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Critical review of small sample calorimetry: improvement by auto-adaptive thermal shield control

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Abstract

The paper reviews measuring and data computation procedures in heat-step calorimetry, for small samples (<100 mg mass) and at low temperatures ($T < 100$ K) under semi-adiabatic (isoperibol) measuring condition. In conjunction with an auto-adaptive heat-shield control, a method is described how the heat losses, occurring during an isoperibol measuring cycle, are correctly taken into account in order to achieve an absolute uncertainty of C_p of 1% or lower. The basic features of the method are strictly adiabatic condition at the beginning of each heat capacity measuring point, achieved by an extremely small temperature drift of the sample, and a very constant temperature of the heat-shield during the whole measuring cycle.

Keywords: Heat capacity measurement; Adiabatic calorimetry; Low temperature calorimetry

1. Introduction

Thermal analysis, today, focus on the use of heat-flow instruments, based essentially on comparative methods and use of thermal reference samples [1,2] and are mostly limited to the temperature range above about 100 K. Adiabatic calorimetry, using the Nernst method with stepwise sample heating, although time-consuming, is the unique ‘absolute’ method which is based on the direct heat (energy) measurement. Adiabatic (heat-pulse) calorimetry is still the *most accurate and direct* method for the determination of heat capacities. Traditionally, the method was applied in low temperature calorimetry by use of numerous home-made and individually designed equipment [3–8]. In addition, low temperature calorimetrists have been the inventor of a number of powerful and ingenious calorimetric methods, especially suited for the measurement of small samples, e.g. ‘ac’ calorimetry and other modulation techniques, relaxation-time and continuous heating (or cooling) calorimetry as well as a number of rather sophisticated designs, partially for the investigation of microgram samples. Development and progress in low temperature calorimetry were reviewed recently in [5].

Today, there is a world-wide need for high accuracy calorimetric data, for the optimisation of thermochemical processing, for the calibration of commercially available differential scanning calorimeter (DSC) and for improved (higher accuracy) values of known substances. Unfortunately, metrological calorimetry declined in the last two decades and the potential of

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systematic errors of DSC (and heat-flow calorimetry) is still notoriously underestimated. DSC calorimetry needs more discipline. Unfortunately, the time spend on theoretical and practical training of the operators of DSC's, in many cases, has been drastically reduced. Often, there is blind believe in the instrument's manual. As a consequence, it is not surprising how few reasonably accurate values exist for heat capacities with an inaccuracy of <1%, for the range 4–300 K.

A focal point in establishing high-precision caloric data remained the correct and fully-perfect monitoring and careful control of heat, heat-flow and heat-loss in the calorimetric cell. In principle, this can be guaranteed only by the adiabatic or semi-adiabatic step-heating method which displays directly the occurring heat losses: the losses are reflected in the internal (sample/sample–support assembly) and external (caloric cell to the surrounding) relaxation times, denoted here as τ_i and τ_e. The adiabatic (or semi-adiabatic) method is the most versatile and transparent technique to account for losses, since the sample temperature is directly monitored as a function of time. Therefore, most standard reference substances, needed for DSC or dynamic heat capacity experiments, refer to adiabatically measured specific heat values (C_p). As a matter of facts, non-adiabatic conditions increasingly occur when the heat capacity is reduced, i.e. isoperibol measuring conditions are unavoidable with decreasing temperature (when the heat capacity drops by several orders of magnitude below 100 K) and/or a decreased amount of sample mass, as often required in modern material science. Thus, small samples (e.g. <100 mg) and low temperatures ($T < 100$ K) *dictate*, in most cases, non-adiabatic measuring conditions.

The purpose of this paper is to show, how under isoperibol surrounding conditions heat capacity experiments can be properly performed and how eventual heat losses can be taken into account correctly, so that the accuracy of the C_p-results is equal to a perfect adiabatic measurement.

Our more than two-decades experience with automated low temperature and small sample heat-step calorimetry lead us to the following four requirements if samples of <100 mg mass should be measured with an absolute accuracy of 1% or better:

(i) start each heat-step from perfect adiabatic conditions, i.e. thermal equilibrium and lowest possible temperature drift of the sample before it is heated, e.g. well below 10^{-5} K/s (and as low as 10^{-6} K/s below 10 K for samples of the order of 10 mg);

(ii) hold a constant temperature for the surrounding (thermal shield) during the C_p-measuring cycle;

(iii) online correction and visualisation of the isoperibol heating and post-heating curves; and

(iv) storage of all measured data for an improved post-experiment data computation.

2. Analysis of isoperibol (or semi-adiabatic) step-heating experiments

The heat-pulse experiment is the direct transposition of the thermodynamic definition of the (isobaric) heat capacity C_p into a measurement:

$$C_p = \left(\frac{\delta H}{\delta T}\right)_p = \lim_{\Delta T \to 0}\left(\frac{\Delta Q}{\Delta T}\right)_p \approx \left(\frac{\Delta Q}{\Delta T}\right)_p \qquad (1)$$

where H denotes the enthalpy, T the absolute temperature, ΔQ the heat supplied to the sample and addenda (sample–support, heater and thermometer) and ΔT is the resulting temperature increment. A full C_p-measuring cycle is schematically shown in Fig. 1 (upper part). The heat-pulse experiment includes four distinct time intervals (1)–(4): the pre-heating driftline (or fore-drift), the heating period Δt_H, a thermal delay time Δt_D, i.e. the time during which the sample/addenda assembly comes into internal equilibrium (about three to five times τ_i), and the post-heating driftline (after-drift). For a more general analysis of the heating cycle see [3,6,8].

The accuracy of heat capacity experiments critically depends on the thermal relaxation-times and the individual length of the four time periods (Fig. 1): (i) how fast is the internal equilibrium reached in the calorimetric cell, i.e. a uniform temperature between the sample and sample-holder (with thermometer and heater), characterised by τ_i, (ii) how quickly relaxes the sample to the heat-shield temperature T_0, characterised by τ_e, and (iii) how long the four intervals are with respect to each other. The errors originating from energy, time and temperature measurements are, in most cases, much smaller. Several cases may occur.

(1) *Fully adiabatic conditions* (see Fig. 1, upper panel, curve a), with Δt_H, $\tau_i \ll \tau_e$ [3,6–15]. This

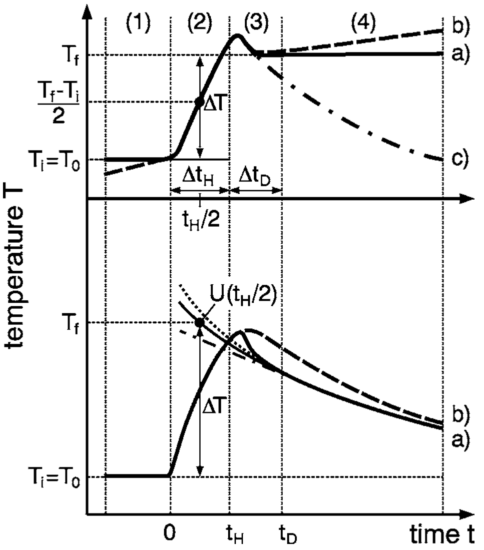

Fig. 1. Temperature (T) vs. time (t) behaviour of a sample in a heat-pulse calorimeter. Upper part: strictly adiabatic case with isothermal fore- and after-heating driftline (curve a, ——), imperfect isothermal, but still parallel fore- and after-drift (curve b, – – – –), isoperibol or so-called relaxation-time case with isothermal fore-drift and exponentially relaxing after-drift (curve c, —·—·—). T_i and T_f denote initial and final temperatures in the heating phase of the sample, ΔT the resulting temperature increment, Δt_H the heating time, Δt_D the thermal equilibrium (or delay) time after the heat-pulse. In the ideal case, T_i equals T_0, the temperature of the (isothermal) heat-shield. Lower part: Quasi- or semi-adiabatic case with short, i.e. $\tau_i \ll \tau_e$ (curve a, ——), or longer, i.e. $\tau_i \approx \tau_e$, (curve b, – – – –) internal relaxation-times. For curve a, the end of the heating period can be extrapolated from the after-drift either linearly (—·—·—), exponentially (......) or according to Eq. (4) (——), to determine T_f and ΔT, respectively.

'ideal' case is realised only if 'large' heat capacities are determined, i.e. samples with a mass $m > 1$ g. In general, adiabatic heat-shield control is preferred, i.e. the surrounding thermal shield follows as closely as possible the sample temperature, so that losses become negligible. Then, the heat capacity can be computed by a linear extrapolation of the fore-drift and after-drift (as shown in Fig. 1 (upper panel) by the thin lines) and determining the ΔT according to the method of equal areas, or more simple, to $t_H/2$, the middle of the heating interval Δt_H.

(2) *Non-adiabatic or isoperibol conditions* (Fig. 1, curve c) exist when the measured heat capacities (or sample mass, respectively) are so small that, after the heating period the sample temperature drops exponentially to the initial temperature T_0, due to unavoidable heat losses in the calorimeter [16–18]. Then the measuring cycle is computed by an exponential fit of the after-drift, provided however, that the fore-drift temperature is constant and the heating interval is very short ($t_H \ll \tau_e$). This so-called isothermal heat-shield control is most suitable for heat-pulse experiments under isoperibol conditions. In addition, when measuring τ_e and evaluating C_p by the relation $C_p = \tau_e/k$ (relaxation method), a properly selected heat leak of the thermal resistance k is required in order to well-define τ_e [4].

(3) *Semi-adiabatic conditions* (Fig. 1, curve b) [19–25] is the case, mostly met today, when smaller samples (10 mg–1 g) are measured. The heat losses then prevent a linear extrapolation of the after-drift, or seem to allow it only in a rather short time interval after the end of the relaxation period (example shown in Fig. 1) leading to systematic errors in the data computation. Two further systematic inaccuracies may occur: (i) fore-drift and after-drift-lines are not parallel, and (ii) the heating curve does not show a temperature which linearly increases with time (as illustrated in Fig. 1, lower panel), due to losses from the (increasing) temperature difference between sample and surrounding during heating. Note that under strong isoperibol conditions and short enough τ_i, the latter two errors can be reduced by choosing extremely short heat-pulses $\Delta_H t$, e.g. ms range.

The most critical period—with all calorimetric methods—is the internal thermal relaxation. Serious problems, i.e. too long τ_i, may arise from poor thermal contact between sample and addenda. Only for method (1), τ_i is clearly defined and displayed on the post-driftline, namely when thermal equilibrium is reached. For methods (2) and (3), the exponentials, resulting from τ_i and τ_e may superimpose. For a proper data computation, $\tau_i \ll \tau_e$ is then required. The problem of long τ_i (often called as "τ_2 effect") was often discussed in the literature [16,18,26–29]. The problem could partially be ravelled by a full curve-fitting of the temperature response curve of the post-driftline (sometimes called "curve-fitting method") [29].

Nevertheless, the best feature is to arrange experimentally a sufficiently good thermal contact inside the sample–addenda system. This presents a challenge because τ_i can vary (for the same sample) strongly as a function of absolute temperature. The specific heat capacity of the materials and the heat conduction of sample and sample-holder, and the thermal contact between both can influence the internal relaxation-time τ_i. Especially near phase transitions, where the thermal diffusivity is very small, τ_i increases and the evaluation of the after-drift must be done with care.

Taking *semi-adiabatic* conditions as unalterable fact, two questions arise which mathematical formalism describes properly the calorimetric temperature versus time curve, and how to implement the required experimental conditions? The answers are given in an earlier paper [30] (by one of the authors) based on [31–33]. Therefore, only a short outline of the procedure is given here.

The thermal equation describing the calorimeter is:

$$C\left(\frac{\mathrm{d}T_S}{\mathrm{d}t}\right) = P - k(T_S - T_0) \tag{2}$$

where P is the heating power, T_S the sample temperature and T_0 the temperature of the surrounding (heat-shield, respectively) as well as the sample temperature before applying heat. Indispensable conditions are that (i) sample, addenda and surrounding are in true thermal equilibrium before heating ($t \gg \tau_e,\ \tau_i$), and (ii) T_0, the heat-shield temperature, is held constant during the measuring cycle and at least the fore-drift is 0. The heating period and the post-heating driftline, as displayed in Fig. 1 (lower panel), are described by

$$U(t) = \left[\frac{P}{C\beta}\right] \times (1 - \exp(-\beta t_H))\exp(-\beta(t - t_H)) \tag{3}$$

with $\beta = \tau_e^{-1} = k/C$ and the heating starts with $t = 0$ and ends at t_H (time interval Δt_H). It follows the establishing of the thermal equilibrium during a ‘thermal delay’ time, Δt_D, before the post-heating driftline is registered. The post-heating temperature drift is least-square fitted to a non-linear expression according to Eq. (3). The fitted expression is then extrapolated to the middle of the heating period ($t = t_H/2$) to obtain $U(t_H/2)$. The heat capacity itself is calculated iteratively from:

$$U\left(\frac{t_H}{2}\right) = \left[\frac{2P}{C\beta}\right]\sinh\left(\frac{\beta t_H}{2}\right) \approx \left[\frac{Pt_H}{C}\right]\left\{1 + \left(\frac{1}{24}\right)(\beta t_H)^2\right\} \tag{4}$$

The values of $U(t_H/2)$ and β are obtained from the fit of Eq. (3), and P and t are known experimentally.

This method practically performs two corrections. First, the exponential fit takes into account the thermal losses in the post-heating period in contrast to a linear fit that leads to too large C-values (underestimation of $U(t_H/2)$). Second, the corrective term, $(\beta t_H)^2/24$, in Eq. (4) accounts for heat losses which occur during the heating period, otherwise the exponential extrapolation alone would give a too small C-value (overestimation of $U(t_H/2)$). To our experience, application of both corrections show a further advantage: random variation of the thermal losses, which modify τ_e, e.g. changes of the heat of radiation, electrical noise, influence of liquid helium or nitrogen level, a.o. These disturbances become more or less enclosed in the calculation of C. For example, a sudden burst of gas desorbed from the surface of the calorimeter-vessel increases for short time the thermal coupling. As a consequence τ_e becomes temporarily shorter, i.e. β larger and thus, $U(t_H/2)$ too large. This effect is remedied by the correction term in Eq. (4). To our experience, application of the full form of Eq. (3), in practise by Eq. (4), results in three to five time lower scatter of the measured C_p-data [30].

The described method proofed particularly suitable when measuring mg samples at low temperatures ($T < 20$ K) or 100 mg samples at temperatures above 100 K where large heat exchange results from thermal radiation.

3. Experimental

For the last two-decades, the essentials of the design of the calorimeters used in our laboratory remained nearly unchanged. A detailed description was given in previous work [3,25]. Different calorimeters of similar design were used from 15 to 300 K, from 1.5 to 100 K, in the liquid Helium-3 range or in magnetic field cryostats up to 16 T. The calorimeters are equipped with one thermal shield for measurements below 100 K, or with two thermal shield for above 100 K. Various sample-holders, designed according [34] consist of a sapphire plate supporting a ca. 2 kΩ evaporated stainless steel meander as heater and a commercially calibrated thermometer, glued on the lower side by use of IMI-7031 varnish. The thermometers are selected appropriately for the temperature range in use, i.e. encapsulated germanium or platinum resistors or, in case of an experiment in a magnetic field, a hermetically sealed CERNOX sensor. The samples to be measured, having mass between a few mg to ca. 1.5 g, typically however 100 mg, are placed on the sapphire platform with a tiny amount (ca. 2 mg) of Apiezon N grease in between [35].

Electronics and software, as described earlier [25], have been permanently improved and modernised and led to a significant increase in accuracy. Much of the electronics consists of modern digital nano-voltmeters and highly stable dc current sources, used primarily for the sample temperature measurement and for the heat-pulse generation. In conjunction with a computer (Hewlett-Packard, series 300, running under HP-UX) and IEEE-bus technique the experiment is controlled by a software written in HP-BASIC. One advantage here is the 'life-keyboard' that allows to modify the measuring parameters during the experiment is running, e.g. when a phase transition occurs in the C_p-curve. Instead of focussing on details, we prefer to point out the important features of the functioning of our calorimeter systems.

Small sample *low-temperature* calorimetry requires a set-up that covers an energy range of six orders of magnitude in $C_p(T)$. A temperature resolution of 10^{-4} to 10^{-6} is necessary in order to yield data with <1% inaccuracy. To our experience, the basic problem remains the control and measurement of the sample and heat-shield temperatures and their drifts.

A single measurement of the heat capacity is performed with the measuring cycle as shown in Fig. 1 (lower panel). The total duration (in time) for a single cycle now varies with the given condition, i.e. according to the absolute temperature, for different τ_i, for a given sample mass, etc. Such a cycle may last 1.5 min for a 100 mg sample near 4 K or 15 min for a 1 g sample at 120 K. The relations of the four time intervals, labelled in Fig. 1 with (1)–(4), however, are held more or less equal in all experiments: the heating time t_H equals approximately the thermal delay time t_D, and fore-drift and after-drift take about three to five times $(t_H + t_D)$. Thus, τ_i related to t_D ($t_D \approx 5\tau_i$ is an appropriate selection) is the basic parameter that determines the time needed for one measuring cycle. The total time needed to take a single C_p point, however, depends on the time needed for the temperature of sample and heat-shield to come in thermal equilibrium (i.e. τ_e).

The automated experiment is realised with input of a certain number of semi-empirical parameters (i.e. thermal delay time t_D after heat-input, desired percentage or absolute temperature increment ΔT during the heat-pulse, duration of temperature measurement on the fore-drift and after-drift, first heating current and first heating time, etc.) which may be programmed also such to vary as a function of temperature or total heat capacity, e.g. around phase transitions. During the cool-down of the calorimeter the sample cooling rate can be registered to detect possible phase transitions. The measurement is started at the bath temperature. The driftlines comprise between 30 and 300 s of continuous sample temperature measurements. The resistance to temperature relations $T(R)$ of the used thermometers, and magnetoresistive corrections $T_{\mathrm{true}}(T(R), H)$, are stored as polynoms. The temperature increments of the heat-pulse range from 0.1% T (near a phase transition) to 5% T below 4 K and is typically about 1% of T above 50 K. The heat capacity C_p of the specimen is computed online, using the correction procedure described in Section 2. For the calculation of C_p, the necessary addenda heat capacities for the sample–support (determined in a separate run), the amount of Apiezon N [35], the mass of eventually used Duran-glass [35] (in which our air-sensitive samples are often encapsulated) are also stored as polynoms.

It is important to note that all monitored data of each single measuring cycle are stored in separate files to allow individual data inspection after the experiment was terminated. Although, an online computation is performed, it is advisable to control and optimise some parameters later in order to avoid systematic errors. In particular, the delay time t_D for the internal relaxation process (τ_i) and the time interval for which the post-heating driftcurve is fitted (not longer than $2\tau_e$) can be adjusted. Fig. 2 illustrates in a plot sample temperature

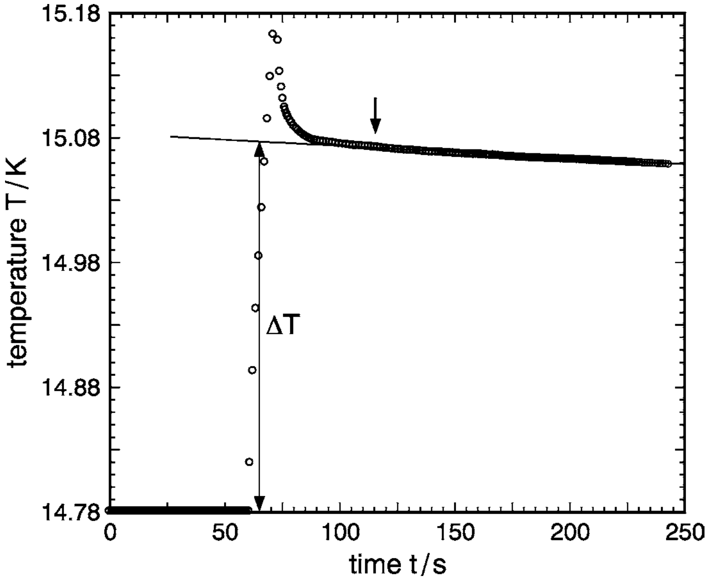

Fig. 2. Example of a heat capacity measurement as plotted for the post-experiment data computation. The basic data are as follows—sample: sapphirine ((Mg, Al)$_8$(Al, Si)$_6$O$_{20}$), 0.1584 g, encapsulated in Duran glass, 0.3068 g and thermally contacted to the sample–support by Apiezon N grease, 3.5 mg. The computed data are: start temperature $T_0 = 14.78035$ K (with a fore-drift of -2.435×10^{-6} K/s), heating time $t_H = 12.045$ s, supplied heat $Q = 1.88615$ mJ (with a heating current of 0.27353 mA), resulting temperature increment $\Delta T = 0.298578$ K (according to Eq. (4)) and heat capacity $C = 6.31716$ mJ/K; the relaxation of the after-drift yields $\tau_e = 2496$ s, when the curve is fitted for the range $t > 130$ s, whereby the τ_2-effect is determined by visual inspection to cover about 1 min (from 70 to 130 s).

T versus time *t*, how quickly the internal equilibrium takes place and indicates (for a given temperature) in which time interval the post-heating driftline exponential is properly computed. The post-experiment computation allows to calculate ΔT, and thus, the heat capacity, correctly by inclusion of the effect of the thermal losses.

An important knowledge based on our experience is that C_p-determination on small samples are better performed with isothermal shields (thermal shield temperature held constant) than with an adiabatic shield (i.e. thermal shield follows the sample temperature). As a consequence, we stabilise separately for each individual C_p-point the shield temperature within 5×10^{-6} of the absolute temperature! This high-temperature stability is only achievable by the most recent commercial digital temperature controllers. Before their advent we used different control systems depending on the temperature range. The most simple version is a constant voltage source which proved useful for temperatures below 25 K. For higher temperatures, the use of digital ac-bridges in connection with analogue PID controllers was troublesome. This equipment offered a good temperature stability only after careful manual adjustment of control parameters (which vary with temperature) and after a time-consuming approach to the next temperature setpoint (temperature overshooting can not be tolerated for many calorimetric experiments). With modern computers a software simulation of an advanced PID-controller was implemented. This system utilises a high-resolution A/D converter (e.g. a nano-voltmeter) as input and a $16+2$ bit digitally controlled voltage source as heater output. The system can be used at all temperature ranges and proved to be very flexible. This way of heat-shield control has many advantages, especially for C_p-measurements, and still offers superior performance.

4. Auto-adaptive thermal shield control

The current technique to provide quasi-adiabatic conditions is to surround the sample and addenda with a heat-shield either controlled adiabatically or isothermally. The reason why we use an isothermal shield are twofold: (i) small/low heat capacity samples are highly sensitive to any temperature variations of the surrounding, (ii) applied computation procedure (Eq. (4)) requires a constant shield temperature during the measurement cycle.

Differential thermocouples are suitable for adiabatic shield control but for isothermal control sensors measuring the absolute temperature have to be used. A problem, and often the major source of uncertainty, arises from real or apparent temperature differences between the thermal shield thermometer and the sample thermometer. First, the thermometers will show differences in their calibration which even within the errors the ITS90 can be larger than admissible for the heat-shield stabilisation. Second, strong differences in the reflectivity of sample and heat-shield may lead to one-way heat-flow. Third, temperature gradients along the heat-shield (and along the calorimeter) as well as thermal resistance between the location of the shield thermometer and other parts of the shield will prevent perfect adiabacity, even if both thermometers, those on shield and sample-holder, show exactly the same temperature. Fourth, self-heating of the sample thermometer and thus, of the sample can be an important contribution for very small samples.

Thus, the idea was not to perfect the heat-shield temperature controlling by application of more thermometers and better calibration, but to choose another method: *the temperature drift of the sample itself is taken as sensor*. In fact, it has shown as the best sensor. Zero drift of the sample temperature indicates adiabatic condition, in other words, the integral heat-flow between sample and surrounding heat-shield equals to zero if the drift becomes zero. Even if possibly some parts of the shield are warmer (than the sample) and others are colder, zero-drift indicates that an integral dynamic thermal equilibrium between sample/sample–support and the surrounding exists. This occurs only when the average sample/addenda temperature is equal to the effective shield environment temperature. The meaning of 'effective' is determined by the specific situation. At low temperature this might be the temperature of the point where the wires leading to the sample are attached to the shield, at high-temperatures thermal radiation dominates and average temperature and reflectivity count more. Thermometer self-heating is included in the dynamic equilibrium. But, since the sensor resistance changes during the heating cycle, the heat-input to the sample is not constant and the sensor excitation has to be kept as low as possible.

In practise, before starting a measurement cycle, the computer waits so long that the temperature versus time drift (fore-drift) reaches a critical pre-set parameter-value, e.g. $dT/dt < 1 \times 10^{-5}$ K/s. Then monitoring of the fore-drift is started, followed by the heating period, etc. During the measuring cycle, however the shield temperature is held strictly constant by the 'software' or hardware PID controller.

After termination of the after-drift, the heat capacity is calculated, all relevant parameters are printed and stored, and then, both, sample and shield, are heated to the starting temperature (setpoint T_0) of the next C_p-point. The effective temperatures reached by sample (T_S) and heat-shield (T_H), however, are not necessarily equal. Therefore, the measured sample temperature ($T_{S,meas}$) will show a positive drift (if the sample is colder than the heat-shield) or a negative temperature drift. Nevertheless, the heat-shield is not adjusted in its temperature but simply held at constant setpoint temperature T_0, and thermal equilibrium is awaited for. After some time the effective (and measured) sample temperature stabilises at a zero-drift, and the software registers the initial difference $\Delta T = T_{S,meas} - T_0$, in order to apply the corresponding correction when sample and heat-shield temperature are approached to the next measuring temperature setpoint. $T_S - T_H$ will be much smaller (or even zero) in the following measuring cycle and zero-drift of T_S will be reached in a much shorter time. By this auto-adaptive method, the software practically performs a type of heat capacity measurement separately for the heat-shield to know how much heating power is required to apply to the sample heater and to the heat-shield, so that they reach simultaneously identical effective temperature for the next fore-drift measurement.

The heat-shield, thus, adapts itself to establish adiabatic conditions for the sample. In addition, a calibration of the heat-shield thermometer is unnecessary. Sensorless heat-shield control is possible (as recently used in [36]). Further, eventual small temperature gradients on the heat-shield are "averaged" and the thermal coupling of the shield thermometer and between the different parts of the shield remain uncritical. In summary, in this procedure, used by us successfully during the last 10 years, the entire heat-shield temperature control is based on an analysis of the temperature behaviour of the sample fore-drift.

The major disadvantage of the presented method is the long time needed for sufficiently low sample temperature drift rates. From our experience, however, we found that better C_p-data can only be obtained at the cost of more time-consuming experiments. Another disadvantage concerns samples containing meta stable phases and having glass transitions. Small heat release rates (see e.g. [37]) of such sample materials are not detected by our method. The investigation of such effects remains the domain of true adiabatic calorimetry.

We note that one of the calorimeters, which was used with preference in the temperature region above liquid nitrogen temperature, was equipped with a second thermal shield. This shield was controlled to a constant temperature value a few Kelvin below the inner (first) heat-shield temperature, e.g. 2.5 K lower. The outer shield minimises the influence of, e.g. changes in the coolant level and leads to a more homogeneous temperature distribution on the inner shield.

5. Conclusion

In conclusion, as a result of many years of experience with semi-adiabatic calorimeters, we describe various procedures, for isoperibol step-heating calorimetry with small samples, which, in applied combination, enable to yield similar high accuracy (inaccuracy <1%) as achieved by fully adiabatic calorimetry with large samples. It seems that isothermal heat-shield control under the given conditions—non-adiabacity and small sample—is the most favourable solution. Further, the fore-drift must be strictly zero and a full computation of the heating curve and the post-heating driftline, both perturbated by heat losses, is mandatory.

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