

Chapter 1

DEFINITIONS, NOMENCLATURE, TERMS AND LITERATURE

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1. INTRODUCTION

This introductory chapter of the Handbook of Thermal Analysis and Calorimetry will present the tools for the exchange of unequivocal, clear information in these fields.

Communication free from misunderstandings is possible only if the meaning and contents of the terms used have been defined and generally accepted. Prerequisite for this is the *definition* of methods of thermal analysis and calorimetry, which leads to a *nomenclature* describing the methods and the instruments. In addition, measuring systems must be clearly characterized on the basis of suitable performance criteria, and it must finally be possible to describe characteristic measurement results by means of suitable *terms*. It is therefore the primary objective of this chapter to present a vocabulary applicable to both thermal analysis and calorimetry. In addition, reference will briefly be made to important *literature* in these fields.

1.1. Basic considerations

The terms *thermal analysis (TA)* and *calorimetry* denote a variety of measuring methods, which involve a change in the temperature of the sample to be investigated.

These methods include the measurement of the time dependence of the sample temperature, when the sample follows a temperature-time variation imposed on it.

Many thermoanalytical instruments and calorimeters can also be used for isothermal measuring methods. Methods allowing the experiment to be

conducted under isothermal conditions therefore also belong to the field of thermal analysis and calorimetry.

Which are the physical quantities measured by methods of thermal analysis and calorimetry?

The quantities concerned are either changes in variables of state of the sample (temperature, mass, volume, etc.) which are used to determine process or material properties (e.g. heat of transition, heat capacity, thermal expansivity, etc.) or changes in the sample's material properties (chemical composition, interatomic forces, crystalline structure, etc.). These changes take place at varying or constant sample temperature. If these processes are connected with the generation/consumption of heat, one also speaks of *thermal events* as the events underlying the measurement (even if the generated/consumed heat itself is not measured).

In modern measuring instruments, many of these changes in the variables of state and material properties are picked up by specific sensors and transformed into electric signals (indirect measuring methods). To obtain quantitative information about these changes, the true value of the quantity sought must be assigned to this signal through calibration.

Direct measuring methods, by which the quantity to be measured is directly related to the SI base units (International System of Units (SI): The coherent system of units adopted and recommended by the General Conference on Weights and Measures (CPGM)) are not commonly used. It would be a direct measurement if, for example, the thermal expansion of a sample was measured with a line scale or if the change in the sample mass was determined by means of a beam scale and weights.

1.2. Definition ranges and limits of thermal analysis

In connection with the definition of thermal analysis and the description of thermoanalytical methods, the problem arises of how to delimit thermoanalytical techniques from the large number of other well-established measuring techniques. The definition of thermal analysis used to date (cf. section 2.2.) has been made in such general terms and it is so comprehensive that almost all measurements of physical and chemical quantities can be included (measurements of viscosity, density, concentration, hardness, electrical resistance, emittance, thermal conductivity, for example) in which the quantity to be measured is influenced by the temperature.

This conflict between the high degree of comprehensiveness claimed by thermal analysis and the fact that almost all of the long-established measuring techniques are independent can be solved only by pragmatic agreement. It is expedi-

ent and useful to define those methods as thermoanalytical methods for which perfected instruments are commercially available (the so-called classical thermoanalytical methods, e.g. thermogravimetry (TG), differential thermal analysis (DTA)) and those methods in which the forced change of the sample temperature is of primary importance, even if conventional physical quantities are measured. Such a pragmatic delimitation is, of course, neither conclusive nor sharp.

1.3. General aspects related to classification principles

It is the aim of a system of definitions, and of the nomenclature resulting from it for the field of thermal analysis and calorimetry, to clearly describe and denote

- metrological principles and
- characteristic measured quantities.

The use of the recommended terms reflects a *classification system*, and it will be ensured in this way that a certain term always furnishes the same information. The system of definitions should have a hierarchical structure, from the general to the particular. In many cases, basic definitions (e.g. that of thermal analysis, cf. section 2.2.) are by no means necessarily given on the basis of scientific or metrological arguments; they are defined taking historical facts and/or their suitability into consideration.

Measuring techniques (and, therefore, measuring instruments as well) must be sorted on the basis of suitable criteria, i.e. classification characteristics must be found which allow measuring techniques and measuring instruments to be assigned to groups which can be described in uniform terms. These groups in turn must be hierarchically structured as far as this is necessary. This means that primary, secondary etc. classification characteristics must be found. Here, too, nothing has been defined in advance on the part of science; differing primary criteria are possible and are in fact used.

Calorimeters are an example of this. Many measuring instruments applying different measuring principles come under this generic term. Several classification systems have been proposed, none of them has so far become generally accepted (cf. section 2.5.1.).

1.4. Features common to all methods of thermal analysis

Thermoanalytical methods are usually not equilibrium methods. In general, the change in the sample temperature does not take place so slowly that there is thermal equilibrium both between the sample and its surroundings and inside the sample.

The fact that, in dynamic operation, there is no thermal equilibrium between the sample and the surroundings can be taken into account by the determination

of the *thermal lag*. In addition, it should be borne in mind that the sample temperature is usually not homogeneous and that the conditions become very complex as soon as the sample generates or consumes heat and/or changes its mass, its volume, its composition or its structure. Thermoanalytical methods usually furnish integral measurement results, i.e. data which are non-specific as regards the sample volume; the values concerned are mean values. In general, it cannot be found out where a reaction/transition begins or how quickly a certain crystallite grows in a structure.

Thermoanalytical methods may be specific for certain reactions/transitions, for example thermogravimetry for reactions involving a gaseous component, or magneto-gravimetric methods for magnetic transitions of solids.

The results obtained by thermoanalytical and calorimetric methods can depend both on operational parameters (heating rate, atmosphere, pressure, etc.) and on sample parameters (mass, geometrical shape, structure, etc.). Interpretations should not be based on a single method. It is convenient to use simultaneous techniques (cf. section 2.3.1.) or several thermoanalytical methods and in addition, if possible, investigational methods of another kind (electrochemical, wet-chemical, spectroscopic, etc.).

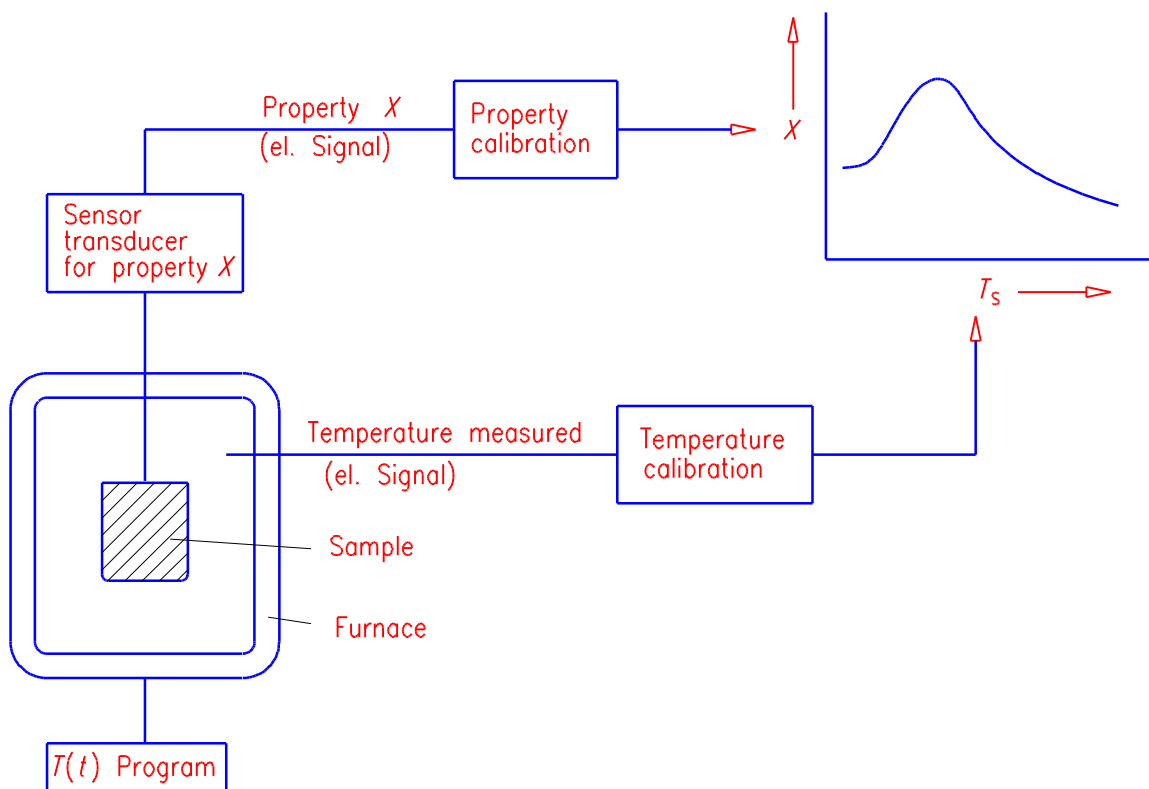


Figure 1. Basic principle of a thermoanalytical instrument.

The design of thermoanalytical instruments is usually such that the sample to be investigated is in an environment whose temperature can be varied in a defined way (cf. Figure 1). It depends on the conditions of heat transfer between sample and environment, in which way the sample temperature follows the temperature of the environment. In general, the precise determination of the sample temperature is not a trivial matter and must be made through temperature calibration.

Calorimeters exist in a large variety of designs and the principles of measurement applied differ. A feature common to all calorimeters is that they are instruments to measure heat and/or heat flow rates.

1.5. The temperature scale

The temperature scale valid on the international level from 01.01.1990 is the *International Temperature Scale of 1990 (ITS-90)* [1]. It superseded the *International Practical Temperature Scale of 1968 (IPTS-68)* [2] valid until that date.

The ITS-90 is realized by a number of fixed points, by means of standard instruments and on the basis of prescriptions for the interpolation between the temperature fixed points. The fixed points are realized by transition temperatures (freezing or melting temperatures) and by triple points of suitable pure substances. Platinum resistance thermometers are used as interpolating standard instruments in the temperature range from 13.8033 K to 961.78 °C. Above 961.78 °C (the freezing point of silver), radiation thermometers (spectral pyrometers) are used.

There are differences between the ITS-90 and the temperature scales valid before, which may be of significance in certain cases (comparison with data in the literature). The temperature $t_{90} = 20.000$ °C (ITS-90), for example, corresponds to the temperature $t_{68} = 20.005$ °C (IPTS-68), that is to say, there is a difference of 5 mK between the two scales. The different temperature scales and the conversion of one scale to the other are described in [1 - 4].

(In thermal analysis, thermocouples are normally used for temperature measurement. In rare cases, resistance thermometers or semiconductor sensors are used. These temperature sensors are usually calibrated *in situ* with the aid of reference materials (cf. section 1.6.)).

1.6. Definitions related to calibration

Calibration means [5]: "The set of operations that establish, under specified conditions, the relationship between values of a quantity indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material, and the corresponding values realised by standards.

Notes:

- (1) The result of a calibration permits either the assignment of values of measurands* to the indications or the determination of corrections with respect to indications.
- (2) A calibration may also determine other metrological properties such as the effect of influence quantities."

A *standard* can be represented by a (certified) reference material (cf. below), but also by a material measure (e.g. weight), a measuring instrument (e.g. micrometer) or a measuring system (e.g. current-carrying electrical resistor).

A *reference material (RM)* is a "Material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for

* particular quantity subject to measurement

2.4. Classification, names and definitions of thermoanalytical methods

This section gives definitions of the most important thermoanalytical methods. Reference is made to basically different patterns or measuring principles of the instruments concerned. If necessary, directions are given as regards the presentation of the measured curve.

2.4.1. Heating or cooling curve analysis

A technique in which the change of the temperature of the sample is analysed while the sample is subjected to a temperature alteration (heated or cooled). (Cf. Figure 2).

2.4.2. Differential thermal analysis (DTA)

A technique in which the change of the difference in temperature between the sample and a reference sample is analysed while they are subjected to a temperature alteration.

Two different designs exist:

- *measuring systems with free standing crucibles* (cf. Figure 3);
- *block measuring systems* (cf. Figure 4).

Table 2

Secondary classification scheme of methods of thermal analysis

| Property under study | Secondary classification criteria/distinguishing features | Method, Abbreviation (Remarks) |
|---------------------------------|---|---|
| Dimension/mechanical properties | With or without any kind of force acting on sample | Generic term: Thermomechanical Analysis, TMA |
| | Static force | Static Force Thermomechanical Analysis, sf-TMA |
| | Special case: Negligible force | Thermodilatometry |
| | Dynamic force | Dynamic Force Thermomechanical Analysis, df-TMA |
| | Special case: Modulated force | Modulated Force Thermomechanical Analysis, mf-TMA |
| Electrical properties | With or without any kind of electric field | Generic term: Thermoelectrical Analysis, TEA |
| | Without superimposed electric field | Thermally Stimulated Current Analysis, TSCA |
| | Alternating electric field (dynamic mode) | Generic term: Alternating Current Thermo-electrical Analysis, ac-TEA |
| | | Special case: Dielectric Thermal Analysis, DETA |
| Magnetic properties | With or without any kind of magnetic field | Generic term: Thermomagnetic Analysis (Various techniques to measure susceptibility, permeability etc.) |
| Optical properties | | Generic term: Thermooptical Analysis, TOA |
| | Intensity of radiation emitted | Thermoluminescence Analysis |
| | Intensity of total radiation reflected or transmitted | Thermophotometric Analysis |

Continuation Table 2

| Property under study | Secondary classification criteria/distinguishing features | Method, Abbreviation (Remarks) |
|---|---|---|
| | Intensity of radiation of specific wavelength(s) | Thermospectrometric Analysis |
| | The refractive index is measured | Thermorefractometric Analysis |
| | The sample is observed by means of a microscope | Thermomicroscopic Analysis |
| Acoustic properties | Acoustic waves are monitored after having passed through the sample | Generic term: Thermoacoustic Analysis, TAA |
| | Acoustic waves emitted by the sample are monitored | Thermally Stimulated Sound Analysis |
| Chemical composition/ crystalline structure/ microstructure | Analysing the change in chemical composition and/or in the crystalline structure and/or in the microstructure of the sample | Various techniques (optical, nuclear, X-ray, electrical, etc.) |
| | Special case: Use of diffraction technique | Thermodiffractometric Analysis, TDA |
| | Special cases: Investigation of the gas exchanged with the sample | Generic term: Thermally Stimulated Exchanged Gas Analysis, EGA |
| | Determination of the composition and/or amount of gas | Various techniques |
| | Monitoring of the amount only | Thermally Stimulated Exchanged Gas Detection |
| | Determination of the composition (and the amount) | Thermally Stimulated Exchanged Gas Determination (e.g. by gas chromatography, mass spectrometry etc.) |
| | Special case: Release of trapped radioactive gas from the sample is monitored | Emanation Thermal Analysis, ETA |

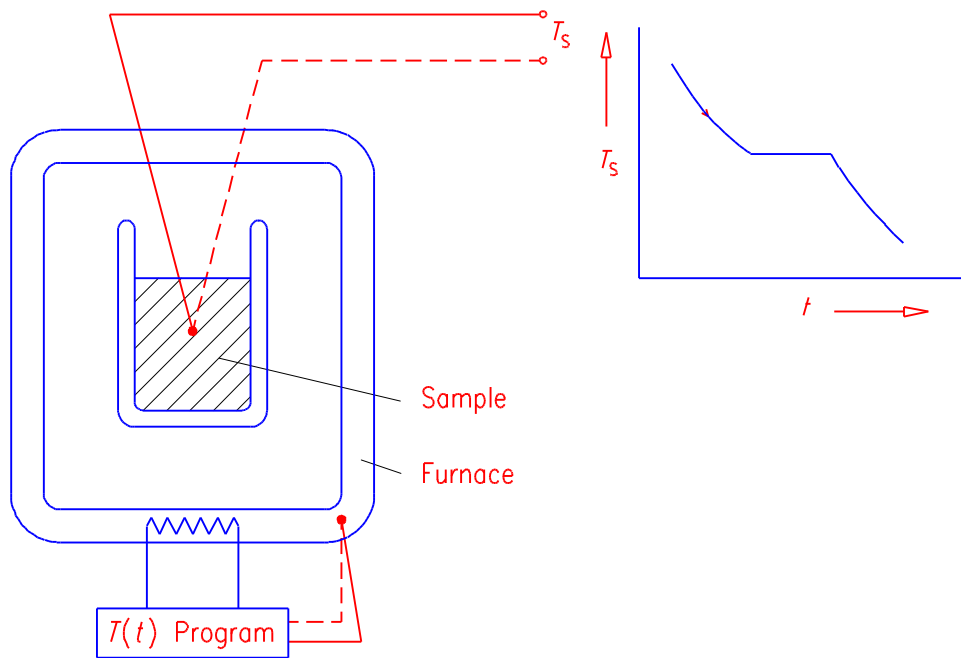


Figure 2. Device to determine the heating or cooling curve.

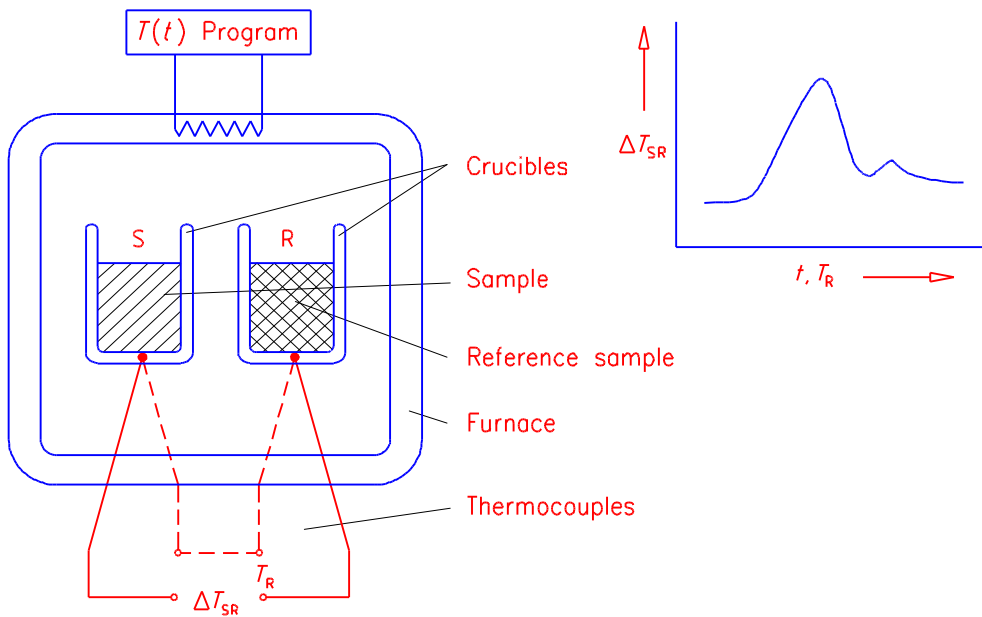


Figure 3. DTA measuring system with free standing crucibles. The crucibles are contacted by thermocouples to measure ΔT_{SR} and the reference temperature T_R .

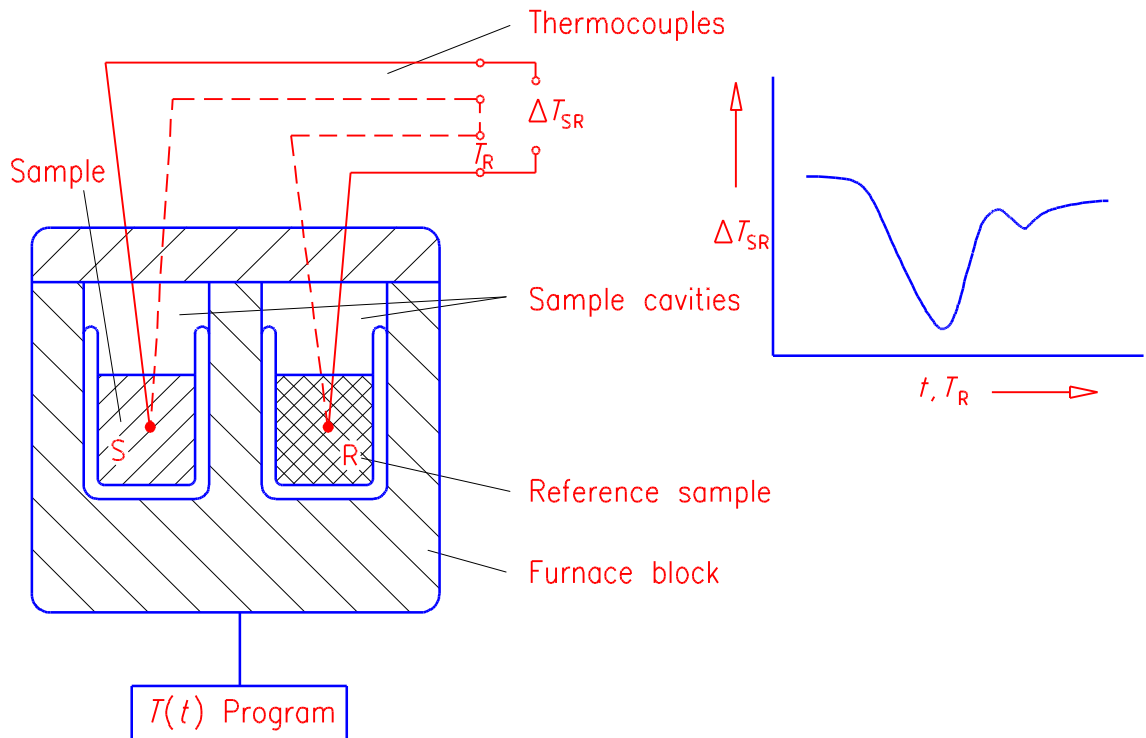


Figure 4. DTA block measuring system.
The temperature sensors are located inside the specimens.

2.4.3. Differential scanning calorimetry (DSC)

A technique in which the change of the difference in the heat flow rate to the sample and to a reference sample is analysed while they are subjected to a temperature alteration.

Note : The difference between DTA and DSC is the assignment of a heat flow rate difference (by calibration) to an originally measured temperature difference. To allow this assignment to be carried out, the instruments' design must be such that they are capable of being calibrated.

Two designs of DSC are available, whose measuring systems differ:

- *heat flux DSC* with two modifications (disk-type and cylinder-type measuring system);
- *power compensating DSC*.

2.5. Classification, names and definitions of calorimetric techniques

Calorimeters are used to measure heat and heat flow rates. Depending on which kind of heat-generating or heat-consuming process is concerned (combustion, solid-state transition or the like), which kind of sample is concerned (solid, liquid, gaseous, living being, of great volume, etc.) and under which conditions the calorimeter is to be used (temperature, pressure, atmosphere, etc.), a great variety of different calorimeters has been developed.

2.5.1. Classification system

The arrangement of the calorimeters in a classification system should be based on a simple and sensible order structure suitable for practical application. Several classification criteria have been suggested, see e.g. [10,11]. The attempt to classify every calorimeter in every detail leads to unclarity and insignificance in practice.

A particular difficulty in the classification of calorimeters arises from the fact that many calorimeters can be operated in various modes (cf. below) so that a certain instrument must often be classified in different ways, depending on the mode of operation. The same is often true of the measuring principle (cf. below) which can be changed in certain calorimeters. The problem of calorimeter classification thus is that, firstly, a simple primary classification criterion orientated to the instruments available must be found and that, secondly, a clear and flexible classification must be guaranteed without too many additional criteria being applied.

To achieve this aim, three primary groups of criteria are taken as a basis of classification, which in turn comprise secondary criteria (the classification system used here follows the suggestions in reference [10]).

The groups of primary criteria are related to:

- (1) *the principle of measurement;*
- (2) *the mode of operation;*
- (3) *the construction principle.*

The individual groups of primary criteria comprise the following secondary criteria:

(1) ***The principle of measurement***

- *heat-compensating principle:* determination of the energy (power) required for compensating the heat (heat flow rate) to be measured;
- *heat-accumulating principle:* measurement of the temperature change caused by the heat to be measured;

- *heat-exchanging principle*: measurement of the temperature difference between sample and surroundings caused by the heat (heat flow rate) to be measured.
- (2) ***The mode of operation*** (temperature conditions)
- *static*: isothermal;
isoperibol¹⁾;
adiabatic²⁾;
 - *dynamic*: scanning of surroundings;
isoperibol scanning³⁾;
adiabatic scanning.
- (3) ***The construction principle***
- *single measuring system*;
 - *twin or differential measuring system*.

Most of the calorimeters can be classified by means of these criteria. Not all secondary criteria from the three groups can be combined. As the heat to be measured (first) appears as a heat flow to be exchanged, there are always temperature gradients in calorimetric measuring systems so that, for example, an ideally isothermal state cannot be established. In addition, temperature differences always occur between sample and environment so that there are undesired heat leaks which must be taken into consideration as a correction, i.e. there are no ideal adiabatic operating conditions. In the following a few examples show the suitability of the classification system.

2.5.2. Examples

Heat compensating calorimeters

The effect of the heat to be measured is compensated, either passively by the phase transition of a suitable calorimeter substance (e.g. ice), or with the aid of an active control system which compensates a temperature change in the sample or the sample container through electrical heating/cooling or other suitable heat sources/sinks. The compensation energy is to be determined, for example, from the mass of the transformed calorimeter substance or from the electrical heating/cooling energy. Advantages of the compensation method are that the

¹⁾ *isoperibol* refers to constant temperature surroundings with the temperature of the measuring system possibly differing from this.

²⁾ *adiabatic* refers to a prevention of the heat exchange between measuring system (sample) and surroundings.

³⁾ *isoperibol scanning* refers to the scanning of the measuring system (sample) in surroundings at constant temperature.

measurement is carried out under quasi-isothermal conditions and heat leaks thus remain unchanged to a first approximation. Possible instruments:

- ***Ice calorimeter***

Principle of measurement: heat compensation (passive, by latent heat);

mode of operation: isothermal;

construction principle: single measuring system.

At 0 °C, a heat exchange between sample and calorimeter substance (ice) takes place; the mass of the transformed ice is determined. From this and from the known heat of transition, the heat emitted by the sample is determined.

- ***Adiabatic scanning calorimeter***

Principle of measurement: heat compensation (active, by electronic control);

mode of operation: adiabatic scanning;

construction principle: single measuring system.

A known electric heating power is fed into the sample. Heat losses into the surroundings are minimized by matching the environmental temperature. The sample's heat capacity may be obtained from the heating power and the heating rate. Heats of transition are determined from the time integral of the heating power. During a first-order transition, the calorimeter's behaviour is quasi-isothermal.

- ***Power compensating DSC***

Principle of measurement: heat compensation (active, by electronic control);

mode of operation: isoperibol scanning;

construction principle: twin measuring system.

The temperature of the surroundings remains constant (isoperibol). The twin measuring system is heated; each specimen has its own heater and temperature sensor. The temperature difference between is maintained at a minimum by increasing or decreasing the sample heating. The difference in heating power is related to the sample heat flow rate to be measured.

Heat accumulating calorimeters

The effect (e.g. an increase in temperature) of the heat to be measured is not minimized by any compensation, but leads to a temperature change in the sample and the calorimeter substance with which the sample is thermally connected. This temperature change is the quantity to be measured. It is proportional to the amount of heat exchanged between the sample and the calorimeter substance. Possible instruments:

- ***Drop calorimeter***

Principle of measurement: heat accumulation (measurement of the resulting temperature change);

mode of operation: isoperibol;

construction principle: single measuring system.

The sample is dropped into the calorimeter that consists of a calorimeter substance (e.g. water, metal) which is thermally insulated from the isoperibol surroundings (thermostat, furnace). The temperature change in the calorimeter substance is measured. Calibration is performed by means of electrical heating. Heat leaks between the calorimeter substance and the surroundings must be taken into consideration as a correction.

- ***Adiabatic bomb calorimeter***

Principle of measurement: heat accumulation;

mode of operation: adiabatic;

construction principle: single measuring system.

The combustion bomb (a metallic, pressure-tight vessel) shows an increase in temperature after ignition of the sample. The temperature of the surroundings (thermostat) is continuously matched to the bomb temperature by means of an electrical control system. The increase in temperature is the measured signal; a correction (as with the drop calorimeter) is not necessary.

- ***Flow calorimeter***

Principle of measurement: heat accumulation;

mode of operation: isoperibol;

construction principle: single measuring system (twin design also feasible).

In a *gas calorimeter* which serves to measure the heat of combustion of fuel gases, the heat to be measured is transferred to a flowing liquid (e.g. water) or gas (e.g. air). The temperature increase in the flowing medium is the measured signal. Other types of flow calorimeters are used to measure heats of reaction, for example by mixing two liquids in a reaction tube. The temperature difference between the liquids flowing in and the reaction product flowing out is the measured signal.

Heat-exchanging calorimeters

In heat-exchanging calorimeters, a defined exchange of heat takes place between the sample (sample container/crucible/support) and the surroundings. The amount of the flowing heat, the heat flow rate, is determined on the basis of the temperature difference along a "thermal resistance" between sample and surroundings. Registration of the dependence of the heat flow rate on time allows kinetic investigations to be carried out. Possible instrument:

- ***Heat flux differential scanning calorimeter (heat flux DSC)***

Principle of measurement: heat exchange;
 mode of operation: scanning of surroundings;
 construction principle: twin measuring system (disk-type or cylinder-type).
 Two containers/supports with sample and reference sample are provided with temperature sensors which measure the temperature difference between the specimens. This temperature difference is proportional to the difference in the heat flow rates flowing from the surroundings (furnace) to both specimens. Due to the twin construction, a direct measurement of the temperature difference between sample and surroundings is not necessary; the main heat flow must not be registered, only the differential one.

3. CHARACTERIZATION OF MEASURING INSTRUMENTS

The requirements to be met by the measuring instrument follow from the kind of problem to be investigated. To be able to judge whether a thermoanalytical instrument or a calorimeter is suitable for the task in question, the instrument must be clearly characterized.

The following can be used for characterization:

- the general specifications of the measuring instrument;
- the performance characteristics of the measuring system.

All specifications and characteristic data given in the following account thus serve to select the best instrument from among those offered by various manufacturers. Prior to purchasing an instrument, all necessary information should be obtained from the manufacturer.

3.1. General specifications of the measuring instrument

A comprehensive general description of the measuring instrument should specify:

- Type of measuring instrument (thermobalance, dilatometer, etc.). In addition, closer details of the design (DTA: block system or free-standing crucibles; TG: weighing system above or below the load receptor; DSC: of the heat flux or power compensating type, etc.).
- Temperature range.
- Atmosphere (which gases, vacuum, pressure).
- Range of heating and cooling rates, temperature-time programs.

5.4. Terms, symbols and units

The *International System of Units (SI)*, which is founded on the *Metric System*, is binding for the presentation and description of physical quantities. (The SI has been adopted worldwide (e.g. by ISO 1000)).

A distinction must be made between the quantity, the name of the quantity and the symbol of the quantity, and between the name of the unit and the symbol of the unit. As an example, the seven *base units of the SI* are listed in the following (Table 4).

Table 4
Base units of the SI

| Quantity (name and symbol) | | Name of unit | Symbol of unit |
|-------------------------------|--------|--------------|----------------|
| length | l | metre | m |
| mass | m | kilogram | kg |
| time | t | second | s |
| electric current | i, I | ampere | A |
| temperature | T | kelvin | K |
| amount of substance | n | mole | mol |
| luminous intensity | I_v | candela | cd |

From the base units, SI derived units are formed (Table 5). Certain derived units have been given special names and symbols (e.g. newton: N, volt: V).

Table 5
Examples of SI derived units

| Quantity (name and symbol) | | Name of unit | Symbol of unit | Relation and Remarks |
|-------------------------------|-----|--------------------------|----------------|---|
| area | A | square metre | m^2 | |
| volume | V | cubic metre | m^3 | do not use "cbm" |
| | | litre | l or L | 1 l = 1 dm ³ = 10 ³ cm ³ do not use "ccm" |
| mass | m | gram | g | 1 g = 10 ⁻³ kg do not use "gr." |
| | | unified atomic mass unit | u | 1 u = 1.6605402 · 10 ⁻²⁷ kg |

Continuation Table 5
Examples of SI derived units

| Quantity (name and symbol) | | Name of unit | Symbol of unit | Relation and Remarks |
|-------------------------------|-------------------------|----------------|-----------------------------------|---|
| time | t | minute | min | 1 min = 60 s |
| | | hour | h | 1 h = 3600 s |
| | | day | d | 1 d = 86400 s |
| frequency | n, f | hertz | Hz | 1 Hz = 1 s ⁻¹ |
| force | F | newton | N | 1 N = 1 kg m s ⁻² |
| pressure | p, P | pascal | Pa | 1 Pa = 1 N m ⁻² |
| | | bar | bar | 1 bar = 10 ⁵ Pa |
| dynamic viscosity | h | pascal second | Pa s | 1 Pa s = 1 N s m ⁻² |
| kinematic viscosity | g | | m ² s ⁻¹ | |
| energy | E } W } Q } | joule | J | 1 J = 1 N m |
| work | | | eV | 1 eV = 1.60218 · 10 ⁻¹⁹ J |
| heat | | | | |
| heat capacity | C | | J K ⁻¹ | 1 J K ⁻¹ = 1 m ² kg s ⁻² K ⁻¹ |
| power | P } F } | watt | W | 1 W = 1 J s ⁻¹ |
| heat flow rate | | | | |
| heat flux | J_q | | W m ⁻² | |
| thermal conductivity | l | | W m ⁻¹ K ⁻¹ | |
| heat transfer coefficient | h | | W m ⁻² K ⁻¹ | |
| voltage (difference) | U | volt | V | 1 V = 1 W A ⁻¹ |
| electric resistance | R | ohm | Ω | 1 Ω = 1 V A ⁻¹ |
| resistivity | r | | Ω m | |
| electric conductance | G | siemens | S | 1 S = 1 Ω ⁻¹ = 1 A V ⁻¹ |
| conductivity | K, s | | S m ⁻¹ | |
| celsius temperature | q, t | degree Celsius | °C | |

There is a number of units which should not be used any more in scientific and technical literature (Table 6).

Table 6
Examples of units not to be used any more in scientific and technical reports

| Name | Symbol | Relation |
|------------------------------|-------------------|---|
| inch | in | 1 in = $2.54 \cdot 10^{-2}$ m |
| dyne | dyn | 1 dyn = 10^{-5} N |
| pond | p | 1 p = 9.80665 N |
| millimetre of mercury | mm Hg | 1 mm Hg = 133.322 Pa |
| standard atmosphere | atm | 1 atm = 1.01325 bar |
| technical atmosphere | at | 1 at = 0.980665 bar |
| Torr | Torr | 1 Torr = 1.333224 mbar |
| pounds per square inch | psi | 1 psi = 6895 Pa |
| poise | P | 1 P = 0.1 Pa s |
| stokes | St | 1 St = 10^{-4} m ² s ⁻¹ |
| erg | erg | 1 erg = 10^{-7} J |
| calorie, international table | cal _{IT} | 1 cal _{IT} = 4.1868 J |
| calorie, thermochemical | cal _{th} | 1 cal _{th} = 4.184 J |

The *International Union of Pure and Applied Chemistry (IUPAC)* recommends a number of Quantities, Units and Symbols in Physical Chemistry [8], which are listed below for the quantities most frequently used in thermal analysis and calorimetry (Table 7).

Table 7
Recommended quantities, units and symbols (reference [8])

| Name | Symbol | Definition | SI unit |
|---|--------|------------------------------|----------------------------------|
| molar mass (applied to entities B) | M | $M_B = \frac{m}{n_B}$ | kg mol ⁻¹ |
| relative atomic mass (atomic weight) | A_r | $A_r = \frac{m_a}{m_u}$ | |
| molar volume (applied to entities B) | V_m | $V_{m,B} = \frac{V}{n_B}$ | m ³ mol ⁻¹ |
| mass fraction (applied to component j) | w | $w_j = \frac{m_j}{\sum m_i}$ | |
| mole fraction (applied to entities B) | x, y | $x_B = \frac{n_B}{\sum n_A}$ | |

Continuation Table 7

Recommended quantities, units and symbols (reference [8])

| | | | |
|---|--------------------|---|--|
| solubility | s | | mol m^{-3} |
| molality (applied to entities B, solvent A) | m, b | $m_B = \frac{n_B}{m_A}$ | mol kg^{-1} |
| heat | q, Q | | J |
| heat flow rate | F | $F = \frac{dQ}{dt}$ | W |
| heat flux | J_q | $J_q = \frac{F}{A}$ (A: Area) | W m^{-2} |
| internal energy | U | | J |
| enthalpy | H | | J |
| thermodynamic temperature | T | | K |
| Celsius temperature | \mathbf{q}, t | | $^{\circ}\text{C}$ |
| entropy | S | | J K^{-1} |
| Helmholtz energy | A | | J |
| Gibbs energy | G | | J |
| heat capacity at constant pressure | C_p | $C_p = \left(\frac{\partial H}{\partial T} \right)_p$ | J K^{-1} |
| heat capacity at constant volume | C_V | $C_V = \left(\frac{\partial U}{\partial T} \right)_V$ | J K^{-1} |
| chemical potential | μ | $\mu_B = \left(\frac{\partial G}{\partial n_B} \right)_{T,p,n_{j \neq B}}$ | J mol^{-1} |
| equilibrium constant | K | | |
| rate of conversion | $\dot{\mathbf{x}}$ | $\dot{\mathbf{x}} = \frac{d\mathbf{x}}{dt}$ | mol s^{-1} |
| fraction reacted | \mathbf{a} | | |
| order of reaction | n | | |
| activation energy (Arrhenius) | E_a, E_A | | J mol^{-1} |
| pre-exponential factor | A | | $(\text{m}^3 \text{mol}^{-1})^{n-1} \text{s}^{-1}$ |
| partial molar quantity X | X_B | $X_B = \left(\frac{\partial X}{\partial n_B} \right)_{T,p,n_{j \neq B}}$ | |
| rate of change of quantity X (flow) | \dot{X} | $\dot{X} = \frac{dX}{dt}$ | |
| flux of a quantity X | J_X | $J_X = \frac{1}{A} \cdot \left(\frac{dX}{dt} \right)$ | |

Remarks:

specific means related to mass (e. g. specific heat capacity c)

molar means related to amount of substance (e. g. molar energy E_m)

Note: In thermal analysis and calorimetry, the rate of change of temperature (heating rate, cooling rate, scanning rate) is denoted by symbol ***b***.

Symbols for states of aggregation (should be appended to the formula symbol in parentheses):

| | |
|-----|------------------|
| g | gas, vapour |
| l | liquid |
| s | solid |
| cd | condensed |
| fl | fluid |
| cr | crystalline |
| lc | liquid crystal |
| sln | solution |
| aq | aqueous solution |
| am | amorphous solid |

Examples: $H_2O(g)$ water in the gaseous/vapour state

$C_p(s)$ heat capacity at constant pressure of a solid

$H(cr)$ enthalpy of a crystalline solid

Subscripts to denote a chemical transformation or reaction:

| | |
|-----|---------------------------------|
| vap | vaporization |
| sub | sublimation |
| fus | fusion, melting |
| trs | transition |
| mix | mixing of fluids |
| sol | solution (of solute in solvent) |
| dil | dilution (of a solution) |
| ads | adsorption |
| r | reaction |
| c | combustion |

Superscripts:

| | |
|------------------|-------------------|
| \ominus, \circ | standard |
| * | pure substance |
| ∞ | infinite dilution |
| id | ideal |
| E | excess quantity |

Symbol for change in an extensive thermodynamic quantity Δ :

Examples:

$$\Delta_{\text{vap}}H = H(\text{g}) - H(\text{l})$$

$$\Delta_{\text{fus}}H_{\text{m}} \quad \text{molar enthalpy of fusion}$$

$$\Delta_{\text{r}}S^{\ominus} \quad \text{standard reaction entropy}$$

Subscripts used in thermal analysis and calorimetry

If related to an object: capital letters (e.g. m_{S} , mass of the sample ; T_{R} , S temperature of the reference sample R).

If related to a phenomenon: lower case (e.g. T_{g} , glass transition temperature).

If related to a specific point in time or temperature: lower case (e.g. T_{e} , extrapolated peak onset temperature).