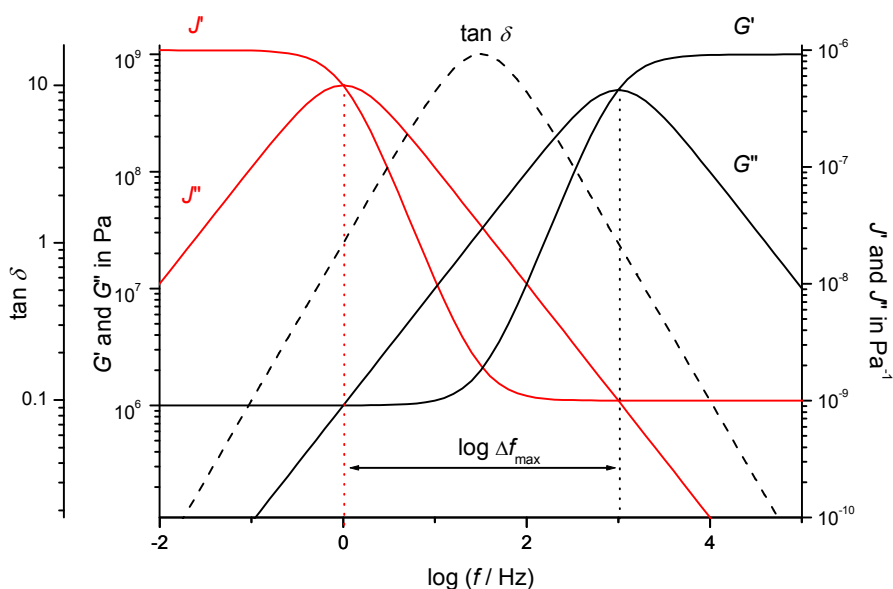


Figure 11.18. Theoretical curve shapes of moduli, compliances and $\tan \delta$ as a function of frequency.

The mechanical behavior of a material can be expressed equally well using the modulus or the compliance. In practice, the quantity used depends on what you are accustomed to and practical considerations. For example, the modulus is often used when discussing mechanical behavior in the rubbery plateau, whereas the compliance is used to separate different processes.

11.5.2.2 The Frequency Dependence of Modulus and Compliance

11.5.2.2.1 An Overview of Frequency Dependence

Theoretical modulus and compliance curves of an amorphous polymer are shown schematically in Figure 11.19. The curves are displayed in log-log presentation. At low frequencies, one can see the flow region in which G' and G'' increase with frequency and J' and J'' decrease. There then follows the region of flow relaxation and the rubbery plateau in which G' and J' are almost constant. A large step in the storage part is characteristic for the main relaxation region. In the transition region, the loss components exhibit peaks. At higher frequencies, secondary relaxation (β -relaxation) occurs, which can be recognized by the relatively broad steps in G' and J' and the peaks in G'' and J'' . A number of different relaxation processes occur over the entire frequency range. The frequency corresponds to the characteristic length of the molecular rearrangement considered. The greater the frequency, the smaller the characteristic length. In the case of secondary relaxation, the characteristic length is about 0.5 nm, whereas at the main relaxation (maximum of G'') it is about 2.5 nm and about 5 nm at the corresponding maximum of J'' .

The β -relaxation observed in polymers is often attributed to the side chains. For polymers that do not have a movable side chain, it is interpreted as a conformational variation. The nature of these relaxation effects cannot however be reduced to polymer specific processes because it is also measured in low molecular weight glass formers.

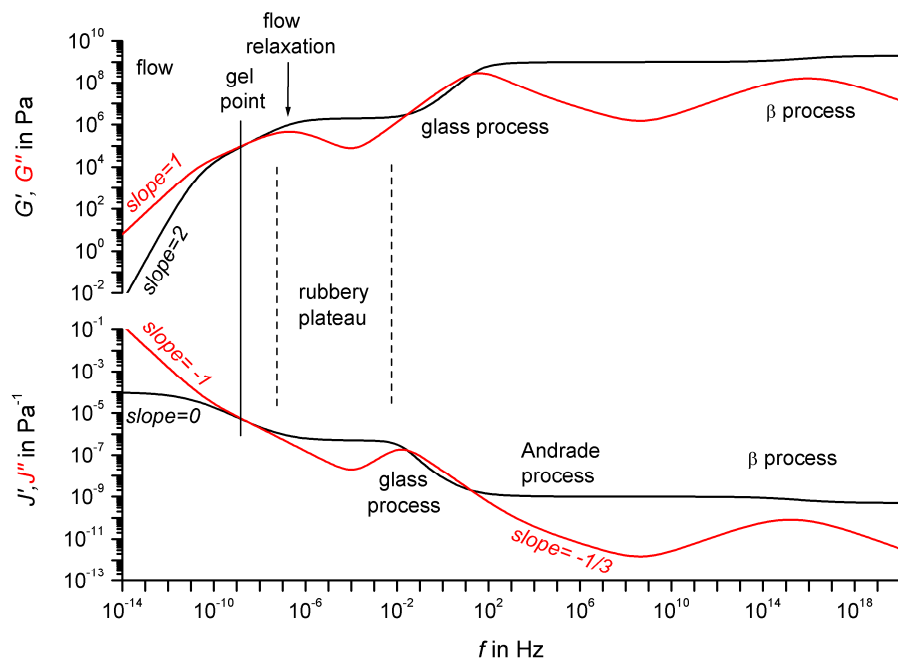


Figure 11.19. Schematic curves of the moduli and compliances of a viscoelastic material.

Figure 11.20 displays the modulus of unvulcanized styrene-butadiene rubber (SBR) at -10 °C. The individual effects are discussed in the following sections.

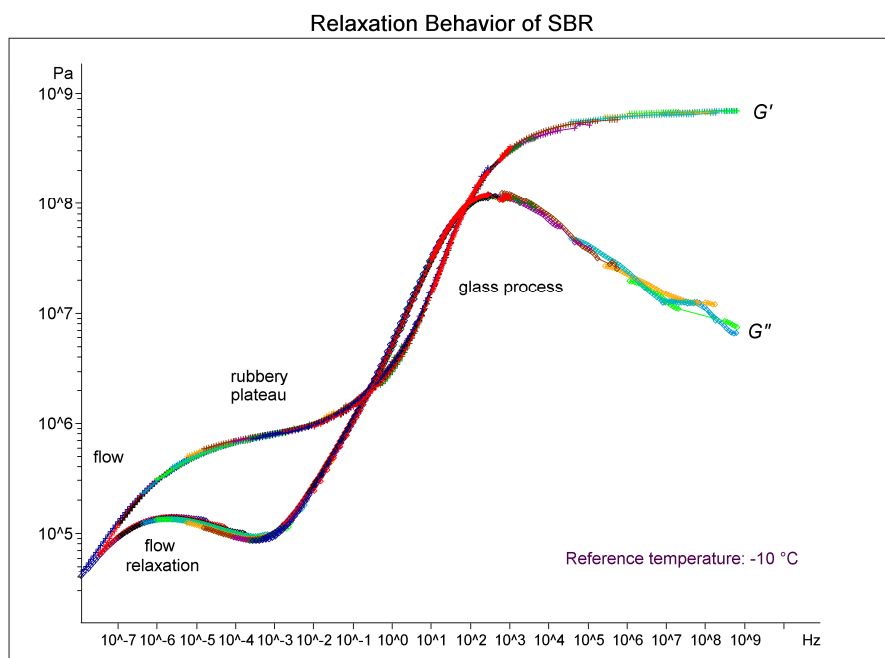


Figure 11.20. Storage G' and loss modulus G'' of SBR at -10 °C.

11.5.2.2.2 Behavior in the Glassy State

We begin the discussion of the mechanical behavior at the high frequencies. In Figure 11.20, the storage modulus, G' , is almost constant above 10^5 Hz and the loss modulus is orders of magnitude (decades) less than G' . The frequency of the mechanical excitation is much greater than the characteristic frequency of the liquid-specific cooperative rearrangements. This means that these molecular processes, which are the origin of the liquid properties, are not activated. The material behaves just like an elastic solid. As shown in Figure 11.19, the secondary or β -relaxation occurs at high frequencies. For SBR, this process lies outside the actual range measured. At frequencies below the β -relaxation, the Andrade process is often observed. Here, the frequency dependence of J'' is described by a power law: $J'' \propto \omega^{-1/3}$. The loss compliance has a slope of $-1/3$ in the log-log presentation. In the case of SBR, this region can be seen between 10^5 and 10^8 Hz (see Figure 11.21).

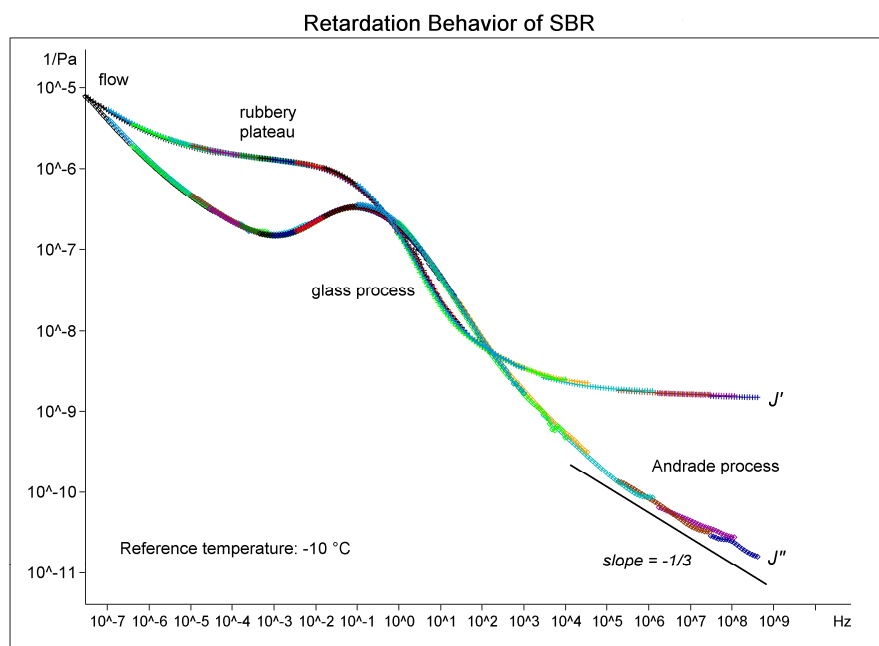


Figure 11.21. Storage and loss compliance of SBR at -10 °C.

11.5.2.2.3 The Glass Process

The relaxation region in which the storage modulus changes by several orders of magnitude is the glass transition (the main relaxation or α -relaxation). This relaxation process is measured when the measuring frequency lies in the frequency range of the cooperative rearrangements. If the frequency is lowered still further, the material loses its solid-state properties. For SBR (Figure 11.20), G' changes from about 10^9 Pa to 10^6 Pa with decreasing frequency. At -10 °C the maximum of the corresponding peak of G'' is at a frequency of $3 \cdot 10^2$ Hz. The compliance shows analogous behavior except that J' increases with decreasing frequency (Figure 11.21). The maximum of the J'' peak is at 10^{-1} Hz (Figure 11.21). The characteristic quantities of the cooperative rearrangements are the relaxation time, τ_G , and the retardation time, τ_J . At the maximum of the loss peak, $\omega \tau \approx 1$. The retardation time of SBR at -10 °C is therefore given by $\tau_J = 1/(2 \cdot \pi \cdot 10^{-1})$ s, that is, 1.6 s. Since the relaxation region is measured at higher frequencies in the modulus, the relaxation time, τ_G , is $5.3 \cdot 10^{-4}$ s. The difference between τ_G and τ_J is explained below. If one considers the simplest possible process for retardation, the Debye process (which describes a retardation process with just one single retardation time), then the following equation applies:

$$J^*(\omega) = J_0 + \frac{J_\infty - J_0}{1 + i\omega\tau_J} \quad (11.8)$$

where J_0 and J_∞ are the limiting values of the compliance at low and high frequencies. The relationship between the retardation time and the relaxation time is then given by

$$\tau_G = \tau_J (\log J_0 - \log J_\infty) \text{ and}$$

$$\tau_J = \tau_G (\log G_\infty - \log G_0).$$

The logarithmic distance, $\log \Delta f$, between the maxima of the J'' and G'' peaks can then be estimated to be 3.0 (see Figure 11.18). The experimental result of about 3.5 from Figure 11.21 shows that this simple estimate is also approximately true for real processes. The relatively large distance between the J'' and G'' peaks therefore results from the large change in G' and J' at the glass transition.

Further information about the relaxation behavior is supplied by the shape of the transition. The curve shape of an isolated process is shown in Figure 11.22 using J'' as an example. In the log-log presentation, the Debye process has two linear limiting tangents with slopes of 1 and -1. The width at half-height of the peak is 1.14 frequency decades. Real processes show appreciably broader peaks – due to molecular interaction there is not just one retardation time but rather a wide spectrum of times. This results in a broader J'' peak with limiting slopes of α and $-\alpha\gamma$ ($0 < \alpha \leq 1$ and $0 < \alpha\gamma \leq 1$). The quantities α and γ are called Havriliak-Negami (HN) parameters and describe the width of the relaxation transition.

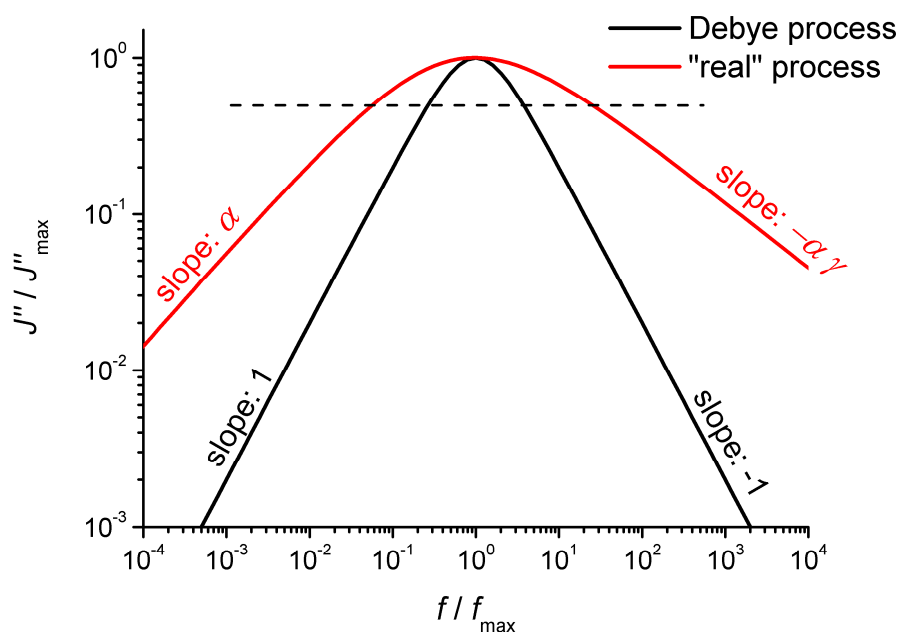


Figure 11.22. Curve shape of the loss compliance in the retardation region in log-log presentation. The dashed line marks half the peak height

The location and width of the relaxation transitions are very sensitive to changes in chemical and physical structure (e.g. due to crystallization and changes in the polymer chain) as well as to fillers, plasticizers, and the composition in the case of polymer blends or copolymers. Some examples are illustrated in Figure 11.23.

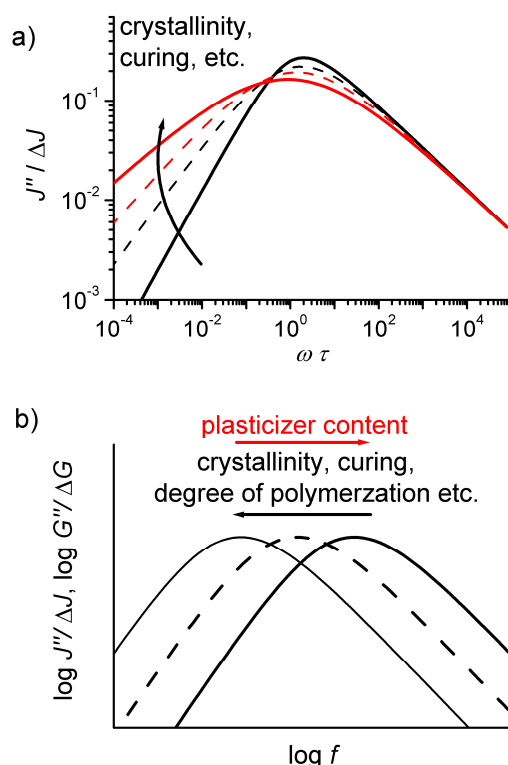


Figure 11.23. Schematic diagram showing the effect of different factors on the glass process: a) influence of curve shape; b) shift of the frequency position (the arrows indicate the direction of increase of the corresponding quantities).

11.5.2.2.4 The Rubbery Plateau

Low molecular mass substances begin to flow immediately after the glass transition. Polymers have a characteristic modulus, G_0 , of about 1 MPa in the rubbery plateau. The plateau arises through the entanglement of macromolecules to form a physical network. The width of the plateau, $\log \Delta f$, depends on the molecular weight, M , where $\log \Delta f \propto M^{3.4}$ (Figure 11.24). In the rubbery plateau, G'' is smaller than G' and exhibits a minimum in the middle (Figure 11.20). At the end of the plateau, flow relaxation can be seen on the G'' peak (with SBR in Figure 11.20 at 10^{-6} Hz). This process cannot usually be directly seen in the compliance curve because it is overlaid by flow.

In cross-linked materials such as vulcanized elastomers, the plateau modulus, G_0 , is proportional to the mean crosslinking density, κ , where $\kappa \approx G_0 / (2RT)$. Flow relaxation can only be observed with very lightly crosslinked materials (Figure 11.24).

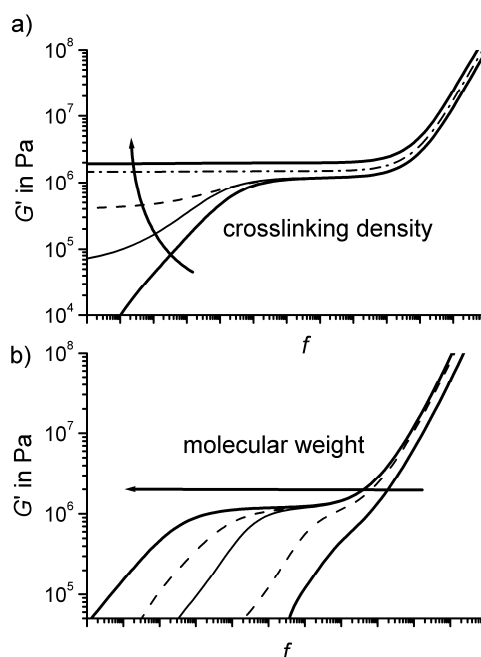


Figure 11.24. Schematic diagram showing the influence of the degree of crosslinking (a) and the molecular weight (b) on the rubbery plateau (the arrows indicate the direction of increase of the corresponding quantity).

11.5.2.2.5 Viscous Flow

At very low frequencies, un-crosslinked polymers exhibit flow. In the ideal case, the power laws: $G' \propto \omega^2$ and $G'' \propto \omega$ apply. Here the slopes of the modulus curves in log-log presentation are 2 for G' and 1 for G'' . At the gel point, the G' and G'' curves intersect one another.

11.5.2.2.6 Conclusions

Knowledge of the frequency dependence of mechanical behavior is very important for the practical application of materials and for material optimization. One obtains information for material optimization because the frequencies at which the different processes occur correlate with characteristic volumes of the corresponding molecular regions. At higher frequencies, smaller molecular regions are observed.

In comparison to temperature-dependent measurements, frequency-dependent measurements provide additional information about material properties and on molecular processes in particular.

11.6 DMA Evaluations

The result of a DSC measurement is a single measurement curve. In contrast, in dynamic mechanical analysis a number of different curves are calculated from the raw data (force and displacement amplitude, phase shift, frequency).

The most important DMA curves are include the following:

Storage modulus	}	These are plotted against time or sample temperature.
Loss modulus		
Complex modulus	}	Numerical values are obtained in tabular form.
Loss factor		

The evaluation of these curves is usually limited to the determination of the onset or peak temperatures or step heights (see Chapter 5, General Thermal Analysis Evaluations).

Other signals that are only needed in certain cases are for example:

- In isothermal measurements, the sample temperature shows (especially with isothermal steps) when the isothermal phase really begins.
- Frequency is of interest especially with isothermal measurements at different frequencies (“frequency sweep”).
- Force amplitude, displacement amplitude can be used to determine the automatic transition from a force-controlled to displacement-controlled experiment.

11.6.1 Master Curve Technique

This evaluation technique allows DMA curves to be overlaid that have been measured at different frequencies and temperatures, in order to cover a much greater frequency range than that experimentally accessible. Low measurement temperatures allow extrapolation to high frequencies (e.g. 10^{10} Hz); and high temperatures to low frequencies (e.g. 10^{-10} Hz).

The evaluation consists of graphically shifting individual measurement curves, called TTS segments, using the mouse to create a complete curve, the master curve. Each TTS segment consists of an isothermal measurement performed at different frequencies (Figure 11.25). The reference temperature of the master curve corresponds to the sample temperature of the TTS segment that was not shifted. A master curve can therefore be created for any available temperature by selecting the segment that is not shifted.

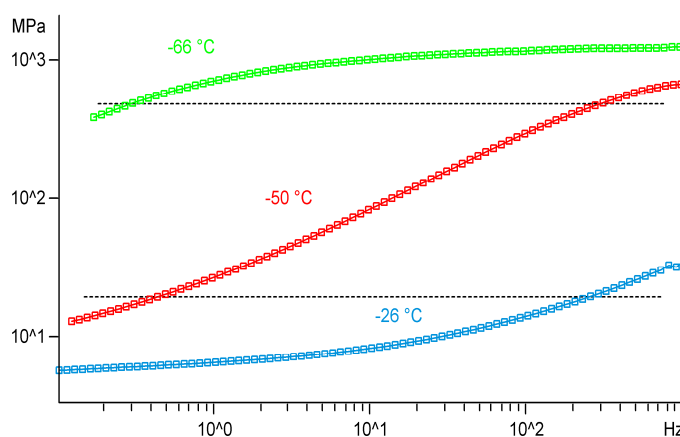


Figure 11.25. The individual TTS segments of a measurement series.

It is also possible to calculate the so-called shift factors according to the WLF model (named after Williams-Landel-Ferry).

$$\log A_f = \frac{-C_1 \cdot (T - T_0)}{C_2 + (T - T_0)} \quad (11.9)$$

C_1, C_2 : Constants

T_0 : Reference temperature in K (of the segment not shifted)

T : Sample temperature in K of the segment to be shifted

A_f : Shift factor

Each TTS segment that is shifted gives a shift factor. The shift factors obtained can be shown graphically in a shift diagram.

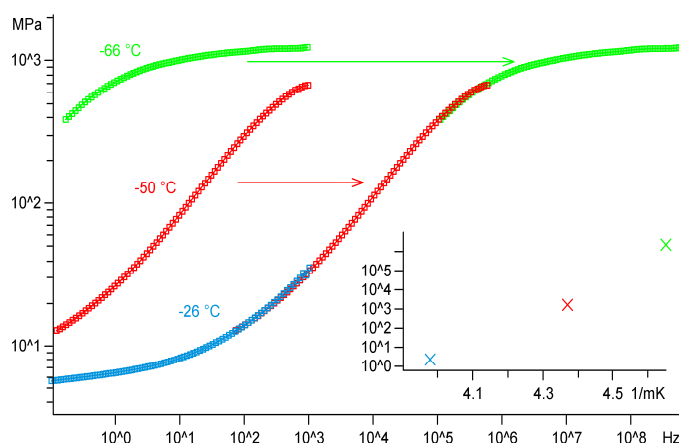


Figure 11.26. Shifting the TTS segments from Figure 11.25 creates a master curve with a reference temperature of -26 °C. At the same time, the shift diagram can be displayed.

From the shift diagram, an activation diagram can be calculated that is plotted against the inverse temperature. The ordinate values are calculated using the following equation:

$$\log f = \log f_{\text{ref}} - \log A_f \quad (11.10)$$

- f : Frequency
 f_{ref} : Characteristic frequency
 A_f : Shift factor

The characteristic frequency corresponds to the internal frequency of the sample with which it reacts to an external oscillation. It corresponds to the frequency at the maximum of the master curve of the loss modulus.

In the simplest case, a relaxation transition shows a linear relationship in the activation diagram ($\log f$ versus $1/T$). This means that one measures a thermally activated process with an average activation energy. According to Arrhenius, the greater the activation energy, the steeper the activation energy curve. The reason for this is that the molecular rearrangements causing the relaxation must overcome a potential barrier in order to change from one stable position to the next. This mechanism is only observed with local processes such as which occur in secondary or β -relaxations.

If the transition in question is a glass transition (α - or main relaxation), then the activation energy diagram is curve-shaped. Cooperative movement processes (relaxation processes) are responsible for this process. The size of the cooperative regions is temperature-dependent. They are larger at lower temperatures. This is why the apparent activation energy is larger at lower temperature.

A curve in the activation energy diagram can be described using empirical equations, for example the Vogel-Fulcher or Williams-Landel-Ferry equation. The curve shape behavior is measured above the thermal glass transition temperature (DSC). In the glassy region, the cooperative rearrangements are almost completely frozen. For this reason, a linear dependence of the relaxation frequency on the reciprocal temperature is observed at this temperature.

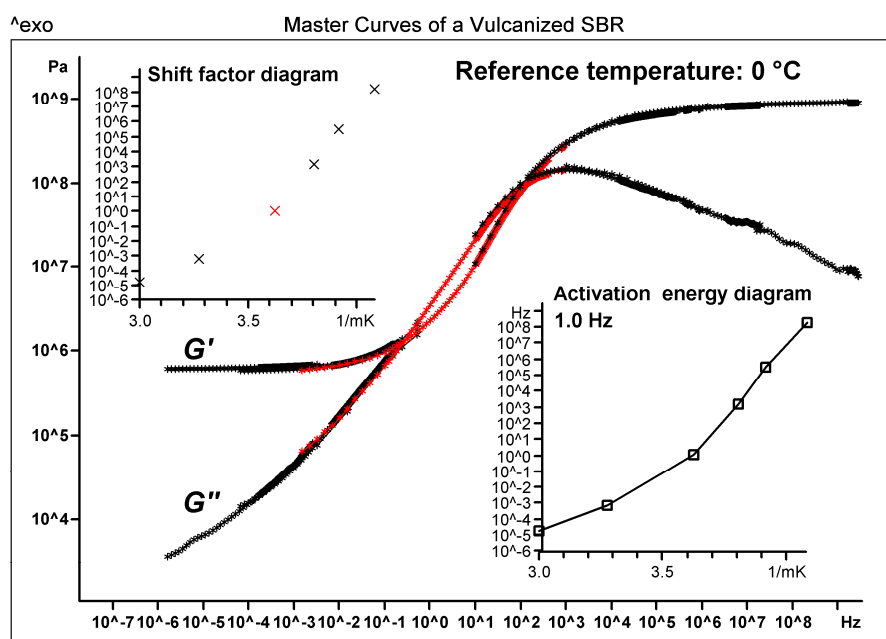


Figure 11.27. Master curve with shift diagram and activation diagram.

11.7 DMA Application Overview

Table 11.3 shows effects and properties that can be studied by DMA.

Viscoelastic behavior
Relaxation behavior
Glass transition
Mechanical modulus
Damping behavior
Softening
Viscous flow
Crystallization and melting
Phase separation
Gelation
Structural change
Composition of blends
Filler activity
Material defects
Curing reactions
Crosslinking reactions
Vulcanization systems

Table 11.3. Effects and properties that can be studied using DMA.

11.8 Calibration of the DMA/SDTA861^e

Definitions and basic principles can be found in Chapter 4, Basic Measurement Technology.

11.8.1 What Needs to Be Calibrated in DMA?

- Temperature: The thermocouples of the clamping assembly and the sample temperature measurement require calibration.
- The heating rate dependence of temperature, expressed by the time constant τ_{lag} between the furnace temperature and the temperature of the clamping assembly, serves to calculate the increased value of the furnace temperature. In DMA, large samples are used and the heating rates are correspondingly low so that this calibration is not necessary.
- The displacement sensor, the LVDT, is adjusted using accurate gauges.
- The force sensor is adjusted using a certified spring.

Temperature calibration: The sheathed thermocouple used in the DMA/SDTA861^e as the sample temperature sensor normally has a temperature error of less than 1 K. This can be checked by dipping it in a mixture of ice/water.

Temperature calibrations analogous to TGA or TMA would lead to much larger errors with the typical size of samples used in DMA. This is why the sample temperature calibration is normally not performed.

In contrast, it is very convenient if the temperature of the clamping assembly is adjusted to the sample temperature (the furnace control uses the temperature of the clamping assembly). This means that a measurement starts at the right temperature and any isothermal steps that have been programmed take place at the desired temperature.

It is very useful for beginners to perform a “modulus calibration”. This uses a reference sample of known modulus. For example: the silicon rod available from METTLER TOLEDO for 3-point bending.

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UserCom: Many of the application examples in this chapter have been taken from UserCom, the METTLER TOLEDO technical customer journal that is published twice a year. Back issues of UserCom can be downloaded as PDFs from the Internet at www.mt.com/ta-usercoms .

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12.1 Glasses and the Glass Transition

A glass is an amorphous substance whose molecular structure is in a disordered state. In contrast, the building blocks (molecules, atoms or ions) of crystalline substances are arranged regularly in a crystal lattice.

The glass transition is a phenomenon that can occur with all glasses, that is, with all non-crystalline or semicrystalline materials.

Thermodynamically, a glass is looked upon as a frozen supercooled liquid. In the liquid phase, cooperative rearrangements occur continuously in addition to the molecular vibrations and rotations (of atoms or groups of atoms) that take place in solid materials. These cooperative rearrangements involve the participation of several molecules or segments of molecules.

The rearrangements typically extend over a range of several nanometers. The actual characteristic length decreases with increasing temperature. Another characteristic quantity is the time required for the cooperative rearrangements. It can be described by an internal relaxation time, τ , or a characteristic frequency (reciprocal value of the relaxation time). The relaxation time is also strongly temperature dependent; it becomes shorter with increasing temperature.

If the relaxation time is shorter than the observation time, the material appears liquid-like. If the cooperative rearrangements are so slow that they do not occur during the measurement, they appear to be frozen.

Example to illustrate cooperative rearrangements:

Cooperative rearrangements can be understood by considering the situation in a local bus crammed full with passengers. During the journey, everyone is standing close together and cannot move; their movement is frozen. If someone has to get out at the next bus stop and is carrying a large bag, then a number of passengers all have to move together “cooperatively” to make this possible. A little additional free space (free volume) is also needed in order to increase mobility – perhaps someone near the door has to get out for a moment. The bus passengers thus experience a series of cooperative rearrangements.

The thermal glass transition is observed when a melt that is not able to crystallize undergoes supercooling. This phenomenon can be explained by assuming that during cooling the characteristic time of the cooperative rearrangements approaches the same order of magnitude as the time determined by the measurement conditions (i.e. through the cooling rate). This causes the rearrangements specific to the liquid state to “freeze”. On heating, the rearrangements “thaw”.

As an amorphous solid, the glass is not in thermodynamic equilibrium. The transition to the liquid state is a relaxation process and is therefore kinetically controlled. The glass transition does not therefore occur at a specific temperature such as for example melting, but rather over a wide temperature range. In addition, it depends on the experimental conditions.

When a glass former is cooled, the characteristic relaxation time, τ , increases because the cooperative rearrangements become slower. As shown in Figure 12.1, the continuous cooling process can be thought of as a series of small steps. At high temperatures (point marked 1 in Figure 12.1) the relaxation time, τ , is so short that the sample can completely relax to equilibrium during such a step. The sample is then in equilibrium (liquid). At point 2, the relaxation time is already significantly longer. Molecular rearrangements are still rapid enough for the sample to reach equilibrium during the step. At point 3, the cooperative rearrangements have become so slow that the measurement time for relaxation to equilibrium is not long enough. The corresponding molecular rearrangements freeze. Only the types of movement that are specific to solids remain. The heat capacity is therefore reduced by an amount that corresponds to these rearrangements.

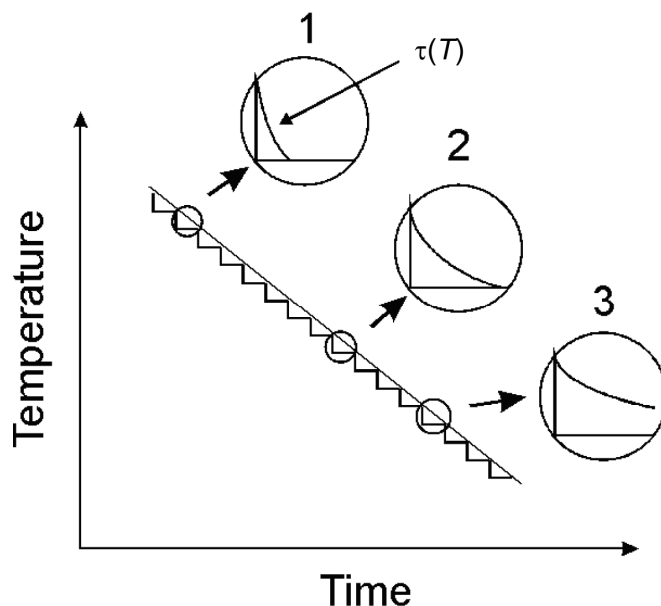


Figure 12.1. Illustration of the thermal relaxation with stepwise cooling in the region of the glass transition. The ordinate of the circular sections corresponds to the deviation from the equilibrium state.

The glass transition can be observed in two ways:

1. **By changing the temperature:**

On heating, the cooperative rearrangements thaw (devitrification), and on cooling, freeze (vitrification). The “thermal glass transition” is therefore observed on changing the temperature.

2. **At constant temperature by changing the frequency:**

If an amorphous substance is mechanically stressed at low frequency, the cooperative rearrangements are able to follow the stress and the material appears liquid. At higher frequency, the cooperative rearrangements are no longer able to follow the stress and the material appears hard. The “dynamic glass transition” is therefore observed when the frequency is changed at constant temperature (i.e. isothermally).

Note on polymers

All polymers are more or less hard and sometimes brittle below the glass transition temperature, T_g . Above the glass transition, thermoplastics are liquid or can at least undergo plastic deformation. The molecules of elastomers and thermosets are fixed in place due to their crosslinked network structure. This is the reason why such polymers cannot undergo plastic deformation. They do however become rubbery soft.

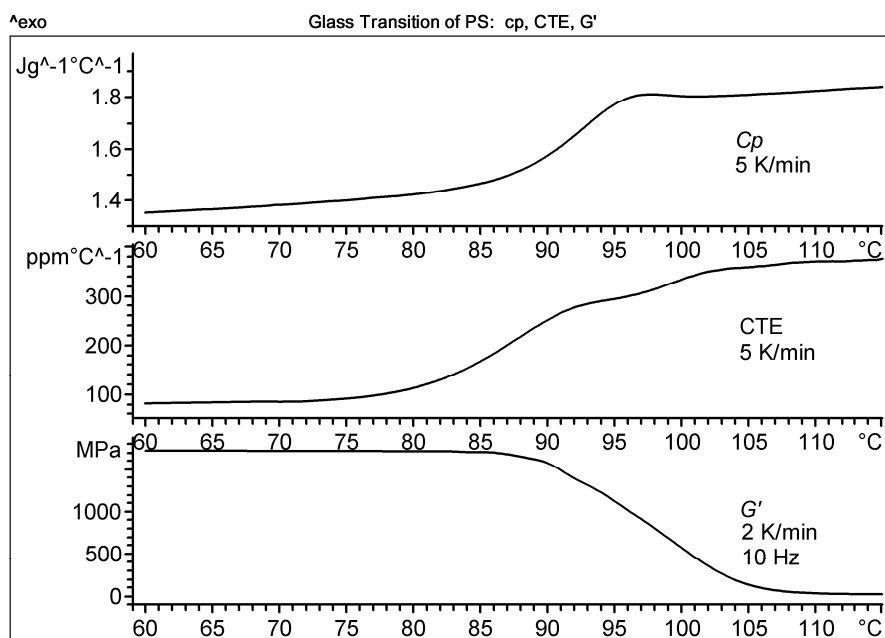


Figure 12.2. Physical properties such as the heat capacity, c_p , the coefficient of thermal expansion (CTE) and the storage modulus (G') change at the glass transition. The figure shows different curves obtained from a polystyrene (PS) sample. The c_p curve was determined from a DSC heating run at 5 K/min (the PS was shock-cooled beforehand). The CTE was obtained from the second heating run in the TMA, and G' from a DMA shear measurement (10 Hz).

12.2 Measurement of the Glass Transition by DSC

Since DSC is widely used for measuring the glass transition, it will be discussed first. DSC is a popular technique because it offers adequate sensitivity, simple sample preparation and the use of small samples.

At the glass transition, the liquid-specific cooperative mobility of the molecules changes and is accompanied by a corresponding change in the heat capacity. With unfilled amorphous plastics, c_p increases from typically 1.5 J/gK to 1.9 J/gK.

The change of the enthalpy (integral of the heat capacity curve) at the thermal glass transition is shown schematically in Figure 12.3.

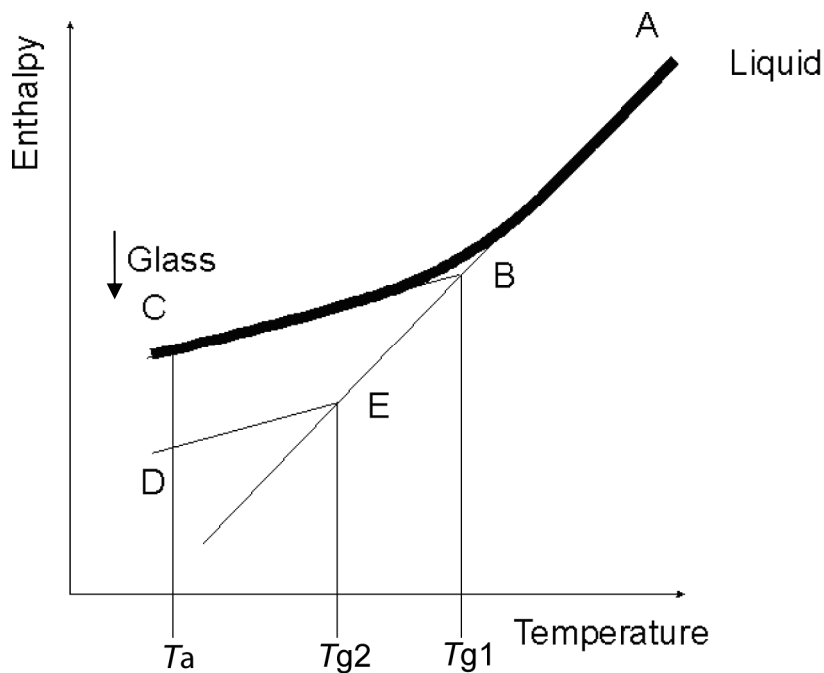


Figure 12.3. Schematic diagram showing the change of the enthalpy at the thermal glass transition.

The sample is cooled from A to C at a constant rate. Around B, it passes through the region of the glass transition with the glass transition temperature, T_{g1} . If the sample is immediately heated to the point A again, the same glass transition temperature is measured. Any differences in the glass transition temperature determined in this way in heating or cooling measurements have to do with thermal conductivity effects within the sample. If the sample is held for some time at a temperature T_a , it ages and the enthalpy decreases (physical aging or enthalpy relaxation). It reaches the state designated by the point D. On heating again, the enthalpy intersects the extrapolated liquid line at the temperature T_{g2} (point E). The glass transition temperature has clearly changed through aging.

The glass transition temperature, T_{g2} , can also be attained by cooling from the melt using a lower cooling rate. The cooperative units have more time for their rearrangements to take place, which results in them freezing at a lower temperature. The lower the cooling rate, the lower the glass transition temperature.

As can be seen in Figure 12.4, hysteresis is observed between the cooling curve and the heating curve under the otherwise same conditions. This effect can be explained by assuming that the frozen-in cooperative rearrangements do not thaw until a higher temperature is reached.

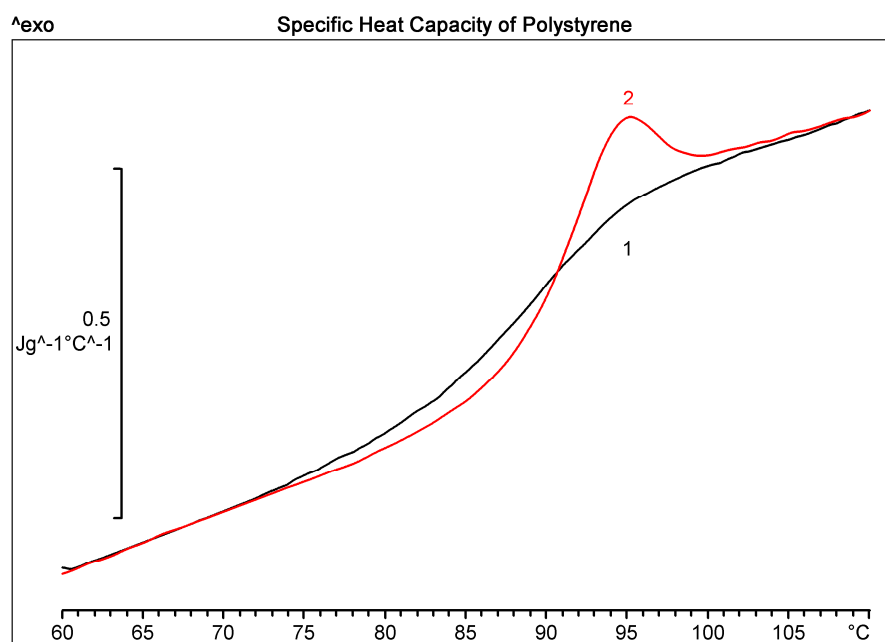


Figure 12.4. Specific heat capacity of polystyrene in the glass transition region. Curve 1 is the cooling curve measured at a cooling rate of 2 K/min. Curve 2 is the heating run performed immediately after at 2 K/min.

Figure 12.5 shows differences between the heating and cooling curves in the enthalpy versus temperature diagram. Curve 1 is a cooling curve. The slope of the curve continuously decreases in the transition region. The glass transition temperature, T_{g1} , is the point of intersection of the curves of the liquid and the glass. Curve 2 is the corresponding heating curve measured at the same rate. In the transition region, the slope of this curve shows a weakly defined maximum, which is equivalent to a maximum in the c_p temperature function (and a peak in the DSC curve). The glass transition temperature is T_{g1} . Curve 3 differs from Curve 2 only in that it was measured at a more rapid heating rate. This leads to a larger relaxation effect at the same glass transition temperature. If the heating rate is lower than the cooling rate, the glass transition temperature does not change but the relaxation effect is reduced.

Curve 4 is a measurement of a sample that was heated at the same rate as Curve 2, but which had been previously stored for some time below the glass transition temperature at a temperature T_a . Two effects occur: the glass transition temperature is lower (T_{g2}) and the slope shows a pronounced maximum (equivalent to a peak in the c_p temperature function or the DSC curve).

Note: T_{g2} is a fictive temperature that is not measured with the usual methods. It can however be calculated from the DSC curves using the Richardson evaluation method (Figure 12.8).

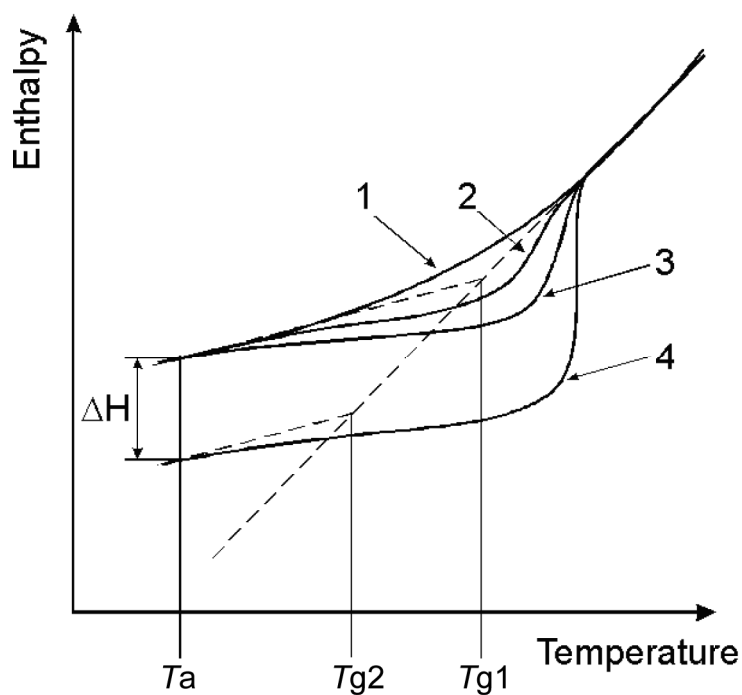


Figure 12.5. Theoretical enthalpy curves at the glass transition to illustrate the differences between cooling and heating curves. The curves are described in the text.

The measurement curves of samples of polyethylene terephthalate (PET) that had been subjected to different periods of physical aging are shown in Figure 12.6. The shift and the increase in size of the enthalpy relaxation peak can be clearly seen.

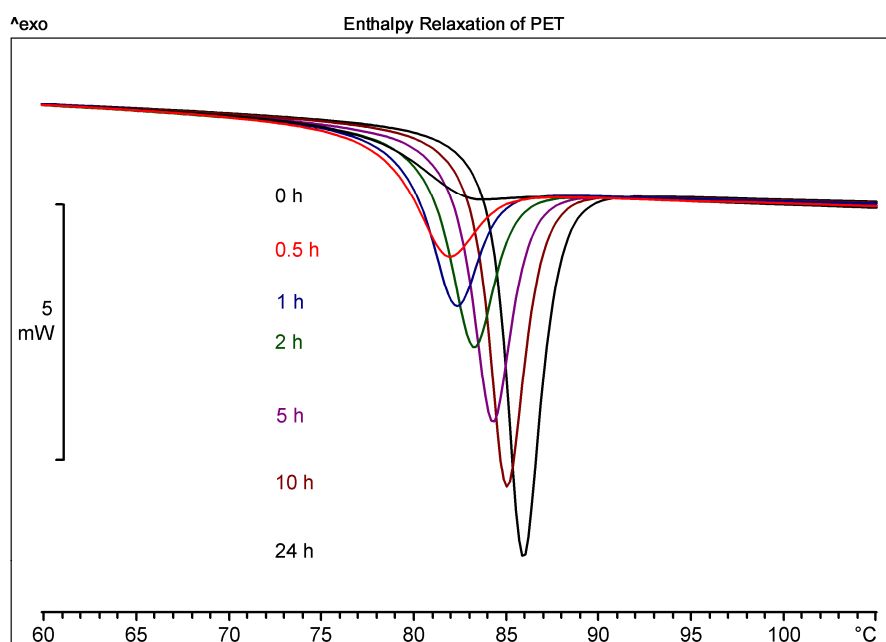


Figure 12.6. Heating curves of PET samples after different periods of physical aging at 65 °C. Heating rate 10 K/min; sample mass 23 mg. Before the physical aging, the sample was heated to above the melting temperature and cooled within a few seconds to room temperature using the sample robot.

12.3 Determination of the DSC Glass Transition Temperature

Various different quantities can be used to characterize the glass transition. Besides the glass transition temperature (T_g), the height of the c_p step (Δc_p) and the width of the glass transition (ΔT) are often determined. Other quantities sometimes used are the height of the enthalpy relaxation peak and its temperature maximum. A number of such characteristic quantities are shown in Figure 12.7.

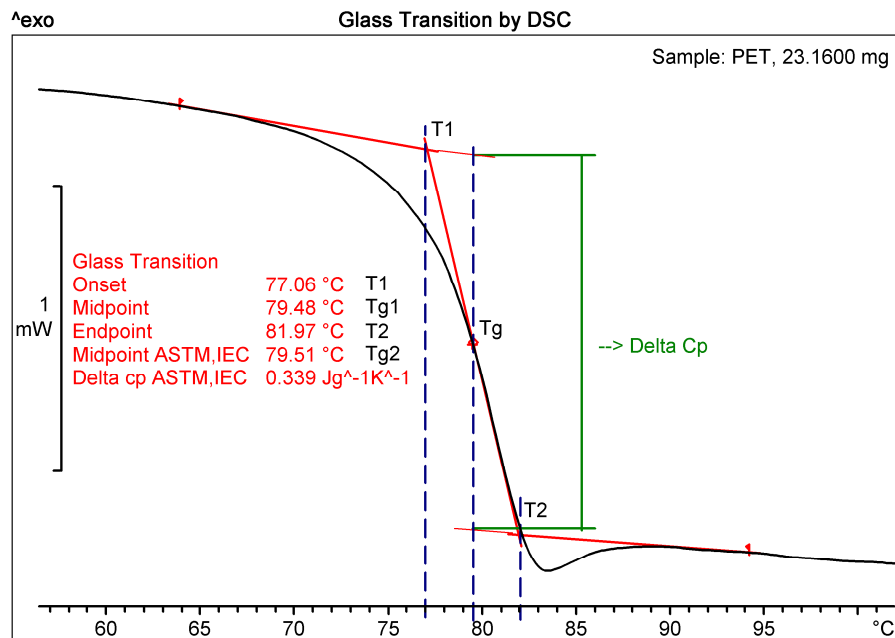


Figure 12.7. The figure shows several characteristic quantities at the glass transition. T_{g1} : glass transition temperature using the angle bisector; T_{g2} : glass transition temperature by ASTM D3418; width of the glass transitions: $\Delta T = T_2 - T_1$; Delta Cp: step height).

Various methods are used to determine the glass transition temperature. Because each method gives a somewhat different result, the evaluation method and the measurement parameters should always be stated. If a large enthalpy relaxation peak occurs, greater differences are to be expected (see Figure 12.8)

- Bisector method: T_g is the temperature at which the bisector of the angle between the two tangents intersects the curve.
- Point of inflection: T_g is the temperature of the point of inflection of the DSC curve.
- ASTM D 3418: T_g is equal to the mean value between T_1 and T_2 .
- Richardson method: Determination of the fictive temperature of the glass as the glass transition temperature. This temperature corresponds to the point of intersection of the extrapolated enthalpy curves of the glass and the liquid in the enthalpy or heat capacity versus temperature diagram as shown in Figure 12.3 or Figure 12.4. The determination is performed using an area calculation method (see Figure 12.8). At T_g , $A_1 + A_3 = A_2$.

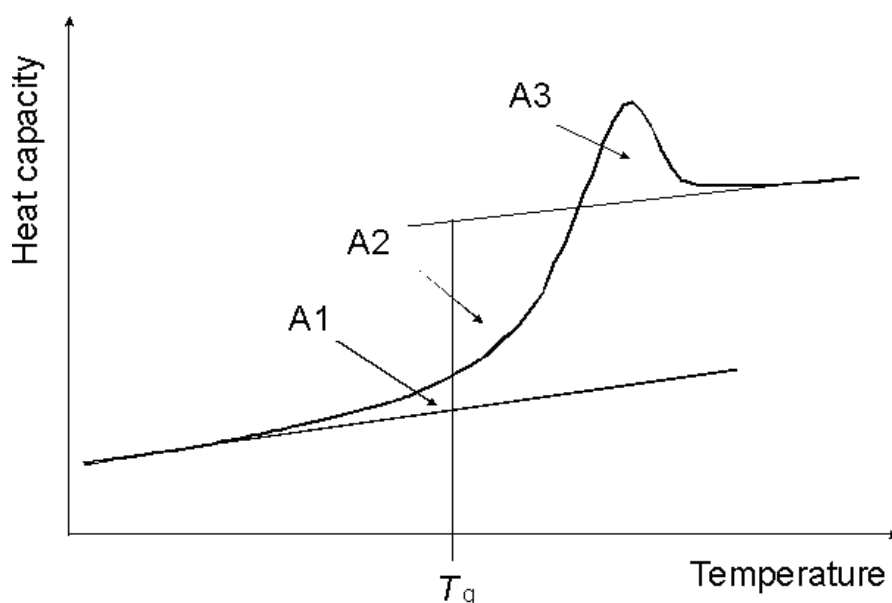


Figure 12.8. Determination of the glass transition temperature, T_g , of a sample with pronounced enthalpy relaxation as the fictive temperature using an area calculation. With samples that do not exhibit a relaxation peak, the glass transition temperatures determined according to point of intersection with the angle bisector, ASTM D 3418 and Richardson are about the same.

The fictive temperature describes the actual state of the glass. The glass transition temperature determined in this way therefore includes definite information about the structure of the material. All the other T_g values are not only influenced by the state of the glass but also by the thermal history and the actual experimental conditions. They are however useful for identifying a sample by its T_g or for evaluating comparative measurements. In addition, they characterize the actual softening of the sample.

Practical notes:

- One problem in the measurement and evaluation of the glass transition is that the change in heat capacity can be very small (particularly with filled or semicrystalline materials). To increase measurement sensitivity, relatively large samples should therefore be used (with polymers typically 10 to 20 mg). Furthermore, thermal contact should be optimized, for example by compressing powders or premelting. Frequently a combination of heating, cooling and heating measurements is very informative.
- The investigations can be complemented by measuring samples that have previously been annealed for a short period below the glass transition temperature. Such samples show temperature and time-dependent peaks. Broad and flat glass transitions are difficult to detect. The evaluation can be facilitated by subtracting a blank curve.
- The construction of tangents to curves is very important and should be done with the utmost care in the evaluation. The section of interest should be expanded sufficiently to make this possible. If several glass transitions are to be compared, curves normalized to sample mass or heat capacity curves should be evaluated. Furthermore, it is advantageous to display the curves in one coordinate system and to draw the tangents so that they run parallel before and after the effect in all the curves. This allows even small differences of the glass transition temperature to be systematically detected and evaluated.

12.4 Physical Aging and Enthalpy Relaxation

As has already been discussed at the beginning of this chapter, both the shape of the curve in the glass transition region and the glass transition temperature itself depend on the physical aging of the sample that takes place during storage below the glass transition temperature. Longer storage times give rise to an enthalpy relaxation peak on the DSC curve.

The glass transition temperature was determined from the curves in Figure 12.6 according to two methods: First as the point at which the bisector of the angle between the two tangents intersects the measurement curve (T_{g1}) and secondly as the “fictive temperature” according to the Richardson method (T_{g2}). While T_{g1} increases with aging, T_{g2} decreases continuously as expected from Figure 12.5.

In addition, the enthalpy relaxation was determined using the method described further down. The results are shown in Figure 12.9. It can be clearly seen that the course of T_{g2} with time is analogous to that of enthalpy relaxation.

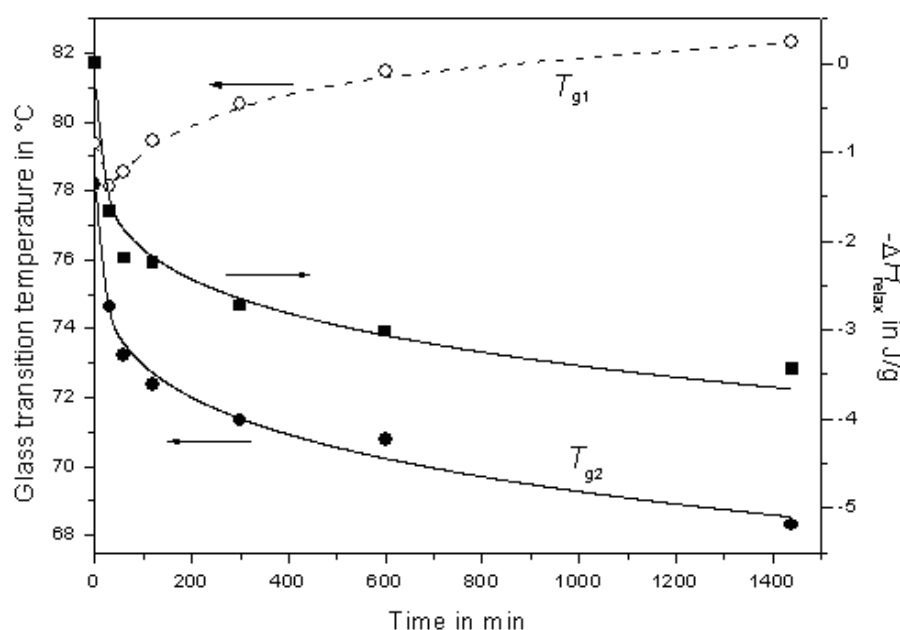


Figure 12.9. Glass transition temperature T_{g1} (intersection of the bisector; open circles) and T_{g2} (according to Richardson; black circles) as well as the enthalpy relaxation $-\Delta H_{relax}$ (filled black squares) of PET as a function of aging time at 65 °C.

The degree of enthalpy relaxation in a glass depends on the mechanical and thermal conditions during its manufacture and storage.

A method frequently used to determine enthalpy relaxation is to first heat the sample, then cool it at the same rate as in heating run, and afterward immediately heat it a second time. Subtraction of the second heating run from the first heating run yields the enthalpy relaxation.

$$\Delta H = \int_{T_1}^{T_2} (c_1(T) - c_2(T)) dT \quad (12.1)$$

The method is illustrated in Figure 12.10. Direct determination of the enthalpy relaxation from the area of the peak can lead to large errors.

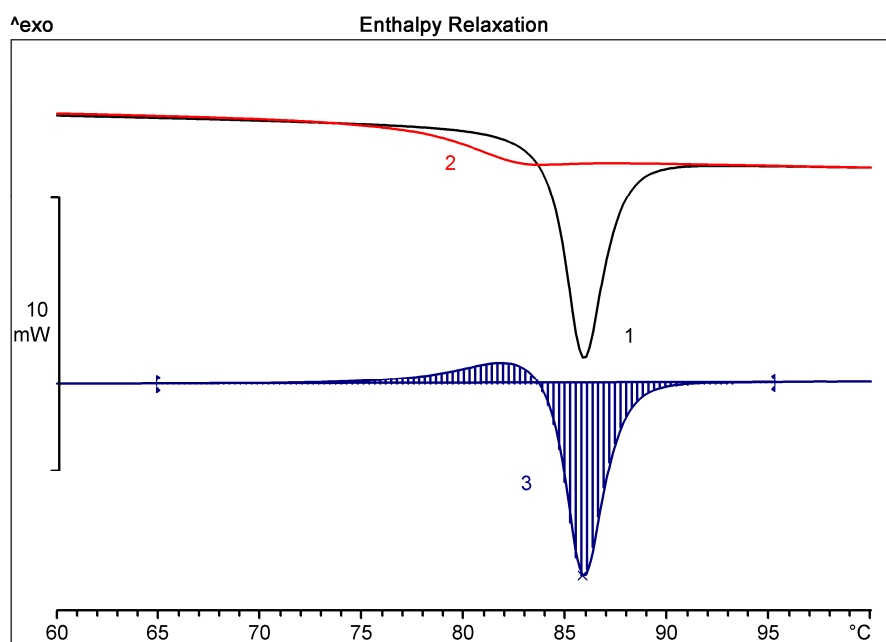


Figure 12.10. Determination of the enthalpy relaxation (3.34 J g^{-1}) using a sample of PET. 1: first heating run; 2: second heating run; 3: difference between the first and second runs.

12.5 The Glass Transition for Materials Characterization

12.5.1 Introduction

The glass transition is very sensitive to changes in molecular interactions. The measurement and evaluation of the glass transition can therefore be used to characterize structural differences or changes in materials. The following sections present a number of examples to illustrate the type of information that can be obtained from such analyses.

12.5.2 Semicrystalline substances

Besides materials that are completely amorphous or completely crystalline, there are of course materials that are partially crystalline. In such semicrystalline materials, crystallites and amorphous regions coexist together. As the degree of crystallinity of the material increases, the amorphous content decreases and the glass transition (step height, Δc_p) becomes smaller.

Particularly with polymers, molecular mobility in the amorphous regions is influenced by the presence of crystallites because some macromolecules are part of both the crystalline and the amorphous phases. As a result, the glass transition is broader and shifted to higher temperature. This behavior is illustrated in Figure 12.11 using polyethylene terephthalate (PET) that had been crystallized at 120°C for different times as an example.

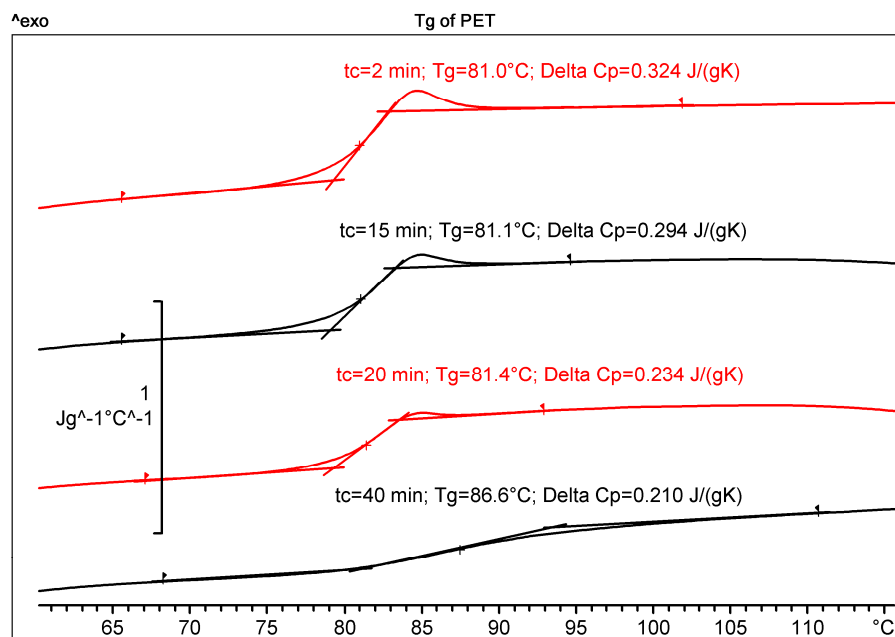


Figure 12.11. The specific heat capacity of PET as a function of temperature in the glass transition region. The sample was crystallized at $120^{\circ}C$ for different times (t_c). The crystallinity increases with the crystallization time, while ΔC_p (ΔC_p) decreases. (Sample mass 14 mg, heating rate $10 K/min$).

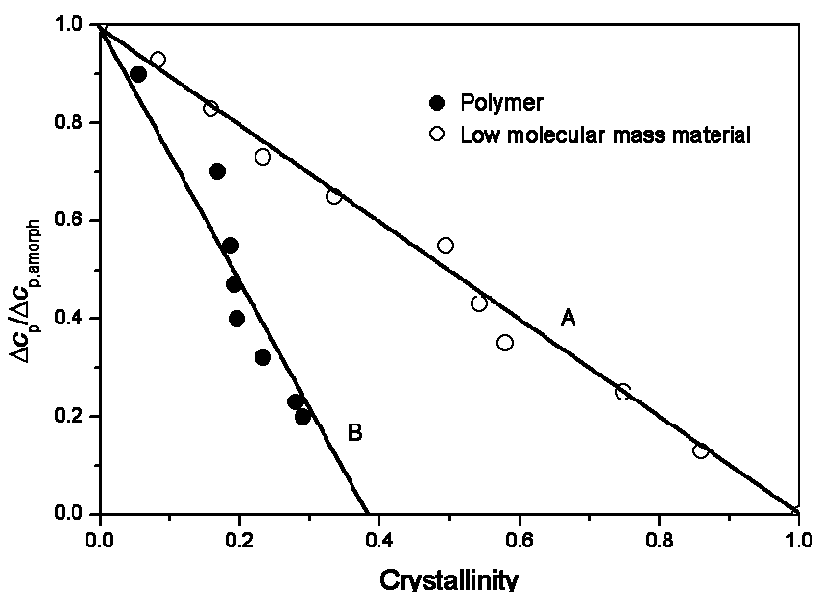


Figure 12.12. Normalized step height of the specific heat ($\Delta C_p / \Delta C_{p, \text{amorph}}$) at the glass transition as a function of crystallinity. A: behavior of a two-phase system. B: measured behavior of the polymeric three-phase system (PET crystallized isothermally at $120^{\circ}C$).

In Figure 12.12, the normalized step height at the glass transition is shown as a function of crystallinity for a number of different PET samples that had been allowed to crystallize for different times at $120^{\circ}C$. The line marked A represents two-phase behavior that can occur with substances of low molecular mass in which only crystals and mobile amorphous material are present. Deviations from this behavior occur with polymers due to molecular size because some of the amorphous regions cannot participate in the cooperative rearrangements and thus do not contribute to the glass transition. This rigid amorphous phase is located at the surface of the chain-folded crystals. This allows the proportion of the rigid amorphous material in polymers to be determined by measuring the step height as a function of the degree of crystallinity. From Figure 12.11, it can be inferred that the maximum degree of crystallization is about 0.4 and the proportion of the rigid amorphous region is about 0.6 for the PET investigated.

If a material can be prepared that is completely amorphous (e.g. by shock-cooling or freeze drying), for low molecular weight substances (two-phase systems), it is possible to determine the degree of crystallinity by measuring ΔC_p .

12.5.3 Orientation

When thin films or fibers are manufactured from polymers, molecular orientation occurs that influences the glass transition. Analogous to the behavior of semicrystalline polymers, the glass transition temperature is shifted to somewhat higher temperatures and the glass transition itself becomes broader. Orientation (e.g. stretching) of semicrystalline polymers can result in a significant increase in crystallinity.

Stretched polymers, however, often shrink on heating. This changes the thermal contact between the sample and the DSC sensor during the measurement. Shrinking begins at the glass transition and can lead to DSC curves that are completely unusable. Only a preheated sample (a sample that has already shrunk) can be reproducibly measured. However, preheating the sample eliminates the thermal and mechanical history.

Figure 12.13 shows the glass transition of an oriented PET fiber. The beginning of the glass transition is visible in the 1st run. However, recrystallization begins to occur during the glass transition (exothermic peak between 80 and 140 °C). The fiber shrinks in this temperature range. If the fiber is heated to a temperature just below the melting temperature and then cooled, the sample is semicrystalline and shows a broad glass transition at a somewhat higher temperature (2nd run). If the fiber is melted and then shock-cooled (3rd run), it is amorphous. In this case, the glass transition and the subsequent exothermic recrystallization are measured.

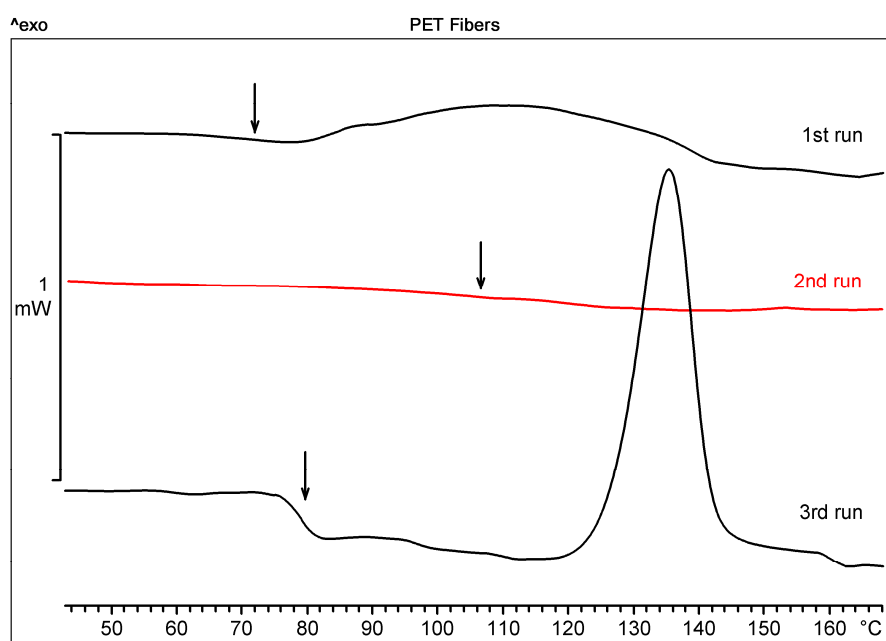


Figure 12.13. Glass transition of a stretched PET fiber (see text for details). The arrows mark each glass transition. Sample mass 2.5 mg, heating rate 10 K/min.

12.5.4 Thermomechanical History

The enthalpy relaxation peak caused by physical aging also depends on internal stresses that originate from the production process and the thermal history during processing and storage. As can be seen in Figure 12.14, these peaks can occur at different places in the glass transition region depending on the sample and its thermal history. Before performing the second run, the samples were rapidly cooled. Heating to well above T_g followed by controlled cooling eliminates the influence of thermal history.

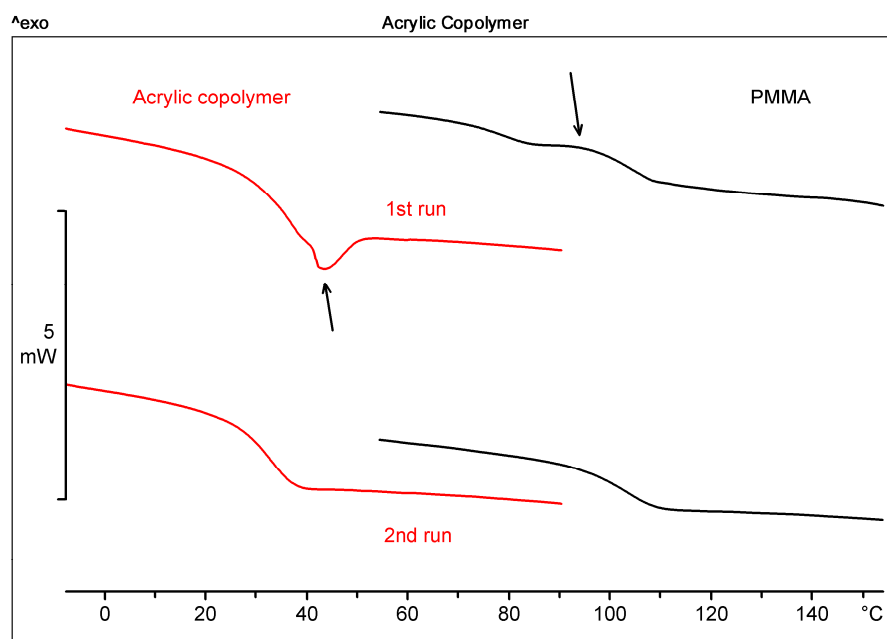


Figure 12.14. The 1st and 2nd heating runs of the glass transition of an acrylic copolymer and PMMA. The arrows mark the relaxation peaks.

12.5.5 Crosslinking

In crosslinked systems (thermosets, e.g. epoxy resins), the glass transition temperature depends on the degree of crosslinking. With increasing crosslinking (conversion), the glass transition shifts to higher temperatures (see Figure 12.15).

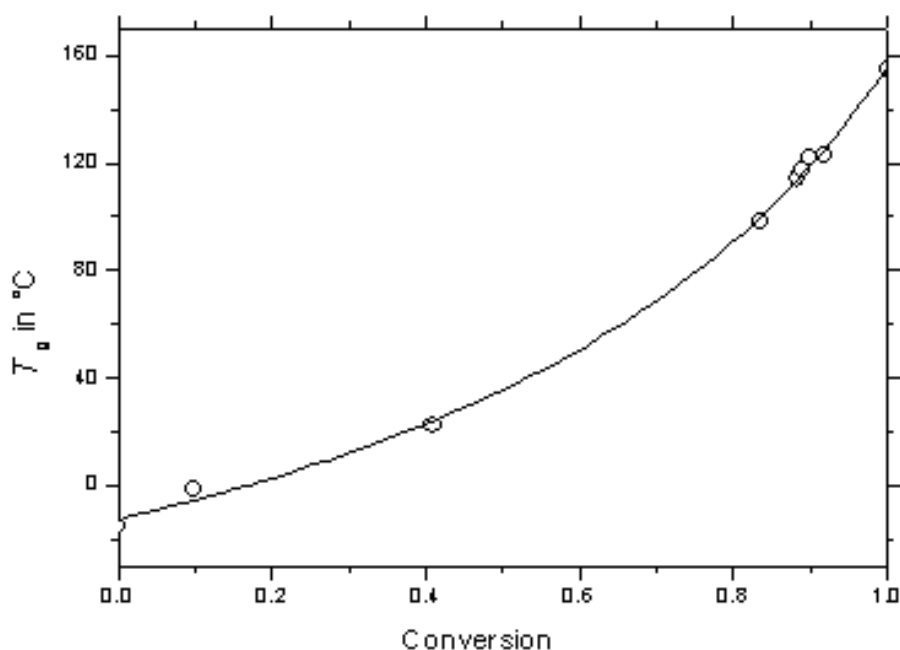


Figure 12.15. Glass transition temperature as a function of the crosslinking (conversion) of an epoxy resin system.

If an epoxy resin is cured isothermally at a temperature T_c , the glass transition temperature also increases with increasing crosslinking. If the glass transition temperature of the material undergoing curing becomes higher than the curing temperature, T_c , vitrification occurs. The sample changes from a liquid to a glassy state. The reaction rate decreases drastically and from then on the glass transition temperature changes only very slowly (see Figure 12.16). At the vitrification time, t_v , the glass transition temperature is equal to the curing temperature.

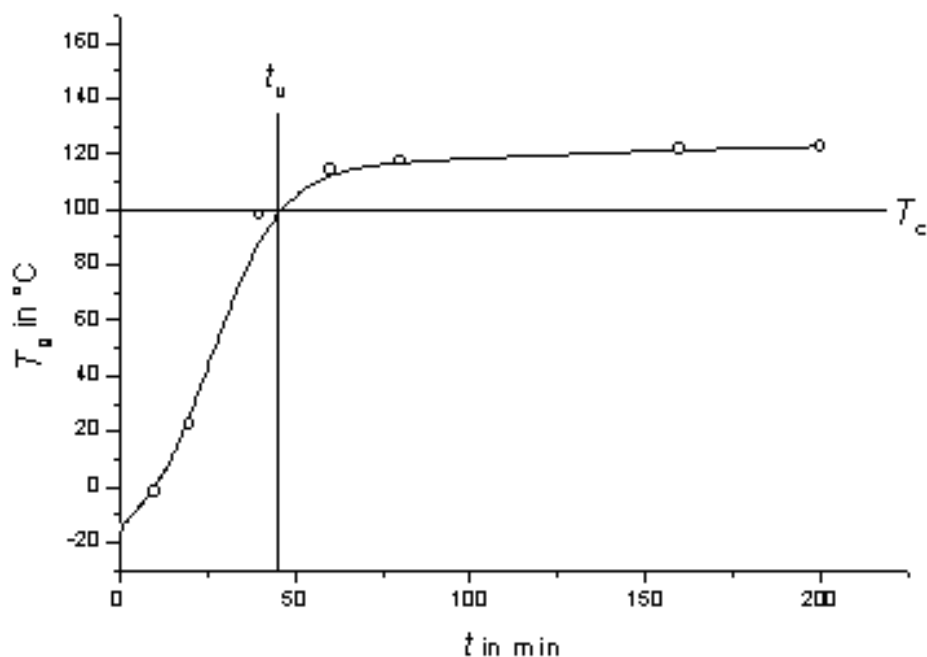


Figure 12.16. Glass transition temperature of an epoxy resin system during isothermal curing at a curing temperature, T_c , of 100 °C. New samples were cured for different times at T_c and then cooled rapidly. The glass transition temperature was determined from a heating measurement performed afterward at 10 K/min.

A similar relationship between the glass transition temperature and the degree of crosslinking (degree of vulcanization) is observed with many elastomers. However, the changes are rather small because the crosslinking density is relatively low (see Figure 12.17).

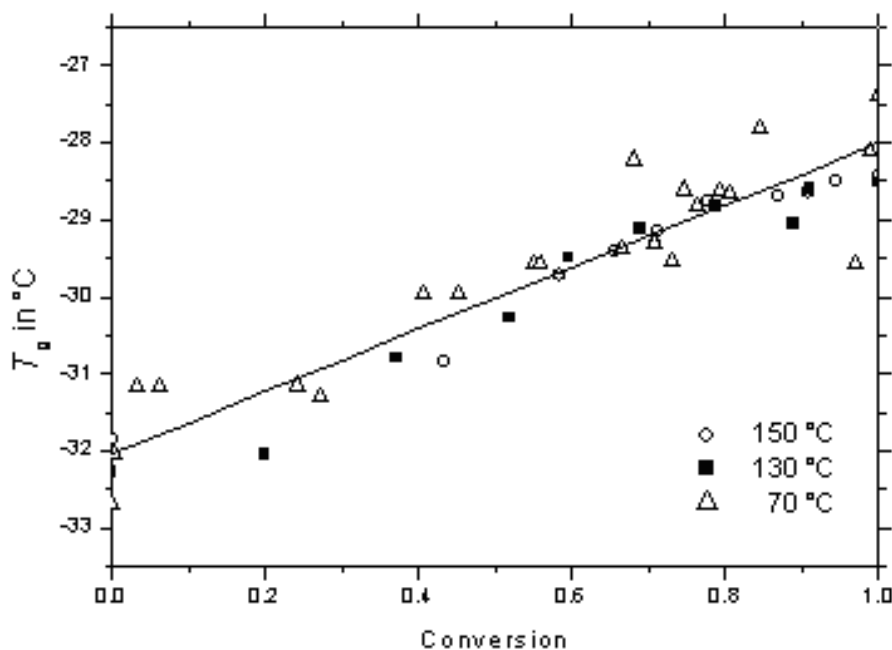


Figure 12.17. Glass transition temperature as a function of the degree of vulcanization of an NBR rubber (acrylonitrile-butadiene rubber). The samples were isothermally vulcanized at 70, 130 and 150 °C.

12.5.6 Molar Mass

Similar to in a crosslinking reaction, the glass transition temperature in a polymerization reaction increases with increasing molar mass, M_w . In the range 10^4 to 10^5 g/mol it asymptotically reaches the maximum value $T_{g\infty}$. To a good approximation, the relationship (Figure 12.18) can be described by the equation

$$T_g = T_{g\infty} - \frac{J}{M_w} \quad (12.2)$$

where J is a polymer-specific constant.

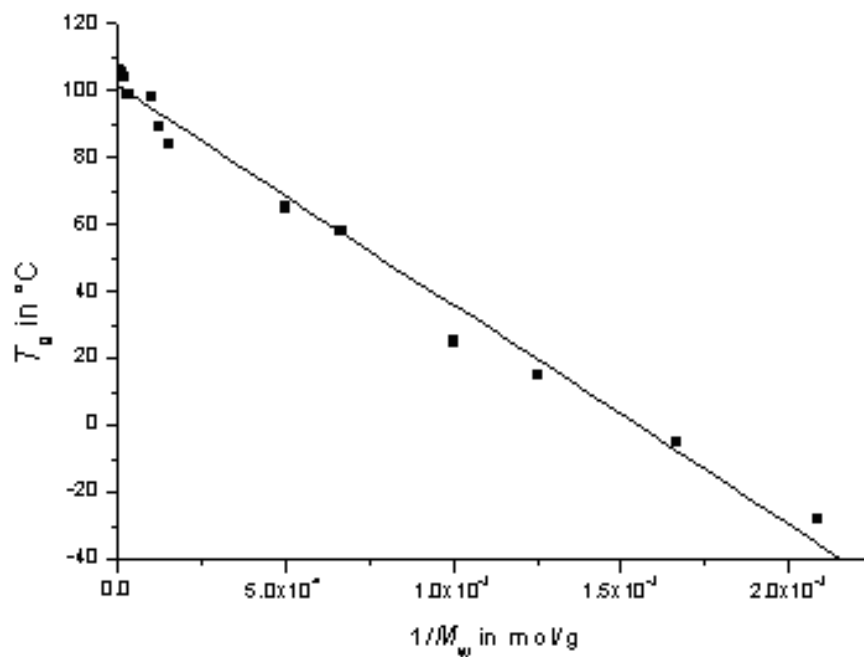


Figure 12.18. Glass transition temperature of polystyrene (PS) as a function of the reciprocal molar mass ($T_{g\infty} = 101$ °C, $J = 2.2$ kgK/mol).

12.5.7 Plasticizers

The curves in Figure 12.19 demonstrate the influence of plasticizer content on the glass transition using polyvinyl acetate (PVAc) as an example. Increasing concentrations of plasticizer shift the glass transition to lower temperatures (Figure 12.20). In some materials, water (moisture) absorbed from the atmosphere can act as a plasticizer. Solvent residues originating from the manufacture or processing of the material can also behave as (unwanted) plasticizers.

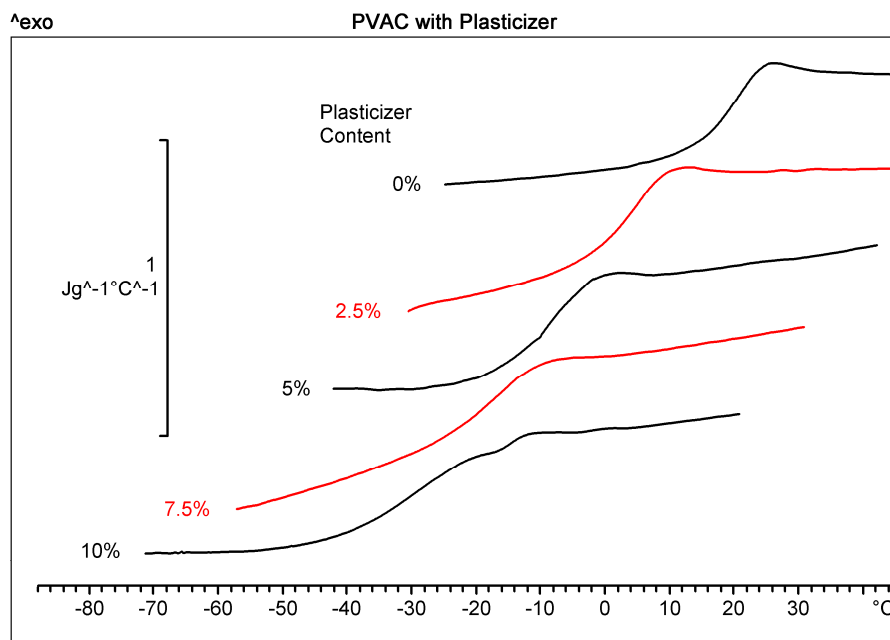


Figure 12.19. Heat capacity as a function of temperature in the region of the glass transition of PVAc containing different concentrations of plasticizer.

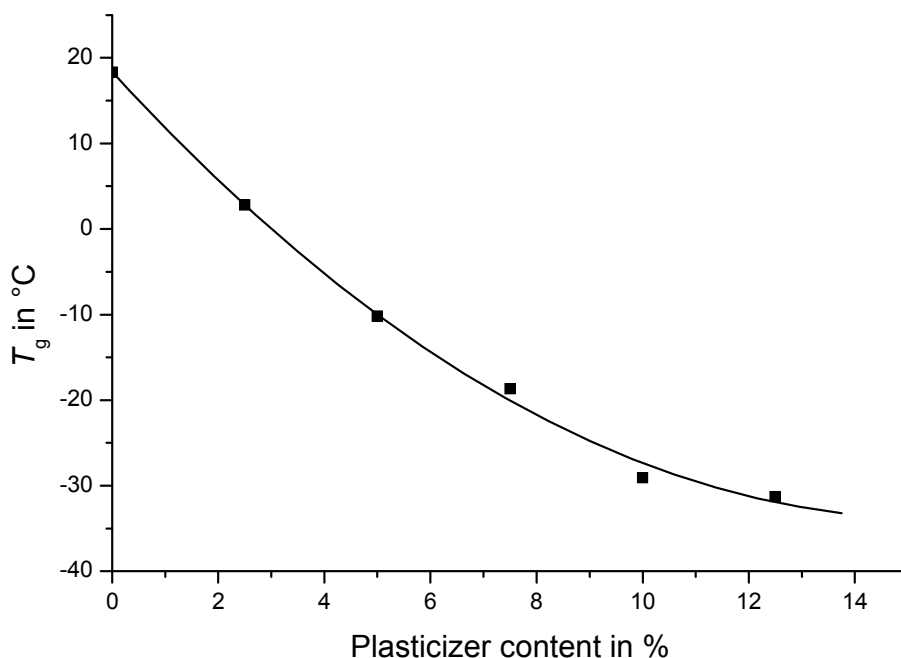


Figure 12.20. Glass transition temperature of PVAc as a function of plasticizer content (data from the measurements in Figure 12.19).

12.5.8 Polymer Blends

Because of the large variety of polymer blends (mixtures), only a few aspects of the glass transition will be mentioned here.

In principle, polymers are either miscible (compatible, e.g. PS and PPE) or immiscible (incompatible, e.g. PS and PAN). The individual components of immiscible polymers behave as separate phases. Regions of different phases simultaneously exist alongside each other. Each of these phases can individually undergo a glass transition, which is why several different glass transitions are measured. A comparison of the step heights and glass transition temperatures with those of the pure components can provide information on the relative content of the phases and possible interactions between the phases, as well as on the quality of the blending process. If the different glass transitions lie close to each other, it is difficult to separate them in a “normal” analysis. Annealing at a temperature just below T_g produces relaxation peaks that often facilitate a separation.

An example of an incompatible mixture, a polycarbonate (PC) blended with ABS, is shown in Figure 12.21. The measurement curve clearly shows two glass transitions. The PC glass transition temperature is lowered by about 3 K due to interaction with the ABS. From the ratio of the step height of the PC glass transitions ($\Delta c_{p,pure}/\Delta c_{p,mixture}$), it can be estimated that the blend consists of 67% PC and 33% ABS.

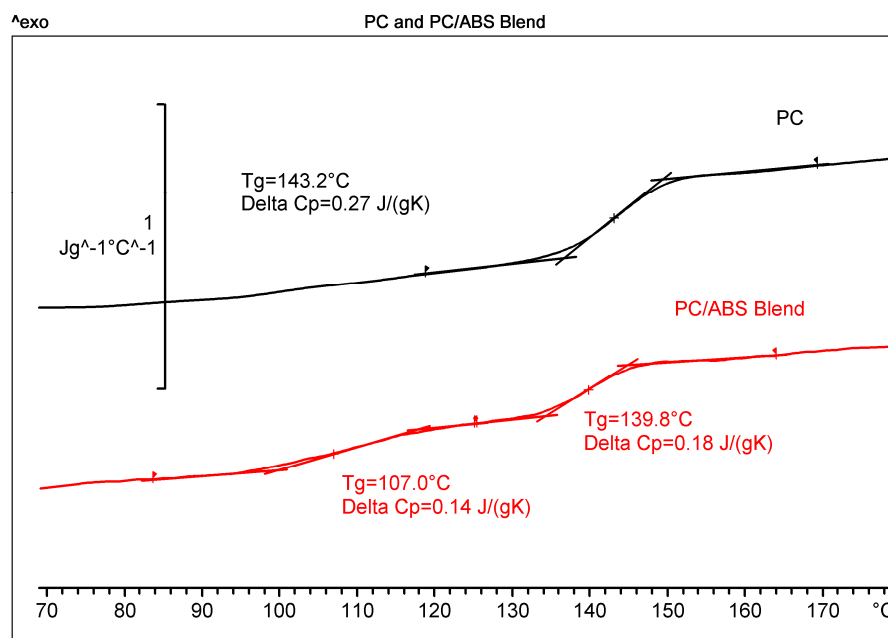


Figure 12.21. Glass transitions of pure PC and a PC/ABS blend. Sample mass about 10 mg, heating rate 10 K/min.

Miscible substances form only one phase and only one glass transition is measured. The glass transition temperature, T_g , depends on the relative concentration of the individual components. The relationship between the glass transition temperature and composition is given by the semi-empirical Gordon-Taylor equation

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (12.3)$$

where T_{g1} and T_{g2} are the glass transition temperatures of the pure components, and w_1 and w_2 are the proportions by mass. Here, k can be regarded as a fit parameter.

An example is shown in Figure 12.22. This displays the change in the glass transition temperature as a function of the content of different PS/PPE blends (PPE is polyphenylene ether).

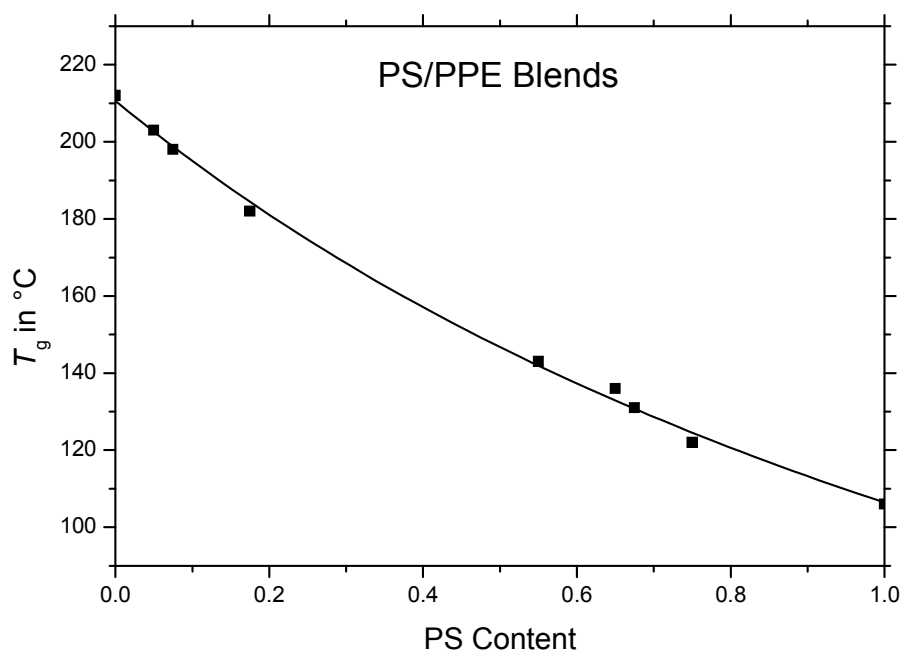


Figure 12.22. Glass transition temperature as a function of the composition of PS/PPE blends. The continuous curve corresponds to the Gordon-Taylor equation with $k = 0.63$.

A homogeneous blend need not necessarily be stable. A phase separation may occur as a result of a temperature increase or decrease depending on which components were mixed together. In such cases, at least two glass transitions are observed after the phase separation.

12.5.9 Copolymers

The glass transition of copolymers depends on the type of the polymerized monomers and their arrangement in the macromolecule. If the monomers are miscible or statistically distributed, then one single glass transition is measured. With block and graft copolymers, a phase separation often occurs. Two glass transitions are then measured. If the blocks are too short, then a phase separation cannot take place for chemical reasons, and only one transition is observed. Figure 12.23 shows the glass transitions of two block copolymers. The substances differ only in the length of the blocks. In Sample 2, the blocks are relatively long and a phase separation occurs. In Sample 1, a phase separation is not possible because the blocks are too short.

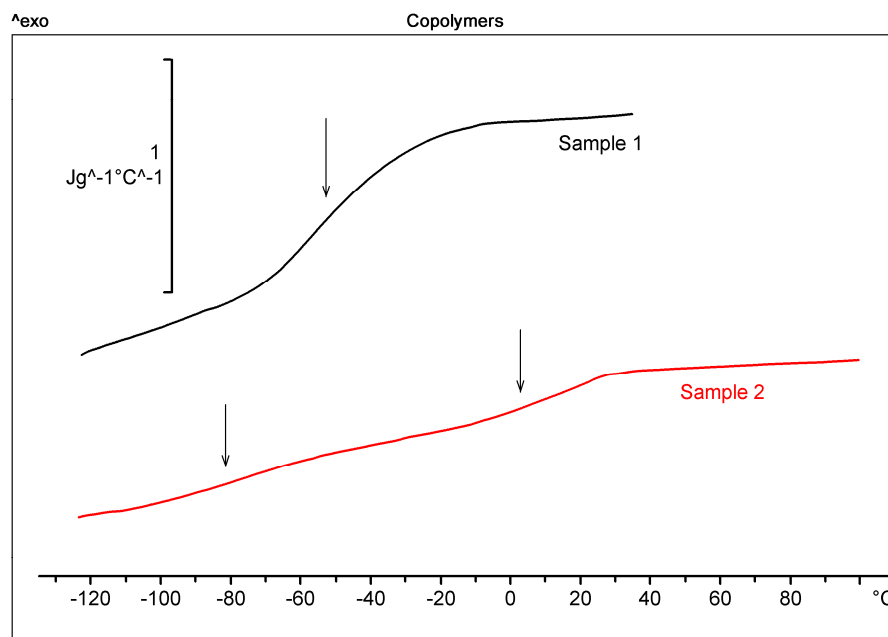


Figure 12.23. Glass transition region of block copolymers made of the same components but with different block lengths. The arrows mark the glass transitions (Sample 1: short blocks; Sample 2: long blocks).

12.5.10 Chemical Modification

Molecular mobility can also be influenced by chemical modification of a polymer. Besides this, a second phase can also occur. The chemical reaction can be intentional or occur through chemical aging. In chemical aging, degradation or oxidation reactions take place.

An example of an intentional modification is the chlorination of polyvinyl chloride (PVC). The influence of the chlorine content on the glass transition is shown in Figure 12.24. Higher concentrations of chlorine decrease the molecular mobility. As a result, the glass transition temperature shifts to higher temperatures.

The broadening of the glass transition with increasing chlorine content is particularly noticeable. The reason for this lies in relatively large degree of inhomogeneity of the chlorine distribution.

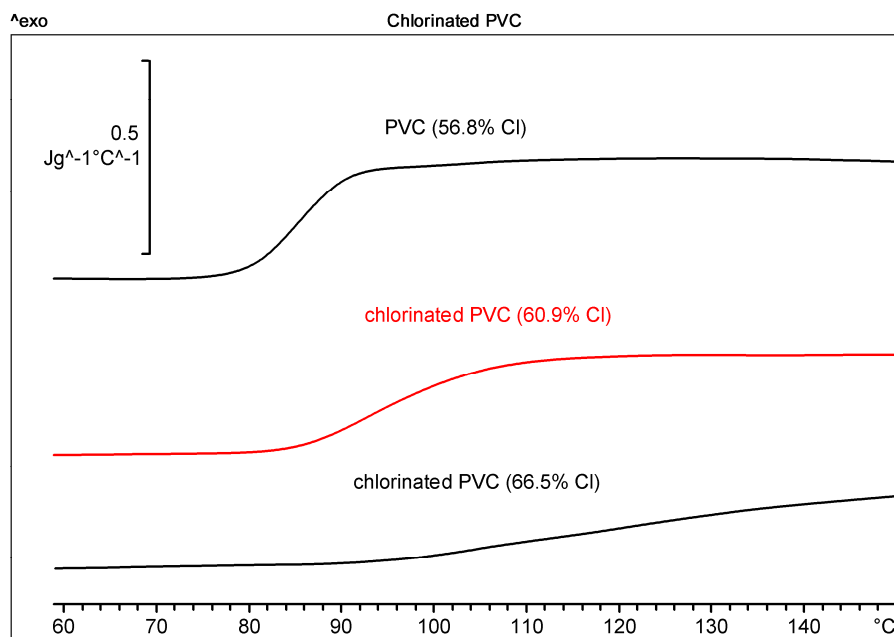


Figure 12.24. Glass transition of samples of PVC that have been chlorinated to different extents. In the sample with 66.5% Cl, the glass transition region is very broad indicating that the transition is still not finished even at 150 °C.

In the chlorination process, a hydrogen atom is replaced by a chlorine atom. This does not change the number of degrees of freedom of a monomer unit. The step height (Δc_p) with respect to a mole remains uninfluenced by chlorination. The reduction of the step height with increasing chlorination, apparent in Figure 12.24, is therefore due to the increase in size of the molar mass. This means the change in Δc_p can be used to estimate the chlorine content. The molar mass of a PVC monomer unit, M_{PVC} , is 65.5 g/mol. Using the molar mass of chlorine (35.5 g/mol) one obtains a value of 56.8% for the chlorine content of PVC. The Δc_p step height, $\Delta c_{p\text{PVC}}$, is 0.28 J/gK. This corresponds to 18.34 J/molK. The height of the Δc_p step of the chlorinated PVC sample with the lower content of chlorine can be relatively accurately determined ($\Delta c_{p\text{PVCC}} = 0.24 \text{ J/gK}$). The molar mass of the chlorinated PVC, M_{PVCC} , can be estimated from the equation

$$M_{\text{PVCC}} = M_{\text{PVC}} \frac{\Delta c_{p\text{PVC}}}{\Delta c_{p\text{PVCC}}} \quad (12.4)$$

In the case considered, this gives a value of $M_{\text{PVCC}} = 76.41 \text{ g/mol}$. This corresponds to 1.31 chlorine atoms per monomer unit and hence a chlorine content of 60.8%. This value agrees well with the data known for this sample.

12.5.11 Fillers

Inert substances such as glass fibers, chalk or carbon black are added to polymers as fillers. They lower the polymer content of the material and thereby reduce the step height of the glass transition. The step height, Δc_p , is proportional to the polymer content. In general, the glass transition temperature is independent of the filler content. Relatively small changes in T_g are only observed with active fillers.

12.5.12 Conclusions

The glass transition is a phenomenon that can be observed in amorphous substances as a step in the heat capacity curve. It is normally characterized by the glass transition temperature, T_g , the step height, Δc_p , and the width of the transition. Various methods can be used to determine the glass transition temperature. All the evaluation methods yield similar results except for the Richardson method. The glass transition is primarily determined by molecular interactions and can therefore be used to detect small differences in the structure of substances.

The glass transition temperature is not a thermodynamic fixed point. It depends on the heating and cooling rates, the thermal and mechanical history of the sample and the method used to determine it. Especially when large enthalpy relaxation peaks occur, Richardson's method (glass transition temperature as fictive temperature) gives glass transition results that are more significant and reproducible than those obtained with other methods. For practical purposes, however, the fictive temperature is of minor importance because it does not coincide with the softening of the material.

The step height should definitely be included in the evaluation because this value contains important information about the material under investigation.

12.5.13 Summary

	Effect on the glass transition	Special comments
Crystallinity	Increasing crystallinity leads to a smaller step height. Especially with polymers, T_g increases and the glass transition becomes broader.	The degree of crystallinity of low molecular weight substances can be determined from Δc_p and with polymers, the proportion of the rigid amorphous phase.
Crosslinking, curing, polymerization, molar mass	T_g shifts to higher temperature with increasing molar mass or crosslinking.	T_g is practically constant from a molar mass of about 104 g/mol onward.
Orientation and storage below T_g	Internal stresses and storage shift T_g and increase the size of the enthalpy relaxation peak.	Crystallization may possibly occur in the glass transition region. The first measurement frequently cannot be used. Possibly use the evaluation according to Richardson. The relaxation peaks contain information about the thermal history of the sample.
Plasticizer	Plasticizers shift T_g to lower temperatures.	Solvent residues and moisture often behave as plasticizers (higher T_g in the 2nd measurement, and mass loss.)
Mixtures/blends	Incompatible mixtures give two transitions, compatible mixtures only one.	The relative proportions can be determined from T_g as a function of the composition or the step height.
Copolymers	Block and graft copolymers of compatible monomers and statistical copolymers show one transition; otherwise two transitions occur.	T_g and the width of the transitions depend on the interactions of the phases.
Chemical modification	T_g , step height and width of the transition can change. Several changes can occur.	Modification due to specific chemical modification, oxidation, or thermal degradation.
Fillers	The step height decreases with increasing filler content.	Hardly any effect on the T_g .

Table 12.1. Factors influencing the glass transition temperature.

12.6 Other Thermal Analysis Techniques for Measuring the Glass Transition

Determination of the thermal glass transition:

12.6.1 TMA

The free volume in the glassy state is less than in the liquid state, where the cooperative rearrangements require additional space. This means that the coefficient of thermal expansion, α , (CTE) measured by TMA changes at the glass transition. The method is relatively sensitive because with plastics α increases from 50 to 150 ppm/K. Its use is, however, somewhat limited because sample preparation is more difficult and because of the possibility of sample deformation at the glass transition. If the viscosity above the glass transition is low, the flow properties of the material are measured rather than the expansion coefficient. The change in hardness and viscosity at the glass transition can however be made use of. For example, TMA measurements under conditions of high probe loading or force are suitable for the determination of the softening temperature, which is related to the glass transition temperature. This mode can therefore also be used to measure thin samples or coatings.

12.6.2 Modulated Techniques

In modulated techniques, two overlapping stresses are simultaneously applied to the sample. One is the periodic component; the other is the underlying heating or cooling program. The dynamic glass transition is evaluated from the frequency-dependent parts. Vitrification or devitrification is determined by the underlying temperature program (linear heating or cooling).

12.6.2.1 DMA, DLTMA

At the glass transition, the mobility of the molecules increases greatly. This is accompanied by a corresponding decrease in the elastic modulus. For example, on passing from the glassy to the rubbery state, the Young's modulus of a polymer decreases from about 1000 MPa to about 1 MPa, that is, by about three decades. The large change means that the glass transition can be measured with good sensitivity. This is of great importance with composites and filled materials. DMA can even measure secondary relaxation effects and glass transitions with very small changes in c_p or α .

Bending measurements are especially suitable for composites and self-supporting systems. Thin samples such as films or fibers are usually measured in tension. Samples that have a very low viscosity above T_g can really only be measured in the shear mode.

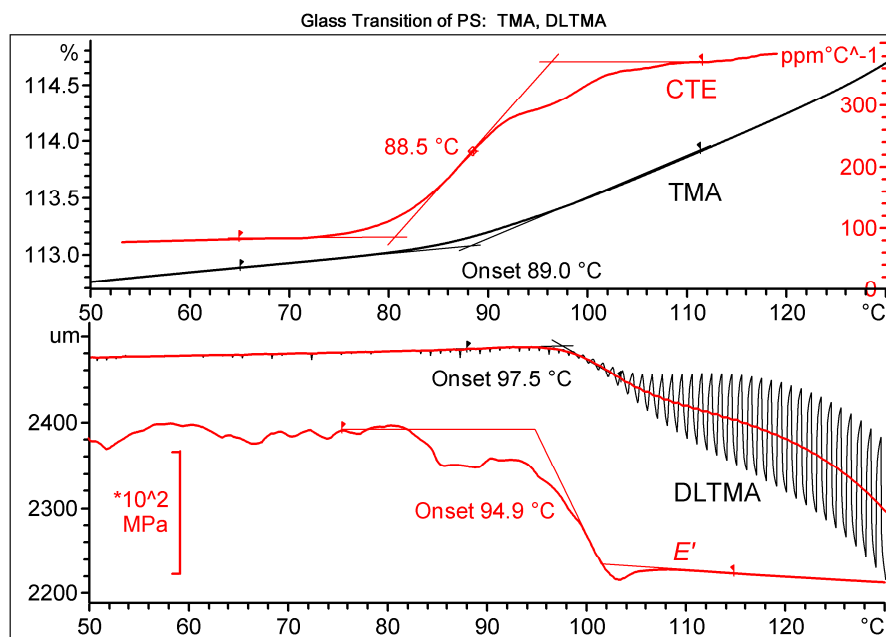


Figure 12.25. Above: The TMA measurement and the calculated curve of the coefficient of thermal expansion (CTE) of polystyrene. Below: The DLTMA curve (compression mode) with the calculated Young's modulus curve. Heating rate 5 K/min. Initial sample dimensions 4.5 x 4.5 x 2.2 mm. The first heating run showed a pronounced volume relaxation effect in which the sample thickness increased by about 13%. The figure shows the second heating run measured after uncontrolled cooling in the TMA.

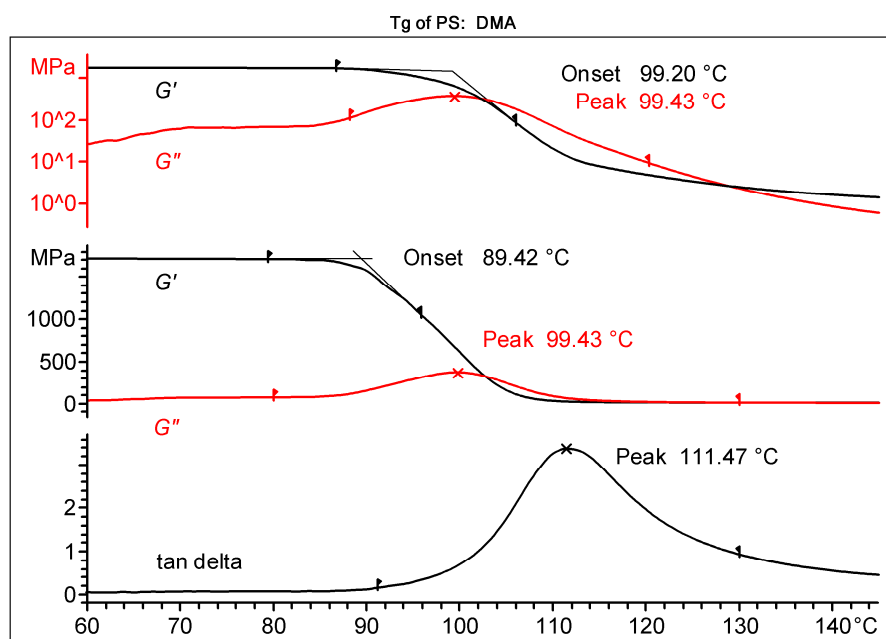


Figure 12.26. Different presentations of DMA curves of polystyrene: shear measurement at 10 Hz and 2 K/min. The sample was not thermally pretreated. Above: logarithmic ordinate scale. Middle: the same curves (storage and loss moduli, G' and G'') on a linear scale. Bottom: the mechanical loss factor, $\tan \delta$. If the onset of the decrease of the storage modulus is to be evaluated, attention must be paid to the scale used for the presentation. The peak temperatures of G'' and $\tan \delta$ are also very different!

12.6.2.2 ADSC

Temperature-modulated DSC (ADSC, IsoStep[®], TOPEM[®]) allows the glass transition to be measured in a frequency-dependent mode. Another aspect of this technique is however also important because the change in the specific heat capacity at the glass transition is often overlapped by effects due to vaporization, enthalpy relaxation, phase transitions and chemical reactions. Temperature modulation makes it possible to separate changes in heat capacity from other effects and thus determine the glass transition temperature.

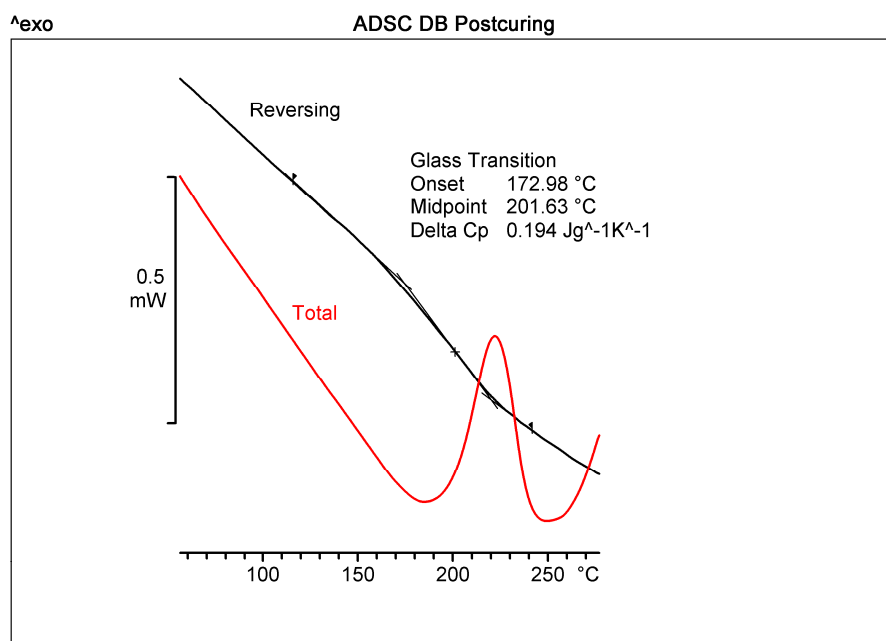


Figure 12.27. The evaluation of an ADSC measurement of the postcuring of a resin yields different curves. The reversing curve shows the glass transition free of other effects.

12.6.3 Determination of the Dynamic Glass Transition by DMA

Because of its large frequency range (6 decades) and sensitivity, DMA can be used to determine the dynamic glass transition under isothermal conditions and obtain information on molecular mobility. This allows one to study the influence of molecular structure on mechanical properties.

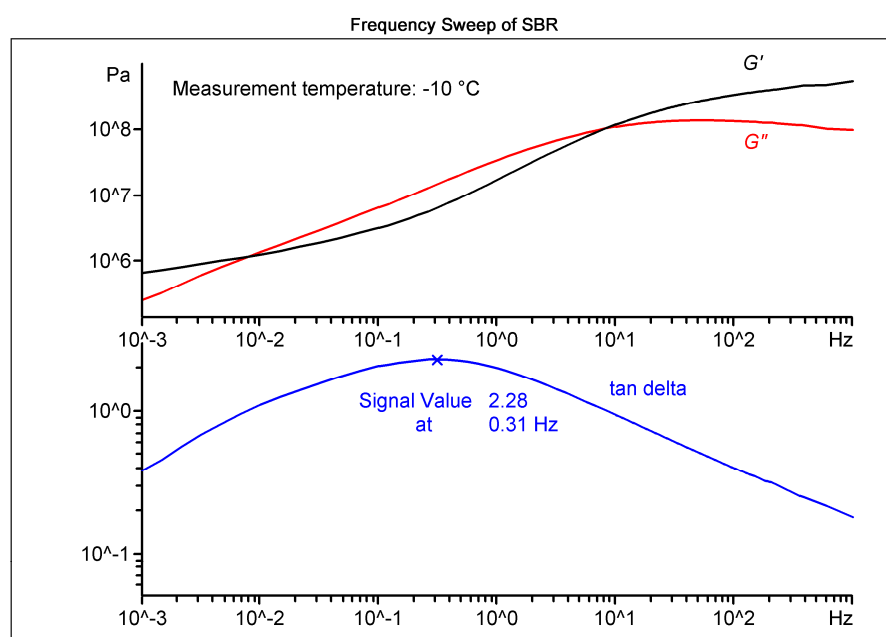


Figure 12.28. Isothermal DMA frequency sweep showing the glass transition of SBR.

12.6.4 Comparison of Thermal Analysis Techniques for Measuring the Glass Transition

Technique	Advantages	Disadvantages	Important points
DSC	Ease of use. Standard methods. Also suitable for low viscosity materials (e.g. solvents); no special sample preparation.	Only a small step is observed with filled samples and at low heating or cooling rates.	Good heat transfer is required between crucible and sample; possible overlapping by other effects (e.g. relaxation).
ADSC	Separation of non-reversing effects. The influence of frequency can be studied. No special sample preparation.	Measurements usually take longer due to the low heating rates used.	Very good heat transfer is required between crucible and sample.
TMA dilato-metric	Even low heating rates give good results. Standard methods.	The viscosity must be sufficiently large above the T_g . Only small changes of expansion are measured with filled materials. Overlapping with stress relaxation effects.	Probe should exert only a low pressure on the sample. Flat parallel samples are required for CTE determination.
TMA penetrometric	Thin films. Standard methods.	Probe geometry and force influence the result.	Ball-point probe is usually used.
DLTMA	Young's modulus determination, especially the bending measurement of highly filled materials.	Low frequency (1/12 Hz or less).	
DMA	Offers the highest sensitivity for determination of glass transitions. Standard methods. Wide frequency range.	Relatively long measurement time due to the low heating rate.	Proper choice of sample geometry and sample holder. Sample preparation can be complicated.

Table 12.2 Overview of measurement techniques for determining the glass transition.

12.6.5 Results of Different Thermal Analysis Techniques

Technique	Cooling/Evaluation conditions	T_g in °C at 2 K/min	T_g in °C at 5 K/min	T_g in °C at 20 K/min
DSC	Shock cooled Cooling = heating rate Cooling measurement	89.3 87.2 84.7	91.6 89.5	95.6 94.0
TMDSC Frequency 0.02 Hz	Shock cooled	93.6		
TMA	Uncontrolled cooling in the TMA Standard evaluation Expansion coefficient		89.0 88.5	

Technique	Cooling/Evaluation conditions	T_g in °C at 2 K/min	T_g in °C at 5 K/min	T_g in °C at 20 K/min
DLTMA Frequency 0.08 Hz	Uncontrolled cooling in the TMA Onset penetration Onset E'		97.5 94.9	
DMA Frequency 10 Hz	Onset, G' (linear) Onset, $\log G'$ Peak, G'' Peak, $\tan \delta$	89.4 99.2 99.4 111.5		

Table 12.3. Glass transition temperatures (T_g) of polystyrene, measured using different thermal analysis techniques under different conditions.

The results show that the glass transition temperature can be measured with different techniques. Each technique however yields different results. The values lie in the range 87.2 to 99.4 °C except for the peak temperature $\tan \delta$ (DMA) and the cooling measurement (DSC).

An exact comparison of measurement results from different laboratories can only be made when the thermal analysis instruments are in proper working order and properly calibrated and, just as important, when the following experimental details are given:

- Thermal analysis technique.
- Heating rate.
- Thermal pretreatment of the sample.
- Evaluation method.

Depending on the thermal analysis technique foreseen for the measurements, the following points should also be specified:

- **DSC**: type of crucible (open or hermetically sealed), range of sample mass
- **TMDSC**: the period and the amplitude
- **TMA, dilatometry**: range of sample dimensions, applied force
- **TMA, penetrometry**: range of sample dimensions, shape of the probe, applied force
- **DLTMA**: shape of the probe; probe either directly on the sample or on the quartz glass disk as interface; applied force (min., max.), period
- **DMA**: type of stress (compression, tension, bending, shear), range of sample dimensions, average force, force amplitude, frequency

If all the conditions are satisfied, the T_g values of identical samples measured in different laboratories should not deviate by more than 2 K.

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UserCom: Many of the application examples in this chapter have been taken from UserCom, the METTLER TOLEDO technical customer journal that is published twice a year. Back issues of UserCom can be downloaded as PDFs from the Internet at www.mt.com/ta-usercoms.

13 Binary Phase Diagrams and Purity Determination

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13.1 Introduction

A binary phase diagram shows the range of existence of phases obtained when two components, A and B, are mixed.

In a phase diagram, the ordinate axis is usually the temperature and the abscissa is the concentration of component B.

The concentration is normally expressed as the **mole fraction** x_B , which is the ratio of the number of moles of component B (n_B) to the sum of moles of component A and B ($n_A + n_B$) (i.e. as 0 to 1, or 0 to 100 mol%).

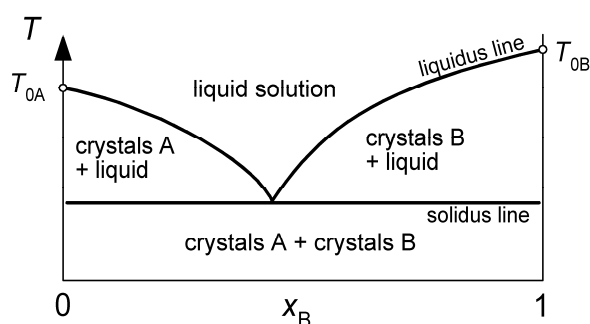


Figure 13.1. A hypothetical binary phase diagram. T_{0A} is the temperature of melting (or fusion) of the pure component A, and T_{0B} that of pure component B.

Some definitions:

The **liquidus line** is the boundary between the liquid solution and the areas where liquid and solid phases coexist (crystals A or B + liquid).

The **solidus line** is the boundary between the areas where liquid and solid phases coexist and the completely solid phase (crystals A + crystals B).

In the two-phase region where solid and liquid phases coexist, there are two different compositions (pure solid and liquid). The composition of the liquid phase at any temperature can be determined by drawing a horizontal line (a so-called **tie-line**) through this point. The intercept with the liquidus line gives the composition of the liquid phase. In the above diagram, the other end of the tie line intersects the ordinate of the diagram at pure solid A or pure solid B.

Components: In principle, the components of a binary phase diagram can be any two substances, A and B. Normally A and B belong to the same class of substance, for example metals, or pharmaceutical substances. A and B can even be the optical antipodes (enantiomers) of a chiral compound.

13.2 The Most Important Binary Phase Diagrams

The type of phase diagram depends on the solubility of the components in the solid and liquid states. The following table summarizes five basic cases:

Type, name	Solubility		Examples
	solid	liquid	
1. Empty or inert (Figure 13.2)	-	-	Naphthalene and indium Typical for inert substances of different classes
2. Eutectic system (Figure 13.3)	-	+	Phenacetin and benzamide Typical for organic substances
3. Limited solid solution (Figure 13.5)	limited	+	Pb and Sn Typical for certain metal alloys
4. Solid solution (Figure 13.6)	+	+	Au and Ni (substitutional) Ni and C (interstitial) Typical for certain metal alloys
5. Compound formation (Figures 13.7 and 13.8)	-	+	Phenol and aniline The racemate of a chiral substance is also a compound.



Figure 13.2. Empty phase diagram obtained with inert substances. Any mixture shows both melting points and does not exhibit any interactions. The crucible and sample in thermal analysis should behave in this way.

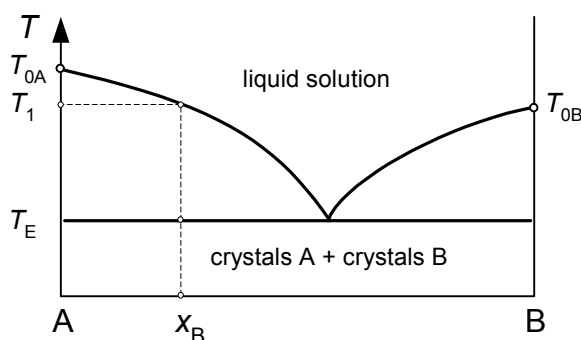


Figure 13.3. The eutectic binary phase diagram is the most important in thermal analysis. Most organic substances exhibit this type of behavior. The eutectic point is the intersection of the liquidus lines with the solidus line and is the unique composition of A and B with the lowest melting point. If a mixture with a mole fraction x_B is slowly heated, all the B crystals melt at the so-called eutectic temperature, T_E . The mole fraction in the liquid phase reaches the eutectic concentration while the solid phase consists of pure A crystals. On further heating, more and more A crystals dissolve in the liquid phase and the concentration of B in the liquid phase therefore decreases. At T_1 all the A crystals have dissolved; the melting point (of the last remaining crystals) has been reached.

The liquidus line of a component that forms a eutectic system can be calculated using the van't Hoff equation (note that the temperatures are in K and ΔH_f is in J mol⁻¹):

$$T_f = T_0 + \frac{RT_0 T_f}{\Delta H_f} \ln(1 - x_B)$$

or after rearranging,

$$T_f = \frac{T_0}{1 - \frac{RT_0}{\Delta H_f} \ln(1 - x_B)} \quad (13.1)$$

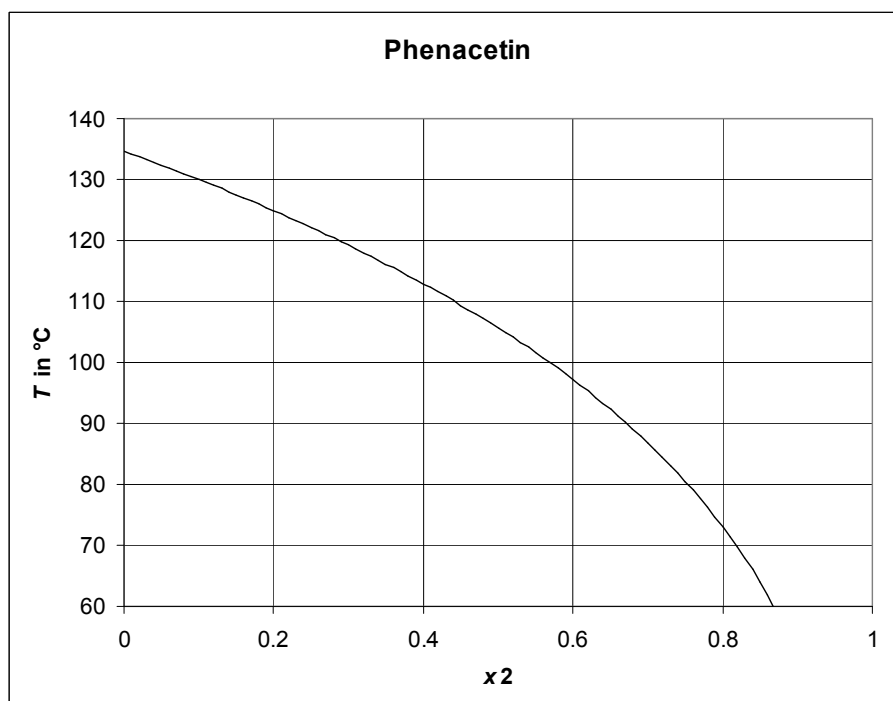


Figure 13.4. Calculated liquidus line for phenacetin, using $T_f = 134.7$ °C, $\Delta H_f = 171$ J/g, $M = 179.2$ g/mol. The shape of the liquidus line is independent of component B.

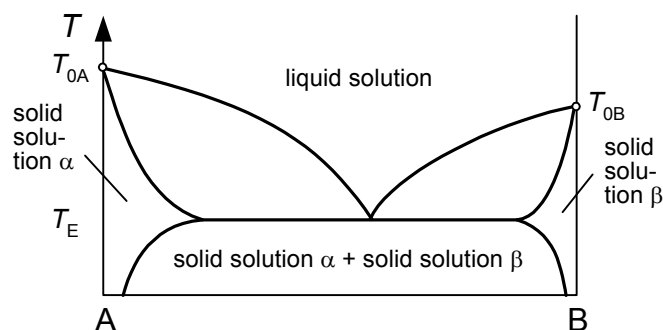


Figure 13.5. Limited solid solution. In the solid phase, small amounts of B are soluble in A (solid solution α) and vice versa (solid solution β). The solid phase, α , is therefore a homogenous solid solution containing small amounts of B in A ("impure" A); and β is a solid solution containing small amounts of A in B ("impure" B). α and β are separate solid solution phases in equilibrium. The lines emerging from the horizontal eutectic line are called solute lines.

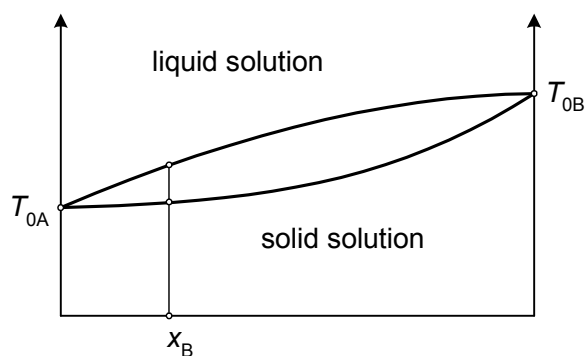


Figure 13.6. Continuous solid solution. Mixtures exhibit a melting range between the solidus and liquidus temperatures.

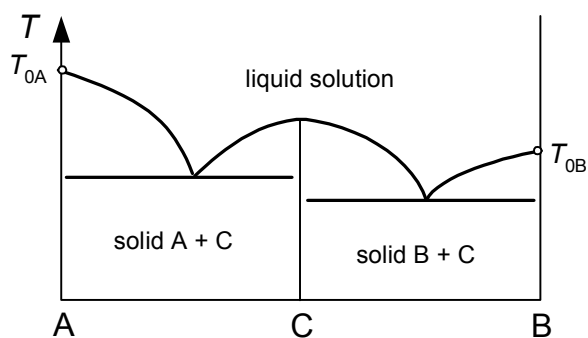


Figure 13.7. Formation of a compound, C, with a composition given by the vertical line at C. The compound interacts in a eutectic manner with A on the left and with B on the right. On melting, C decomposes to A and B. In this example the compound is AB; other common possibilities are A_2B , A_2B_3 , and generally, A_nB_m .

The racemate of a chiral substance is also a compound (always of the type 1:1). The corresponding phase diagram is perfectly symmetrical (Figure 13.8).

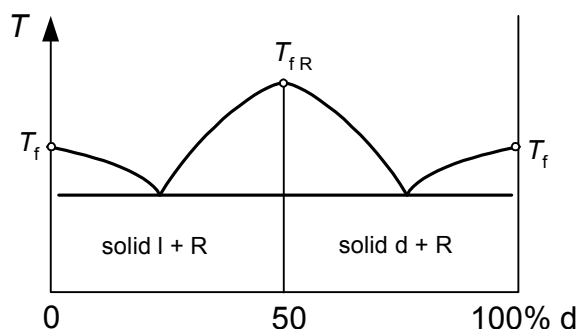


Figure 13.8. Optical antipodes. T_f is the temperature of fusion of pure antipode, and T_{fR} the temperature of fusion of the racemate.

Comment on chiral substances: The two components are the **optical antipodes** or **enantiomers** of an optically active compound. In organic compounds, optical activity occurs due to so-called asymmetric carbon atoms. These are C-atoms whose four equally spatially oriented (tetrahedral) bonds are attached to four different entities. Such a molecule is called chiral and can not be superimposed on its mirror image. The two versions rotate plane-polarized transmitted light to the right or left and are therefore given a small d or l (from the Latin dexter, right and laevus, left), for example l-lactic acid.

Apart from the fact that the two antipodes rotate polarized light in the opposite directions, their physical properties such as density and melting point are the same. 1:1 mixtures of d and l enantiomers of the same compound form either a **racemate** with a higher melting point (symmetrical eutectic phase diagram) or a **conglomerate** with a lower melting point than the antipodes.

13.3 The Use of the Tie-Line to Predict DSC Curves

As mentioned earlier, **tie-lines** (or conodes) are horizontal lines in a region of coexisting phases linking two compositions on the phase boundaries. Application of the **lever rule** and tie-lines allows you to determine the fraction that has melted, F :

$$F = \frac{xs}{ls} \quad (13.2)$$

“ xs ” is the distance x to s ; “ ls ” is the length of the tie-line.

If the solid solution of composition x_B is heated, it begins to melt at the solidus line. F is still about zero. On further heating, xs and thus F slowly increase. When the liquidus line is reached, the solid phase disappears. The rate of fusion is the first derivative of F and is proportional to the DSC curve.

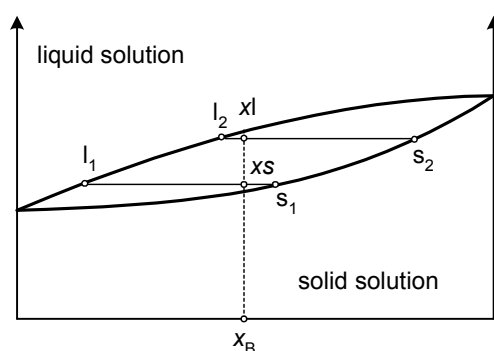


Figure 13.9. A solid solution diagram with two tie-lines drawn to illustrate the method of calculating the fraction melted.

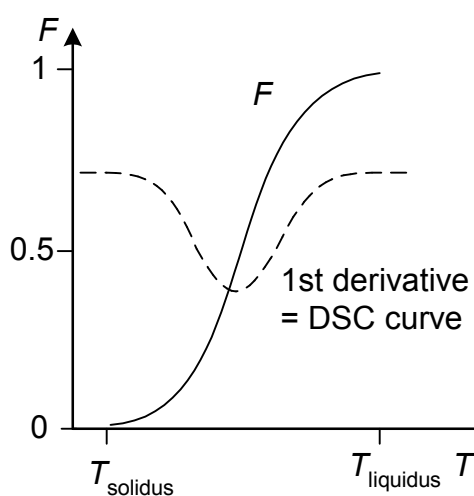


Figure 13.10. F , the calculated fraction melted of the solid solution diagram (Figure 13.9). The first derivative is multiplied by -1 to conform with the ICTAC rule for the DSC sign (exothermic direction upward).

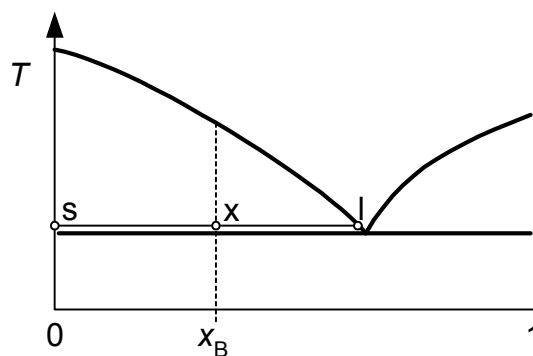


Figure 13.11. A eutectic diagram with a tie-line drawn to illustrate the calculation of the fraction melted.

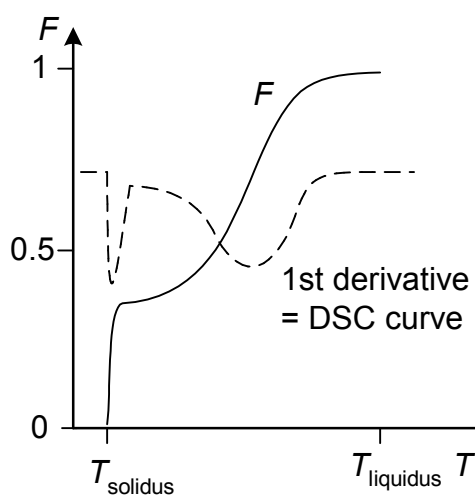


Figure 13.12. In the eutectic diagram (Figure 13.3), the distance xs immediately jumps to quite a high value on crossing the solidus line which corresponds to the melting of the eutectic. xs then remains constant while the length of the tie-line slowly decreases as the remaining A crystals melt. Again, the first derivative signifies the corresponding DSC melting curve.

13.4 Constructing Phase Diagrams from DSC Measurements

With simple phase diagrams, it is sufficient to measure the two pure components and about four mixtures with x_B values of approx. 0.2, 0.4, 0.6 and 0.8. The heating rate used should not be greater than 5 K/min.

The crucible should be sealed to prevent evaporation of the component with the higher vapor pressure.

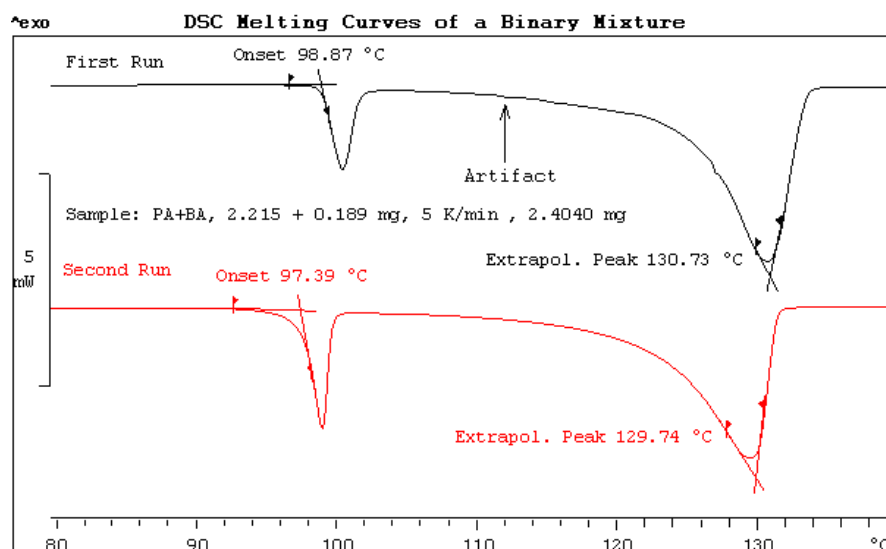


Figure 13.13. The DSC curves show the difference between the first and second heating runs of a two-component mixture (PA is phenacetin; BA is benzamide). Artifacts (spikes) may occur in the first heating run, which indicates that the components were not properly mixed (just weighed into the crucible). This results in the characteristic temperatures being shifted to values that are too high. The second heating run should be used if no decomposition occurs and the molten sample crystallizes on cooling.

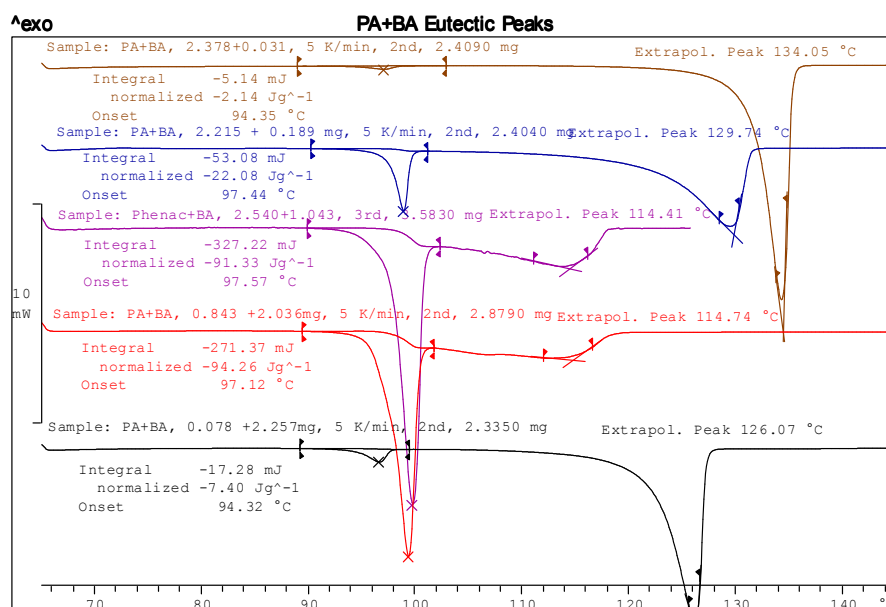


Figure 13.14. Five mixtures of phenacetin and benzamide measured by DSC at 5 K/min.

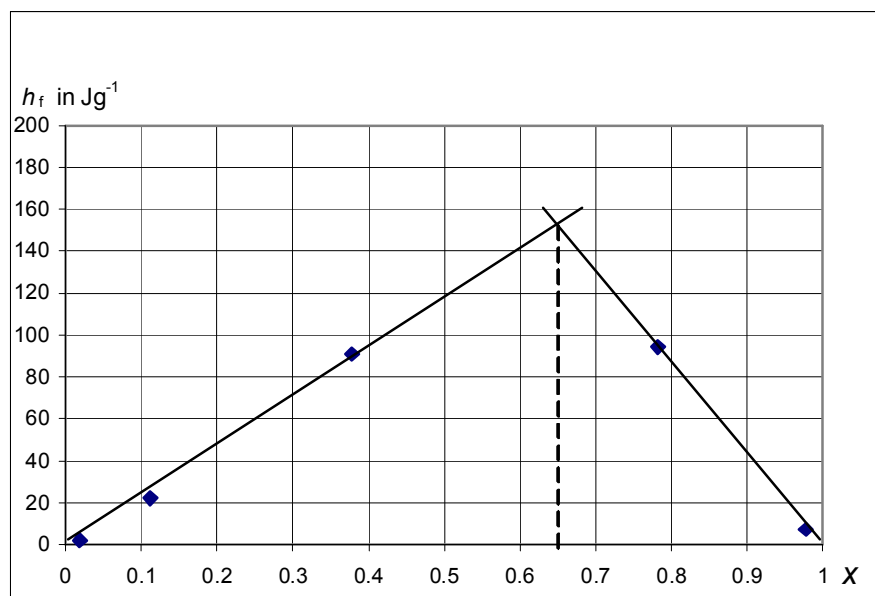


Figure 13.15. The eutectic composition is obtained by linear extrapolation of the enthalpy of fusion of the eutectic peak of the DSC curves of Figure 13.14 plotted against x_B . Zero values of the pure compounds are also included.

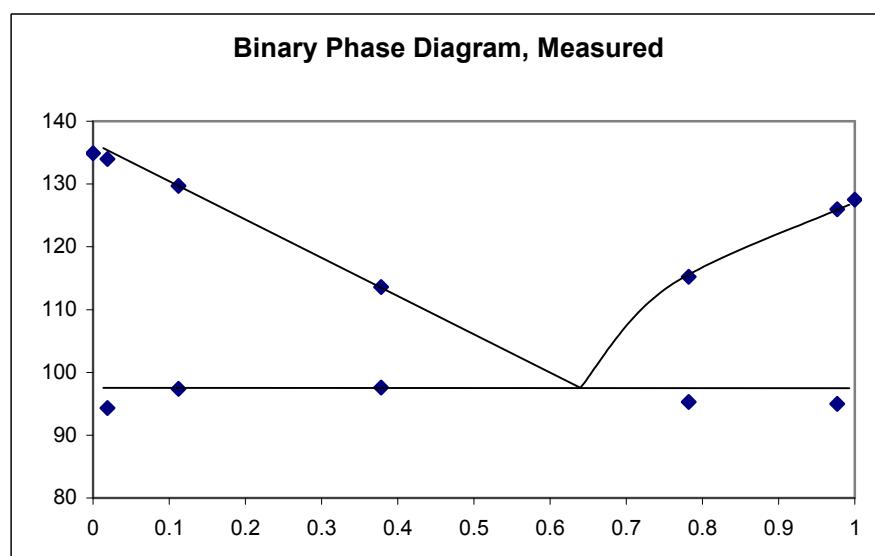


Figure 13.16. The solidus and liquidus points obtained from the DSC measurements in Figure 13.14. The melting points of pure phenacetin (134.4 °C) and of pure benzamide (127.5 °C) are also used. The eutectic concentration comes from Figure 13.15.

Besides the simple binary melting diagrams discussed here, there are also more complicated ternary (three-component) melting and boiling point diagrams. These are not so important in this context and will not be further discussed.

13.5 DSC Purity Determination

The first section describes the basic principles of purity determination. The sections that follow deal with problems that can occur in practice and give information on sample preparation and measurement parameters for the STAR^e evaluation method.

13.5.1 Basic Principles

DSC purity determination is based on the fact that eutectic impurities lower the melting point of eutectic systems. This effect is described by the modified **van't Hoff equation** (13.3) or its simplified version (13.4):

$$T_f = T_0 + \frac{R T_0 T_{\text{fus}}}{\Delta H_f} \ln \left(1 - x_2 \frac{1}{F} \right) \quad (13.3)$$

$$T_f = T_0 - \frac{R T_0^2}{\Delta H_f} x_2 \frac{1}{F} \quad (13.4)$$

where

T_f is the melting temperature in Kelvin, which moves along the liquidus line of the binary phase diagram during melting,

T_0 is the melting point of the pure substance in Kelvin,

T_{fus} is the clear melting point of the impure substance in Kelvin

R is the gas constant,

ΔH_f is the molar enthalpy of fusion (can be calculated from the DSC peak area, A_{tot} , eq 13.6),

x_2 is the unknown concentration of impurity to be determined (mole fraction), x_2/F (δ) is the momentary concentration of impurity in the liquid phase. During melting, it sinks from the eutectic concentration to the original impurity concentration (at the clear melting point),

F is the fraction melted (during the measurement it increases from 0 toward 1). It corresponds to the ratio of the partial area to the total area of the melting peak (DSC conversion), eq 13.7,

$\ln$ is the natural logarithm,

A_{part} is the partial area of the DSC peak,

A_{tot} is the total area of the peak,

M is the molar mass of the main component, and

m is the sample mass.

$$\Delta H_f = A_{\text{tot}} \frac{M}{m} \quad (13.5) \quad \text{and} \quad F = \frac{A_{\text{part}}}{A_{\text{tot}}} \quad (13.6)$$

The simplifications used in converting eq 13.3 to eq 13.4 are the following:

- $T_0 T_{\text{fus}} \sim T_0^2$: because T_0 and T_{fus} are close to one another
for example: $400 \text{ K} \times 398 \text{ K} = 159,200 \text{ K}^2$ and $(400 \text{ K})^2 = 160,000 \text{ K}^2$
- $\ln(1 - \delta) \sim -\delta$: if $\delta \ll 1$, e.g. $\delta = 0.05$, $\ln(1 - 0.05) = -0.0513$

According to eq 13.4, T_f is a linear function of $1/F$. The ordinate intercept (see inserted diagram in Figure 13.17) is T_0 , and x_2 is calculated from the slope. In practice, a linearization correction, c , is necessary. The graph $T_f = f(1/F)$ is called the van't Hoff plot. It shows the function with and without correction. The correction can partly be explained by the area of the eutectic peak, which is normally not measured. The inverse melted fraction becomes:

$$\frac{1}{F} = \frac{A_{\text{tot}} + c}{A_{\text{part}} + c} \quad (13.7)$$

$$T_f = T_0 - \frac{RT_0^2}{A_{\text{tot}}} \frac{M}{m} x_2 \frac{A_{\text{tot}} + c}{A_{\text{part}} + c} \quad (13.8)$$

Equation 13.8 is obtained when eqs 13.5 and 13.7 are inserted in eq 13.4.

The three unknowns, T_0 , x_2 and c can then be calculated because an almost unlimited number of measurement points T_f , A_{part} are available for the equation. Usually only measurement points between 10 and 50% of the peak height are used because in the range below 10% the concentration of impurity is very high, and above 50% the melting rate is too high (the van't Hoff equation applies to equilibrium conditions). In Figure 13.17, the evaluation range on the DSC curves is marked by crosses (x).

On the assumption that the linearization correction, c , corresponds to the “neglected” enthalpy of fusion, A_{tot} can be replaced by $A_{\text{tot}} + c$ in eq 13.5. Equation 13.8 is then reduced to eq 13.9:

$$T_f = T_0 - RT_0^2 \frac{M}{m} x_2 \frac{1}{A_{\text{part}} + c} \quad (13.9)$$

In eq 13.8, the total area of the peak no longer occurs. This is the reason why it can be applied to incomplete melting peaks, for example at the beginning of decomposition. The **STAR**[®] software automatically applies this short form (“Short”) if peak maximum does not lie in the evaluation range. This of course means that when “Short” is used, results such as T_f and Δh are not available.

13.5.2 Applicability of DSC Purity Analysis

Note: Non-eutectic impurities can also affect the melting point, and in the case of mixed crystal systems even increase the melting point. Impurities that form an empty binary phase diagram (mutually insoluble in the liquid phase, e.g. vanillin and iron oxide), do not change the melting point of the main component at all. This type of impurity is therefore not detected by the DSC purity analysis (except via the lower enthalpy of fusion).

When validating a method for purity determination of a particular chemical substance, the first thing to check is whether it exhibits eutectic behavior with the main impurities presumed to be present. If the chemical process used for the production of the substance is known, then usually the by-products are also known; otherwise the chemist must make some intelligent guesses. If necessary, the impurities can be identified by HPLC. As soon as the main impurity has been identified, samples containing specific amounts of impurity can be prepared and investigated by DSC.

This assumes that the main component is available with a purity level >99.5 mol%. Whenever possible, the purity should be checked using different methods and not just by DSC purity analysis alone. The degree of purity can often be improved by recrystallization, zone melting or drying. A relatively small amount of substance (about 100 g) is usually sufficient for these investigations.

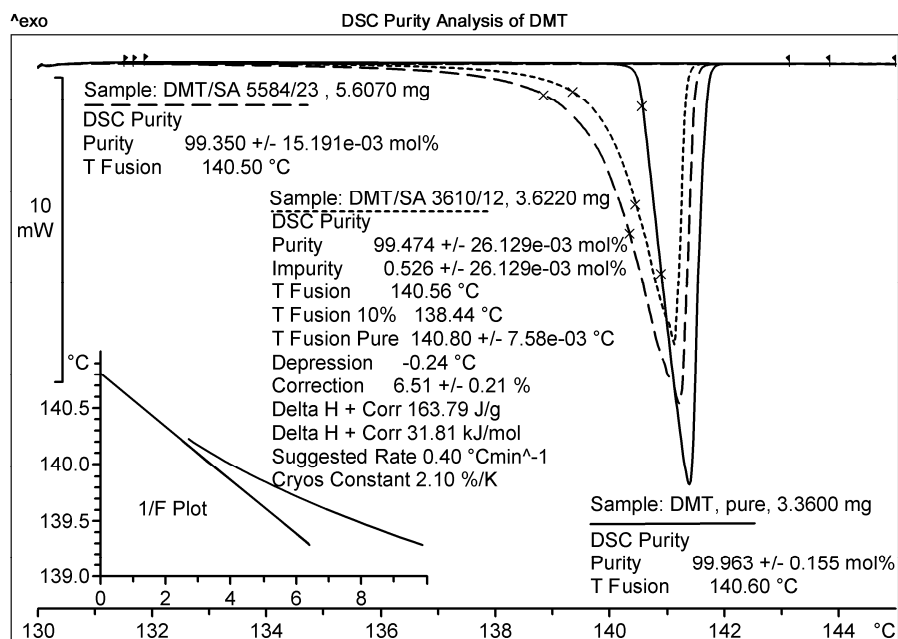


Figure 13.17. DSC heating runs of samples of dimethyl terephthalate (DMT) containing increasing amounts of salicylic acid impurity (SA) are listed in Table 13.1. Two curves are evaluated with the minimum possible number of results: the purity in mol%, the confidence interval of the purity, and the clear melting point. Optional results from the second curve are also presented. The inserted van't Hoff plot diagram also belongs to the second curve. The heating rate used was 1 K/min.

First, DSC purity determinations are performed on a number of test specimens of the pure main components and the mean value of the impurity concentration, x_2 , is determined. If the substances concerned are not in a finely powdered form, they should be ground and powdered in a mortar and possibly dried in a desiccator. Prepare three or more samples of different impurity in 100x12 mm test tubes by weighing-in the components using several micrograms of the impurity and a corresponding mass of the main compound. Use a 4-decimal place analytical balance for the main component and a microbalance for the impurity in order to achieve the desired degree of impurity. Plug the test tubes using a rubber plug, seal with Parafilm and melt the mixture in an FP83 or equivalent oven. Mix carefully in the liquid state by shaking. To obtain a homogeneous mixture, cool the samples rapidly in ice/water. Divide the final mixture using a spatula and put about 3.5 mg of the mixture into a 40- μ L aluminum crucible. Seal the crucible hermetically with an aluminum lid and indent the lid to minimize free volume. Insert the crucible containing the sample into sample position of the DSC. An empty identical crucible with lid is placed in the reference position.

If the molar masses of the two components are similar, impurity concentrations of about 0.2, 0.5, 1 and 2% are desirable. In order to calculate the degree of impurity of the preparations, the molar masses of the main component M_1 , the impurity M_2 and the masses of the components m_2 and m_1 have to be entered in the following equation.

$$x_2 = \frac{\frac{m_2}{M_2}}{\frac{m_1}{M_1} + \frac{m_2}{M_2}} \quad (13.10)$$

To obtain more convenient numbers in mol%, the mole fraction is usually multiplied by 100%.

If the “pure” substance exhibits a significant DSC impurity concentration, this is added to the added concentration.

The DSC purity determination of the artificially prepared impure samples is then performed at a heating rate of 1 K/min. If the samples melt without decomposition and crystallize on cooling to room temperature, they can be measured a second time. In this case, the peak shape around the maximum is often better. Slight decomposition in the first melting run as well as polymorphism can of course change the shape of the peak.

If possible, try to detect the eutectic peak, at least with the most impure sample. Since the eutectic typically melts some 10 to 50 K lower than the pure component 1, it is better to look for the eutectic peak using a heating rate of 10 K/min with a sample that is no longer required (start temperature about 100 K below the melting point of component 1). The eutectic peak (Figure 13.13, at about 98 °C) confirms the presence of a eutectic system.

The error in x_2 (x_2 measured by DSC minus x_2 added) is now plotted. Ideally, this should be a horizontal line with no error (Figure 13.18). If the error is clearly on the positive side, a possible explanation could be dissociation of the impurity. For example, sodium chloride in water gives an “error” of 100% due to the complete dissociation to Na^+ and Cl^- ions.

m_1 DMT [μg]	m_2 SA [μg]	Impurity added [mol%]	Impurity measured [mol%]	Error (impurity measured – impurity added) [mol%]
3360	0	0.0	0.037	0.037
3610	12	0.465	0.526	0.061
5584	23	0.58	0.65	0.07
3224	36	1.55	1.45	-0.1
3868	94	3.30	2.77	-0.52

Table 13.1. Added and measured impurities. The main component is dimethyl terephthalate (DMT); the impurity is salicylic acid (SA). In this case, the DSC purity determination of the pure main component yielded a negligible impurity concentration of 0.003 mol%.

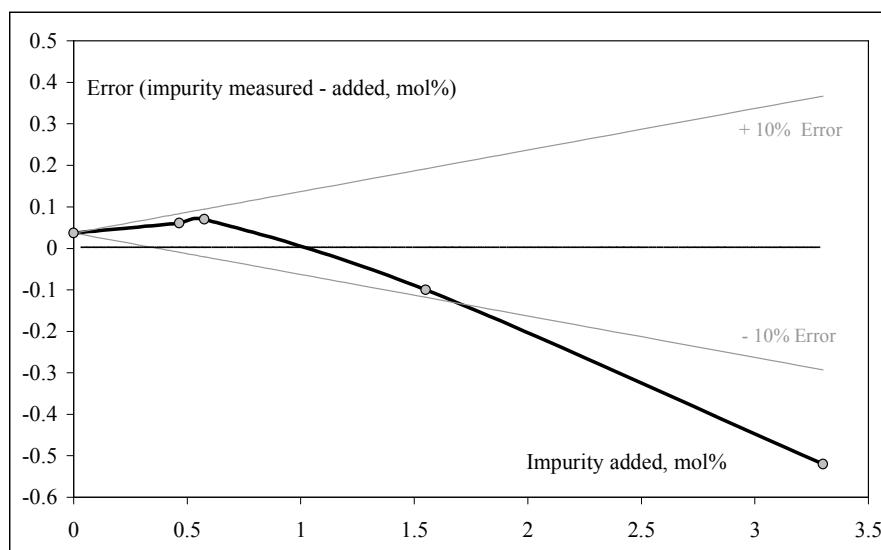


Figure 13.18. Error of x_2 as a function of the concentration of impurity added. Component 1 is high purity dimethyl terephthalate ($M_1 = 194.2$ g/mol); component 2 is salicylic acid ($M_2 = 138.1$ g/mol). The sample masses and results of the DSC purity determination are summarized in Table 13.1. The relative error of the DSC purity analysis for this system is less than 10% up to about 1.7% mol%.

13.5.3 Volatile Impurities

The presence of moisture (i.e. water) with its low molar mass has a particularly large influence on the result of a DSC purity determination. For organic samples with a typical ratio of M_2/M_1 of 10, one mass% of water corresponds to a value ten times greater in mol%.

Organic solvents are also examples of volatile compounds. They are detected if the measurements are performed in sealed crucibles.

If only the nonvolatile impurities are of interest, which is normally the case for pharmaceutical active ingredients, the crucible should be sealed with a pierced lid. Holes with diameters of 0.3 to 1.0 mm are ideal. The volatile impurities of substances with melting points above about 80 °C can then evaporate and do not affect the results. The endothermic vaporization peak can of course give rise to baseline problems in the evaluation. This can be avoided by means of an isothermal drying period at about 10 K below the expected melting point. In this case, it is important to purge the measuring cell with nitrogen (in general gases from gas bottles are extremely dry).

When pierced lids are used, there is of course the possibility that not only solvents but also other relatively volatile impurities are lost and not measured.

Small holes (<0.3 mm) slow down diffusion and result in the formation of a self-generated atmosphere, which greatly retards the drying process. If the holes are too large (>1.0 mm), or if crucibles without lids are used, then quite often part of the main component is lost through sublimation.

13.5.4 Thermal Stability of the Main Component

If the main component undergoes partial decomposition during the melting process, the decomposition products immediately depress the melting point. This effect decreases noticeably with increasing heating rates because at higher heating rates there is less time for decomposition to occur.

There are also substances that do not decompose at the beginning of the melting process but whose baselines are at a different level after melting due to decomposition. In such cases, one uses a horizontal baseline beginning on the left (low temperature) side and the “Short” evaluation according to eq 13.9.

In principle, the decomposition can be shifted to higher temperature using high-pressure DSC at pressures of about 5 MPa. The melting behavior changes only slightly compared to that at normal pressure.

13.5.5 Polymorphism

Polymorphism interferes with purity determination especially if a polymorphic transition occurs in the middle of a melting peak. Usually the transition can be allowed to take place beforehand in an isothermal segment and the resulting stable modification then measured in a dynamic segment.

(see Chapter 14, Polymorphism)

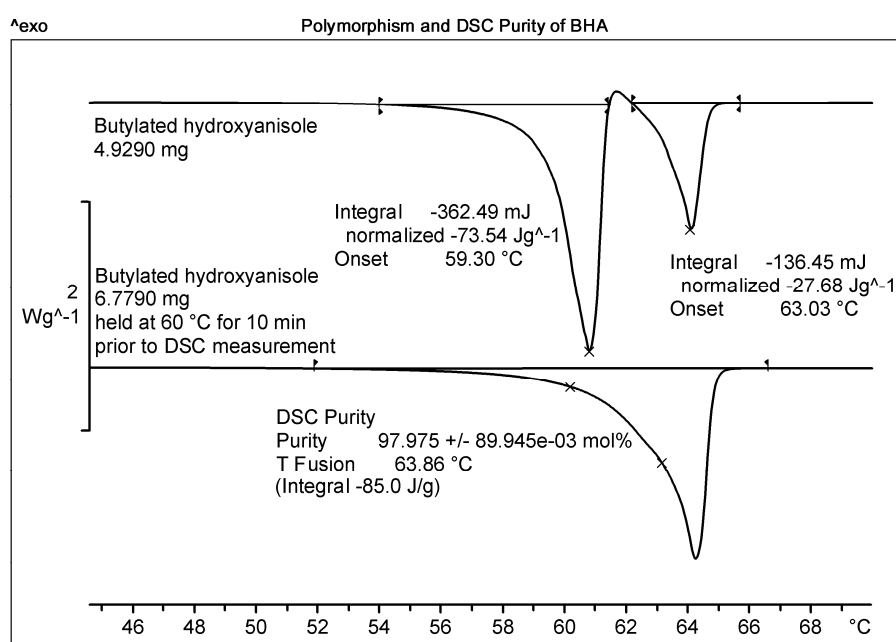


Figure 13.19. Above: The diagram shows the melting curve of butylhydroxyanisole (BHA) with the characteristic melting of the metastable modification at about 60 °C. This is followed by crystallization of the stable modification, which then melts at about 63 °C. Polymorphism interferes with both melting peaks and thereby prevents purity determination. Below: The transition to the stable modification is complete after annealing for 10 minutes at 60 °C. The sample is then cooled to 35 °C and the melting curve measured at 2.5 K/min. This curve can be evaluated but the results are questionable because BHA contains isomers.

The different modifications of a chemical substance do not mutually depress their melting points.

Certain substances may be partially amorphous. This manifests itself in a noticeably smaller enthalpy of fusion. A more serious problem for DSC purity determination is, however, exothermic “premelting crystallization” that occurs at the beginning of the melting curve. This leads to completely erroneous evaluation results. Here again, crystallization can be allowed to take place isothermally before measuring the melting curve.

With hydrates (or solvates), two melting points can often be measured. In a hermetically sealed crucible, the hydrate melts in “its own water of crystallization” quasi like a eutectic with maximum depression of the melting point. In an open crucible, the water of crystallization evaporates on warming and the anhydrous form melts at a correspondingly higher temperature.

13.5.6 Sample Preparation and DSC Measurement Parameters

Sample shape: The thermal resistance between the sample and the crucible should be as small as possible. In this respect, fine powders are much more favorable than coarse agglomerates of particles. Furthermore, a fine powder is more likely to be a representative sample of the substance under investigation.

For these reasons, about 1 g of the substance is ground in a clean agate mortar using as little pressure as possible (the crystal lattice of some substances can be destroyed by excessive pressure). The powder is then stored in a small bottle.

Samples that are liquid at room temperature are prepared by transferring a drop to a previously weighed aluminum crucible using a fine spatula. The crucible is then hermetically sealed and weighed. The drop solidifies later on cooling in the low temperature DSC.

Sample mass: The enthalpy of fusion of most organic substances is quite large (about 150 J/g). For this reason, relatively small sample masses can be used. This reduces the effect of temperature gradients within the sample. A sample mass of 2 to 3 mg is optimal for very pure substances, 3 to 5 mg for 2 mol% impurity, and 5 to 10 mg for 5 mol% or more impurity. It is good practice to weigh the sample before and after the measurement in order to check for any loss of mass. This is also advisable when using hermetically sealed crucibles since dust or traces of the samples between crucible and the lid prevent successful cold sealing.

It is often preferable to perform three measurements in order to obtain information about the homogeneity of the sample.

Crucibles: The 40- μ L standard aluminum crucibles are normally used because they can be hermetically sealed. The low mass 20- μ L aluminum crucibles are also very suitable due to their shape and low heat capacity. They cannot however be hermetically sealed. Sometimes the molten substance is able to seep through the gap between the lid and the wall of the crucible with the risk of contaminating the DSC sensor.

Start temperature: This depends on the expected degree of contamination and is usually 10 to 30 K below the melting point of the pure substance.

End temperature: This is usually about 5 K above the melting point of the pure substance.

Heating rate: The optimum heating rate is 0.5 to 1 K/min for very pure substances, 1 to 2 K/min for samples with about 2 mol% impurity and 2 to 5 K/min for samples with impurity levels above 5 mol%. Heating rates of up to 10 K/min can be successfully used for substances that decompose. According to ASTM E928, heating rates of 0.3 to 0.7 K/min must be used.

Our experience with numerous stable substances shows that the results are not very dependent on the heating rate up to 5 K/min. At 10 K/min, the measured impurity concentration tends to be lower (by about 10%).

If the substance melts without decomposition and crystallizes on cooling, the effect of heating rate can be investigated by measuring the same sample at different heating rates.

Atmosphere: The DSC measuring cell is normally purged with nitrogen at 50 mL/min in order to prevent oxidative decomposition and to flush out any volatile components that are produced.

References and Further Reading

- [1] Further information and results from inter-laboratory tests can be found in the publication “Purity Determinations by Thermal Methods” (R. L. Blaine, C. K. Schoff, eds.), ASTM-PCN 04-838000-40 ASTM STP 838 (1984).
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- [5] METTLER TOLEDO Collected Applications Handbook: “Validation in Thermal Analysis”.

14 Polymorphism

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14.1 Introduction and Terms

Polymorphism is the property possessed by certain chemical compounds of being able to crystallize in two or more forms which are structurally distinct. A substance that can exist in different crystalline forms or modifications is called a **polymorph**. The various crystalline forms such substances have very different physical, chemical, or biological properties, sometimes with important consequences across a range of industries from pharmaceuticals to foods.

As indicated above, the individual polymorphic forms of a substance differ in their major physical properties such as melting temperature, color, solubility, refractive index, hardness or conductivity. The different modifications however yield the same liquid phase when they melt.

Polymorphism in the case of elements is known as **allotropy** and is for example exhibited by sulfur, carbon (graphite, diamond), phosphorus and a large number of minerals and organic compounds. Polymers can also occur in polymorphic forms, for example isotactic polypropylene or polytetrafluoroethylene.

The polymorphic forms of drug substances [1] are of major practical importance. Since the solubility and the dissolution rate of individual polymorphic forms are often very different, resorption and bioavailability in the human body [2] are also different. The therapeutic efficacy therefore depends on the modification present, so that for example a **metastable** form might be twice as active as the stable form.

Polymorphism is not only important for pharmacological efficacy but even at an earlier stage in production (crystallization and drying conditions), processing and formulation (stickiness, flowability, appearance) of a polymorphic substance.

The individual crystalline modifications are each stable in a particular temperature range and are assigned the Greek letters (α , β) or Roman numbers (I, II, III). Furthermore, metastable modifications can also exist and are denoted for example by β' . Their gradual transformation to the stable form takes hours and sometimes even years. In practice, one distinguishes between two types of polymorphism, enantiotropy and monotropy:

- Reversible solid-solid transitions are called **enantiotropic** (Figure 14.1, left). The transition from $\alpha \rightarrow \beta$, starting from the low temperature form α to the high temperature form β is endothermic. In this case, the enthalpy of fusion of the α -form is therefore higher than that of the β -form [3]. The melting point of the α -form is of course only observed if the transition $\alpha \rightarrow \beta$ is very slow.
- The exothermic solid-solid transition of metastable forms into stable forms is called **monotropic** (Figure 14.1, right) because it only proceeds in one direction and is irreversible. The enthalpy of fusion of the lower melting β' -modification is usually smaller than that of the more stable, higher melting form β [1]. The difference between the heats of fusion corresponds to the monotropic transition enthalpy. In accordance with **Ostwald's rule**, the less stable modifications often crystallize first on cooling from the melt. These then undergo stepwise transformation to the more stable forms. This process is known as Ostwald ripening. Metastable modifications can often be obtained in the DSC by slowly warming amorphous materials (obtained by shock cooling the melt) to above the glass transition temperature [4]. Metastable forms also often crystallize from solutions of the substance in particular solvents.

Many compounds form **solvates** with different physical properties on crystallizing out from solution. If the solvent is water, they are called **hydrates**. If such a solvate is heated in a gas-tight and pressure-tight container, it melts at a considerably lower temperature than the non-solvated compound. The different melting temperatures resemble the behavior of polymorphic compounds so the behavior is often referred to as **pseudo-polymorphism** [2].

Some organic compounds consisting of long-stretched molecules with dipole properties do not reach the **isotropic** (having identical properties in all directions) liquid aggregate state in one single transition. A special liquid phase known as a **mesophase** occurs above the melting process first observed. This phase is a **liquid crystalline** state that exists between the crystalline and isotropic liquid phases. The isotropic liquid phase is then formed on further heating. Finally, there are also more spheroidal-like molecules which on heating first of all form a **plastic crystalline** state. The isotropic melt is obtained on further heating.

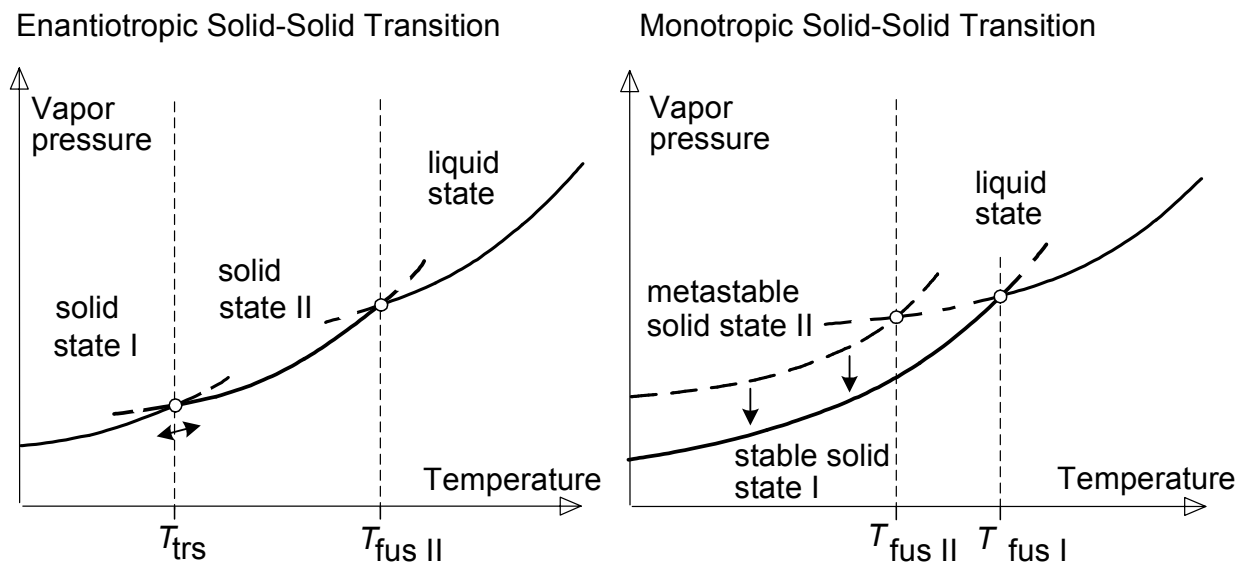


Figure 14.1. Schematic representation of an enantiotropic (left) and a monotropic (right) phase diagram. It shows the vapor pressure temperature function of the different phases. The melting point of the metastable modification β' is often only reached on fast heating, otherwise the stable modification β is formed through a monotropic transition.

14.2 Detection of Polymorphism

The different physical properties of the individual polymorphic forms of a compound allow them to be characterized. The methods most often used to investigate polymorphism include the following:

- DSC: All first-order phase transitions involve enthalpy changes. Free enthalpy temperature functions can be calculated from c_p temperature functions.
- Thermo-optical analysis [1]: Here the sample is observed between crossed polarization filters. If the sample is subjected to a temperature program, the individual phase transitions are detected as a change in birefringence (Figure 14.2). See Chapter 18, Thermooptometry.

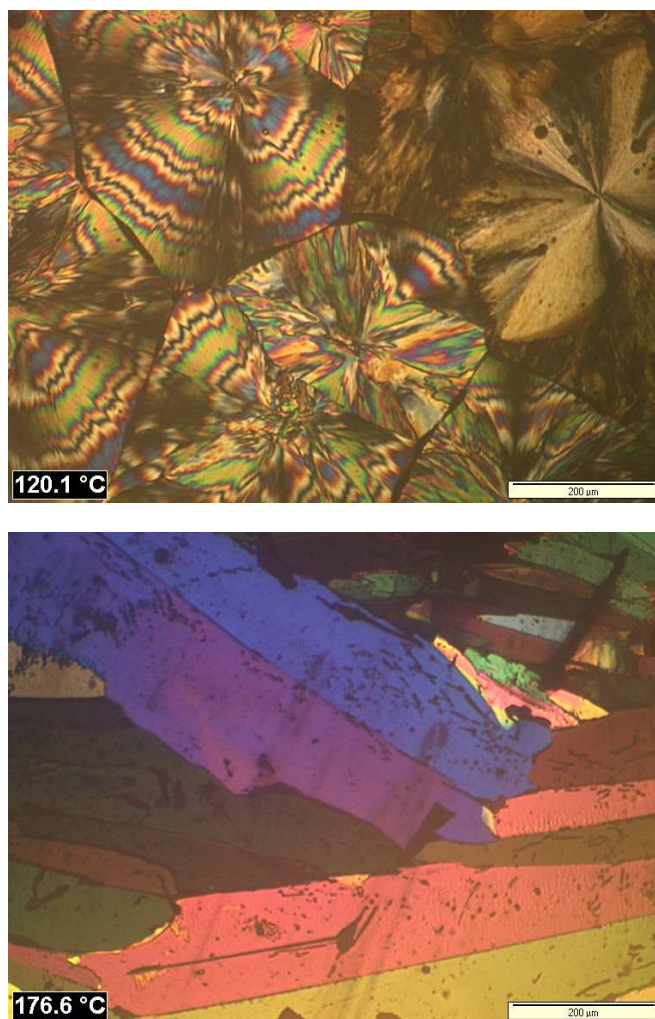


Figure 14.2. Two polymorphic forms of sulfapyridine that exhibit different birefringence in polarized light.

- Solubility studies.
- X-ray methods, e.g. Debye-Scherrer powder diffractometry.
- Infrared spectroscopy.

14.3 The DSC Investigation of the Polymorphism of Sulfapyridine

The sample was first heated to melting (first heating run in Figure 14.3). It was then shock cooled in the sample robot by placing the hot crucible with the molten sample onto the turntable at 25 °C. An amorphous glass was formed. The second heating run (red curve in Figure 14.3) shows a glass transition followed by exothermic cold crystallization. The metastable phase formed changes to a more stable modification through an exothermic monotropic solid-solid transition. This modification then melts at 179 °C. Finally, the stable phase crystallizes from the melt and melts at 190 °C.

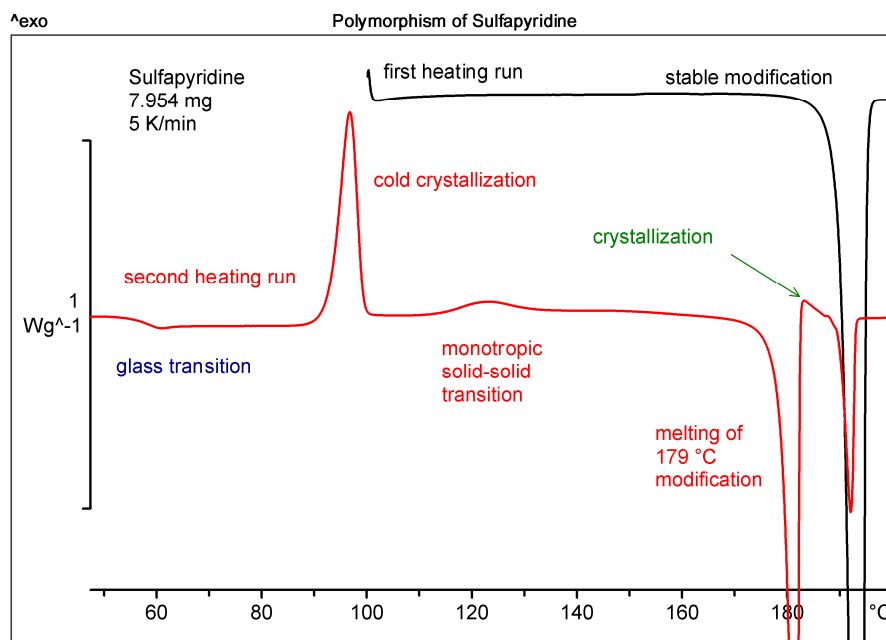


Figure 14.3. First heating run of sulfapyridine at 5 K/min (black). The melting temperature of the stable modification is about 190 °C. The second heating curve is shown below in red. The monotropic solid-solid transition occurs at about 125 °C.

References and Further Reading

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15 Temperature-Modulated DSC

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15.1 Introduction

The classical temperature program used in DSC is to heat or cool the sample at a constant rate. In temperature-modulated DSC (TMDSC) or modulated-temperature DSC (MTDSC), the heating rate changes in a more complex fashion. In the isothermal step method, IsoStep®, the sample is heated in a series of steps of just a few degrees separated by isothermal periods. In alternating DSC (ADSC), the linear temperature change is overlaid with a periodically changing (usually sinusoidal) modulation. The temperature change can be set to zero and other periodic modulations (e.g. saw-tooth) are possible. The aim is to achieve 4 to 6 cycles during the thermal event of interest. In the most advanced technique, TOPEM®, a stochastic temperature change in the form of pulses is superimposed on the underlying heating rate. The advantage of these three techniques lies in the fact that the heat flow can be separated into two components. One of these corresponds to the specific heat of the sample and the other to so-called “kinetic” processes such as chemical reactions, crystallization processes or vaporization processes.

15.2 IsoStep®

IsoStep® [1] is the simplest type of temperature-modulated DSC. In this technique, the temperature program consists of a large number of dynamic segments that each begin and end with an isothermal segment (Figure 15.1). The length of the isothermal or dynamic segment is typically 30 s to 2 min and the heating rate during the dynamic segments is about 0.5 to 3 K/min. The isothermal and dynamic segments are usually of equal length and the same heating rate is used in all dynamic segments.

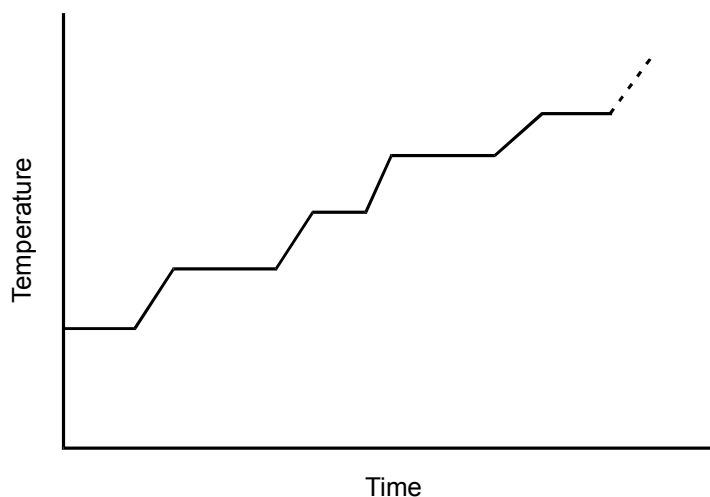


Figure 15.1. An IsoStep® temperature program consisting of different isothermal and dynamic segments.

The idea behind the DSC IsoStep® technique is that only “kinetic” phenomena (e.g. crystallization, chemical reactions, vaporization) are measured during isothermal segments, whereas the heat flow occurring in the dynamic segments is mainly due to the thermal mass and the specific heat capacity, c_p , of the sample. This allows c_p information to be separated from “kinetic” information; the c_p information is calculated from the dynamic segment and the “kinetic” information from the isothermal segments. Isothermal drift is eliminated by subtracting a blank curve. Furthermore, the

heat flow is calibrated using a sapphire sample in order to obtain accurate c_p values. The specific heat capacity of the sample (c_p sample) is then given by eq 15.1 (see also Figure 15.2).

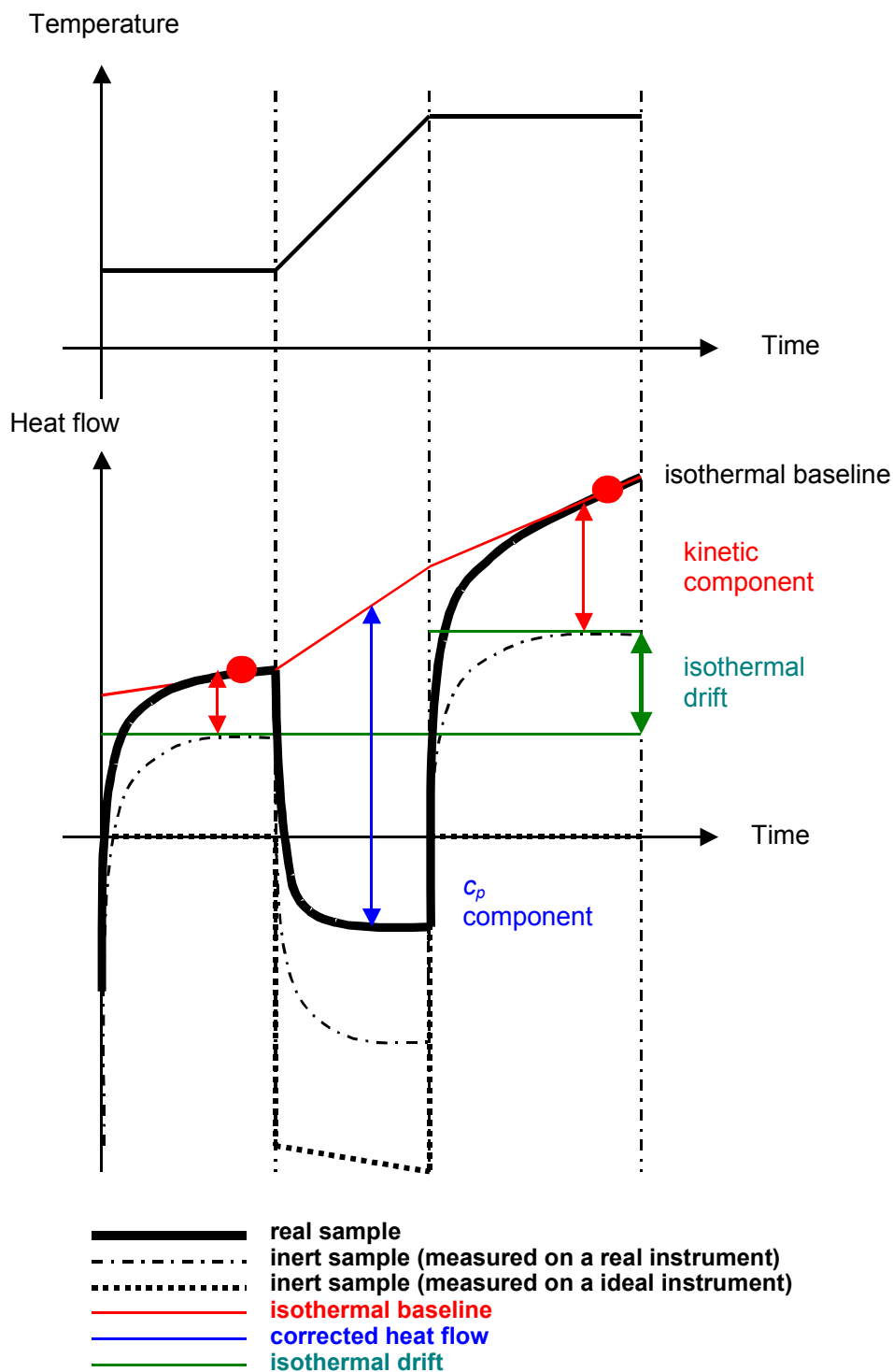


Figure 15.2. Schematic diagram of an IsoStep® temperature program with the corresponding heat flow curve separated into components for ideal and real systems.

$$c_p \text{ sample} = (\phi_{\text{sample}}(T) - \phi_{\text{blank}}(T)) \cdot c_p \text{ sap. lit.}(T) / (\phi_{\text{sap.}}(T) - \phi_{\text{blank}}(T)) \cdot m_{\text{sap.}} / m_{\text{sample}} \quad (15.1)$$

where

c_p is the specific heat capacity,

ϕ is the heat flow, and

m is the mass.

Figure 15.3 shows a typical experiment to illustrate the IsoStep[®] technique using PET as an example. First, the blank corrected curves of PET and the sapphire sample are measured (the two uppermost curves). The lower envelope of each corresponds to the heat flow during the dynamic segments and is used to calculate the specific heat capacity. The upper envelope corresponds to the heat flow during the isothermal segments and gives the values for the “kinetic” phenomena, that is, for the so-called non-reversing heat flow. Conversion of the results for the specific heat to heat flow (by multiplying the specific heat by the sample mass and the heating rate) yields the so-called reversing heat flow.

The heat capacity and reversing heat flow curves of the PET sample show a glass transition at about 75 °C. In the non-reversing heat flow curve, a small endothermic peak can be seen at roughly the same temperature. This is a result of enthalpy relaxation during storage of the sample (see Chapter 12, The Glass Transition). At about 125 °C, an exothermic peak occurs due to cold crystallization. The crystallization of the sample affects the specific heat capacity, which is slightly lower for the semicrystalline material than for the liquid (step in the c_p curve at about 130 °C).

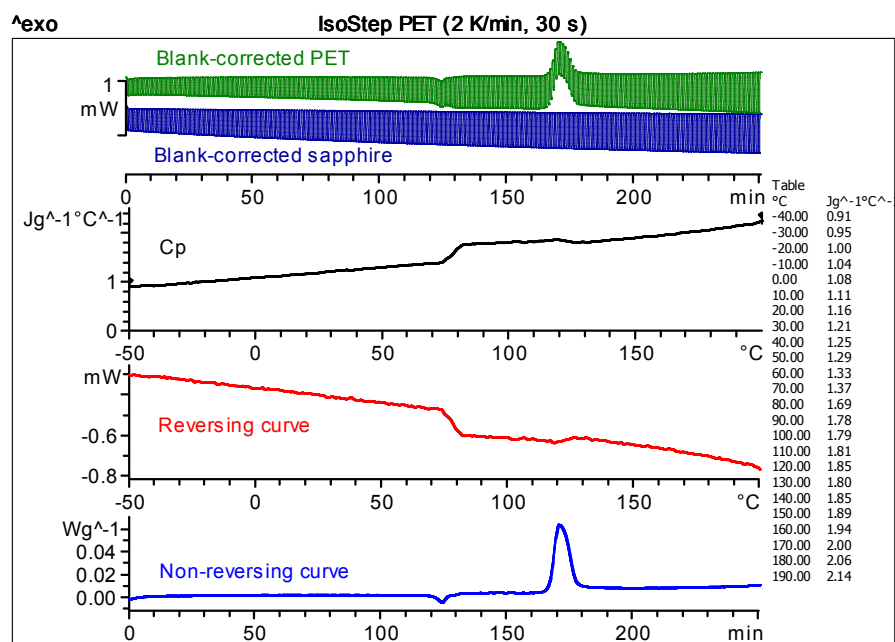


Figure 15.3. IsoStep[®] measurements of PET.

15.3 Alternating DSC

In alternating DSC (ADSC) [2] the temperature program is characterized by the underlying heating rate, β_0 , the temperature amplitude, T_a , and the duration of the periodically changing temperature, t_p , (Figure 15.4). For quasi-isothermal measurements, the underlying heating rate can also be set to zero. The choice of the parameters (β_0 , t_p , T_a) depends to a large extent on the sample. Typical values are 1 to 3 K/min for β_0 , 30 to 120 s for t_p and 0.5 to 2 K for T_a .

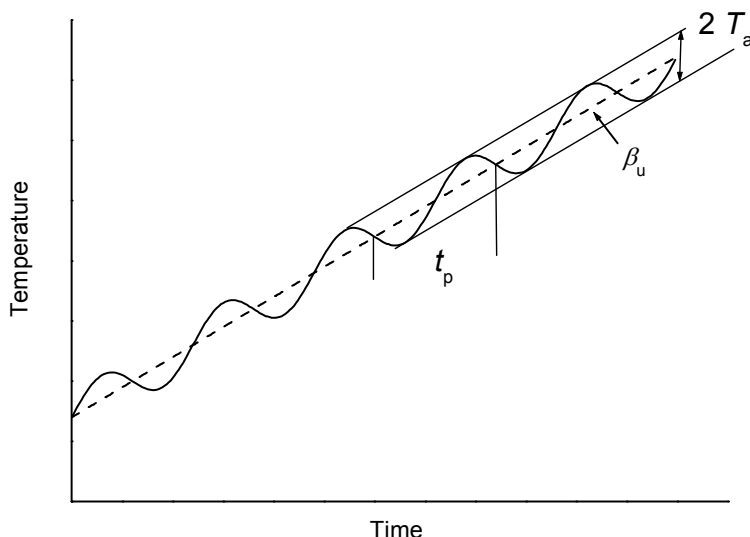


Figure 15.4. Typical ADSC temperature program: β_u is the underlying heating rate, T_a the temperature amplitude, t_p the period.

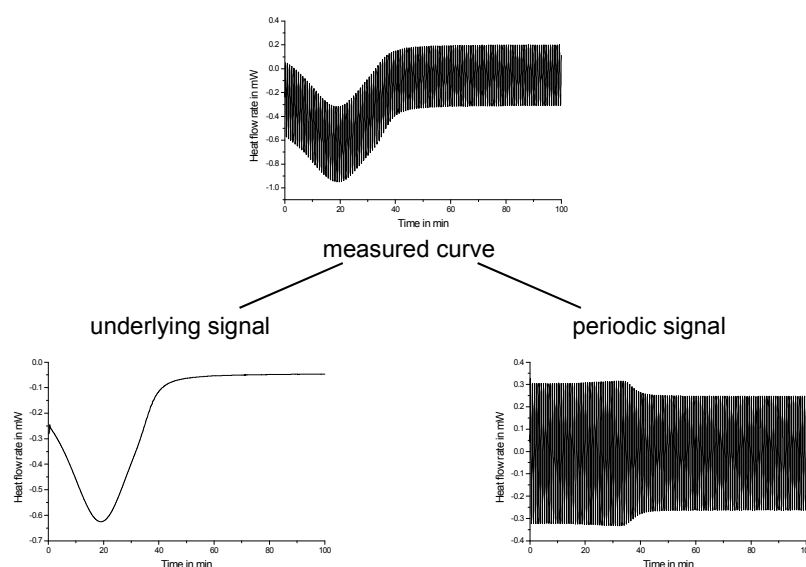


Figure 15.5. Separation of the measured ADSC curve into the underlying and the periodic signal components.

As a result of temperature modulation, the measured heat flow changes periodically. This can be separated into two parts as shown in Figure 15.5. Signal averaging yields the underlying signal (total heat flow), which corresponds to the conventional DSC curve. Additionally, one also obtains the periodic signal component. This is characterized by the amplitude of the heat flow and the phase shift between the actual (modulated) heating rate and the heat flow. The heat capacity (complex heat capacity) can then be determined from the amplitudes of the heating rate and the heat flow and the phase shift. One advantage of this technique is that it allows processes that occur simultaneously to be separated. For example, the change in heat capacity during a chemical reaction can be measured directly.

The evaluation of an ADSC measurement provides information about the complex heat capacity of the sample, which is frequency dependent, and in addition about different heat flows. The individual results can be calculated as follows (see also Figure 15.6):

$$\text{Complex heat capacity:} \quad \left| c_p^* \right| = \frac{\hat{\Phi}_m}{m \cdot (\beta_0 + \frac{2\pi}{t_p} T_A)} \quad (15.2)$$

$$cp \text{ in-phase:} \quad c_p' = \left| c_p^* \right| \sin \varphi \quad (15.3)$$

$$90^\circ \text{ phase-shifted component:} \quad c_p'' = \left| c_p^* \right| \cos \varphi \quad (15.4)$$

Here Φ_m is the amplitude of the modulated heat flow, β_0 the underlying heating rate, t_p the period and T_A the amplitude of the modulation, and φ the phase angle between the modulated heat flow and the modulated heating rate.

The total heat flow, Φ_{tot} is the moving average of the modulated heat flow:

$$\Phi_{\text{tot}}(t) = \int_{t-T/2}^{t+T/2} \Phi_m(t') dt' \quad (15.5)$$

The reversing heat flow, Φ_{rev} is the amplitude of the “in-phase” component of the modulated heat flow:

$$\Phi_{\text{ref}} = m \cdot c_p' \cdot \beta_0 \quad (15.6)$$

The non-reversing heat flow, Φ_{nr} is the total heat flow – reversing heat flow.

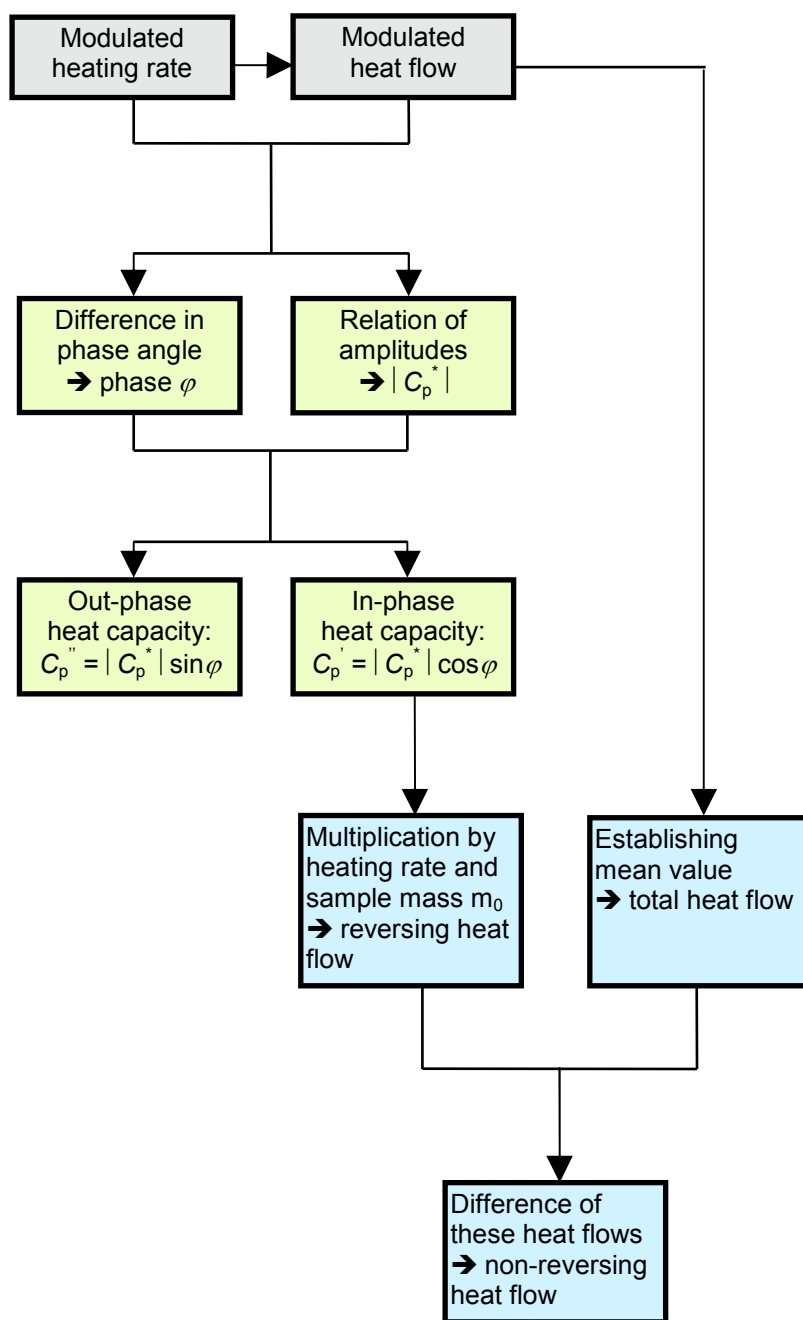


Figure 15.6. Flow diagram describing the ADSC evaluation.

Application Examples of ADSC

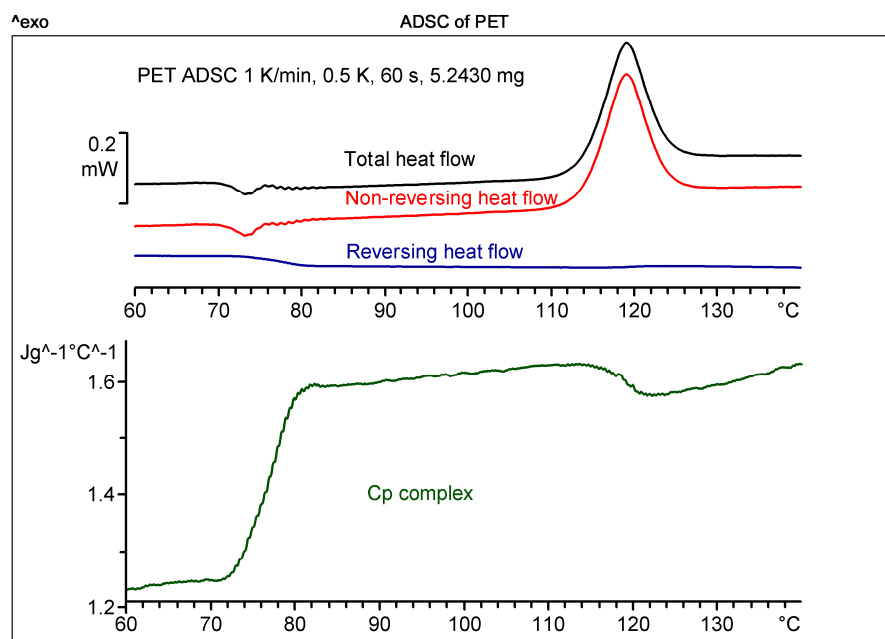


Figure 15.7. Glass transition and cold crystallization of PET.

Figure 15.7 shows the results of an ADSC experiment performed on PET. Measurement conditions: underlying heating rate 2 K/min, modulation amplitude 0.8 K, period 1 min. The total heat flow corresponds to the curve obtained in a DSC experiment at constant heating rate. The glass transition with the enthalpy relaxation peak and the cold crystallization can be clearly seen. In the reversing heat flow curve the glass transition is observed without the relaxation peak. The non-reversing heat flow shows the enthalpy relaxation and the exothermic crystallization. After the cold crystallization, the reversing heat flow increases slightly as a result of the change in the heat capacity of the sample. This can also be seen in the complex heat capacity curve.

A comparison of the measurements obtained with IsoStep[®] with those from ADSC shows that both techniques provide similar results. The difference between the two techniques is that a complex heat capacity can be determined with ADSC, whereas this is not possible with IsoStep[®].

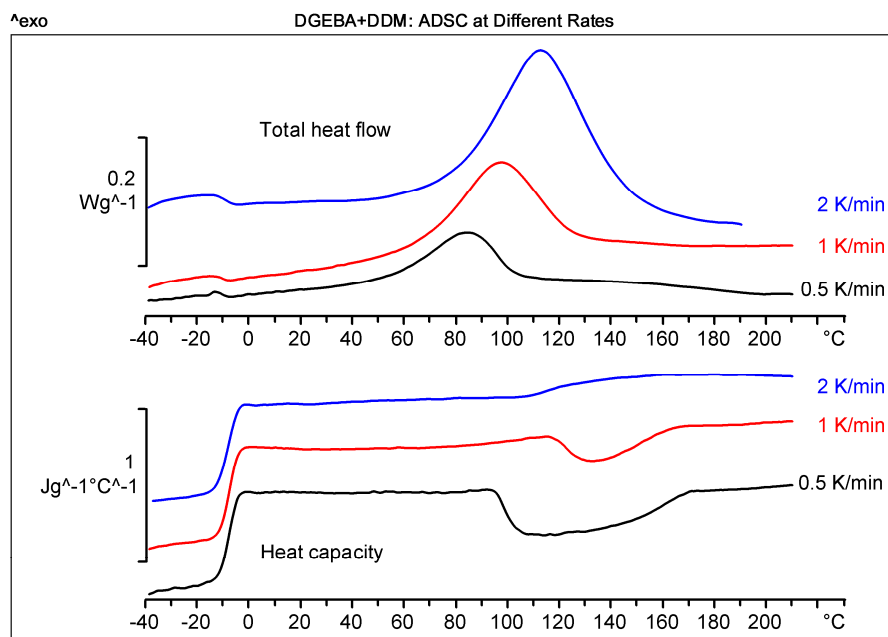


Figure 15.8. Vitrification of a DGEBA (diglycidylether of bisphenol A) and DDM (diaminophenylmethane) epoxy system during curing.

Figure 15.8 shows the curing reaction on an epoxy system. During curing, the glass transition temperature of the partially cured sample can reach the current sample temperature. In this case, the sample vitrifies and the curing process practically stops. The result is a sample that is not completely cured. This vitrification process can be detected by ADSC. The total heat flow curve exhibits a broad exothermic peak whose area corresponds to the energy released in the curing process. The total heat capacity curve shows whether the sample vitrifies and at what temperature this occurs; vitrification results in the curing reaction practically stopping. When the sample is heated at 0.5 K/min, vitrification takes place at about 95 °C. Devitrification (the glass transition of the cured sample) can also be seen at about 163 °C. Vitrification of the sample cannot be observed without the use of temperature-modulated DSC.

15.4 TOPEM[®]

TOPEM[®] is a TMDSC technique that is based on a full mathematical analysis of the response of a DSC (both the apparatus and the sample) to a stochastically modulated underlying temperature program [3]. Figure 15.9 illustrates the basic measurement principle of the DSC TOPEM[®] technique.

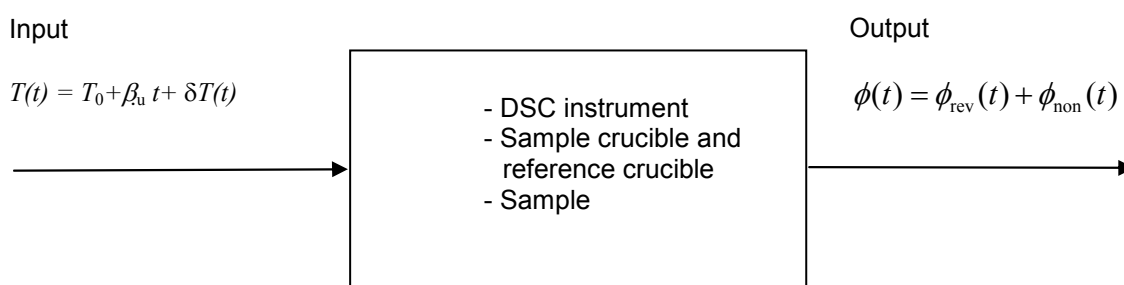


Figure 15.9. Schematic representation of a DSC measurement.

In a TOPEM[®] measurement, the input signal is the sum of the underlying temperature ramp $T_0 + \beta_u t$ where T_0 is the start temperature, β_u the underlying heating rate, and t the time, and $\delta T(t)$ a stochastic temperature modulation. The measured heat flow consists of a reversing component $\phi_{rev}(t)$ and a non-reversing component $\phi_{non}(t)$.

The analysis of the DSC system is based on the following assumptions:

1. The DSC is considered as a linear, time invariant system during a sufficiently long time interval and for a reasonably small temperature modulation.
2. The sample response to the temperature program can be separated into a linear response (reversing heat flow) and a non-linear response (non-reversing heat flow). It assumes that the non-reversing processes are slow. This assumption applies to the sample - only slow non-reversing effects are allowed. An effect is considered to be slow if its timescale is larger than what has been called a sufficiently long time interval.

These assumptions are in fact made for all known TMDSC techniques.

To sample the response of the DSC system, TOPEM[®] makes use of a stochastic temperature modulation. Ideally, the modulation consists of step-like temperature increments and decrements with random interval lengths along the underlying heating rate. The actual DSC cell temperature (see Figure 15.10) as well as the resulting heat flow (see Figure 15.11) are recorded.

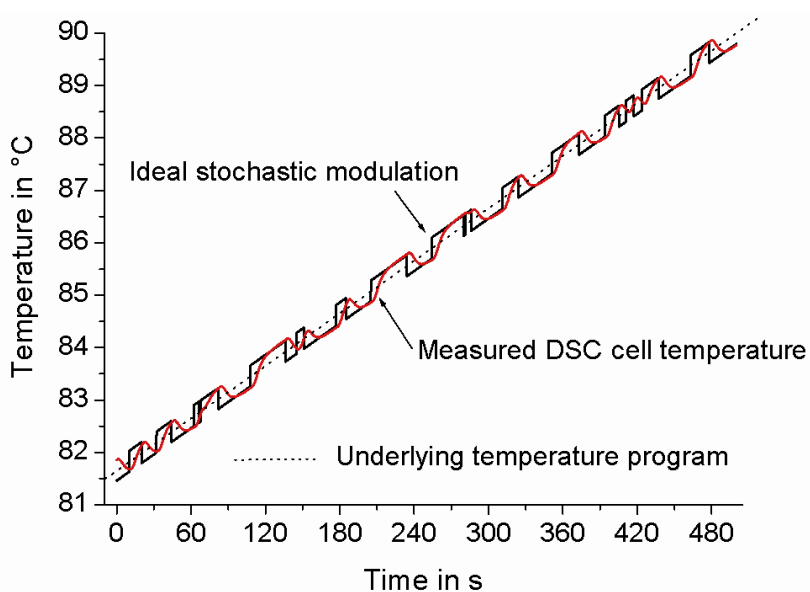


Figure 15.10. TOPEM[®] temperature program and measured DSC cell temperature.

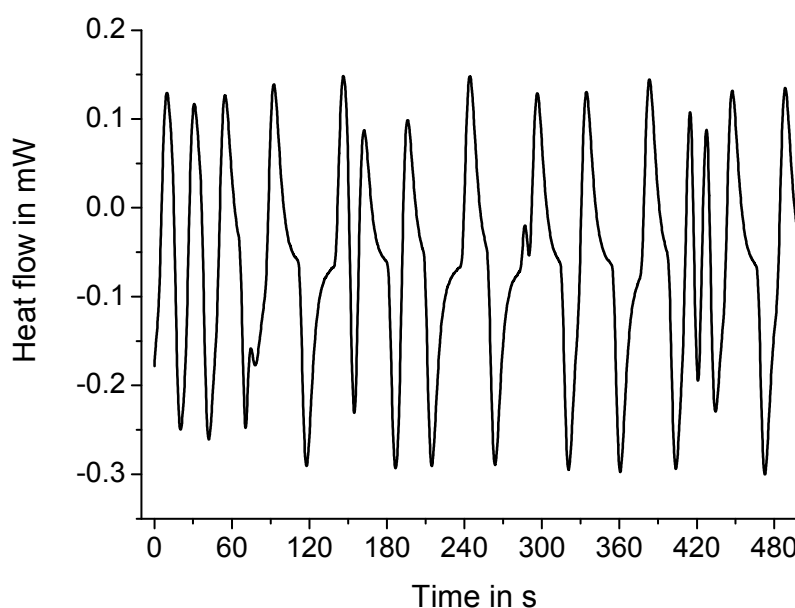


Figure 15.11. TOPEM[®] heat flow signal.

The TOPEM[®] technique consists of four main steps.

Step 1: The input signal is the measured temperature of the DSC resulting from a superimposition of a conventional temperature program with a small stochastic temperature modulation. The measured heat flow is the output signal.

Step 2: The analysis of the correlation between the input signal and the output signal uses a mathematical procedure. As a result, the heat flow is separated in two components: a component that correlates with the input signal, and another component that does not correlate with the input signal. The correlated component characterizes the linear behavior of the system sample-instrument. The heat flow component that does not correlate with the heating rate is determined from the excess heat capacity. This is the non-reversing heat flow.

Step 3: The cross-correlation function between heating rate and heat flow is determined from the characterized system. This function is equivalent to the heat flow signal measured as the response to a small temperature step normalized with respect to the height of the temperature step. The integration of this function delivers the quasi-static heat capacity $c_{p,0}$ and the reversing heat flow $\Phi_{\text{rev}} = m c_{p,0} \beta_u$. The total heat flow is the sum of reversing and non-reversing heat flows.

Step 4: Using the multi-frequency evaluation of the characterized system, the frequency-dependent complex heat capacity can be determined for any frequency.

TOPEM[®] allows the dynamic behavior of the sample to be analyzed over a wide frequency range in one single measurement. The reversing heat flow signal based on the quasi-static heat capacity and the non-reversing heat flow signal is a direct result of the correlation analysis.

Application examples of TOPEM[®]

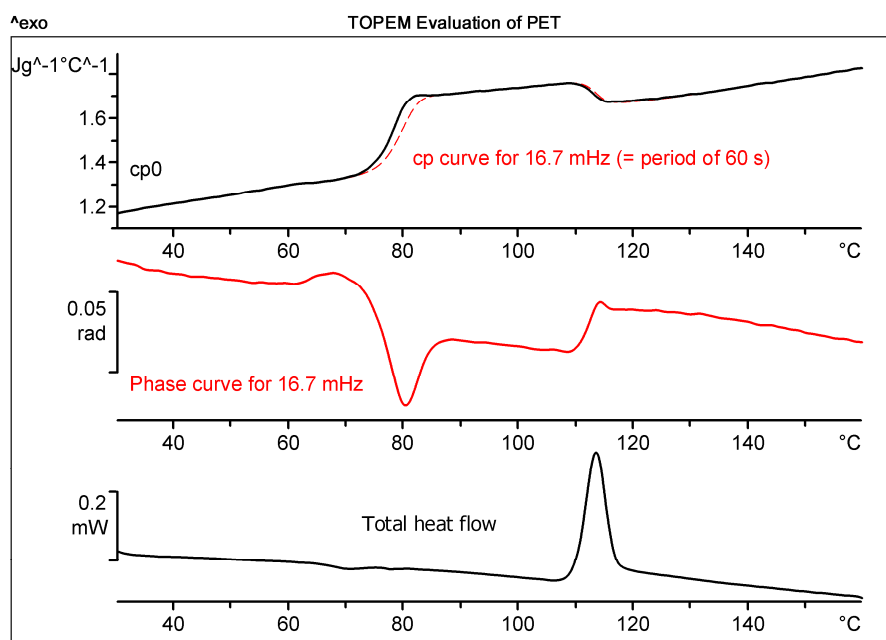


Figure 15.12. Curves obtained from a TOPEM[®] measurement show the glass transition and cold crystallization of amorphous PET.

Amorphous polyethylene terephthalate (PET) exhibits a glass transition at about 75–80 °C and then begins to crystallize. This behavior was measured at an underlying heating rate of 0.1 K/min (Figure 15.12). The maximum pulse height was 0.5 K. Just as in a conventional DSC curve, the total heat flow shows a step at the glass transition and at the crystallization peak at 110 °C. The quasi-static heat capacity, $c_{p,0}$, increases at the glass transition but decreases on crystallization because the content of mobile amorphous material decreases. The different molecular dynamics associated with these two c_p steps is apparent in their frequency dependence. The glass transition step is shifted to higher temperatures with increasing frequency, whereas in the crystallization region the frequency curves are identical. At the glass transition, the peak temperature of the phase is determined by the molecular relaxation process.

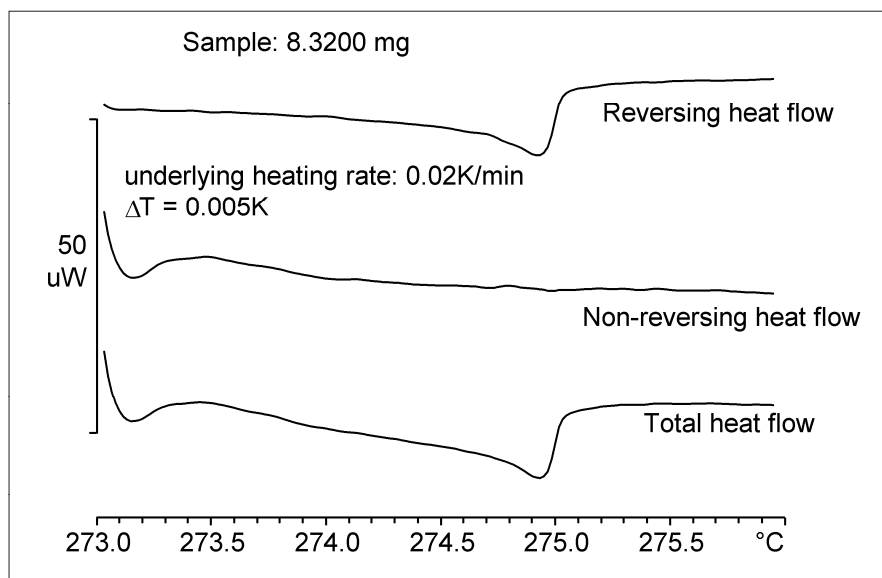


Figure 15.13. Total, reversing and non-reversing heat flow curves of the solid-solid phase transition of sodium nitrate at 275 °C.

In second order phase transitions, the heat capacity first increases to a critical temperature and then suddenly decreases. It is a phenomenon that does not involve latent heat. Correspondingly, no measurement effects are expected in the non-reversing heat flow curve.

As an example, the solid-solid transition of sodium nitrate at 275 °C was measured (see Figure 15.13). Since the change in heat capacity after the critical temperature is expected to take place over a very narrow temperature range (about 0.1 K), a measurement can only be successful if it is performed at a very low heating rate using a very small temperature modulation. In this case, an underlying heating rate of 20 mK/min and a pulse height of 5 mK were used. The resulting heat flow curves are shown in Figure 15.13. As expected, only the reversing and total heat flow curves exhibit the transition peak. The non-reversing heat flow curve does not show any effect despite the sharp change after the critical temperature. This proves that TOPEM[®] is clearly able to differentiate between effects involving latent heat and sensible heat.

Compared with other TMDSC techniques, TOPEM[®] offers the following advantages:

1. The quasi-static heat capacity as well as quasi-static reversing and non-reversing heat flows are available.
2. The frequency dependency of the complex heat capacity (c_p^* , c_p' , c_p'' , phase angle) is determined from one single experiment.
3. The frequency-dependent complex heat capacity can be calibrated by using the quasi-static quantities.

TOPEM[®] is therefore a unique tool for heat capacity measurements (quasi-static and frequency dependent) as well as for the separation of the heat flow into reversing and non-reversing components.

Quantity	IsoStep [®]	ADSC	TOPEM [®]
Total heat flow	No	Yes	Yes
Sensible heat flow	Yes (c_{p0} based)	Yes (c_p based)	Yes (c_{p0} based)
Latent heat flow	Yes	Yes	Yes
Quasi-static c_{p0}	Yes	No	Yes
Complex $ c_p^* $	No	Yes	Yes
Real c_p'	No	1	Yes, unlimited number*
Imaginary c_p''	No	1	Yes, unlimited number *
Phase φ	No	1	Yes, unlimited number *
Comments	• Easy to understand • Based on the c_p sapphire standard method • Sapphire used as reference	• Widely used TMDSC method • Aluminum used as reference	• Simultaneous, multi-frequency technique • Sapphire used as reference
* means that for each selected frequency such a curve can be calculated			

Table 15.1. Comparison of the three TMDSC techniques.

References and Further Reading

- [1] METTLER TOLEDO Data Sheet: “IsoStep[®]”.
- [2] METTLER TOLEDO Data Sheet: “ADSC”.
- [3] METTLER TOLEDO Data Sheet: “TOPEM[®] - the new advanced multi-frequency TMDSC technique.”
- [4] Mike Reading and Douglas J. Hourston, Modulated-Temperature Differential Scanning Calorimetry: Theoretical and Practical Applications in Polymer Characterisation (Hot Topics in Thermal Analysis and Calorimetry), Springer Netherlands, paperback, 2006.
- [5] Peter Haines, Principles of Thermal Analysis and Calorimetry, Royal Society of Chemistry, 2002.
- [6] Paul Gabbott, Principles and Applications of Thermal Analysis, Blackwell Publishing, 2008.

UserCom: Many of the application examples in this chapter have been taken from UserCom, the METTLER TOLEDO technical customer journal that is published twice a year. Back issues of UserCom can be downloaded as PDFs from the Internet at www.mt.com/ta-usercoms.

16 Evolved Gas Analysis

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Thermogravimetric Analysis (TGA) is a technique that provides quantitative information on the change in mass of a sample as a function of time as it is heated, cooled or held at constant temperature. TGA alone, however, is not an identification technique.

The combination of TGA with a mass spectrometer (MS) or a Fourier transform infrared spectrometer (FTIR) allows the nature of the gaseous products formed in the TGA to be investigated online. When several compounds are evolved, the MS or FTIR can track their evolution profiles. Mass spectra and infrared spectra are substance-specific. The spectra can be used to characterize the substance or class of substance through spectral interpretation and comparison with database reference spectra. Decomposition pathways can thereby be elucidated.

	Features	Benefits
TGA-MS	High sensitivity coupled with very fast measurement	Extremely small amounts of substances can be detected. Ideal for the online characterization of all types of volatile compounds.
TGA-FTIR	High chemical specificity and fast measurement	Characterizes substances by identifying their functional groups, i.e. the class of substance. Ideal for the online measurement of substances that exhibit medium to strong infrared absorption.

16.1 Brief Introduction to Mass Spectrometry

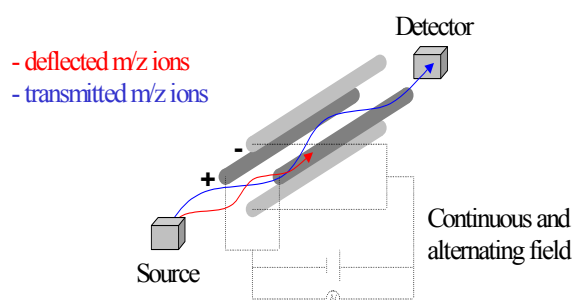


Figure 16.1. Operating principle of a quadrupole mass spectrometer.

Mass spectrometry characterizes substances by identifying and measuring the intensity of molecular fragment ions of different mass to charge ratio (m/z).

The gas molecules entering the mass spectrometer from the thermobalance are first ionized in the ion source. The positive molecular ion and fragment ions formed are then separated according to their m/z value by a combination of magnetic and electrostatic fields. A mass spectrum is recorded by scanning the field strength so that ions of increasing m/z ratio arrive at the detector.

In a TGA-MS system, the mass spectrometer is usually set to monitor particular m/z values that are characteristic for specific structural features.

16.2 Brief Introduction to Fourier Transform Infrared Spectrometry

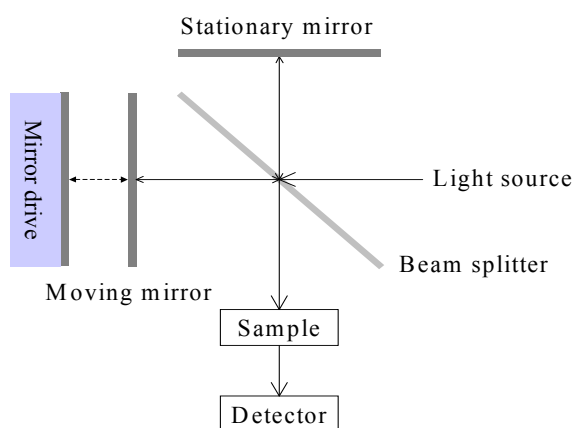


Figure 16.2. Operating principle of an FTIR spectrometer.

Infrared spectroscopy measures the light absorbed by different types of vibration in molecules.

Infrared radiation from the light source is divided into two beams by the beam splitter. One beam is reflected onto a moving mirror and the other onto a stationary mirror. Both beams are then recombined and pass through the sample to the detector. Fourier transformation of the resulting interferogram yields an infrared transmission spectrum.

In TGA-FTIR, the absorption bands of each spectrum are usually simultaneously integrated over the entire spectral range or over characteristic spectral regions. The intensity is presented as a function of time as so-called Gram-Schmidt curves or chemigrams.

16.3 Coupling the TGA to a Gas Analyzer

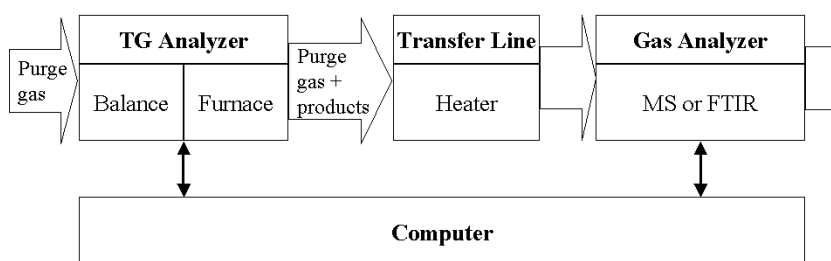


Figure 16.3. Coupling the TGA to a gas analyzer.

In the **TGA-MS combination**, the TGA is coupled to the MS using a fused silica capillary tube heated at 200 °C to prevent condensation. A small part of the gases evolved from the sample in the TGA is sucked into the MS. The sensitivity is so great that only about 1% of the effluent gas is required. The purge gas is argon or nitrogen.

In contrast, the **TGA-FTIR combination** uses the total volume of purge gas and gaseous decomposition products from the TGA. The gases are transferred through a heated glass-coated steel transfer capillary line into a heated gas cell installed in the FTIR spectrometer. Nitrogen, which does not exhibit IR-absorption, is used as the purge gas.

These so-called hyphenated techniques are used in research and development, in quality control and to investigate material failure. Typical applications are for example:

- Thermal degradation processes (oxidation, pyrolysis).
- Vaporization and sublimation.
- Detection of additives in a matrix.
- Characterization of starting materials and end products.
- Investigation of chemical reactions (catalysis, syntheses, polymerization).
- Outgassing and adsorption/desorption behavior.

16.4 Examples

16.4.1 Decomposition of Calcium Oxalate Monohydrate (TGA-MS)

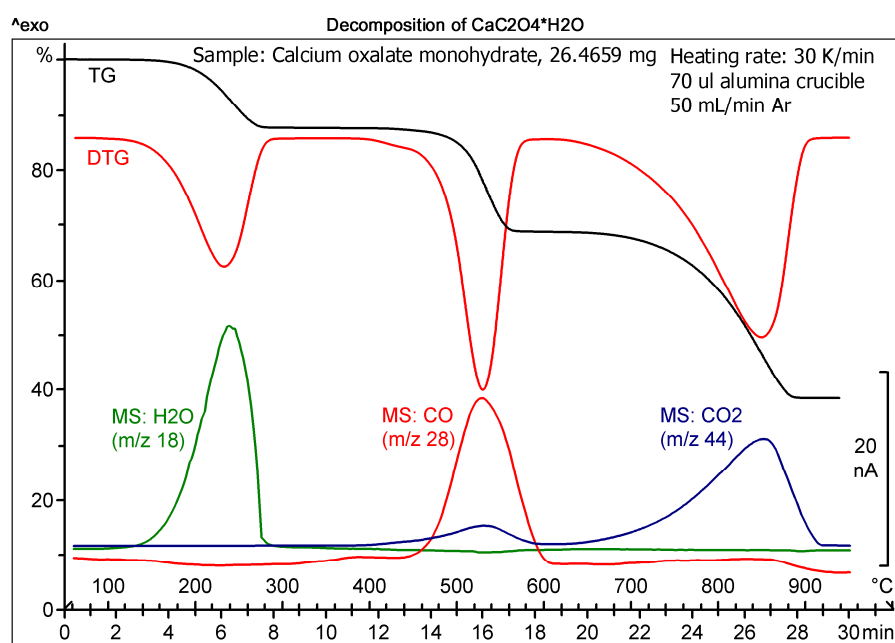


Figure 16.4. TGA-DTG-MS curves of the thermal decomposition of calcium oxalate monohydrate.

The diagram shows that calcium oxalate monohydrate decomposes in three distinct steps. The MS fragment ion curves for water (m/z 18), CO (m/z 28) and CO_2 (m/z 44) display peaks that correspond closely to the individual steps in the TGA curve. The first mass loss step relates to the elimination and vaporization of water of crystallization; the second step to the decomposition of anhydrous calcium oxalate with formation of CO; and the third step to the decomposition of calcium carbonate to calcium oxide and CO_2 . The m/z 44 ion curve shows that CO_2 is also formed in the second step at 550 °C (besides CO). This is due to the disproportionation reaction of CO to CO_2 and carbon.

16.4.2 Pyrolysis of PVC (TGA-FTIR)

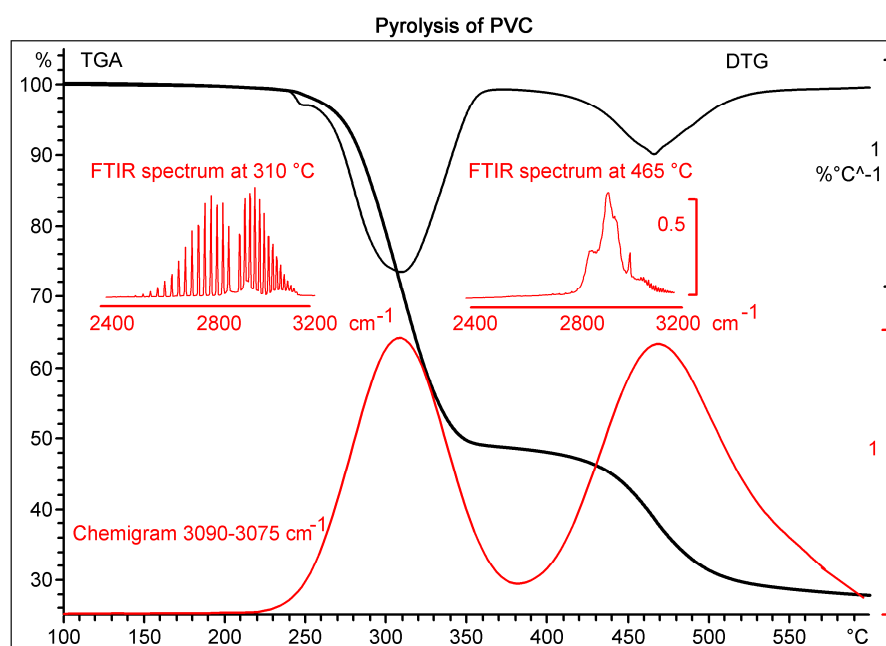
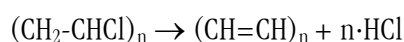


Figure 16.5. The thermal degradation of polyvinylchloride.

This example describes the thermal degradation of PVC. The TGA weight loss curve exhibits two clear steps. The IR spectrum (above left) measured at the maximum of the peak at 310 °C corresponds to HCl formed through the reaction



The spectrum measured at the maximum of the second peak at 465 °C (above right) is due to benzene formed through the cyclization of $(\text{CH=CH})_n$. The curve in the lower part of the diagram shows a chemigram in the wavenumber range 3090 to 3075 cm^{-1} . Absorption bands in this region are characteristic for molecules with aromatic rings (C-H stretching vibrations).

16.4.3 Detection of Solvents in Pharmaceutical Substances (TGA-MS)

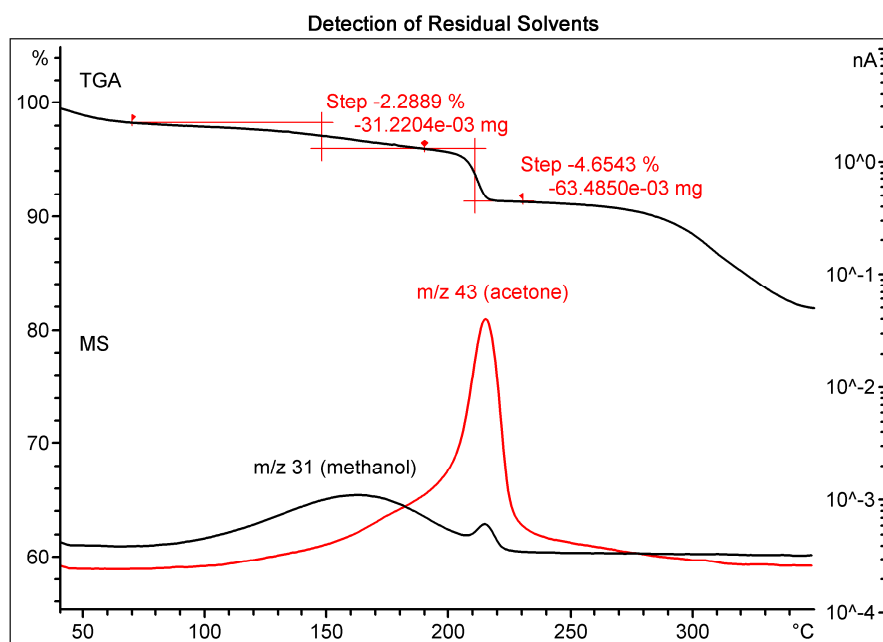


Figure 16.6. Thermogravimetric analysis of a pharmaceutical substance.

Different solvents are often used both in the synthesis of a pharmaceutical substance and afterward for its purification/recrystallization. The presence of residual amounts of solvents in a substance can influence its properties. The solvents concerned must therefore be identified and their concentration kept as low as possible.

The TGA curve exhibits several mass loss steps. In the final step above 250 °C, the substance begins to decompose. The two steps in the range 70–240 °C indicate that moisture or solvents are lost through heating. The simultaneously recorded MS ion curves confirm that the mass loss steps correspond to methanol (m/z 31) and acetone (m/z 43, the main fragment ion of acetone).

The methanol is released over a wide temperature range. In comparison, the acetone is eliminated in a much narrower temperature range. This indicates that the acetone is more firmly bound, possibly as a solvate.

References and Further Reading

- [1] METTLER TOLEDO Collected Applications Handbook: "Evolved Gas Analysis".

17 TGA Sorption Analysis

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Recent surveys among users of thermal analysis equipment have confirmed that one of the current trends in modern thermal analysis is to control the gas atmosphere surrounding the sample. This can involve the use of reactive gases, the application of vacuum or pressure, or setting different levels of relative humidity (RH).

In particular, investigations at defined relative humidity are becoming more and more important. This can be achieved by the application of a TGA Sorption Analyzer System [1].

17.1 Brief Introduction to TGA Sorption Analysis

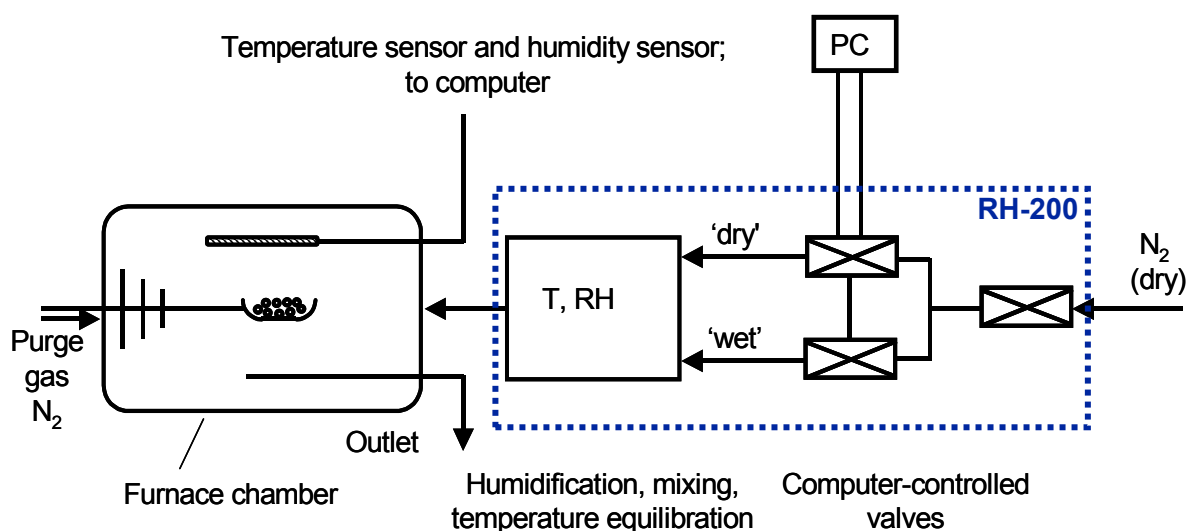


Figure 17.1. Operating principle of a TGA sorption analyzer system.

A specially built water vapor generator is connected to the gas outlet of the TGA. The humidified gas is passed from the water vapor generator via a heated transfer line and a specially designed interface directly into the furnace chamber. The furnace chamber in fact serves as a controlled environmental chamber. The chamber temperature is maintained at a defined constant temperature during the measurement (Figure 17.1).

A dew point sensor inside regulates the water vapor generator so that defined humidity steps can be set.

This type of humidity-sorption measurement (dynamic vapor sorption, DVS) places special demands on the thermobalance:

- The humidified gas must be supplied without condensation or cooling occurring.
- The exhaust gas should flow out of the cell in a defined way without condensation so that further analysis, e.g. online GC-MS, is possible.

To satisfy these requirements, the instrument was specially modified with a thermostated furnace lid, sorption interface, O-ring seal and defined diameter stainless steel inlet and outlet tubes. The outlet tube is maintained at constant temperature by a heat exchanger. A thermostat regulates the temperature at about 5 K higher than the temperature set

for the TGA experiment. A second thermostat maintains the balance housing at 22.0 °C. A flow of 5 mL/min protective gas is used to protect the microbalance from moisture.

The water vapor generator was specially developed for the DVS modification. The most important parts of the generator are the control unit (PC hardware and software) and the water vapor generator with its humidifying and mixing units. The dry inlet gas (N₂) is divided into two parts. One part, the wet flow, is at 100% RH (relative humidity), while the other part, the dry flow, remains dry (< 2% RH). The desired relative humidity in the furnace chamber can be adjusted by mixing dry and wet flow in the right proportions. The mixing ratio from “dry” to “wet” is set by means of computer-controlled valves triggered by the RH program (humidity steps). The total flow of humidified gas into the TGA furnace chamber is normally 100 mL/min.

The RH program can be changed while it is running and the start of the TGA sorption experiment can be triggered from the TGA.

TGA sorption experiments are used in research and development and in quality control. Some typical applications include the

- measurement of the dynamic vapor sorption (DVS) curve,
- determination of sorption isotherms,
- determination of BET and GAB parameters,
- determination of specific surface areas,
- determination of free and bound water,
- determination of sorption enthalpies, and the
- determination of low amorphous content.

17.2 Examples

17.2.1 Dynamic Sorption Curve of Amiloride Hydrochloride Dihydrate

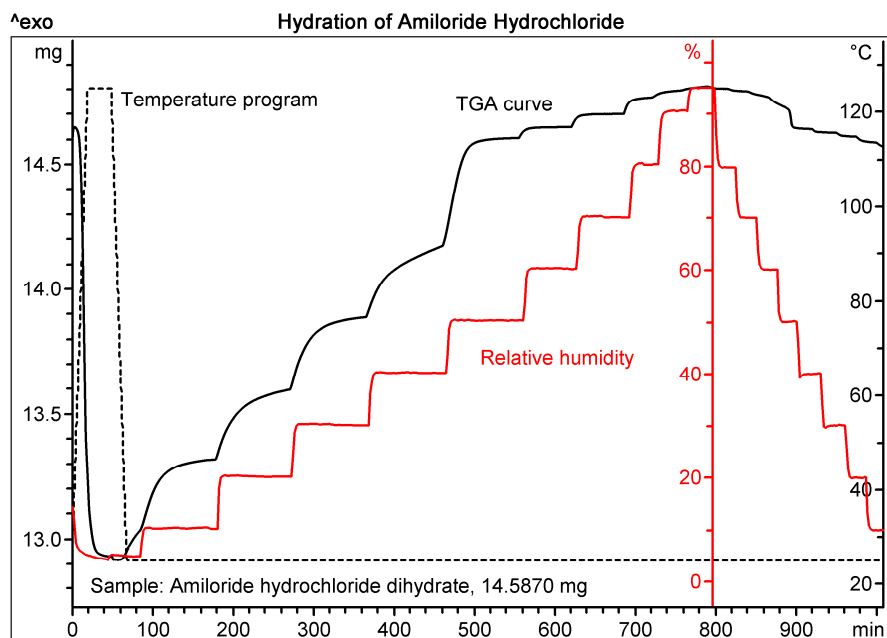


Figure 17.2. Uptake and release of moisture of amiloride hydrochloride dihydrate as a function of RH. The dihydrate can only be converted to the anhydride at a higher temperature in a dry atmosphere.

The TGA curve shows the uptake and release of moisture of a sample of amiloride hydrochloride dihydrate as a function of RH.

The different stages of the analysis consist of the

- temperature program with a pre-conditioning segment (dehydration) at 120 °C (dotted line),
- increase of RH in steps of 5% with equilibration (red curve), and the
- resulting weight changes for each 5% change in RH (black curve).

At a RH of 50%, the substance has regained its original water of crystallization. Further increase of RH results in the uptake of free surface water, which is released again when the RH is decreased [2].

17.2.2 Sorption Isotherm of Maltodextrin

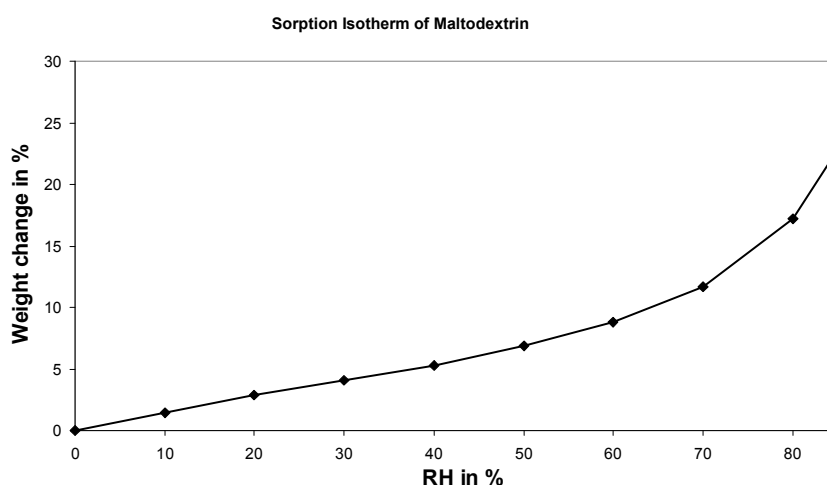


Figure 17.3. Sorption isotherm of maltodextrin.

The sorption isotherm of maltodextrin was calculated from the dynamic sorption curve using the end point of each sorption step [3].

The type of sorption isotherm can be compared with the five classified types of isotherm. This provides information on the type of sorption, the adsorbate surface and the monolayer formation.

The isotherm shown for maltodextrin is of type II and describes adsorption on macroporous adsorbents with strong and weak adsorbate-adsorbent interactions (type III isotherms have the same description but a different shape). Other types of isotherms relate to microporous adsorbents (type I) and adsorption isotherms with hysteresis (type IV and V).

17.2.3 Determination of Sorption Enthalpy of Starch

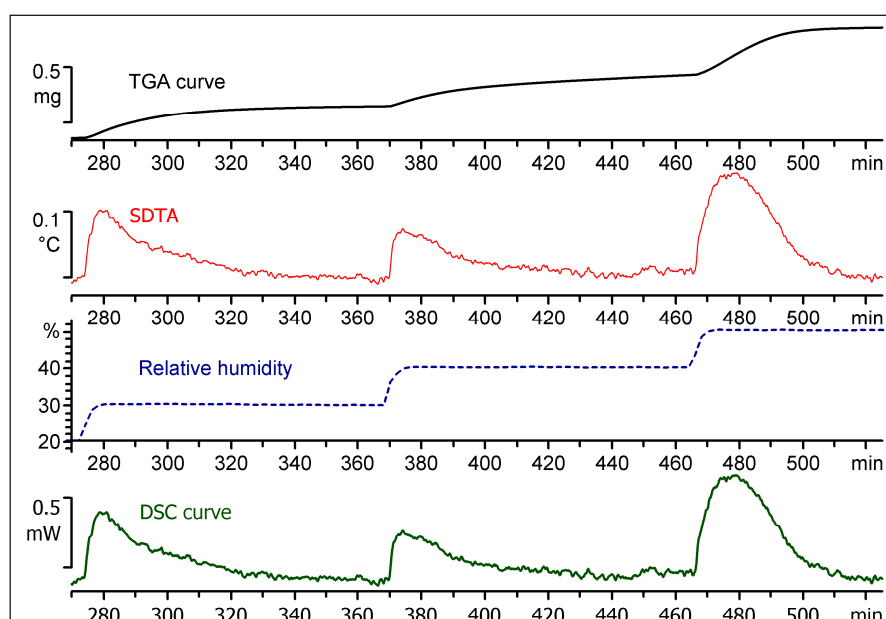


Figure 17.4. Sorption enthalpy of starch.

TGA sorption analyzer systems are equipped with the capability to measure sorption enthalpies.

In the figure, the heat flow data (DSC curve) shows the effect that a dynamic sorption program has on the enthalpy of a modified starch. The DSC curve shows an exothermic peak that slowly falls off after each RH step change. The integral of the area under the peak yields a value of about 42 J/g, which is typical for starch products [4].

The correlation between sorption enthalpies and moisture content allows the temperature dependence of water sorption to be described at any humidity. This offers many advantages in material characterization.

17.3 Calibration

Like any other analytical measurement system, the TGA sorption analyzer system has to be calibrated. Since no standards are available that show a defined weight increase at a certain set RH, the deliquescence behavior of certain compounds is used to calibrate the system [5]. Deliquescence is the process by which a substance absorbs water vapor from the air to form a solution. This occurs when the vapor pressure of the solution is less than the partial pressure of the water vapor in the air. The response is an increase in weight. The relative humidity at which deliquescence begins is called the deliquescence point. The examples shown in the plot at 25 °C cover a wide range of RH values:

- lithium chloride (11.3%)
- sodium bromide (59.1%)
- sodium chloride (75.5%)

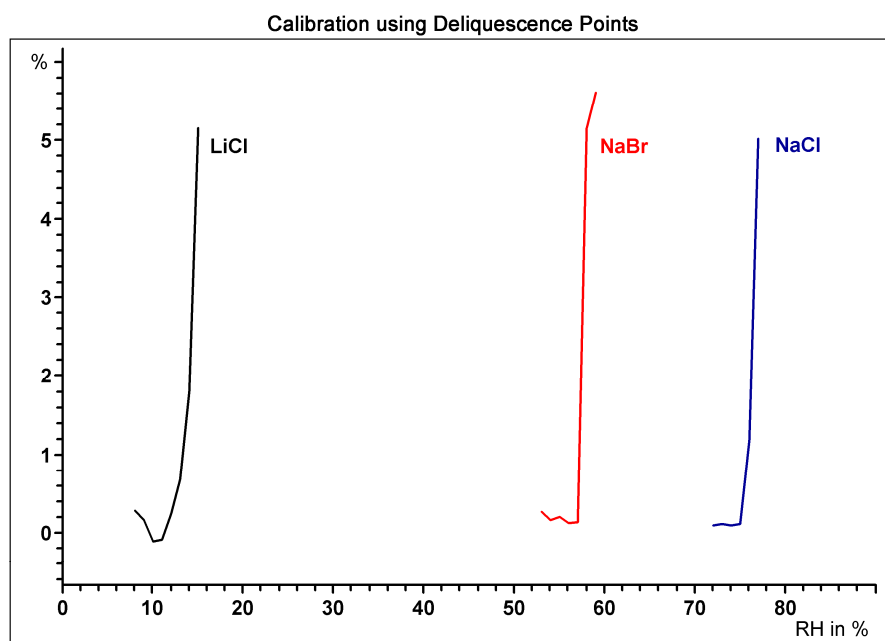


Figure 17.5. Deliquescence measurements of LiCl, NaBr and NaCl.

17.4 Typical Application Areas

Industry	Applications
Common for all industrial segments	Storage and stability, moisture migration, surface adsorption and thermal desorption and the processability of raw materials.
Pharmaceutical and personal care	Activity of ingredients, the effect of fillers, phase transformations, loss on drying, development of spray drying technology, moisture sorption and hydrophilic characterization.
Food flavorings and ingredients	Aging of food products, analysis of dehydrated structures, oxidation, non-enzymatic browning, enzymatic changes, material flow and crystallization, recrystallization of ice, plasticization and swelling characteristics.
Plastics (elastomers, thermosets, thermoplastics), films and fibers	The plasticization influence on material and product performance.
Catalyst and porous support materials	Variations in surface activity.
Construction materials and minerals	Stability of cement. Wood, metal and rust investigation. Impact on explosives.
Chemical	Fertilizers and surface activity.

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18 Thermoptometry

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18.1 Introduction

Thermoptometry is defined by IUPAC as

“A technique in which an optical characteristic of a substance (and/or its reaction product (s)) is measured as a function of temperature whilst the substance is subjected to a controlled temperature program.

Measurements of total light, light of specific wavelength(s), refractive index and luminescence lead to thermophotometry, thermospectrometry, thermorefractometry and thermoluminescence, respectively; observation under the microscope leads to thermomicroscopy.”

18.2 Thermomicroscopy

It is often difficult from a thermoanalytical measurement alone (e.g. DSC) to know what exactly occurs in the sample when it is heated. Additional information derived from the visual appearance can aid interpretation or support hypotheses that have already been proposed.

Results from thermal analysis coupled with optical analysis (thermo-optical analysis) can be obtained by using light transmission microscopy or reflected microscopy during the thermoanalytical measurement.

For thermal analysis transmission microscopy one uses hot-stage microscopy[1], while for thermal analysis reflection microscopy, DSC-microscopy is the method of choice [2].

In both cases, the sample in the measurement cell is observed using microscope optics with a digital or analog camera mounted. The camera is connected to a computer equipped with software that enables images to be captured and evaluated. A suitable image capture software should be able to display the temperature or the time in the case of isothermal measurements. If individual images are not of interest, the image intensity curve alone can also be recorded using a photomonitor. A typical measurement setup is shown in Figure 18.1.

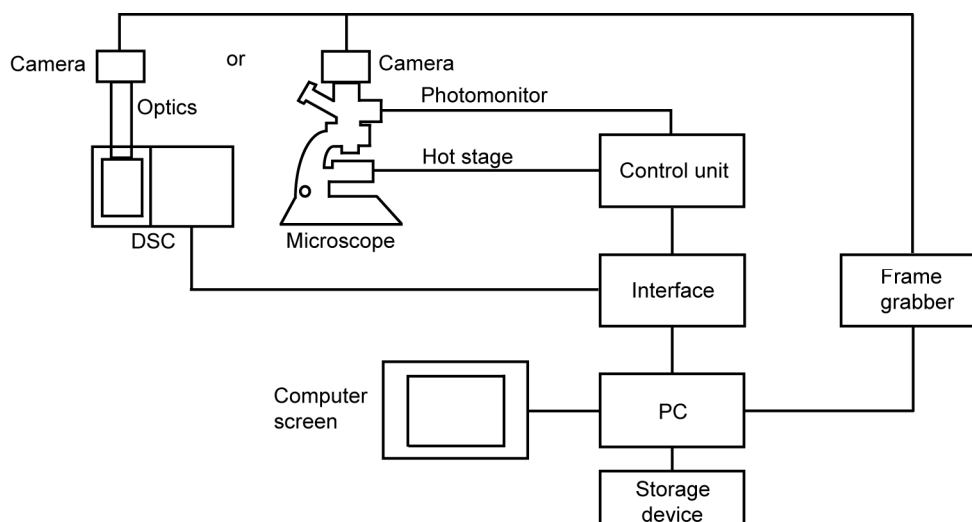


Figure 18.1. Instrumental setup for simultaneous hot-stage microscopy and DSC-microscopy.

Hot-stage microscopy allows samples to be measured in the temperature range $-60\text{ }^{\circ}\text{C}$ to $375\text{ }^{\circ}\text{C}$. Instruments with and without the possibility of simultaneous recording of heat flow are available. The design and focal length of the microscope should be able to accommodate the hot stage. A polarization accessory helps to distinguish between different crystal morphologies.

Typical applications of hot stage microscopy include studies of substances that exhibit polymorphism, investigations on liquid crystals, and the determination of crystallization behavior of polymers.

The following example describes a typical investigation of polymorphism using hot-stage microscopy (see Chapter 14 “Polymorphism”).

Sulfapyridine belongs to a class of drugs known as sulfonamides, which exert a powerful antibacterial action. The most well-known form in which it is used today is sulfasalazine, a substance with a structure derived from sulfapyridine and salicylic acid that is used to treat rheumatic arthritis. Studies of the polymorphism of sulfapyridine can be found in the pharmacological literature.

Sulfapyridine exhibits crystallization and several solid-solid transitions as soon as it is heated from the glassy state. These transitions can be easily observed in the DSC curve (Figure 18.2), but it is not possible to know which transition occurs at any instant.

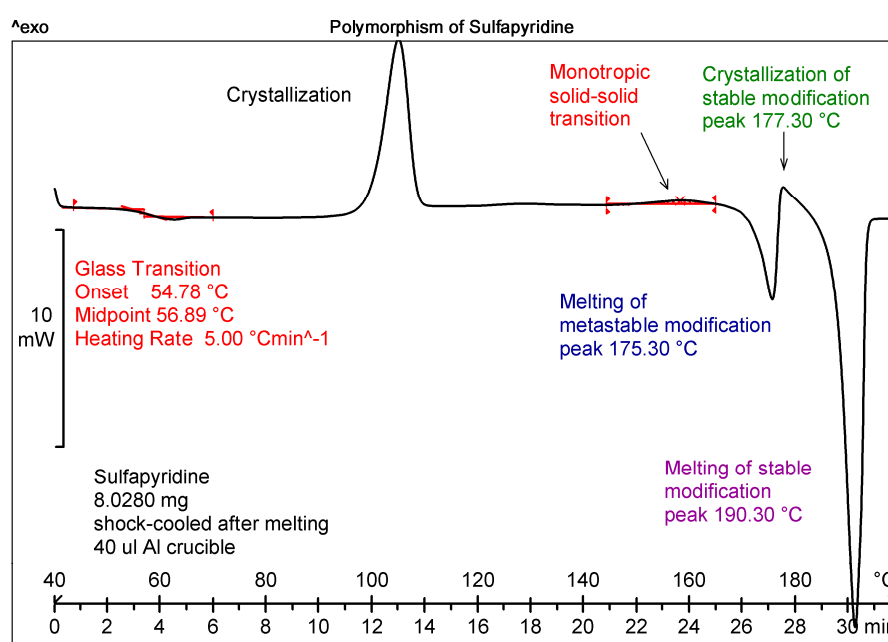


Figure 18.2. DSC curve of sulfapyridine.

By using an FP82 with image display system, it is possible to identify the individual processes that correspond to each DSC peak [1]. Figure 18.3 shows the sample at 120.1 °C. Spherulite crystals have grown out of the glassy phase.

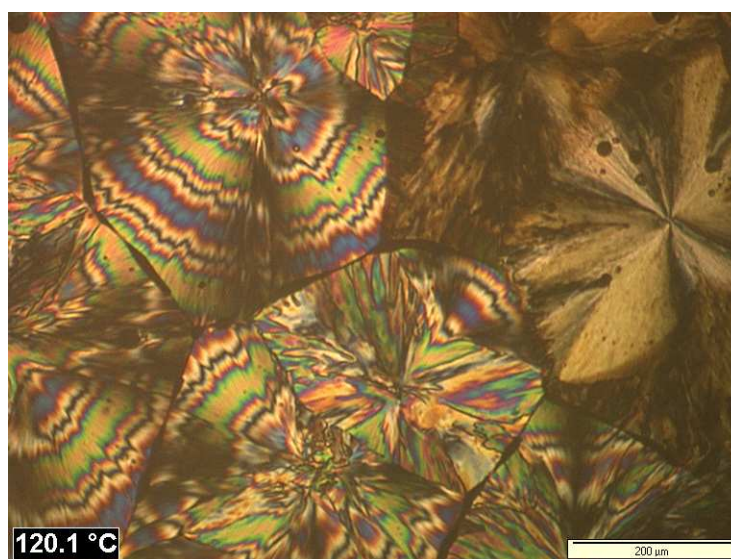


Figure 18.3. Sulfapyridine at 120.1 °C.

At 176.6 °C (Figure 18.4) the spherulites have changed through melting and recrystallization to the new rhombic modification.

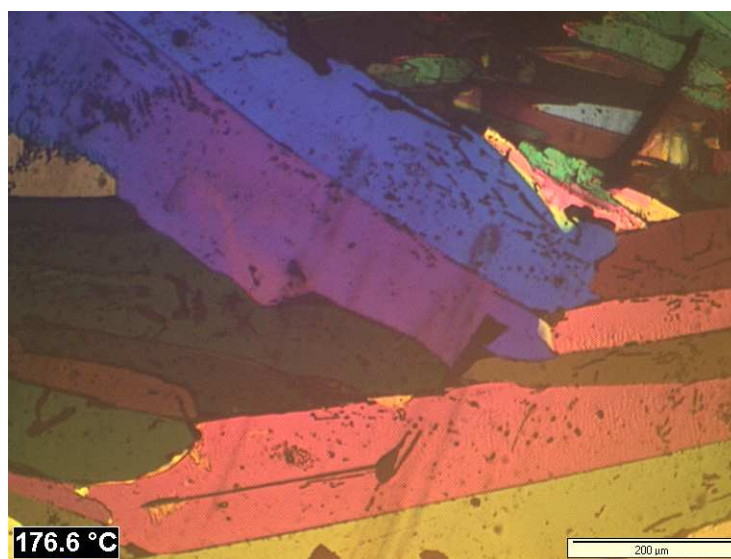


Figure 18.4. Sulfapyridine at 176.6 °C.

DSC microscopy requires a stand and a suitable interface for the microscope optics. The interface allows the optics to be focused and accommodates the light guide from the light source.

The technique can be used in the temperature range from room temperature up to 700 °C. The pressure range is from atmospheric pressure up to 20 bar (2 MPa). Applications include the investigation of thermochromic behavior, crystallization from solution, and the melting behavior of polymers. The example in Figure 18.5 shows the solid-solid thermochromic transition of HgI₂ measured using a high-pressure DSC equipped with microscope optics and a digital camera [2].

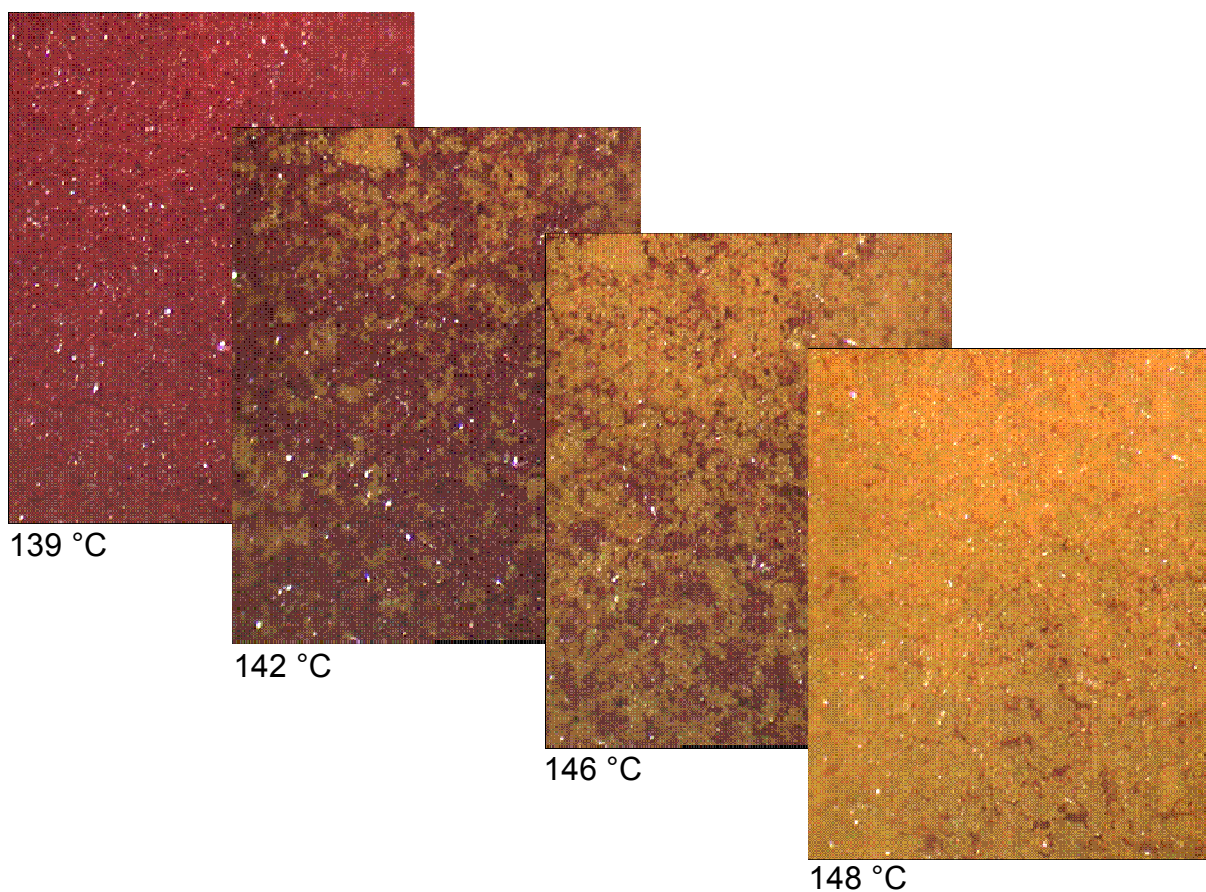
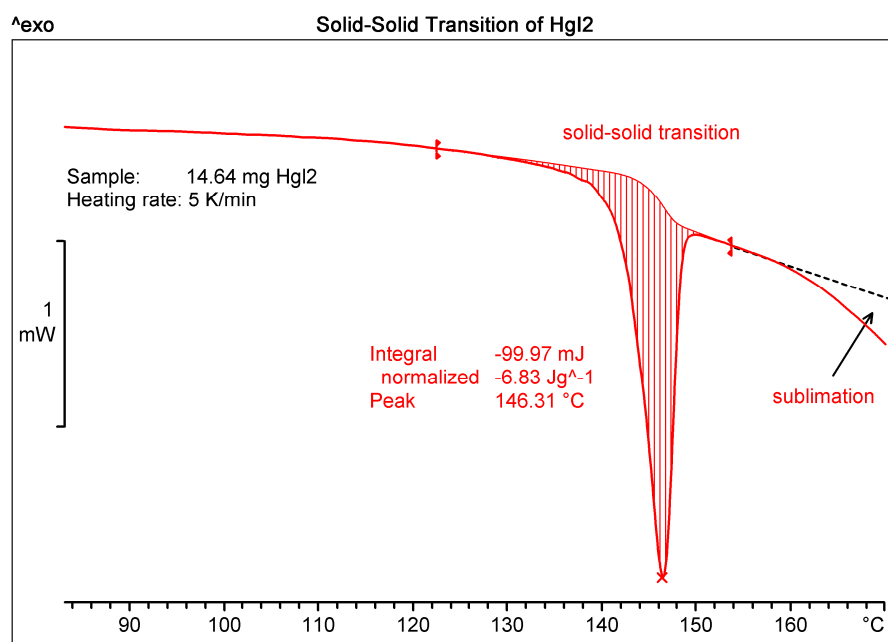


Figure 18.5. Above: DSC curve of HgI₂. Below: Images of the material at different temperatures during the solid-solid transition.

18.3 Chemiluminescence in Thermal Analysis

18.3.1 Introduction

Chemiluminescence (CL) is the term used to describe the emission of (usually) visible light as a direct result of a chemical reaction. The fact that organic materials may emit light under oxidative conditions was recognized early [3] and polymers are no exception. Most common polymers degrade readily during normal use through reaction with oxygen. The first step is the formation of unstable alkyl radicals, which react immediately with the oxygen of the air to form peroxy radicals. These react further and are transformed into a variety of species in an auto-accelerating degradation cycle (autooxidation, Figure 18.6). The luminescent reaction is believed to involve the termination of two peroxide radicals in a Russel mechanism, which leads to an excited “triplet” carbonyl group. The spectral range of emission varies with the type of polymer but is generally in the blue-violet region (380 to 450 nm). As CL originates from oxidation reactions, it is sometimes called oxyluminescence.

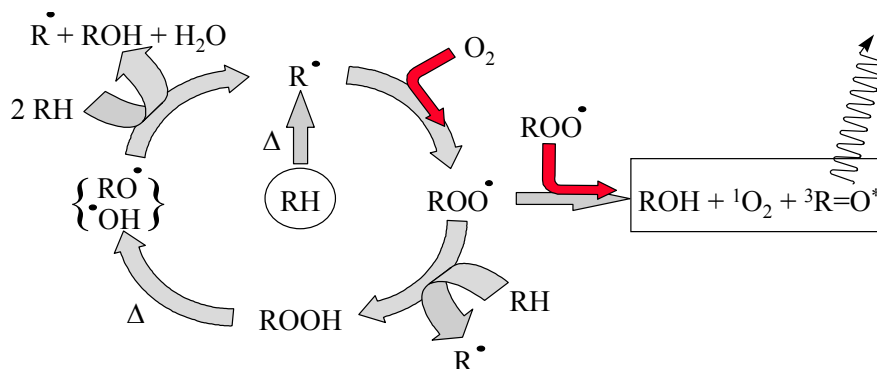


Figure 18.6. A simplified scheme for autooxidation of an organic material, with a chemiluminescent termination reaction.

The first study of CL resulting from polymer oxidation was reported in 1961 [4]. However, despite the considerable interest shown by the scientific community, CL was not recognized as an important thermal analysis method, unlike for example differential scanning calorimetry (DSC). The reasons lie in the low quantum yield of the CL reaction, about 10^{-9} , which requires very sensitive and delicate photon counting instruments to measure the very low emission: the light emission from polypropylene heated at $150^\circ C$ in pure oxygen ($< 10^5$ photons $s^{-1} cm^{-2}$) is about 50 times less than a bright star in the night sky. Moreover, CL instrumentation was not commercially available and equipment had to be specially built. Recent advances in detector electronics, the development of new types of detectors and the availability of commercial CL [5] equipment have changed the situation. CL is now a competitive technique for the study of the degradation and stabilization of polymers and other oxidizable materials.

18.3.2 CL Instrumentation

All CL instruments used in polymer studies consist of a sensitive light sensor linked to an oven. An exact description of different instruments can be found in the literature cited.

The emission rate of most polymers at near ambient temperatures is too low to be detected and samples are usually heated to increase their emission. Requirements for the oven are: rapid heating rate, good temperature stability (experiments are often carried out isothermally), a gas exchange facility and absolute light tightness.

Several different detectors can be used to measure CL. The most common is a conventional photomultiplier tube (PMT) used in photon counting mode [6]. PMTs are very sensitive detectors but their dynamic range is low and exposure to too high a light level will saturate the photocathode. Slow scan charge-coupled device cameras (CCD) have been used recently [7] [8]. Use of a solid-state detector combines the advantages of simplicity of use, high dynamic range and high sensitivity. They also offer the possibility of imaging the CL emission. A third possibility is to use image intensified devices, which typically consist of a micro-channel plate (MCP) photon amplifier coupled with either a CCD camera [9] [10] or a resistive anode encoder [11]. This type of sensor certainly offers the best combination of sensitivity and imaging but with the same low dynamic range as a PMT and at a much higher cost than the CCD.

18.3.3 Application Examples

18.3.3.1 Oxidation Induction Time

A standard method used to determine the thermal stability of organic materials and the performance of antioxidants is the measurement of Oxidation Induction Time (OIT). The measurement is made using DSC in isothermal mode, typically at a temperature between 190 and 220 °C. The OIT is the time needed to reach the onset of oxidation, detected as the start of an exotherm, and can be correlated with the stability of the material. OIT measurements are routinely used in the cable industry to assess the stabilization of polyolefin insulation materials. They are also widely used for assessing the performance of additives in lubricating oils and the stability of food oils.

The rate of formation of peroxy radicals in the induction period of oxidation of an unstabilized sample is expected to be equal to the rate of termination by recombination. Since the termination is also the CL reaction, (Figure 18.6) the CL signal is initially low. At the end of the induction period, the autoacceleration of the oxidation causes the radical concentration to increase, resulting in an increased rate of termination and an increased CL intensity. In the case of a stabilized sample, the effect is more marked. During the induction period, peroxy radicals are efficiently trapped by the antioxidant and CL is too low to measure. Once the antioxidant is consumed, oxidation begins rapidly and there is a corresponding increase in CL. It is therefore easy to measure OITs by CL.

Figure 18.7 shows typical isothermal CL curves obtained from a polybutadiene rubber film stabilized with 3000 ppm BHT (a phenolic antioxidant) and oxidized at different temperatures. OIT data from such curves can be used to predict the inherent stability of the material or to assess the efficiency of stabilizers [12].

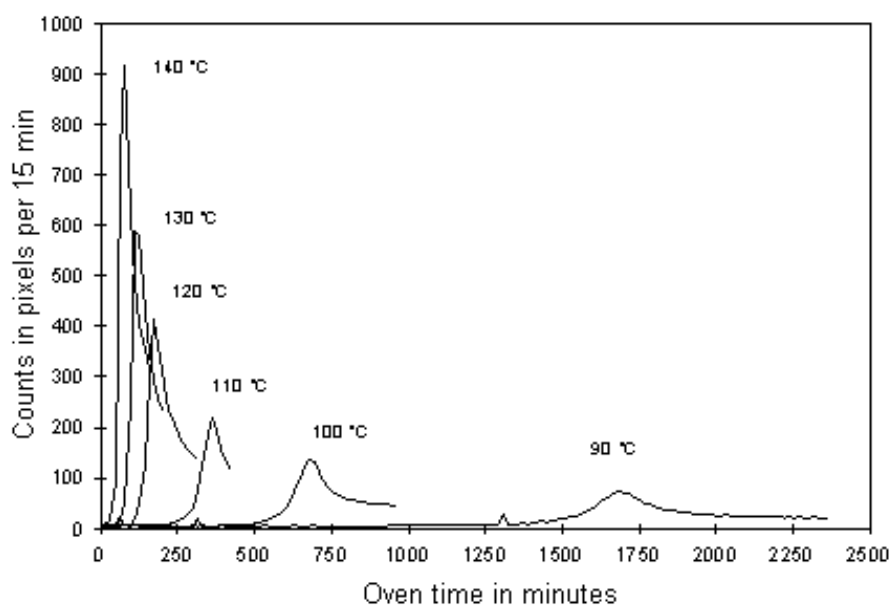


Figure 18.7. CL curves of stabilized polybutadiene films measured at different oven temperatures.

CL offers many advantages over DSC. The much higher sensitivity means that it is possible to make measurements at lower temperature, closer to real degradation conditions. This is especially important for semicrystalline polymers with a melting point lower than the test temperature (e.g. polyolefins). Since both the degradation kinetics and the distribution of additives in the molten polymer are completely different from those of the solid material, conclusions on the thermooxidative stability of polymers drawn from DSC-OIT measurements above the melting point are often misleading. Normal DSC instruments are however usually not sensitive enough to detect the long OITs common in well-stabilized samples below the melting point.

The shape of the DSC curve in an oxidizing atmosphere is the sum of many different exothermic oxidation reactions and is sometimes complex, making the graphical determination of the OIT difficult. In addition, DSC depends on detection of minute changes in sample temperature; baseline stability over very long periods can be difficult to achieve.

In contrast, the CL signal is related to only one reaction. The CL curve is always well defined with a sharp onset and the OIT is easy to determine. Baseline stability is not an issue. Another advantage is the small sample needed for CL. The OIT of a single polypropylene (PP) particle weighing as little as 10 μg can easily be measured [13].

These advantages are illustrated in Figure 18.8, which shows a simultaneous DSC and CL measurement on a sample of PET heated in air at 10 K/min. The glass transition, crystallization and melting peaks of the polymer are all observed in the DSC curve but not the CL. In contrast, the rapid onset of oxidation above the melting point is difficult to distinguish from baseline changes in the DSC trace but is absolutely clear in the CL curve. (Note: This experiment was performed with an experimental DSC head – the baseline performance of a commercial instrument is better).

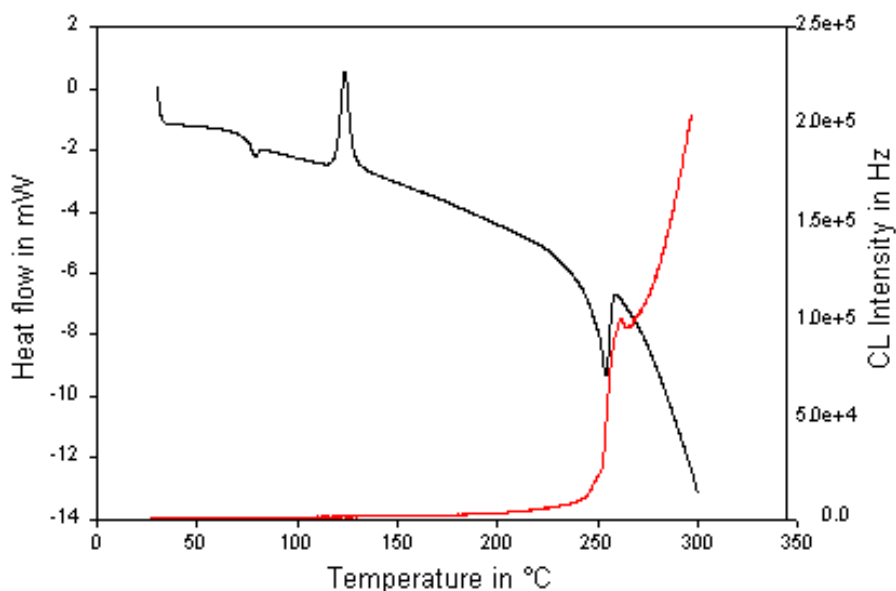


Figure 18.8. Simultaneous temperature-programmed DSC and CL of PET at 10 K/min in oxygen.

18.3.3.2 Thermal Analysis at High Pressures

One significant problem in using DSC to measure OITs at high temperatures is that the sample may be too volatile, or may produce volatile oxidation products which contaminate the calorimeter. This is especially true of samples such as lubricating oils and food oils. The traditional method to study volatile samples is to operate the DSC instrument under high (tens of atmospheres) pressure. This also provides an accelerating effect because the oxygen concentration in the sample is increased.

The design of a good high-pressure DSC system is extremely challenging because the density and thermal conductivity of the gas increase with increasing pressure and it becomes more and more difficult to achieve a noise-free baseline. This problem does not apply to CL detection. Figure 18.9 shows some OIT measurements for a stabilized PP sample at 150 °C. The OITs are very clearly defined and baseline stability and noise are both outstandingly good. It is interesting to note that the OIT is not only shortened by pressure but also becomes more sharply defined. CL detection is potentially a very valuable method for studying volatile samples.

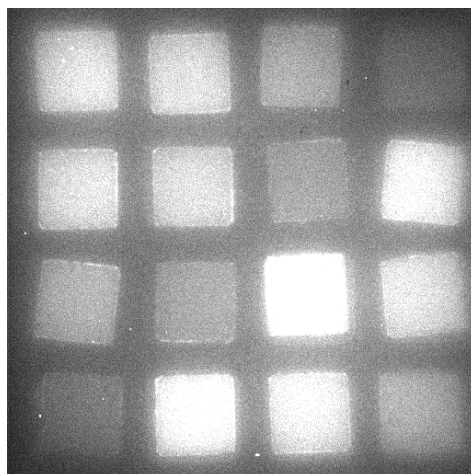


Figure 18.9. CL curves for a sample of stabilized PP heated in oxygen at 150 °C at different oxygen pressures.

18.3.3.3 Determination of Hydroperoxides

It is clear from the degradation scheme in Figure 18.6 that the rate of generation of peroxy radicals depends on the peroxide concentration, so that CL emission can be related to the hydroperoxide (ROOH) content of a polymer. Hydroperoxides are quite stable at ambient temperature but decompose rapidly on heating, forming peroxy radicals which emit CL. If the sample is heated in inert gas, further oxidation is prevented and the amount of light recorded is directly related to the ROOH concentration. By using reference samples standardized by a chemical method, the CL can then be used for the quantitative determination of ROOH with the advantage of simplicity and rapidity. This method has been successfully applied to polyolefins [14] and to automotive coatings [15]. Hydroperoxides are formed in automotive coatings during photo-oxidation in artificial or natural exposure.

Figure 18.10 shows an example of the use of imaging detection. Polyurethane coatings were weathered artificially for different times (48 to 240 h) prior to CL measurement. The difference in emission between the samples is clearly visible. Such data is useful to assess the effectiveness of light stabilizer formulations in coatings or to establish the photostability of materials.

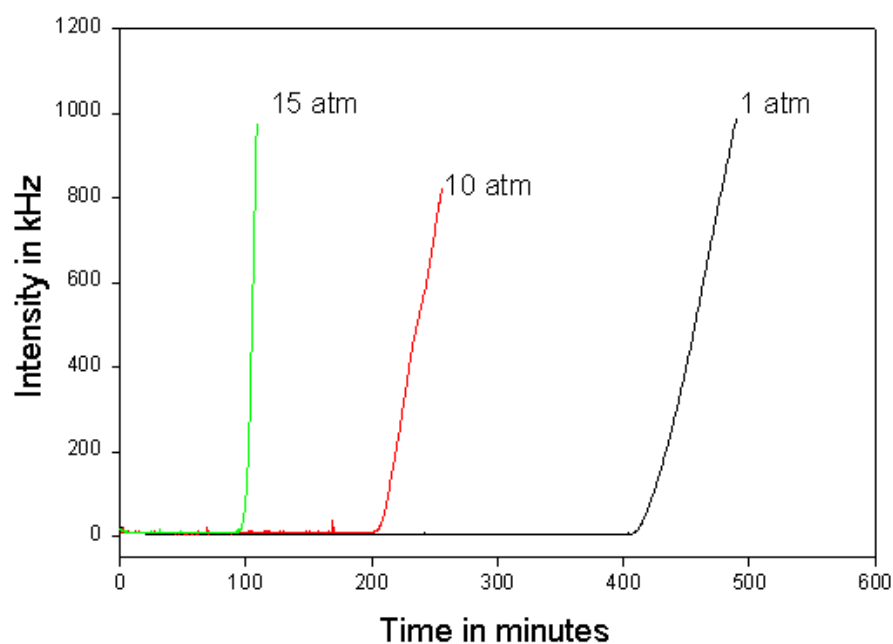


Figure 18.10. CL image of photo-oxidized polyurethane coatings (40 μm thick, on aluminum) heated at 150 °C. Individual sample dimensions 3 x 3 mm. Exposure time 5 min.

18.3.3.4 CL Imaging

When a CL instrument is equipped with an imaging sensor, the technique offers new application possibilities. The first is to image emission from multiple samples onto the detector and to use digital image analysis of a series of such images to carry out multiple sample analysis. Figure 18.9 shows an example in which 16 samples were observed simultaneously. Multiple sample imaging allows a large increase in productivity, for example in the screening of stabilizer formulations. Alternatively, it allows data to be obtained at lower temperatures without loss of productivity.

The most interesting prospect offered by CL imaging is the possibility of studying the heterogeneity of polymer oxidation. Solid polymers typically do not degrade homogeneously. Oxidation initiates at “hot spots”, produced by the presence of a catalyst residue or a mechanical defect, and spreads through the material. This degradation mechanism has still not been fully clarified. CL imaging is one of the few techniques that offers the possibility of studying this phenomenon in real time. For example, the series of images in Figure 18.11 shows the spread of oxidation across a stabilized PP film. The oxidation is initiated on the left of the film by a piece of degraded PP. The degradation products (reactive peroxide species) diffuse into the undegraded film and “infect” it. Antioxidants in the film react with the infectious species and retard the progress of the oxidation.

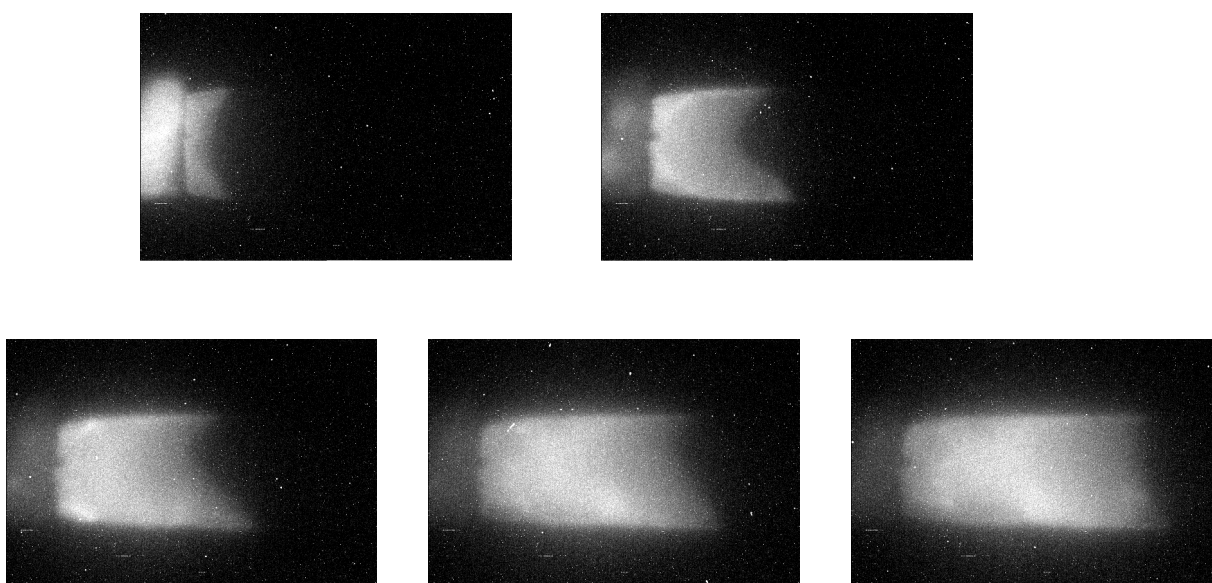


Figure 18.11. CL images showing the spread of oxidation across a stabilized PP film. Image size is 9 x 13 mm. Oxidation conditions are 150 °C, pure oxygen atmosphere. Time scale between first (upper left) and last (lower right) image is about 160 min.

18.4 Conclusions

These applications of CL to polymers are just some examples of the versatility of the method. Almost all polymers exhibit CL under oxidation [16] but most studies have been limited to polyamides and polyolefins. Undoubtedly the development potential of the CL technique is still very large as many polymers and applications have not yet been considered. There is also great scope for development in other materials, for example foods and lubricants.

The development of new commercial instruments allowing simultaneous recording of the enthalpic and photochemical signals (CCD camera or PMT mounted on a high-pressure DSC) should open up new fields of investigation and boost interest in the method [17].

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19 Method Development

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19.1 Introduction

The development and validation of methods is of major importance in today’s quality assurance systems. The starting point is usually a trial method that is then optimized and validated in several iterative steps. The final result is a validated method that is used for SOPs (SOP: **S**tandard **O**perating **P**rocedure). The development and validation of a measurement procedure is time-consuming and costly. This means it is important to start with a good trial method right from the beginning. The following section attempts to systematize the development of thermoanalytical methods and discusses the most important aspects involved. Figure 19.1 presents an overview of this process.

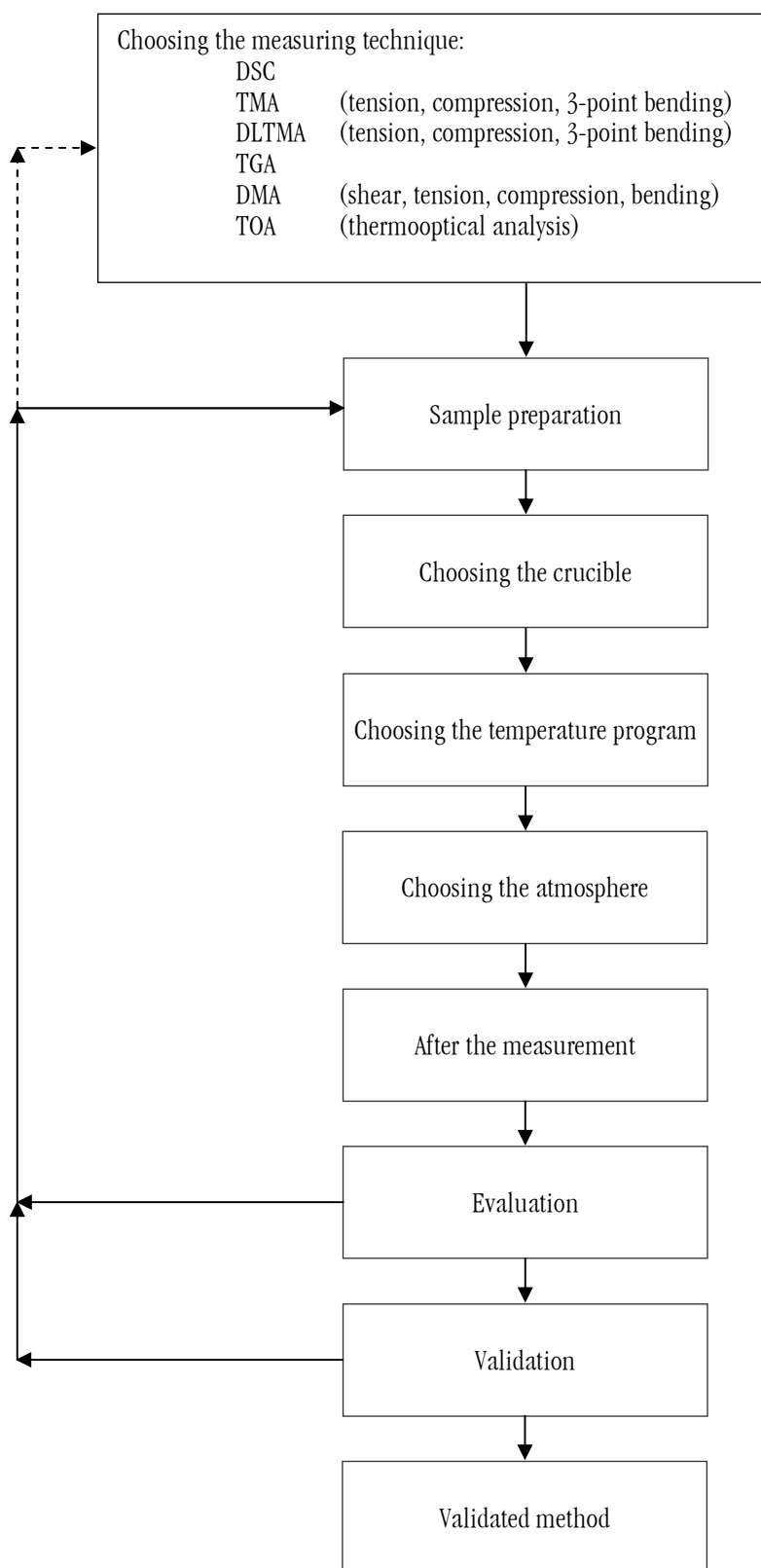


Figure 19.1. Procedure for developing a thermoanalytical method.

19.2 Step 1: Choosing the Right Measurement Technique

19.2.1 The Analytical Task

Method development begins with precisely defining the information you hope to get from an analysis of the sample. Typical questions could be for example:

- At what temperature does the glass transition occur?
- Does the sample exhibit polymorphism?
- How pure is my product?
- What is the moisture content of my sample? and so on.

Depending on the analytical task and the information required, you first have to decide which measurement technique to use. Table 19.1 presents an overview of the application possibilities of various thermoanalytical measurement techniques.

	DSC	TGA/DSC	TMA	DMA
Physical properties				
Specific heat capacity	...	.		
Expansion coefficient			...	
Young's modulus			.	...
Physical transitions				
Melting and crystallization	...	.	.	...
Evaporation, sublimation, drying	...	...		
Glass transition, softening	...		...	...
Polymorphism (solid-solid transitions)	...		...	
Liquid crystals	...			
Purity analysis	...			
Chemical properties				
Decomposition, degradation, pyrolysis, oxidation stability	...	...		
Composition, content (moisture, fillers), ash	.	...		
Kinetics, reaction enthalpies	...	...		
Crosslinking, vulcanization (process parameters)	...		...	...

Table 19.1. Overview of the application possibilities of different thermoanalytical techniques. ... means "very suitable", . means "less suitable".

19.2.2 “Sensitivity”

The most important considerations at this point are basic questions that have to do with the later validation of the method [1]:

- Is the sensitivity of the method good enough to obtain the desired information?
- What possible consequences arise from the sensitivity of the method, e.g. with regard to the size of the test specimen or the heating rate?
- What accuracy can I expect to achieve?
- Is the accuracy sufficient for my purposes?
- Do any interfering effects have to be taken into account? Are the effects more serious with one measurement technique than with another (robustness of method)?

To answer these questions, one needs to understand the operating principles of the instruments concerned and to have had practical experience. Particularly important is information on the signal-to-noise ratio, the long-term stability or drift, and measurement reproducibility.

Example about signal resolution:

Question: What is the smallest mass loss step that can be resolved by TGA?

Answer: The decisive point in this case is the noise of the measurement signal (balance and surroundings). As a rule of thumb, a measurable mass change should be at least four times greater than the background noise signal. Assuming that the noise is 1 μg , the minimum step height is 4 μg . If the mass of the test specimen is 10 mg, this means that mass changes of the order of 0.4 per thousand can be measured. However, the accuracy with which such a small mass step can be measured also depends on the width of the step. An example of a very low mass loss step is shown in Figure 19.2.

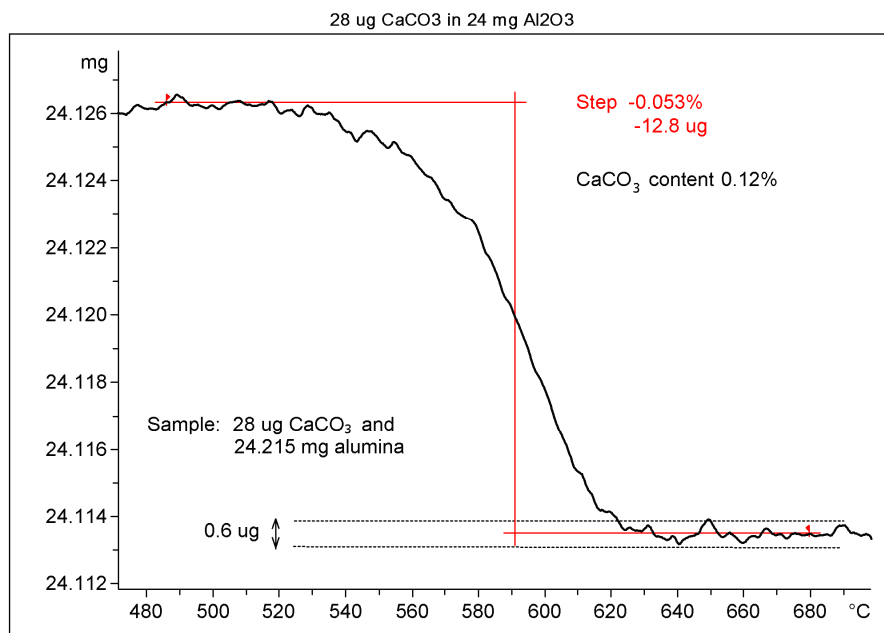


Figure 19.2. Calcination of 28 μg calcium carbonate in 24.215 mg aluminum oxide: The CaCO_3 loses CO_2 up to about 600 $^{\circ}\text{C}$ (calcination). From stoichiometric considerations, a step of 12.3 μg is expected from the decomposition reaction of calcium carbonate.

19.2.3 Measurement Mode

Once you have decided to use a particular measurement technique (here DSC, TGA, TMA or DMA), the next question concerns the measurement mode in which the instrument is to be operated. Table 19.2 summarizes various instrument-specific measurement modes and their use.

Measurement technique	Special measurement modes	Use
DSC	TMDSC (ADSC, IsoStep [®])	Separation of changes in c_p from non-reversing events (vaporization, crystallization, chemical reactions).
TGA	MaxRes	For automated optimized temperature resolution of neighboring mass changes.
TMA/DLTMA	Dilatation (low load on test specimen) Penetration (large load on test specimen) Tension Bending	Mode to measure the coefficient of thermal expansion. Particularly suitable for the analysis of thin films (glass transition, melting temperature, film thickness). For fibers and films, shrinkage behavior. Glass transition of filled materials and other stiff samples.
DMA	Tension Compression Shear Bending	Above all for fibers and thin films. Foams, elastomers. Elastomers, most thermoplastics, powder, pastes. Fiber-reinforced plastics, thermoplastics, thermosets.

Table 19.2. Special measurement modes for different thermal analysis techniques and their applications.

19.3 Step 2: Sampling and Preparation of the Test Specimen

The most important aspects concerning sampling and sample preparation can be summarized as follows:

- Is the test specimen representative of the total sample? To obtain reliable results, you may have to measure several test specimens and compare the results (statistics) [1].
- Sample processing: To obtain optimum thermal analysis results, test specimens often have to be mechanically processed (e.g. cut, ground, polished, etc.). The specimens are thereby unintentionally subjected to mechanical and thermal stress: This may in some cases lead to undesirable changes (e.g. with polymorphous substances).
- Thermal pretreatment: Annealing at a suitable temperature eliminates the thermal history of the test specimen. The information obtained then relates solely to the material under investigation. If the test specimen is not annealed, information about the conditions under which it was produced, i.e. its thermal history, can also be obtained.
- Geometry and size of the test specimen. The specimen should be no larger than is necessary to determine the result with the desired accuracy (i.e. as large as necessary but as small as possible).
- Insertion of the test specimen into the crucible (DSC, TGA) or into the instrument (TMA, DMA). See the table for specific details.

DSC/TGA	TMA	DMA
• Optimum contact of the test specimen with the crucible (thermal conductivity). • Test specimen must not move within the crucible. • Test specimen must not react with the crucible.	• Surfaces of the test specimen should ideally be flat and parallel. • For dilatometry, use a quartz glass disk between the test specimen and the probe to distribute the force exerted by the probe uniformly over the test specimen.	• Geometry of the test specimen must be known exactly. • The test specimen must be properly mounted in the clamp. • Possibly adjust the force on the test specimen at the start temperature. • The thermocouple must not touch the test specimen or the furnace and should always be placed in the same position.

Table 19.3. Important aspects of sample preparation for different thermal analysis techniques.

Typical questions about the size of a test specimen

What is the minimum mass of a test specimen needed to determine a residue of 1% with a precision of $\pm 1\%$?

Answer:

The precision with which residues can be determined in a thermogravimetric measurement depends mainly on the repeatability of the blank curve. Let us assume that the standard deviation of the blank curve in the temperature range considered is $\pm 10 \mu\text{g}$. In this case, the $\pm 10 \mu\text{g}$ represents $\pm 1\%$ of the measured residue. The residue must therefore be at least 1 mg. Since the residue is about 1% of the original test specimen, its mass should be at least 100 mg [1].

How thick does the test specimen have to be to determine a coefficient of thermal expansion (CTE) of 20 ppm/K over a temperature interval of 10 K with a confidence level of $\pm 2\%$?

Answer:

On heating the test specimen with a CTE of 20 ppm/K through 10 K ($\Delta T = 10 \text{ K}$), the thickness increases by 200 ppm ($\text{CTE} = \Delta L / \Delta T \cdot 1 / L_0$). Let us assume that the change in thickness of the test specimen in this temperature interval can be determined with a standard deviation of about 20 nm. For a 95% confidence level, the confidence interval is about 40 nm (coverage factor 2). The change in thickness over this 10-K interval must therefore be about $2 \mu\text{m}$ ($\Delta L = 2 \mu\text{m}$). This change corresponds to 200 ppm in the original thickness (L_0). The original thickness must therefore be at least 10 mm [1].

19.4 Step 3: Choosing the Crucible (DSC and TGA)

The most important considerations regarding the choice of the crucible are the

- volume of the crucible (mass of the test specimen; with the TGA, also gas exchange),
- heat capacity and thermal conductivity of the crucible: this influences the resolution (separation of thermal events) and sensitivity of the DSC or SDTA signal, and the
- crucible material: the test specimen must not react with the crucible material.

Further aspects are presented in Figure 19.3.

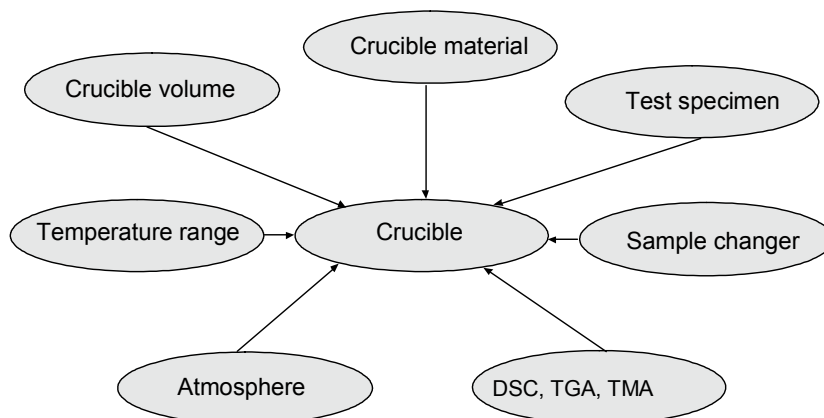


Figure 19.3. Factors influencing the choice of crucible.

Recommendations for METTLER TOLEDO instruments:

For DSC, we recommend the use of the small 20- μ L or the 40- μ L aluminum crucibles: These crucibles have the lowest heat capacity and give the best sensitivity and time resolution.

For the TGA, we recommend the 30- μ L or the 70- μ L alumina crucible as standard crucible. If the temperature range of the measurement is below 600 °C, and if a reaction with the sample is not expected, the 40- μ L aluminum crucible can also be used for TGA. The advantages are the excellent thermal conductivity and a much better DSC signal due to its low heat capacity. In addition, the crucible can be disposed of after use and so does not have to be cleaned.

Besides the standard crucibles, we also offer a variety of special crucibles manufactured from different materials (gold, platinum, copper, sapphire and Pyrex glass) for different conditions (normal, medium and high pressure). They are available in a number of different sizes.

19.5 Step 4: Choosing the Temperature Program

The two main aspects that have to be considered are as follows:

- Type of temperature program (single segment, multi-segment, modulated temperature program).
- Choice of parameters (heating rate, start and end temperatures, and if relevant, amplitude and period).

Table 19.4 displays the different temperature programs and makes recommendations for the different thermal analysis measurement techniques.

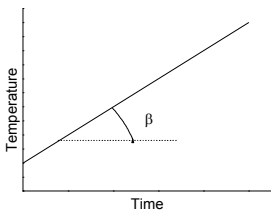
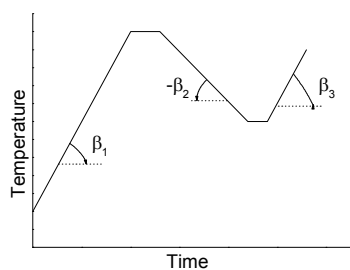
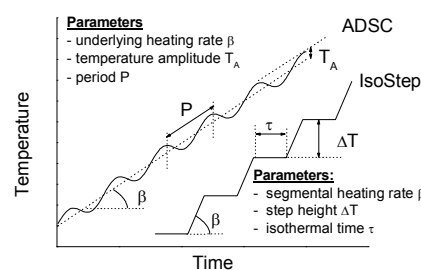
								
	Dynamic heating segment with constant heating rate; this is the usual temperature program.	Temperature program consisting of several segments (isothermal, dynamic heating and cooling segments).	Temperature-modulated heating program: ADSC and IsoStep®, and TOPEM® (not shown).					
DSC	Typical heating rate: 10 to 20 K/min. Low heating rates give good resolution at the cost of sensitivity.	Simplifies interpretation; heating and cooling rates are typically between 5 and 20 K/min. Thermal pretreatment.	Typical parameters					
			<table><tr><td>ADSC</td><td>IsoStep®</td></tr><tr><td>$\beta = 0.5\text{--}2 \text{ K/min}$</td><td>$\beta = 0.5\text{--}2 \text{ K/min}$</td></tr><tr><td>$T_A = 0.2\text{--}2 \text{ K}$</td><td>$T_A = 0.5\text{--}2 \text{ K}$</td></tr><tr><td>$P = 40\text{--}120 \text{ s}$</td><td>$P = 30\text{--}120 \text{ s}$</td></tr></table>	ADSC	IsoStep®	$\beta = 0.5\text{--}2 \text{ K/min}$	$\beta = 0.5\text{--}2 \text{ K/min}$	$T_A = 0.2\text{--}2 \text{ K}$
ADSC	IsoStep®							
$\beta = 0.5\text{--}2 \text{ K/min}$	$\beta = 0.5\text{--}2 \text{ K/min}$							
$T_A = 0.2\text{--}2 \text{ K}$	$T_A = 0.5\text{--}2 \text{ K}$							
$P = 40\text{--}120 \text{ s}$	$P = 30\text{--}120 \text{ s}$							
TGA	Typical heating rate: 10 to 20 K/min.	Only in special cases.	Direct determination of the conversion-dependent apparent activation energy of a reaction					
TMA	Typical heating rate: 5 K/min.	Facilitates interpretation; heating and cooling rates are typically between 3 and 10 K/min. Thermal pretreatment.	Separation of thermal expansion and contraction.					
DMA	Typical heating rate: 3 K/min.	Thermal pretreatment.	Is not used.					

Table 19.4 Overview of different temperature programs and their use.

The heating rate and the start and end temperatures are chosen with the following factors in mind:

- Thermal conductivity of the sample: The temperature distribution in the test specimen should always be as homogeneous as possible (use lower heating rates for poor conductors).
- The lower the heating rate, the better the temperature resolution.
- The higher the heating rate, the more pronounced the effects (DSC).
- Start and end temperatures: The time interval before and after the first and last thermal events should be sufficiently long to enable a clear “baseline” to be estimated. Recommended values: DSC 3 min, TGA: 5 min, TMA: 5 min, DMA 8 min.

In standard methods, for example ASTM and DIN, the temperature program is often specified. According to ISO 17025, such standard methods no longer need to be validated. This should, however, be treated with caution because many standard methods are not fully validated. In practice, variations of standard methods are often used that definitely require validation.

19.6 Step 5: Choosing the Atmosphere

In particular with DSC and TGA, different atmospheric conditions allow different types of information to be obtained. This is illustrated in Figure 19.4, which describes the decomposition of coal. The upper curve was measured in an air atmosphere, the lower curve in nitrogen (up to 900 °C) and then air (above 900 °C). In air, the combustion profile of the sample is of interest, that is, the temperature at which the coal begins to burn, and how the combustion process proceeds. If the measurement is first performed in an inert atmosphere and then finally in air, the main question has to do with the composition of the coal, that is, the content of volatile compounds (moisture, adsorbed gases), whether inorganic compounds are present, and the carbon content.

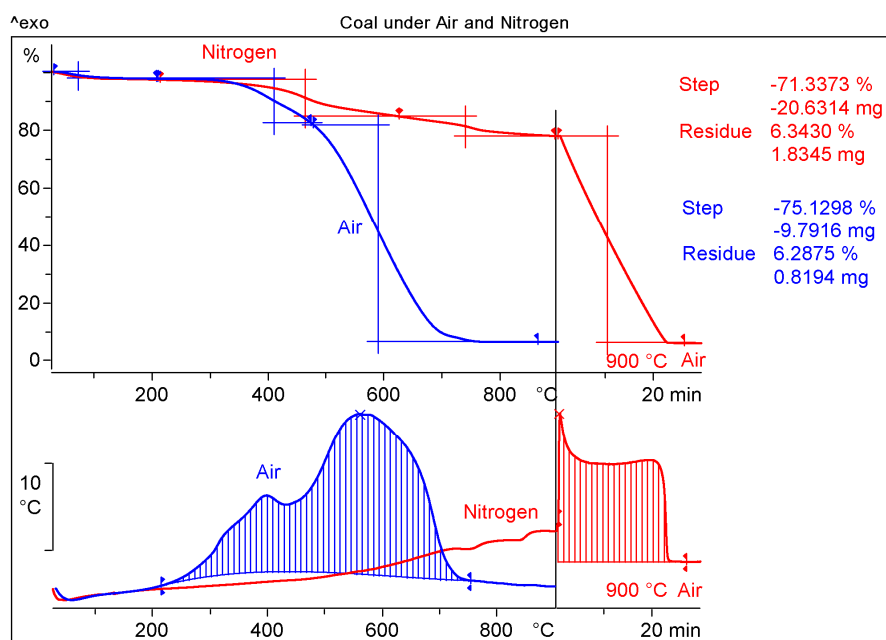


Figure 19.4. Coal measured in air and in nitrogen. Measurement in air allows the combustion process of the coal to be followed; heating in nitrogen is used for quantitative compositional analysis.

In DSC, the atmosphere within the crucible plays an important role. For example, in an open crucible, you can measure the slow evaporation of solvents and moisture. This process gives rise to broad endothermic peaks that sometimes overlap with other interesting effects such as glass transitions and polymorphic transitions. If you seal the crucible with a crucible lid that has been pierced with a small hole, a so-called self-generated atmosphere is created and the evaporation process is delayed almost to the boiling point of the liquid. Above the boiling point, the liquid evaporates rapidly from the crucible. METTLER TOLEDO supplies lids with a hole-diameter of 50 μm for this type of measurement. Finally, in a hermetically sealed crucible, the boiling point can be exceeded. The crucible is then under pressure. This can lead to initial deformation of the crucible and ultimately, on further temperature increase, to bursting (see Figure 19.5). Endothermic evaporation can be completely suppressed by using medium pressure crucibles.

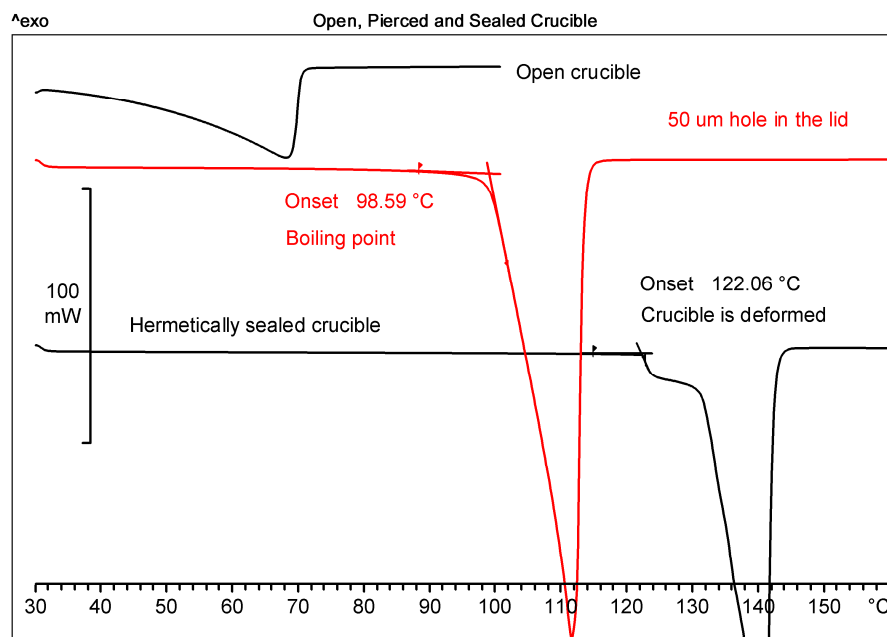


Figure 19.5. DSC measurements of water in an open crucible, in a self-generated atmosphere and in a hermetically sealed crucible.

19.7 Step 6: Examining the Test Specimen after Measurement

You should make a habit of weighing test specimens before and after an experiment (even with TMA and DMA measurements). Small weight changes indicate that evaporation or initial decomposition processes have taken place. This usually has an effect on the measurement curves (not only DSC, but also TMA and DMA curves). These effects are often only weak and may hardly be noticeable so that the gravimetric information is very important.

A further aid to interpretation is a visual examination of the test specimen after the experiment. Points to check are for example:

- Has the color changed?
- Does the sample appear to have melted?
- Has the test specimen undergone deformation?

Answers to such questions can lead to a better interpretation and understanding of the effects observed in the different measurement curves.

19.8 Step 7: Evaluation

For quantitative results, the curves obtained from the measurement instrument have to be properly evaluated. Often, several different procedures are available for calculating numerical results from the curves. These might involve choosing baselines, drawing tangents, etc. and can lead to different measurement results being obtained. For example, the glass transition temperature can be determined from DSC curves according to ASTM and DIN methods, and according to other procedures (Richardson, bisector of tangents). To meaningfully compare measurement results, it is important to evaluate measurement curves in exactly the same way each time and to specify the procedure used to obtain the results (e.g. baseline type, tangent type).

19.9 Step 8: Validation

Once steps 1 to 7 have been specified, the final task is to design a validation plan. This includes specifying the number of replicate measurements (for repeatability) that must be performed, as well as defining the order in which sample and reference sample measurements and blank curves are to be measured. It also includes providing details about the statistical methods to be used for further analysis of the experimental data [1].

19.10 Conclusions

Method development begins with a draft procedure that is optimized in steps and finally validated. A well-designed draft method can greatly facilitate the actual method development and validation process that follow. Table 19.5 summarizes the most important points to consider in method development.

Step	Questions, criteria
Choosing the measurement technique	• What information is required? • Which measurement techniques can be used? • How do the different measurement techniques compare with regard to accuracy of results, and robustness and sensitivity of the method?
Preparation of the test specimen	• Size of the test specimen, geometry. • Contact with crucibles (TGA, DSC), clamping assemblies (TMA, DMA). • Annealing at a constant temperature or a first heating run.
Choosing the crucible	• DSC: if possible use the light 20-μL aluminum crucibles. • TGA: With end temperatures < 600 °C, if possible use the 40-μL aluminum crucibles, otherwise the 30-μL or 70-μL alumina crucibles. • If required: pressure crucibles, crucibles made of special materials (sapphire, platinum) are also available.
Temperature program	• Temperature range - if possible, allow at least 3 minutes before the first event and 3 min after the last). • Heating rate: In general, the heating rate affects the resolution of thermal effects and the temperature distribution in the test specimen. Typical heating rates used are: DSC 10 K/min, TGA 20 K/min, TMA 5 K/min, DMA 3 K/min. • In many cases, a combination of heating, cooling and isothermal segments is recommended (especially for DSC).
Atmosphere	• Open crucible, pierced lid, hermetically sealed crucible; overlapping effects can sometimes be separated from one another. • Inert or reactive atmosphere
After the measurement	• Loss of mass? (off-line thermogravimetric analysis with DSC, DMA, and TMA) • Change in morphology? • Change in color?
Evaluation	• Possibly use a standard procedure? • Should always be performed in the same way.
Planning the experiments	• Specification of the number of measurements (repeatability). • Order of sample, reference and blank measurements, specification of the reference materials to be used for calibration. • Specification of the statistical methods to be used to analyze the different experiments.

Table 19.5. Summary of the most important points to consider in method development.

References and Further Reading

- [1] METTLER TOLEDO Collected Applications Handbook: “Validation in Thermal Analysis”.
- [2] M. Schubnell, Method development in thermal analysis. Part 1, METTLER TOLEDO Thermal Analysis UserCom 21, 1–4.
- [3] M. Schubnell, Method development in thermal analysis, Part 2, METTLER TOLEDO Thermal Analysis UserCom 22, 1–4.
- [4] M. Schubnell, Tips on method development for DMA measurements in 3-point bending, METTLER TOLEDO Thermal Analysis UserCom 28, 9–12.

Back issues of UserCom can be downloaded as PDFs from the Internet at www.mt.com/ta-usercoms .

20 Overview of Standard Methods for Thermal Analysis

The large number of standard methods and test procedures used for thermal analysis makes it impossible to give a fully comprehensive overview in this handbook. Instead, a number of selected international standards are given below as examples (some are in German).

If several standardization organizations are involved, the most international one is listed, e.g. ISO 527 is given instead of DIN EN ISO 527.

Organizations:

ASTM	American Society for Testing and Materials	www.astm.org
ISO	International Organization for Standardization	www.iso.ch
EN	European Committee for Standardization	www.cenorm.be
DIN	Deutsches Institut für Normung	www.din.de
JIS	Japanese Industrial Standards	www.jsa.or.jp
VDA	Verband der Automobilindustrie	www.vda.de
USP	United State Pharmacopeia	www.usp.org
IP	Institute of Petroleum	www.energyinst.org.uk
NF	Norme française	www.afnor.fr
OECD		www.oecd.org
UNI	Ente nazionale italiano di unificazione	www.uni.com
AOCS	American Oil Chemists Society	www.aocs.org
CEI/IEC	The International Electrotechnical Commission	www.iec.ch
IPC	Institute for interconnecting and packaging electronic circuits	www.ipc.org
CEC	Coordinating European Council for the development of performance tests for transportation fuels, lubricants and other fluids	
BS	British Standards	www.bsonline.bsi-global.com
CSA	Canadian Standards Organization	www.csa.ca
IEEE	Institute of Electrical and Electronics Engineers	www.ieee.org

Norm	No.	Year	Title	Short description	Technique
AOCS	Cj 1	1994	DSC Melting Properties of Fats and Oils	Recommended practice: Premelting at 80 °C, cooling at 10 K/min to -40 °C followed by heating at 5 K/min. Onset and endset of melting peak(s).	DSC
ASTM D	3350	1984	Standard Specifications for Polyethylene Plastics Pipe and Fittings Materials.	DSC, oxidation induction time (OIT). Indium in the reference crucible. Start temperature 150 °C, 10 K/min, static air. Onset between extended baseline and a tangent to the exothermic decomposition peak. Requires crimped Al crucible.	DSC Needs special crucibles
ASTM D	3386	1994	Standard Test Method for Coefficient of Linear Thermal Expansion of Electrical Insulating Materials	Sample height 2.5 to 7.5 mm. The thermocouple should be as close as possible to the sample.	TMA
ASTM D	3417	1983	Standard Test Method for Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry (DSC)	Heating/cooling rates: 10 K/min, N ₂ .	DSC
ASTM D	3418	2003	Standard Test Method for Transition Temperatures of Polymers by Differential Scanning Calorimetry	Press the lid against the test specimen. Melting/crystallization: ±10 K/min, N ₂ . Glass transition: 20 K/min, shock-cooled, air or N ₂ .	DSC
ASTM D	3850	1984	Standard Test Method for Rapid Thermal Degradation of Solid Electrical Insulating Materials by a Thermogravimetric Method	Based on the temperatures at weight losses of 10, 20, 30, 50 and 75%.	TGA
ASTM D	3895	2004	Standard Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry	OIT measurement. Heat to 200 °C at 20 K/min and hold isothermally at 200 °C for 5 min in N ₂ . Then switch to O ₂ . After the onset of the oxidative exothermic reaction, hold for 2 min before cooling. The OIT is the intercept between the extrapolated slope and the extended base line.	DSC
ASTM D	3947	1986	Standard Test Method for Specific Heat of Aircraft Turbine Lubricants by Thermal Analysis	Cp determination with diphenyl ether as the reference material.	DSC
ASTM D	4065	1995	Practice for Determining and Reporting Dynamic Mechanical Properties of Plastics	Specifies general procedure, formula, instrumentation and geometry of specimen for torsion, single cantilever, compression and bending.	DMA
ASTM D	4092	1996	Standard Terminology Relating to Dynamic Mechanical Measurements on Plastics	Definitions and descriptions of technical terms.	DMA
ASTM D	4419	1990 (2002)	Standard Test Method for Measurement of Transition Temperatures of Petroleum Waxes by Differential Scanning Calorimetry (DSC)	Solid-solid or solid-liquid transitions in the temperature range 15 to 150 °C, at 10 K/min, in N ₂ . Onset, endset, extrapolated peak.	DSC
ASTM D	4440	1995	Standard Test Method for Plastics: Dynamic mechanical properties melt rheology	Determination of complex viscosity of thermoplastic resins and other types of molten polymers as a function of frequency, strain amplitude, temperature, and time.	DMA
ASTM D	4473	2003	Standard Test Method for Plastics: Dynamic Mechanical Properties: Cure Behavior. The cure behavior of thermosetting resins using dynamic mechanical procedures	Determination of the curing behavior of supported and unsupported thermosetting resins using DMA (shear and compression). see also ASTM D 4065.	DMA
ASTM D	4565	1099	Standard Test Methods for Physical and Environmental Performance Properties of Insulations and Jackets for Telecommunications Wire and Cable	The test methods cover many different test for different types of samples (OIT, melt flow, aging etc.).	DSC
ASTM D	4591	2001	Standard Test Method for Determining Temperatures and Heats of Transitions of Fluoropolymers by Differential Scanning Calorimetry	Defines DSC methods for the analysis of fluoropolymers (PTFE, PVDF, PCTFE, and PVF and their copolymers PFA, FEP, ECTFE, EFEP, VDF/HFP, VDF/TFE/HFP, VDF/CTFE).	DSC
ASTM D	4816	1986	Standard Test Method for Specific Heat of Aircraft Turbine Fuels by Thermal Analysis	Cp determination using n-heptane or sapphire as reference material.	DSC
ASTM D	5023	1999	Standard Test Method for measuring the Dynamic Mechanical Properties of Plastics using 3-Point Bending	Viscoelastic properties of thermoplastic and thermosetting resins and composite systems using 3 point bending. Storage, loss and complex modulus, and tan delta as a function of frequency, time, or temperature; 0.01 to 100 Hz.	DMA
ASTM D	5024	1995	Standard Test Method for Measuring the Dynamic Mechanical Properties of Plastics in Compression	see ASTM D 5023.	DMA
ASTM D	5026	1995	Standard Test Method for Measuring the Dynamic Mechanical Properties of Plastics in Tension	see ASTM D 5023.	DMA
ASTM D	5028	2003	Standard Test Method for Curing properties of Pultrusion Resins by Thermal Analysis	Determination of curing parameters.	DSC

Norm	No.	Year	Title	Short description	Technique
ASTM D	5418	1995	Standard Test Method for Measuring the Dynamic Mechanical Properties of Plastics Using a Dual Cantilever Beam	Viscoelastic properties of thermoplastic and thermosetting resins and composite systems in the form of rectangular bars molded directly or cut from sheets, plates, or molded shapes. The elastic modulus may be used to characterize thermomechanical properties of a plastic material or its composition.	DMA
ASTM D	5483	1995	Standard Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry	Calibration at 10 K/min uses 157.4 °C for indium due to tau lag of 5 s!	HP DSC
ASTM D	5885	1997	Standard Test Method for Oxidative Induction Time of Polyolefin Geosynthetics by High-Pressure Differential Scanning Calorimetry	OIT under 3.4 MPa static O ₂ . No gas switching.	HP DSC
ASTM D	6186	1998	Standard Test Method for Oxidation Induction Time (OIT) of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC)	This test method covers the determination of the oxidation induction time of lubricating oils in oxygen at 3.5 MPa (500 psig) and at temperatures between 130 and 210 °C. Calibration at 10 K/min uses 157.4 °C for indium due to tau lag of 5 s!	HP DSC
ASTM D	6370	1999	Standard Test Method for Rubber - Compositional Analysis by Thermogravimetry (TGA)	Heating from 50 to 560 °C at 10 K/min in nitrogen, cooling to 300 °C, heating to 800 °C at 10 K/min in air or O ₂ .	TGA
ASTM D	6375	1999	Standard Test Method for Evaporation Loss of Lubricating Oils by Thermogravimetric Analyzer (TGA) Noack Method	The test method is applicable to base stocks and fully formulated lubricant oils having a Noack evaporative loss ranging from 0 to 30 wt%. This procedure requires much smaller specimens and is faster, easier and safer than the standard Noack method.	TGA
ASTM D	6382	1999	Standard Practice for Dynamic Mechanical Analysis and Thermogravimetry of Roofing and Waterproofing Membrane Material	DMA: ASTM D5023, D 5024, D 5026, D 5279, and D 5418 are used; 3-point bending, compression, tension, torsion, and dual cantilever modes. TGA: ASTM E 1131 is used for conducting thermogravimetric measurements of roofing and waterproofing membrane materials.	DMA TGA
ASTM D	6456	1999	Standard Specification for Finished Parts Made from Polyimide Resin	Uses ASTM D 4065.	DMA
ASTM D	6558	2000	Standard Test Method for Determination of TGA CO ₂ Reactivity of Baked Carbon Anodes and Cathode Blocks	TGA determination of CO ₂ reactivity and dusting of shaped carbon anodes and cathode blocks used in the aluminum reduction industry.	TGA
ASTM D	6559	2005	Standard Test Method for Determination of Thermogravimetric (TGA) Air Reactivity of Baked Carbon Anodes and Cathode Blocks	TGA determination of air reactivity and dusting of shaped carbon anodes and cathode blocks used in the aluminum reduction industry.	TGA
ASTM D	6604	2000	Standard Practice for Glass Transition Temperatures of Hydrocarbon Resins by Differential Scanning Calorimetry	This covers the determination of glass transition temperatures of hydrocarbon resins using DSC.	DSC
ASTM E	473	2006	Standard Terminology Relating to Thermal Analysis and Rheology	Most definitions are widely accepted.	general
ASTM E	487	1992	Standard Test Method for Constant-Temperature Stability (CTS) of Chemical Materials	Isothermal experiments at several temperatures.	DSC
ASTM E	537	1992	Standard Test Method for The Thermal Stability Of Chemicals By Differential Scanning Calorimetry	Assessing the thermal stability of chemicals in an inert or a reactive atmosphere with an absolute pressure range from 100 Pa to 7 MPa and in the temperature range from 27 to 527 °C.	HP DSC
ASTM E	698	1993	Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials Using Differential Scanning Calorimetry and the Flynn/Wall/Ozawa Method	Uses DSC, based on at least 2 measurements at different heating rates; peak temperatures are used for the evaluation.	DSC
ASTM E	793	2000	Standard Test Method for Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry	Heating and cooling rates of 10 K/min.	DSC
ASTM E	794	2006	Standard Test Method for Melting and Crystallization Temperatures by Thermal Analysis	Heating and cooling rates of 10 K/min. Onset and peak temperature are used to characterize the melting and crystallization.	DSC
ASTM E	831	2006	Standard Test Method for Linear Thermal Expansion of Solid Materials by Thermomechanical Analysis	2 to 5 mm in diameter, 2 to 10 mm in height, accuracy 2.5% for > 5ppm/K. Temperature: 120 to 900 °C.	TMA
ASTM E	928	2003	Standard Test Method for Mol Percent Impurity by Differential Scanning Calorimetry	Based on van't Hoff equation, applicable purity range from 98.5 to 100%, heating rate 0.3 to 0.7 K/min.	DSC

Norm	No.	Year	Title	Short description	Technique
ASTM E	967	2003	Standard Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers	Using 1 or 2 point calibration, table of recommended calibration standards.	DSC
ASTM E	968	2002	Standard Practice for Heat Flow Calibration of Differential Scanning Calorimeters	DSC heat flow calibration using metal standards (melting). Suggested values for the enthalpy of fusion for In (28.58 J/g) and for Zn (108.1 J/g).	DSC
ASTM E	1131	2003	Standard Test Method for Compositional Analysis by Thermogravimetry	Determination of contents of highly volatile, medium volatile and combustible compounds, and of ash. Required resolution of the balance: better than 2 µg.	TGA
ASTM E	1142	2006	Standard Terminology Relating to Thermophysical Properties	Compilation of terms and definitions used for the characterization of thermophysical properties of materials.	general
ASTM E	1231	1996	Standard practice for Calculation of Hazard Potential Figures-of-Merit for Thermally Unstable Materials	Time-to-runaway, and other kinetic parameters. Uses Arrhenius behavior and general rate law.	DSC
ASTM E	1269	2005	Standard Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry	Sapphire method without isothermal drift correction.	DSC
ASTM E	1356	2003	Standard Test Method for Assignment of Glass Transition Temperature by Differential Scanning Calorimetry	Determination of 6 characteristic temperatures during the glass transition.	DSC
ASTM E	1363	2003	Standard Test Method for Temperature Calibration of Thermomechanical Analyzers	One-point and two-point temperature calibration by penetration. Thermocouple needs to be positioned close to sample.	TMA
ASTM E	1545	1995	Standard Test Method for Assignment of the Glass Transition Temperature by Thermomechanical Analysis	Expansion mode: probe 4 to 6 mm diameter, 0 to 5 mN. Penetration mode: probe 2 to 4 mm diameter, 20 to 50 mN. T_g = intersection of tangents. Temperature has to be measured close to the specimen.	TMA
ASTM E	1582	2004	Standard Practice for Calibration of Temperature scale for Thermogravimetry	Replaces ASTM D 914. Use of either melting point or Curie point magnetic transition standards.	TGA
ASTM E	1640	1994	Standard Test Method for Assignment of the Glass Transition Temperature by Dynamic Mechanical Analysis	Peak temperature of $\tan \delta$, loss modulus or onset on storage modulus (log or linear scaling).	DMA
ASTM E	1641	2004	Standard Test Method for Decomposition Kinetics by Thermogravimetry	Requires at least 4 measurements. Determination of the temperature at 5, 10, 15 and 20% conversion. For simulations and predictions the reaction order is set to 1. This method is similar to ISO 11358-2 but differs in the mathematical treatment.	TGA
ASTM E	1782	2003	Standard Test Method for Determining Vapor Pressure by Thermal Analysis	Procedure to determine the vapor pressure of pure liquids or melts from the boiling point as measured by DTA or DSC at different pressures (5 kPa to 2 MPa).	HP DSC
ASTM E	1824	1996	Standard Test Method for Assignment of a Glass Transition Temperature Using Thermomechanical Analysis Under Tension	Glass transition of films and fibers. T_g is given by the intersection of tangents to the TMA curve.	TMA
ASTM E	1858	2003	Standard Test Method for Determining Oxidation Induction Time of Hydrocarbons by Differential Scanning Calorimetry	OIT of polymers and oils at ambient or 3.5 MPa pressure.	HP DSC DSC
ASTM E	1867	2001	Standard Test Method for Temperature Calibration of Dynamic Mechanical Analyzers	Temperature calibration by using reference materials that are filled in PTFE tubes.	DMA
ASTM E	1868	2004	Standard Test Method for Loss-on-Drying by Thermogravimetry	Amount of volatiles released from a test specimen under specific temperature and time conditions.	TGA
ASTM E	1877	2000	Standard Practice for Calculating Thermal Endurance of Materials from Thermogravimetric Decomposition Data	Procedure to calculate a thermal endurance curve and derive a relative thermal index for materials using Arrhenius activation energy data determined by ASTM E 1641.	Calculation only
ASTM E	1953	2005	Standard Practice for Description of Thermal Analysis Apparatus and Rheology Apparatus	General descriptions of apparatus used in thermal analysis; specifies instrument performance parameters for each test method.	general
ASTM E	1970	2006	Standard Practice for Statistical Treatment of Thermoanalytical Data	Definition of mean, standard deviation, relative standard deviation, pooled standard deviation, pooled relative standard deviation and the best fit to a straight line.	general
ASTM E	2008	2004	Standard Test Method for Volatility Rate by Thermogravimetry	Procedures to quantify the volatility of solids and liquids using TGA. Test results are expressed as rates (1 st derivative of the TGA curve with respect to time).	TGA

Norm	No.	Year	Title	Short description	Technique
ASTM E	2009	1999	Standard Test Method for Oxidation Onset Temperature (OOT) of Hydrocarbons by Differential Scanning Calorimetry	Oxidation onset temperature (OOT) at 10 K/min either in oxygen at ambient pressure, in oxygen at 3.5 MPa, or in air at ambient pressure. 3-mg sample in Al-crucible.	DSC
ASTM E	2040	2003	Standard Test Method for Mass Scale Calibration of Thermogravimetric Analyzers	This test method describes the calibration of the mass (or weight) scale of thermogravimetric analyzers.	TGA
ASTM E	2041	2003	Standard Test Method for Estimating Kinetic Parameters by Differential Scanning Calorimetry Using the Borchardt and Daniels Method	n-th order kinetics. Method A assumes $n = 1$. Method B uses multiple linear regression.	DSC
ASTM E	2043	1999	Standard Test Method for Nonvolatile Matter of Agricultural Adjuvant Solutions by Thermogravimetry	Determination of the non-volatile matter content of agricultural tank mix adjuvant solutions by thermogravimetry.	TGA
ASTM E	2069	2000	Standard Test Method for Temperature Calibration on Cooling of Differential Scanning Calorimeters	Difference between transition temperatures upon heating and cooling in the temperature range of 60 to 140 °C using liquid crystals.	DSC
ASTM E	2070	2003	Standard Test Method for Kinetic Parameters by Differential Scanning Calorimetry Using Isothermal Methods	This method describes the determination of activation energy, pre-exponential factor and reaction order using a series of isothermal DSC experiments in a narrow temperature range (~ 10 K). The procedure is applicable to low nth order reactions and to autocatalyzed reactions such as thermoset curing, pyrotechnic reactions or crystallization in the temperature range from 30 to 630 °C. The method can only be applied if DSC curves do not exhibit shoulders or baseline shifts.	DSC
ASTM E	2071	2000	Standard Practice for Calculating Heat of Vaporization or Sublimation from Vapor Pressure Data	Describes the determination of the heat of vaporization or sublimation from measured vapor pressure data obtained by DSC.	DSC
ASTM E	2092	2004	Standard Test Method for Distortion Temperature in Three-Point Bending by Thermomechanical Analysis	The distortion temperature is that temperature at which a test specimen of defined geometry is deformed to a specified extent when exposed to a stress of 0.455 and 1.82 MPa (66 and 264 psig).	TMA
ASTM E	2105	2000	Standard Practice for General Techniques of Thermogravimetric Analysis (TGA) Coupled With Infrared Analysis (TGA/IR)	TGA coupled with IR or MS.	TGA
ASTM E	2113	2004	Standard Test Method for Length Change Calibration of Thermomechanical Analyzers	Calibration of the length scale of a thermomechanical analyzer using a suitable reference material. The temperature range is from -150 °C to 1000 °C.	TMA
ASTM E	2160	2001	Standard Test Method for Heat of Reaction of Thermally Reactive Materials by Differential Scanning Calorimetry	Determination of the heat of reaction as well of the onset and peak heat flow temperature for the exothermic reaction of thermally reactive materials.	DSC
ASTM E	2161	2006	Standard Terminology Relating to Performance Validation in Thermal Analysis	Terminology related to the validation of thermal analysis methods and instrumentation.	general
ASTM E	2206	2002	Standard Method for Force Calibration of Thermomechanical Analyzers	This method describes the calibration of the force applied to a sample in thermomechanical analyzers in the range of 0 to 1 N.	TMA
ASTM E	2254	2003	Standard Test Method for Storage Modulus Calibration of Dynamic Mechanical Analyzers	Describes the calibration of the storage modulus scale in a DMA in the temperature range -100 to 300 °C using various reference materials (steel, Monel, copper, aluminum, PE; respective modulus values are given).	DMA
ASTM E	2347	2005	Standard Test Method for Indentation Softening Temperature by Thermomechanical Analysis	Softening upon heating to a modulus less than 6.0 MPa. This test method describes the determination of the temperature at which the specific modulus of either 6.65 (Method A) or 33.3 MPa (Method B) (equivalent to Test Method D 1525) of a test specimen is realized by indentation (1 mm ² probe).	TMA
ASTM E	2402	2005	Standard Test Method for Mass Loss and Residue Measurement Validation of Thermogravimetric Analyzers	Reference materials with known low, medium and high volatility are measured for validation purposes of the thermogravimetric analyzer. The prescribed procedure is doubtful for high volatile materials.	TGA
ASTM E	2403	2006	Standard Test Method for Sulfated Ash of Organic Materials by Thermogravimetry	Reaction of common metals found in organic materials (such as sodium, potassium, lithium, calcium, magnesium, zinc, or tin) with sulphuric acid to produce the sulfate salts of the metals. The method requires the use of sulphuric acid as reactive gas.	TGA
ASTM E	2425	2005	Standard Test Method for Loss Modulus Conformance of Dynamic Mechanical Analyzers	Uses poly(methylmethacrylate) as a reference material. Tests have to be performed at 21 °C	DMA

Norm	No.	Year	Title	Short description	Technique
ASTM F	2004	2000	Standard Test Method for Transformation Temperature of Nickel-Titanium Alloys by Thermal Analysis	Martensitic transition temperatures of nickel-titanium shape memory alloys.	DSC
BS	7825-3.1	1997	Calibration of rubber and plastics test equipment. Calibration schedules. Thermal properties	Provides schedules for the calibration of a range of methods of tests used for the evaluation and investigation of the dimensional properties of rubber and plastic materials.	TMA
CEC	L-85-T-99	1999	Hot surface oxidation – Pressure DSC (for lubricating oils)	OIT at 0.69 MPa in static air at 210 °C, special crucibles (Seiko) are required.	HPDSC
CEI/IEC	538	1985	Appendix D: Test method for copper-catalyzed oxidative degradation of polyolefin insulated conductors (OIT)	Similar to ASTM D 3895.	DSC
CEI/IEC	1006	1991	Methods of test for the determination of glass transition temperature of electrical insulating materials	Method C: DMA.	DMA
CEI/IEC	1006	1991	Methods of tests for the determination of glass transition temperature of electrical insulating materials	DSC: Midpoint: half heat flow difference between the extrapolated onset and extrapolated endset. TMA: Expansion mode: flat probe 2 to 5 mm diameter, 5 to 10 mN load. Penetration mode: hemispherical probe with a diameter of less than 5 mm, 50 mN to 1 N load.	DSC TMA
CEI/IEC	1074	1991	Determination of heats and temperatures of melting and crystallization of electrical insulating materials by DSC	Heating and cooling rates of 10 K/min. Equivalent to EN 61074.	DSC
CSA	Z245.20	2002	External Fusion Bond Epoxy Coating for Steel Pipe – External Polyethylene Coating for Pipe	Covers the qualification, application, inspection, testing, handling, and storage of materials required for plant-applied fusion bond epoxy (FBE) coating of bare steel pipes.	DSC
DIN	3761 Part 15	1984	Determination of cold resistance of elastomers by DTA, rotary shaft lip type seals for automobiles	Glass transition temperature (inflection point).	DSC
DIN	51004	1994	Determination of the melting temperature of crystalline materials using differential thermal analysis	Peak evaluation; purity.	DSC
DIN	51005	1993	Thermal analysis (TA) - Terms	General terms and principles.	general
DIN	51006	2005-2007	Thermal analysis – Thermogravimetry - Principles	Thermal analysis and TGA terms and principles.	TGA
DIN	51007	1994	Thermal Analysis – Differential Thermal Analysis - Principles	Determination of specific heat capacity by DSC. Based on known specific heat of sapphire. Require isothermal blank drift correction.	DSC
DIN	51045	1989	Part 1: Determination of the thermal expansion of solids; Basics rules	Discussion of different experimental parameters such as load, heating rate, etc.	TMA
DIN	53513	1983	Determination of the viscoelastic properties of elastomers on exposure to forced vibration at non-resonant frequencies	Overview of different standards on the determination of the glass transition temperature and the analysis of crystallization behavior.	DMA
DIN	53535	1982	Testing of rubber, general requirements for dynamic testing	Testing rubbers and elastomers by DMA; general principles.	DMA
DIN	53545	1990	Determination of low-temperature behavior of elastomers; principles and test methods	Testing of rubber and elastomers using DSC, TMA and DMA methods. DMA: see also DIN 53513, DIN 53535.	DMA DSC TMA
DIN	53547	1987	Testing of plastics; determination of the elastic modulus by tensile, compression and bend testing	Replaced by DIN EN ISO 527 Parts 1 and 2, DIN EN ISO 178 and DIN EN ISO 604.	DMA
DIN	53548	1983	Testing of rubber; determination of the freezing behavior of vulcanized rubbers by modulus-temperature measurement (Gehman test)	Gehman test for rubber and elastomers.	DMA
DIN	53765	1994	Testing of plastics and elastomers; thermal analysis, DSC method	Evaluation: specific heat, glass transition, melting, crystallization, chemical reaction (under dynamic and isothermal conditions).	DSC
DIN	57472	1983	Testing of cables, wires and flexible cords; crystallite melting point (VDE specification).	(VDE 0472). Peak temperature DSC.	DSC
DIN	53752	1980	Testing of plastics; determination of the coefficient of linear thermal expansion		TMA

Norm	No.	Year	Title	Short description	Technique
DIN	65467	1989	Aerospace. Testing of organic polymeric materials with and without reinforcement	Determination of glass transition, melting or curing reactions of reactive resins.	DSC
DIN	65583	1999	Aerospace - Fiber reinforced materials - Determination of glass transition of fiber composites under dynamic load.	T _g determination of storage modulus by DMA: A1: single cantilever. A2: 3-point bending. A3: dual cantilever. and torsion-pendulum (Method B). Temperature calibration with PC at 153.4 °C (glass transition, peak maximum in tan δ).	DMA
EN	728	1997	Plastics piping and ducting systems. Polyolefin pipes and fittings. Determination of oxidation induction time.	Samples are heated in N ₂ for example to 210 °C. After stabilization, the gas is switched to oxygen. The time to the onset of the exothermic oxidation peak is reported as OIT.	DSC
EN, IEC	61074	1993	Determination of Heats and Temperatures of Melting and Crystallization of Electrical Insulating Materials by Differential Scanning Calorimetry		DSC
ENV	1159-3	1993	Advanced technical ceramics. Ceramic composites. Thermophysical properties. Part 1: Determination of thermal expansion		TMA
ENV	1159-3	1995	Advanced technical ceramics. Ceramic composites. Thermophysical properties. Part 3: Determination of specific heat capacity	Method B – DSC by step and continuous method; uses sapphire as a reference material.	DSC
IP	389	1993	Wax appearance temperature (WAT) of middle distillate fuels by DTA or DSC	The fuel is cooled at 10 K/min (Method A) or 1 K/min (Method B). The onset temperature of the crystallization exotherm is recorded.	DSC
IPC-TM-650	2.4.24	1994	Glass Transition Temperature and z-axis Thermal Expansion by TMA	Glass transition temperature and expansion in the z-axis of printed circuit boards. T _g is the intersection of the tangents. T _g can also be reported as the midpoint of the step change in the CTE-curve.	TMA
IPC-TM-650	2.4.25	1994	Glass Transition Temperature and Cure Factor by Differential Scanning Calorimetry	The cure factor is the difference of the glass transition temperature between the first and the second heating.	DSC
IPC-TM-650	2.4.24.1	1994	Time to delamination (TMA Method)	Laminate or printed board is heated to 260 °C at 10 K/min and kept isothermally at this temperature until an irreversible thickness change is observed (segment time).	TMA
IPC-TM-650	2.4.41	1986	Coefficient of Linear Thermal Expansion of Electrical Insulating Boards	Heating at 5 K/min.	TMA
IPC-TM-650	2.4.24.2	1995	Glass Transition Temperature of Organic Films - DMA Method	RSA-II is mentioned as example of instrument. 1 Hz, 2 K/min, peak of tan δ.	DMA
IPC-TM-650	2.4.24.3	1995	Glass Transition Temperature of Organic Films - TMA Method	T _g determined by intersection of tangents, 5 K/min, 30 mN with preheating at 20 K/min.	TMA
IPC-TM-650	2.4.24.4	1998	Glass Transition Temperature and Thermal Expansion of Materials Used in High Density Interconnection (HDI) and Microvias - DMA Method	T _g determined by onset of E' (logarithmic scaling), peak of tan δ and peak of E''.	DMA
IPC-TM-650	2.4.41.3	1995	In-Plane Coefficient of Thermal Expansion, Organic Films (TMA)		TMA
IPC-TM-650	2.4.24.5	1998	Glass Transition Temperature and Thermal Expansion of Materials Used in High Density Interconnection (HDI) and Microvias - TMA Method	Inert gas, first heating run at 10 K/min, second at 5 K/min; CTE as mean value below and above T _g ; T _g as intersection of tangents or as midpoint of the instantaneous CTE curve.	TMA
ISO	75-1	1993	Plastics – Determination of temperature of deflection under load – Part 1: General test method	Description of an apparatus for compression and bending.	TMA
ISO	1043-4	1998	Plastics – Symbols and abbreviated terms. Part 4: Flame retardants		general
ISO	1043-1	2001	Plastics – Symbols and abbreviated terms. Part 1: Basic polymers and their special characteristics		general
ISO EN DIN	3146	1985	Determination of melting behavior (melting temperature or melting range) of semicrystalline polymers	T _{onset} , extrapolated T _{peak} .	DSC

Norm	No.	Year	Title	Short description	Technique
ISO	6721-6	1996	Plastics - Determination of dynamic mechanical properties - Part 6: Shear vibration - Non-resonance method	Determination of the complex modulus using shear; for materials with a modulus in the range of 0.1 MPa to 50 MPa.	DMA
ISO	6721-5	1996	Plastics - Determination of dynamic mechanical properties - Part 5: Flexural vibration - Non-resonance method	Determination of the complex modulus using single cantilever; for materials with a modulus in the range of 10 MPa to 200 GPa.	DMA
ISO	6721-4	1994	Plastics - Determination of dynamic mechanical properties - Part 4: Tensile vibration - Non-resonance method	Determination of the complex modulus using tension; for materials with a modulus in the range of 10 MPa to 5 GPa. Sample length should be 10 cm!	DMA
ISO	6721-1	1994	Plastics - Determination of dynamic mechanical properties - Part 1: General principles	Theoretical background and summary of terms and evaluation procedures; valid for all other standards.	DMA
ISO	6964	1986 2001	Polyolefin pipes and fittings – Determination of carbon black content by calcination and pyrolysis	Describes various test method and basic specifications.	TGA
ISO DIN	7884-8	1987 1998	Glass - Viscosity and viscometric fixed points - Part 8: Determination of (dilatometric) transformation temperature		TMA
ISO DIN	7991	1987 1998	Glass - Determination of coefficient of mean linear thermal expansion (ISO 7991:1987)	Determination of coefficient of mean linear thermal expansion: uses a pushrod dilatometer.	TMA
ISO	9924-1	2000	Rubber and rubber products -Determination of the composition of vulcanizates and uncured compounds by thermogravimetry	Part 1: Butadiene, ethylene-propylene copolymer, SBR, and others. Determination of total organic component, carbon black and ash.	TGA
ISO	9924-2	2000	Rubber and rubber products -Determination of the composition of vulcanizates and uncured compounds by thermogravimetry	Part 2: Acrylonitrile-butadiene and halobutyl rubbers (leaving carbonaceous residues). Determination of total organic component, carbon black and ash.	TGA
ISO	10112	1991	Damping materials – Graphical presentation of the complex modulus	Describes how experimental data obtained from DMA can be evaluated and presented.	DMA
ISO (TR)	10837	1991	Technical Report : Determination of the thermal stability of polyethylene (PE) for use in gas pipes and fittings	Heat in N ₂ at 20 K/min to 200 °C; switch to oxygen after 5 min and determine the oxidation induction time.	DSC
ISO	11357-7	1999	Plastics - Differential scanning calorimetry (DSC) - Part 7: Determination of crystallization kinetics	Isothermal and dynamically cooling experiments either at 3 distinct temperatures or 3 different heating rates. Uses the methods developed by Ozawa and Avrami.	DSC
ISO	11357-6	2002	Plastics- Differential scanning calorimetry (DSC) - Part 6: Determination of oxidation induction time	OIT.	DSC
ISO	11357-5	1999	Plastics- Differential scanning calorimetry (DSC) – Part 5: Determination of characteristic reaction-curve temperatures and times, enthalpy of reaction and degree of conversion	Determination of polymerization temperatures and/or times and polymerization kinetics.	DSC
ISO	11357-4	2005	Plastics - Differential scanning calorimetry (DSC) – Part 4: Determination of specific heat capacity	Specific heat capacity by sapphire method (requires blank, sapphire and sample run).	DSC
ISO	11357-3	1999	Plastics - Differential scanning calorimetry (DSC) – Part 3: Determination of temperature and enthalpy of melting and crystallization	Determination of temperature and enthalpy of melting and crystallization.	DSC
ISO	11357-2	1999	Plastics - Differential scanning calorimetry (DSC) – Part 2: Determination of glass transition temperature	Determination of glass transition temperature.	DSC
ISO	11358-2	2005	Plastics - Thermogravimetry (TG) of polymers – Part 2: Determination of activation energy	Determination of kinetic parameters. Uses the Ozawa and Flynn-Wall approach; same as ASTM E1641.	TGA
ISO	11359-3	2002	Plastics - Thermomechanical analysis (TMA) – Part 3: Determination of penetration temperature	Determination of the penetration temperature.	TMA
ISO	11357-1	1997	Plastics - Differential scanning calorimetry (DSC) – Part 1: General principles	Principle of the heat flow DSC; temperature scanning measurement, isothermal measurement.	DSC

Norm	No.	Year	Title	Short description	Technique
ISO	11359-2	1999	Plastics - Thermomechanical analysis (TMA) – Part 2: Determination of coefficient of linear thermal expansion and glass transition temperature	Determination of the linear expansion coefficient and the glass transition temperature.	TMA
ISO	11358-1	1997	Plastics - Thermogravimetry (TG) of polymers – Part 1: General principles		TGA
ISO	11359-1	1999	Plastics - Thermomechanical analysis (TMA) – Part 1: General principles	General principles.	TMA
ISO	11409	1993	Plastics -Phenolic resins - Determination of heats and temperatures of reaction by Differential Scanning Calorimetry	Requires medium pressure steel crucible.	DSC
ISO	12989-2	2004	Carbonaceous materials used in the production of aluminum – baked anodes and sidewall blocks – Determination of reactivity to air – Part 2: Thermogravimetric method		TGA
ISO EN	11357-1	1997	Plastics - Differential scanning calorimetry – Part 1: General principles	Description of general principles.	general
ISO/DIS	22768	2005	Rubber, raw - Determination of the glass transition temperature by differential scanning calorimetry (DSC)		DSC
JIS K	129	1994	General rules of thermal analysis	Definitions of terms and principles for DTA, DSC, TMA, TGA.	general
JIS K	7120	1987	Testing Methods of Plastics by Thermogravimetry		
JIS K	7121	1987	Testing Methods for Transition Temperatures of Plastics		
JIS K	7122	1987	Testing Methods for Heat of Transition of Plastics		
JIS K	7123	1987	Testing Methods for Specific Heat Capacity of Plastics		
JIS K	7196	1991	Testing Method for Softening Temperature of Thermoplastics Film and Sheet by Thermomechanical Analysis		TMA
NF T	46-047		Vulcanized or non-vulcanized rubber. Compositional analysis of mixtures by thermogravimetry	Content of plasticizer, rubber (or organic compounds) and carbon black.	TGA
NF T	54	1986	Plastics - polyethylene pipes and fittings - determination of thermal stability by thermal analysis-isothermal method		DSC
OECD	102	1997	Guidelines for the Testing of Chemicals: Melting Point	Various principles; reference is made to other standards.	DSC
OECD	103	1997	Guidelines for the Testing of Chemicals: Boiling Point	Various principles; reference is made to other standards.	DSC
UNI	8698	2001	Test of raw and vulcanized elastomers by TG	Weight loss and residue.	TGA
46-047VDA	675115	1992	Elastomeric components in motor vehicles. Test methods for the identification of low temperature performance features (in German)	Glass transition temperature.	DSC
VDA	675135	1992	Elastomeric components in motor vehicles (in German)	Organic constituents, oxidizable constituents, inorganic residues.	TGA

Remarks: The last column indicates the thermal analysis technique to which the standard refers; if no technique is given, it means that the standard has not been reviewed in this respect.

Note: Many of the national standards are the same or are similar to the ISO/IEC standards and often even use the same numbers.

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