Dynamic behaviour of power compensated differential scanning calorimeters.
Part 2. The signal flow [1]

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Abstract

The dynamic behaviour of the measured signal of a power compensated DSC is studied in terms of linear response taking into account the measuring system, the sample, the reference, the control circuits, the heat transport coefficients and the heat losses.

As a result it is shown that the apparatus (or Green's) function of the DSC (including sample and heat transfer) is different from that necessary to desmear the sample heat flow.

The quality of the extracted Green's function is discussed for different measuring conditions.

INTRODUCTION

To obtain information about the real thermodynamic functions of a sample from a DSC curve it is necessary to think about the smearing of the signal by the apparatus. In the case of DSC it is not easy to get a correct Green's function (or "apparatus function") to desmear the measured curves, because it depends both on the apparatus and on thermal properties of the sample under investigation. To describe the influence of the temperature profile inside the sample, different kinds of thermal effects must be taken into account [1].

Elsewhere [2] a simple model has been given to quantitatively describe the influence of heat transfer inside the DSC furnace and from the sample itself on the shape of the measured signal. The model is based on the analysis of the signal flow including the heat flow and the temperature profile in the complex system DSC furnace–sample. A proposal to correct the measured curves with the aid of linear response theory is given.

Let Φ_{out} be the measured heat flow rate, Φ_{in} the theoretical heat flow rate

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of an infinitely thin sample which is coupled to the furnace with an infinitely small heat resistance and G the Green's function containing all dynamic properties of the system DSC–sample; then the convolution product

$$\Phi_{out}(t) = \int_0^t G(t - \tau)\Phi_{in}(\tau)\, d\tau = G(t) * \Phi_{in}(t) \tag{1}$$

describes the smearing of Φ_{in} by the heat transfer within the furnace and the sample and by other relaxations (e.g. from electronics) of the DSC.

The heat transport and relaxation processes in the measuring instrument and the sample cause the smearing of the signal. Similar influences may originate from electronics. We term all these smearing processes collectively 'dynamic processes'. They are characterized by the Green's function. An instrument without any dynamic processes (no smearing) has a Dirac δ-function as Green's function $G = \delta(t)$. The Laplace transformed Green's function is then $g = 1$. In this rather uncommon case, the measured function Φ_{out} is identical with thermal event of the sample Φ_{in}.

In order to desmear a DSC curve we need the solution of this integral equation. Thus the Green's function G must be known. One idea is to extract the Green's function from the response of the measured curve on switching the heating rate $(\beta = dT/dt)$ on an off, for instance at the beginning or at the end of the scan. It is also possible to interrupt the scan in between to get this information.

As a change of the temperature profile needs time after the scan rate was switched from zero to the rate in question or vice versa, there is no sharp step in the heat flow as expected from the equation $\phi = m \cdot c_p \cdot \beta$ (with $\beta = 0$ at $t < t_0$ and $\beta = $ const. at $t > t_0$, see Fig. 1). It is possible to extract a
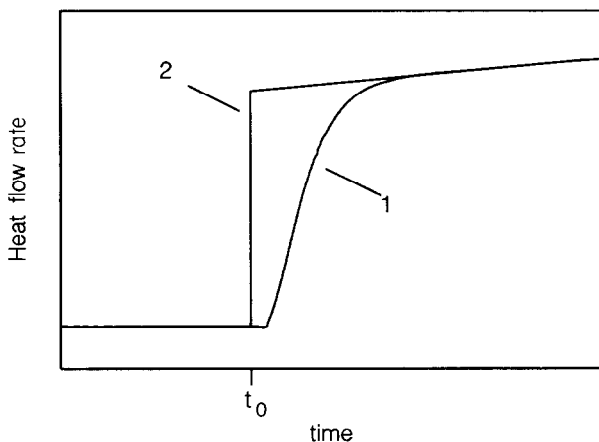

Fig. 1. Schematic behaviour of heat flow rate curves after switching-on the scan rate (1, measured smeared curve; 2, theoretical, unsmeared curve with $\Phi = m \cdot C_p(T(t)) \cdot \beta$; t_0 is the moment at which the heating rate changes from zero to β).

Green's function from the heat flow change at this parts of the DSC curve. On condition that there is only a negligible change of the material properties (specific heat capacity c_p, density ρ, thermal conductivity λ) during the temperature scan this Green's function can be used to desmear the total DSC curve. In other cases the DSC run may be cut into parts by interrupting the scan several times in between. The advantage of this method is that the Green's function can be extracted directly from every DSC curve under investigation.

However, this simple model only describes the behaviour of one furnace. Thereby the dynamic behaviour of the reference, the second furnace and the control circuits of the power compensated DSC are neglected [2]. To investigate the influence of these parts of a power compensated DSC on the measured curve and on the extracted Green's function, a model of the signal flow network in the whole DSC will be discussed in terms of linear response theory (the mathematical background is given in ref. 1). The proposed algorithm is restricted to power compensated DSC, because the description takes into account only the fluxes (no potentials are necessary as is the case for heat flux DSC). The resulting eqn. (10) allows us to describe the influence of sample, reference, both furnaces, heat losses and control circuits on the dynamics of the measured DSC curve.

From this equation the problem of baseline correction and the extraction of the Green's function from the DSC curve under investigation will be discussed. Problems concerned with the influence of thermal effects inside the sample and applications will be presented in subsequent parts of this paper.

THE MEASURING SYSTEM

The measuring system of a power compensated DSC is shown schematically in Fig. 2. The main parts are two symmetric furnaces which are located inside an isothermal surrounding (isoperibol DSC [3]).

Two separate control circuits guarantee firstly that the mean temperature of both furnaces strictly follows the programme temperature (T_P) with the actual rate β, and secondly that the temperature difference ($\Delta T = T_S - T_R$) between the furnaces is minimized. Differences result from the different heat capacities of sample and reference (including thermal effects inside the sample) and asymmetries of the furnaces (strongly dependent on temperature). This is compensated with the aid of an additional power input to the furnace with the lower temperature. As the second control unit works as a proportional controller, the remaining temperature difference (control deviation) is proportional to the difference of the heat capacities of sample and reference supposing absolutely symmetrical furnaces. This temperature difference is used as measuring signal.
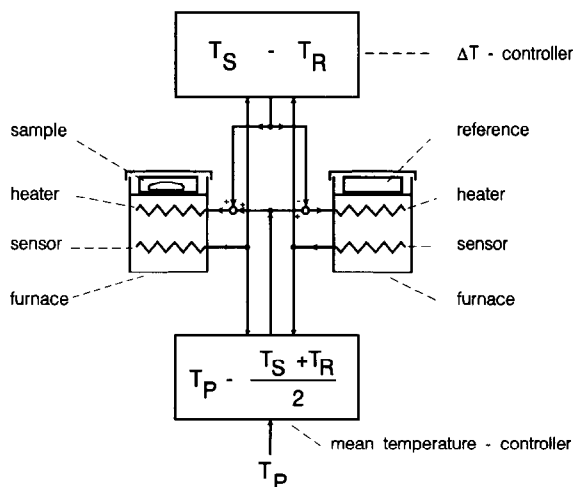
Fig. 2. Schematics of the furnaces and the control system of a power compensated DSC. T_S, temperature of the sample furnaces; T_R, temperature of the reference furnace; T_P, programme temperature (set value).

The temperature sensors and the heaters are Pt10 resistors. A change of the function as a sensor or as a heater is possible by a special electrical plug which exchanges the connections [4]. The influence of this change will be discussed below.

THE SIGNAL FLOW

To investigate the influence of both substances (sample and reference), both furnaces and all control units on the measured curve, it is necessary to describe the total system response of a power compensated DSC including dynamic processes. One possible way to do this is to consider the signal flow in terms of linear response theory. Parts of the measuring system which have an influence on the signals are called transfer elements (e.g. heat transfer paths, heaters, sensors, control units and combinations of them).

To perform an analysis of the influence of the transfer elements on the measured curve the power compensated DSC must be idealized as a "linear" system. Then the behaviour of the transfer elements can be described with the aid of their Green's functions.

As the measuring system of a power compensated DSC is a rather complex one, the discussion of it is split into three steps: (1) description of the signal flow neglecting the influence of the ΔT-control unit (no power compensation); (2) extension of the model by power compensation; (3) the influence of an exchange of the position of heater and temperature sensor within the furnace.

Signal flow without power compensation

Firstly we will discuss the dynamic behaviour of a DSC without power compensation. The corresponding signal flow circuit is shown in Fig. 3. The Green's functions of the transfer elements are called G_{ik}. The index i characterizes the furnace type (1, sample; 2, reference). The second index k illustrates the part of the furnace in question (1, lower part of furnace; 2, upper part of furnace). G_S or G_R stands for the Green's function of the sample and the reference, respectively. G_h characterizes the heaters and G_A the control unit for the average temperature (see Fig. 2).

The physical properties influenced are energy fluxes, for which the generally used symbol is Ψ. The subscripts of Ψ have the following meanings: I, input (scanning programme); h, electrical power (heater input); 1, heat flow in the bottom part (between heater and sensor) of furnace 1 (sample); 2, heat flow in the bottom part (between heater and sensor) of furnace 2 (reference); 1L, losses of furnace 1; 2L, losses of furnace 2; S, unsmeared (theoretical) signal of the sample (the heat flow of an ideal, infinitesimally thin sample which is coupled to an ideal furnace (scanned with rate β) with zero heat resistances); R, unsmeared (theoretical) signal of the reference; m, measured signal. Superscript c refers to a smeared quantity. The losses describe the thermal losses and differences between a real DSC and a true linear system.
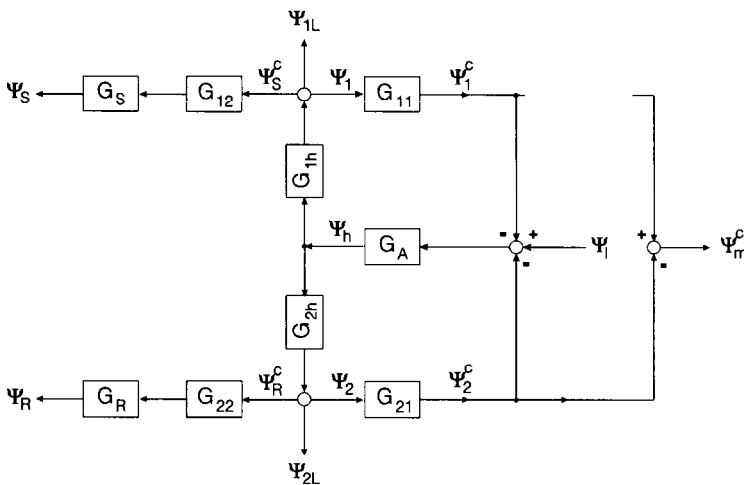

Fig. 3. Scheme of the signal flow in a DSC without power compensation. Key: G, Green's function; Ψ, energy flux. I, input (scanning programme); h, electrical power (heater input); 1, heat flow in the bottom part (between heater and sensor) of furnace 1 (sample); 2, heat flow in the bottom part (between heater and sensor) of furnace 2 (reference); 1L, losses of furnace 1; 2L, losses of furnace 2; S, unsmeared (theoretical) signal of the sample (the heat flow of an ideal, infinitesimally thin sample which is coupled to an ideal furnace (scanned with rate β) with zero heat resistances); R, unsmeared (theoretical) signal of the reference; m, measured signal. Superscript c refers to a smeared quantity.

Factors which are necessary to convert one quantity into another are thought of as a part of the Green's function in question. The operator symbol * stands for the convolution integral (eqn. (1)).

In terms of linear response the smeared output signals of the furances are due to (see Fig. 3)

$$\Psi_1^c = \left(\left(\Psi_I - \frac{\Psi_1^c + \Psi_2^c}{2} \right) * G_A * G_{1h} - \Psi_S^c - \Psi_{1L} \right) * G_{11} \tag{2}$$

and

$$\Psi_2^c = \left(\left(\Psi_I - \frac{\Psi_1^c + \Psi_2^c}{2} \right) * G_A * G_{h2} - \Psi_R - \Psi_{2L} \right) * G_{21} \tag{3}$$

Hence we obtain for the smeared measured signal

$$\Psi_m^c = \left(\Psi_I - \frac{\Psi_1^c + \Psi_2^c}{2} \right) * G_A * (G_{11} * G_{1h} - G_{21} * G_{2h})$$
$$- (\Psi_S^c * G_{11} - \Psi_R^c * G_{21}) - (\Psi_{L1} * G_{11} - \Psi_{L2} * G_{21}) \tag{4}$$

As can be seen the output signals from both furnaces are coupled via the mean temperature controller.

To discuss the influence of the measuring system on the measured signal we have to eliminate Ψ_1^c and Ψ_2^c in eqn. (4). This is done after Laplace transforming [1] eqns. (2) and (3). The transformed functions are characterized by lower case characters. The convolution integral transforms into a normal product (convolution theorem) [1]. From eqns. (2) and (3) we obtain

$$\psi_1^c = \left(\left(\psi_I - \frac{\psi_1^c + \psi_2^c}{2} \right) g_A g_{1h} - \psi_S^c - \psi_{1L} \right) g_{11} \tag{5}$$

or

$$\psi_2^c = \left(\left(\psi_I - \frac{\psi_1^c + \psi_2^c}{2} \right) g_A g_{2h} - \psi_R^c - \psi_{2L} \right) g_{21} \tag{6}$$

respectively.

To obtain ψ_2^c we rearrange eqn. (6)

$$\psi_2^c = \left(\psi_I - \frac{\psi_1^c}{2} \right) g_A g_{2h} b_2 - \psi_R^c b_2 - \psi_{2L} b_2 \tag{7}$$

with

$$b_2 = \frac{g_{21}}{1 + \frac{g_A}{2} g_{2h} g_{21}}$$

After combination of eqns. (5) and (7) and some algebraic calculations we

obtain

$$\psi_1^c = \psi_1 \frac{2d_1(1-c_2)}{1+d_1(1-c_2)} + (\psi_R^c + \psi_{2L})\frac{d_1b_2}{1+d_1(1-c_2)} - (\psi_S^c + \psi_{1L})\frac{g_{11}}{1+d_1(1-c_2)} \tag{8}$$

with $c_2 = \frac{1}{2}g_A g_{2h}b_2$ and $d_1 = \frac{1}{2}g_A g_{1h}g_{11}$.

For ψ_2^c we obtain by analogous changes

$$\psi_2^c = \psi_1 \frac{2d_2(1-c_1)}{1+d_2(1-c_1)} + (\psi_S^c + \psi_{1L})\frac{d_2b_1}{1+d_2(1-c_1)} - (\psi_R^c + \psi_{2L})\frac{g_{21}}{1+d_2(1-c_1)} \tag{9}$$

with

$$b_1 = \frac{g_{11}}{1+\dfrac{g_A}{2}g_{1h}g_{11}}$$

$$c_1 = \frac{1}{2}g_A g_{1h}b_1$$

and

$$d_2 = \frac{1}{2}g_A g_{2h}g_{21}$$

For the measured signal ψ_m^c (ψ_m^c is the difference between ψ_1^c and ψ_2^c) we obtain as the final result of this approximation

$$\psi_m^c = \psi_1 h_D + (\psi_R^c + \omega_{2L})h_2 - (\psi_S^c + \psi_{1L})h_1 \tag{10}$$

or

$$\psi_m^c = \psi_1 h_D - (\psi_S^c h_1 - \psi_R^c h_2) - (\psi_{1L}h_1 - \psi_{2L}h_2) \tag{11}$$

with

$$h_D = \frac{2d_1(1-c_2)}{1+d_1(1-c_2)} - \frac{2d_2(1-c_1)}{1+d_2(1-c_1)}$$

$$h_1 = \frac{g_{11}}{1+d_1(1-c_2)} - \frac{d_2b_1}{1+d_2(1-c_1)}$$

and

$$h_2 = \frac{d_1b_2}{1+d_1(1-c_2)} - \frac{g_{21}}{1+d_2(1-c_1)}$$

To explain eqn. (11) we will first discuss a measured curve without any dynamic processes (deviation from steady state). In this case we can

neglect the influence of the heat transfer and control units on the measured signal (Fig. 3). No smearing effects occur, i.e. $\psi_j^c = \psi_j$ and $h_i = 1$ (with $j = R, S$ and $i = 1, 2$). Equation (11) thus is reduced to

$$\psi_m = -(\psi_S - \psi_R) - (\psi_{1L} - \psi_{2L}) \tag{12}$$

Equation (12) describes an ideal calorimeter. The measured signal is only falsified by the heat losses (ψ_{1L}; ψ_{2L}) of the furnaces. These losses are all heat fluxes from the furnace to the surroundings. In the case of reproducible heat losses the normal baseline correction results in the exact difference of the heat fluxes into the sample and into the reference (see below).

We can see from eqn. (11) that there is always a smearing of the measured signal in the case of any additional dynamic thermal processes inside the sample during the scan. As the Green's functions depends on parameters of the sample–furnace system in a very complicated manner, there is no easy possibility of correcting this smearing.

The first term in eqn. (11) stands for the convolution product of the input with a Green's function, which characterizes the differences between both furnaces. This term influences the measured signal only at the beginning and the end of the scan where the scan rate switches. This effect increases with increasing asymmetry of the furnaces and can be seen as a fluctuation or overscan of the curve at the beginning and end of the measurement.

The information from the sample is included in the second term of eqn. (11). Unlike eqn. (12) this is not an exact difference of the signals from sample and reference but a difference of two different smeared signals (with different Green's functions). This difference is then smeared once more with a Green's function which contains a part of the measuring system. The asymmetriy of the furnaces is taken into consideration by distinguishing between h_2 and h_1.

The third term in eqn. (11) (hereafter called the loss term) characterizes the thermal losses and non-linearities. The losses are a result of heat transfer, convection and radiation. In the case of isoperibolic DSC these losses depend greatly on temperature of the furnaces. The curvature of the baseline is one result of this term. The heat losses are orders of magnitude greater than the measuring signal (e.g. up to 15 W in the case of a Perkin-Elmer DSC), whereas the noise of the measured signal is of the order of 10 μW. For that reason a change of the symmetry of the furnaces of the order of some ppm results in a measurable change of the signal. Dynamic thermal processes in the sample (e.g. latent heat) induce a change of the temperature profile within the whole furnace [5]. This results in a change of the heat losses as well. We emphasize that the heat losses depend on the heat flux into the sample, which we want to measure.

The loss term is also affected by changes of the symmetry, as a result of changes in the heat transport coefficients, the position of the sample or the

shape of the sample. Therefore it is evident that the curvature of the sample run curve is different from that of the baseline run. The error of the baseline correction can be minimized by realizing nearly the same conditions (e.g. block temperature, purge gas flow, heat capacities, position of sample and lid, etc.) for both runs.

Influence of the power compensation on the dynamic behaviour of the DSC

To describe the influence of the power compensation witin the signal flow circuit we have to take into account the Green's function of the ΔT-control unit. Figure 4 shows the extended signal flow. For the functions of interest Ψ_1^c, Ψ_2^c and Ψ_m^c we get from the circuit

$$\Psi_1^c = \left(\left(\left(\Psi_I - \frac{\Psi_1^c + \Psi_2^c}{2} \right) * G_A - (\Psi_1^c - \Psi_2^c) * G_D \right) * G_{1h} - \Psi_S^c - \Psi_{1L} \right) * G_{11}$$

(13)

$$\Psi_2^c = \left(\left(\left(\Psi_I - \frac{\Psi_1^c + \Psi_2^c}{2} \right) * G_A + (\Psi_1^c - \Psi_2^c) * G_D \right) * G_{2h} - \Psi_R^c - \Psi_{2L} \right) * G_{21}$$

(14)

$$\Psi_m^c = \left(\Psi_I - \frac{\Psi_1^c + \Psi_2^c}{2} \right) * G_A * (G_{11} * G_{1h} * G_{2h})$$

$$- (\Psi_1^c - \Psi_2^c) * G_D * (G_{11} * G_{1h} - G_{21} - G_{2h})$$

$$- (\Psi_S^c * G_{11} - \Psi_R^c * G_{21}) - (\Psi_{L1} * G_{11} - \Psi_{L2} * G_{21})$$

(15)

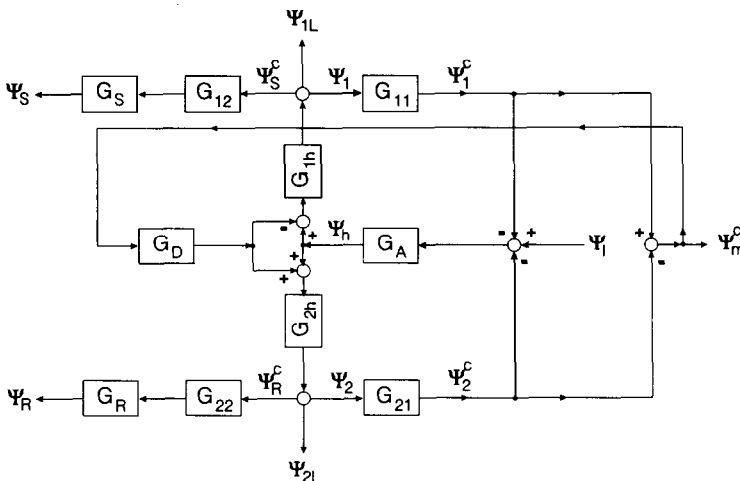Comparison of eqn. (4) with eqn. (15) reveals that there is only a difference

Fig. 4. Scheme of the signal flow in a DSC with power compensation. Symbols as in Fig. 2.

in that term containing the power compensation Green's function. Taking Ψ^c_{md} as the measuring signal without power compensation, we obtain

$$\Psi^c_m = \Psi^c_{md} - \Psi^c_m * G_D * (G_{11} * G_{1h} - G_{21} - G_{2h}) \tag{16}$$

After Laplace transformation and some calculations it follows that

$$\psi^c_m = \frac{\psi^c_{md}}{1 + g_D(g_{1h}g_{11} + g_{2h}g_{21})} \tag{17}$$

We find the dynamic behaviour of the measuring signal with included power compensation being described with the same type of equation as in the case without power compensation, but the (Laplace transformed) Green's function combinations terms h_1, h_2 and h_D are divided by the quotient from eqn. (17). The structure of this equation has the form of a Laplace transformed equation of a feedback system. With a proper g_D function, the Green's functions yields smaller values and the relaxation after a disturbance must be faster than in the case without power compensation.

Changing the position of temperature sensor and heater within the furnace

Generally there are two possibilities for the arrangement of the temperature sensor and the heater in a DSC furnace. One arrangement (with the heater closer to the sample) is shown in Fig. 2. With the aid of a special connector an exchange of the function is possible (heater used as temperature sensor and vice versa). Figure 5 shows the signal flow circuit in this case.
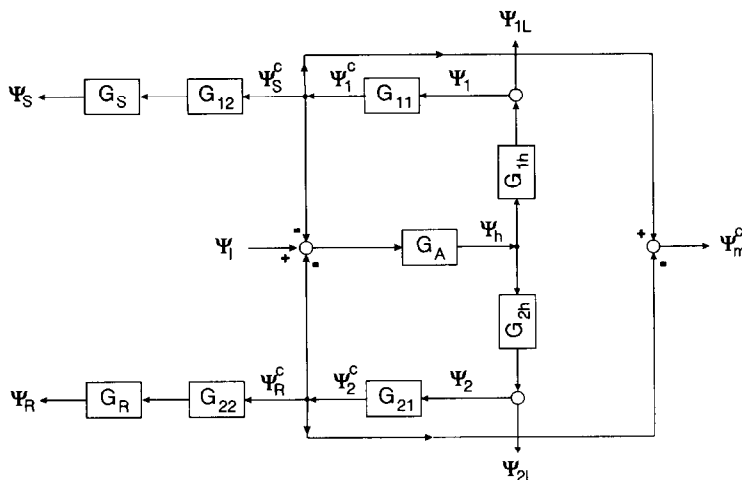

Fig. 5. Scheme of the signal flow in a DSC with power compensation. Same as in Fig. 2, but the position of heater and temperature sensor are exchanged.

As including the power compensation does not change the results generally, for the sake of simplicity it is neglected in the following calculations. From Fig. 5 we find

$$\Psi_1^c = \left(\left(\Psi_I - \frac{\Psi_1^c + \Psi_2^c}{2} \right) * G_A * G_{1h} - \Psi_{1L} \right) * G_{11} - \Psi_S^c \tag{18}$$

$$\Psi_2^c = \left(\left(\Psi_I - \frac{\Psi_1^c + \Psi_2^c}{2} \right) * G_A * G_{h2} - \Psi_{2L} \right) * G_{21} - \Psi_R^c \tag{19}$$

and

$$\Psi_m^c = \left(\Psi_I - \frac{\Psi_1^c + \Psi_2^c}{2} \right) * G_A * (G_{11} * G_{1h} - G_{21} * G_{2h})$$
$$- (\Psi_S^c - \Psi_R^c) - (\Psi_{L1} * G_{11} - \Psi_{L2} * G_{21}) \tag{20}$$

The Laplace-transformed measuring signal is

$$\psi_m^c = \psi_I h_D - \left(\psi_S^c \frac{h_1}{g_{11}} - \psi_R^c \frac{h_2}{g_{21}} \right) - (\psi_{1L} h_1 - \psi_{2L} h_2) \tag{21}$$

Comparing eqns. (11) and (21) reveals that there is only some modification of the Green's function which is connected to ψ_S^c and ψ_R^c. That means that the validity of eqn. (11) is not changed in the case of exchange of temperature sensor and heater.

The eqns. (11), (17) and (21) describe the connection between measured signal on the one hand and the paths of heat flows and the properties of the temperature controllers on the other. If the Green's functions of the controllers [6] and the heat conduction paths [7] are inserted in these equations, the measured signal can be calculated for that model of heat transfer. In this paper we only discuss the general aspects of these equations to obtain basic results.

CORRECTIONS

Baseline correction

Baseline correction without dynamic processes of the DSC
In this case of "classical" baseline correction in the steady state, any dynamic processes needing Green's functions are neglected. In this case the measured curve reads as a sum of unsmeared signals

$$\Psi_m = (\Psi_S - \Psi_R) + \Psi_L \tag{22}$$

and the baseline

$$\Psi_{m,b} = (\Psi_B - \Psi_R) + \Psi_{L,b} \tag{23}$$

where the sample is replaced by an empty pan (with the same mass as the sample pan).

If the loss terms in both runs are not significantly different ($\Psi_L \sim \Psi_{L,b}$) the difference of both curves is

$$\Psi_{m,cor} = \Psi_S - \Psi_B \qquad (24)$$

Ψ_B characterizes the heat flow into the sample-furnace and the sample pan. Ψ_S includes additionally the heat flow into the sample. $\Psi_{m,cor}$ then describes the heat flow into the sample. This method is well known from DSC manuals. However in the case of such a simple correction all dynamic processes are neglected.

Baseline correction including the influences of the Green's functions

Taking into account the smearing of the measured signal by sample and calorimeter influences we obtain for the sample run

$$\Psi_m^c = \Psi_I * H_D - (\Psi_S^c * H_1 - \Psi_R^c * H_2) - (\Psi_{1L} * H_1 - \Psi_{2L} * H_2) \qquad (25)$$

which equals eqn. (10), and for the baseline run analogously

$$\Psi_{m,b}^c = \Psi_I * H_D - (\Psi_B^c * H_1 - \Psi_R^c * H_2) - (\Psi_{1L,b} * H_1 - \Psi_{2L,b} * H_2) \qquad (26)$$

The DSC manual [4] recommends use of an empty pan for the baseline run. Ψ_B describes the heat flow into the contents of the sample furnace during the baseline run. We call these contents the "baseline sample". After baseline subtraction (eqn. (25) − eqn. (26)) we get a function $\Psi_{m,cor}^c$ which contains the difference of the smeared signals of the sample Ψ_S^c and the "baseline sample" Ψ_B^c convoluted with H_1 and another one taking into account the loss terms.

$$\Psi_{m,cor}^c = (\Psi_S^c - \Psi_B^c) * H_1 + (\Psi_{1L} - \Psi_{1L,b}) * H_1 - (\Psi_{2L} - \Psi_{2L,b}) * H_2 \qquad (27)$$

Supposing that there is no significant change in the heat losses of the reference furnace (number 2) between baseline run and sample run the last term can be neglected. This should always be guaranteed by good (reproducible) experimental conditions. The first term in eqns. (25) and (26), describing the asymmetry of the empty furnaces in the moment of a stepwise change of the scan rate, cancels out in the difference. This asymmetry therefore has no influence on dynamic processes during the scan in the baseline corrected curve.

Desmearing

Every desmearing procedure should yield the true heat flow function into the sample.

The idea of the desmearing algorithm proposed in refs. 1 and 2 is to

describe the measuring curve as a simple convolution product with the Green's function in question obtained from the behaviour of the measuring signal on step changes of the heating rate. Comparison of eqns. (1) and (11) shows that this simple description is only a rough approximation of the truth.

Now the question arises as to how erroneous is our result if we desmear the measured results with only one Green's function (as in eqn. (1)). We proceed from eqn. (25) and substitute the smeared sample signal Ψ_S^c and the smeared reference signal Ψ_R^c due to Figs. 3–5 by

$$\Psi_S^c = \Psi_S * (G_S * G_{12})$$

$$\Psi_R^c = \Psi_R * (G_R * G_{22})$$

and obtain

$$\Psi_m^c = \Psi_1 * H_D - (\Psi_S * H_S - \Psi_R * H_R) - (\Psi_{1L} * H_1 - \Psi_{2L} * H_2) \tag{28}$$

with $H_S = H_1 * G_S * G_{12}$ and $H_R = H_R * G_R * G_{22}$. An analogous equation can be derived for the baseline from eqn. (26).

We have also to look at the (one) Green's function commonly used to desmear the measured curves. We determine this function from the response of the measured heat flow on a stepwise change of the heating rate (step response Green's function G_{sr}) [1, 2]

$$\Psi_m^c = \Psi_m * G_{sr}$$
$$\quad = \eta_m \Theta * G_{sr} \tag{29}$$

where η is the step height and Θ the "step function" (0 for $t < t_0$ and 1 for $t \geq t_0$).

The measured curve Ψ_m^c is described by eqn. (28). A step in the scan rate results in a step of Ψ_1, Ψ_S and Ψ_R. Including these step functions in eqn. (28) and comparing with eqn. (29) yields

$$\eta_m \Theta * G_{sr} = \eta_1 \Theta * H_D - (\eta_S \Theta * H_S - \eta_R \Theta * H_R) - \Delta L \tag{30}$$

with ΔL being the total loss term.

After Laplace transformation, eqn. (30) can be solved relative to the Green's function

$$g_{sr} = \frac{\eta_1}{\eta_m} h_D - \left(\frac{\eta_S}{\eta_m} h_S - \frac{\eta_R}{\eta_m} h_R \right) - \Delta l \tag{31}$$

Δl being the Laplace transformed loss term.

Both the step response Green's function (eqn. (31)) and the measuring

function (eqn. (28)) consists of three terms. Their magnitude depends on the symmetry between sample and reference. In the case of good symmetry $\eta_S h_S - \eta_R h_R$, η_m and Δl are small. The step response Green's function is then mainly determined by h_D, the asymmetry of the dynamic behaviour of the furnaces. This asymmetry is only influenced by changing the scan rate but not by a thermal effect inside the sample during the scan.

The signal in which the experimenter is interested is the true heat flow into the sample Ψ_S. If there are some changes within the sample during the steady state region of the measurement, the measured heat flow, in response to these changes, is Ψ_S^c. The connection between Ψ_S^c and Ψ_S reads

$$\Psi_S^c = \Psi_S * H_S \tag{32}$$

If we desmear the measured curve with the step response Green's function G_{sr}, which includes the response function of all parts of the equipment, we are in error. This can be followed from (the Laplace transformed) eqn. (31), as g_{sr} contains much more than h_s.

Upon increasing the asymmetry between sample and reference, the influence of the first term decreases, but the influence of the third term Δl increases. The relation between them are described elsewhere [8].

If we desmear the measured curves after baseline correction it follows from eqns. (25)–(27) that the influence of the asymmetry in the dynamic behaviour of the furnaces at the beginning and at the end of the scan can then be neglected. Therefore we get a minor erroneous step response Green's function from the baseline corrected measuring curves, namely

$$\eta_m \Theta * G_{sr} = (\eta_S \Theta * H_1 * G_{12} * G_S - \eta_B \Theta * H_1 * G_{12} * G_B) - \Delta L \tag{33}$$

after Laplace transformation this equation can be solved for the searched Green's function as well

$$g_{sr} = \left(\frac{\eta_S}{\eta_m} g_S - \frac{\eta_B}{\eta_m} g_B \right) g_{12} h_1 - \Delta l \tag{34}$$

Desmearing the baseline corrected measuring curve with this Green's function (and neglecting the heat losses) we obtain

$$\psi_{m,cor} = \psi_S \frac{g_S}{\dfrac{\eta_S}{\eta_m} g_S - \dfrac{\eta_B}{\eta_m} g_B} - \psi_B \frac{g_B}{\dfrac{\eta_S}{\eta_m} g_S - \dfrac{\eta_B}{\eta_m} g_B} \tag{35}$$

The inevitable difference between the contents of the furnaces in both runs (sample run and baseline run) is the reason for a systematic error. This error is smaller if we desmear the baseline corrected curve instead of desmearing the sample run and the baseline run separately, because the Green's functions of the furnaces are not part of eqn. (35).

The variation of g_B due to the variation of the "baseline-sample" changes the error. If g_B is about zero the desmeared measured signal equals the heat flow into an ideal sample. In this case the second term in eqn. (35) vanishes and the quotient containing the Green's functions in the first term becomes unity and we obtain

$$\Psi_{m,cor} = \Psi_s$$

In this case the asymmetry between both runs is rather high and the heat losses are not allowed to be neglected in eqn. (35).

The case that g_B equals zero arises only if the baseline is an exact straight line (with slope zero) and if there is no change of the heat flow on changing the scan rate. This needs very exact symmetry and practically never occurs in reality. The quantitative estimation of this error will be part of further experimental work.

SUMMARY

The smearing of the measured signal of a power compensated DSC has been studied taking into account the dynamic behaviour of the measuring system, the sample and the heat transfer path.

To desmear the measured DSC curves it is possible to extract the Green's function from that part of the curve where the scan rate switches. Doing this with the measured heat flow curve results in only a rough approximation of the true Green's function. The reason is that there are components in the measured signal immediately after switching the scan rate which originate from the measuring system on changing the steady state conditions and not from the Green's function valid for transitions during the scan. The difference between these Green's functions increases with increasing symmetry between the heat capacities of the sample and the reference.

From the analysis of the signal flow circuit it follows that the Green's function extracted from the baseline corrected heat flow curve is more valid than that extracted from a single sample run. These results can also be used to discuss other dynamic errors in DSC measurements in a similar manner. Experimental results supporting this theory will be presented in further parts of this series [8, 9].

The dynamic behaviour of heat-flux DSC has not been discussed in this paper. To do this, it is necessary to consider both fluxes (i.e. heat fluxes) and additionally potentials (i.e. temperatures) in a theoretical approach. From the differential equation of this type of DSC obtained with the aid of analogous electrical networks [10] we can conclude that similar results, as shown for the power compensated DSC, should also be valid for that type of DSC.

REFERENCES

1 G.W.H. Höhne and J.E.K. Schawe, Thermochim. Acta, 229 (1993) 27.
2 J.E.K. Schawe and C. Schick, Thermochim. Acta, 187 (1991) 335.
3 W. Hemminger and G.W.H. Höhne, Calorimetry, Fundamentals and Practice, VCH Verlags-Gesellschaft, Weinheim, 1984.
4 DSC-2 Manual, Perkin-Elmer Corporation, 1974.
5 H. Hoff, personal communication, 1991.
6 S. Tanaka, Thermochimica Acta, 210 (1992) 67.
7 H. Hoff, Thermochimica Acta, 187 (1991) 293.
8 J.E.K. Schawe, C. Schick, and G.W.H. Höhne, Dynamic behaviour of power compensated differential scanning calorimeters; Part 5, in preparation.
9 J.E.K. Schawe, C. Schick, and G.W.H. Höhne, Dynamic behaviour of power compensated differential scanning calorimeters; Part 4, in preparation.
10 G.W.H. Höhne, Thermochim. Acta, 69 (1983) 175.