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PROBLEMS WITH THE CALIBRATION OF DIFFERENTIAL-TEMPERATURE-SCANNING-CALORIMETERS*

G.W.H. Höhne Sektion für Kalorimetrie der Universität Ulm
Postfach 4066, D 7900 Ulm (F.R.G.)

Abstract

The function principle of differential-temperature-scanning-calorimeters (heat-flux-calorimeters) gives rise to calibration errors in case of phase transitions (and other events within the sample) disturbing the steady-state conditions. The cause of the problems is the temperature dependence of the coefficients of heat transfer, leading to weak non-linearity of the calorimeter and thus to a dependence of the calibration factor on parameters such as mass and thermal conductivity of the sample, heating rate, peak shape and temperature. By theoretical considerations and model calculations quantitative relations can be derived. As a result the uncertainty of the calibration factor for heat-flux-calorimeters due to variation of sample parameters should be supposed as 1 to 5 percent depending on temperature and on the properties of the calorimeter in question.

Introduction

Depending on the method of measuring, two types of scanning calorimeters can be distinguished.

Power compensated calorimeters measure the difference of the elec-

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tric power necessary to heat a sample and a reference at a constant rate, the temperature of the two supports are controlled to be equal to the set-value at every moment. In case of a transition of the sample the greater (or smaller) requirements of heat are covered by increasing (or decreasing) the power input to the sample heater appropriately. An electronic device evaluates the differential power (corresponding to the heat-flux into the sample) and yields it as an analogous voltage on the output calibrated in units of heat-flux.

In heat-flux calorimeters the sample and the reference sample are connected to a furnace via a well defined heat conduction path and the temperature-difference between sample and reference is measured usually with aid of difference-thermocouples. The furnace is heated in a controlled manner such that its temperature increases at a constant rate. Heat arrives at the sample and the reference by conduction, this presumes a temperature difference between the furnace and the sample and reference. A larger heat-flux needs a larger temperature difference, thus the latter is a measure for the former.

This holds both for sample and reference, leading to the conclusion that the temperature difference between sample and reference is a measure for the differential heat flux:

$$\Delta\dot{Q} = K \cdot \Delta T \tag{1}$$

Hence the peak area in case of a transition of the sample is proportional to the total heat of transition:

$$Q_t = \int \dot{Q}^* dt = K \cdot \int \Delta T^* dt \tag{2}$$

The superscript $*$ indicates a proper baseline correction. The factor K must be determined by seperate calibration runs with substances of well known heat of transition. As equation (1) holds for steady-state conditiones only and the steady-state of the heat flux is surely disturbed by the larger need of heat during transition of the sample, the general validity of equation (2) has to be questioned. In particular the independence of the calibration factor K from the peak shape $\Delta T^{*}(t)$ and sample parameters is only true within certain limits, this is leading to an uncertainty connected on principle to this method, what shall be demonstrated with aid of the following remarks.

Differential equation of asymmetric heat-flux calorimeters

In case of pure conduction heat transfer without radiation and convection it is possible to deduce the differential equation proper and integrate it getting instructive results.

Fig. 1 shows a sketch of a heat-flux calorimeter and an equivalent electric network facilitating the set up of the functional equations. The current source i_t corresponds to the additional heat-flux during a transition. Kirchhoff's first law states that the sum of all currents in a junction is zero, this is leading to the following equations for the three junctions of the circuit in fig. 1:

① : $i_F = i_{FS} + i_{FR}$ (3)

② : $i_{FS} + i_t = i_{SR} + i_s$ (4)

③ : $i_{FR} + i_{SR} = i_R$ (5)

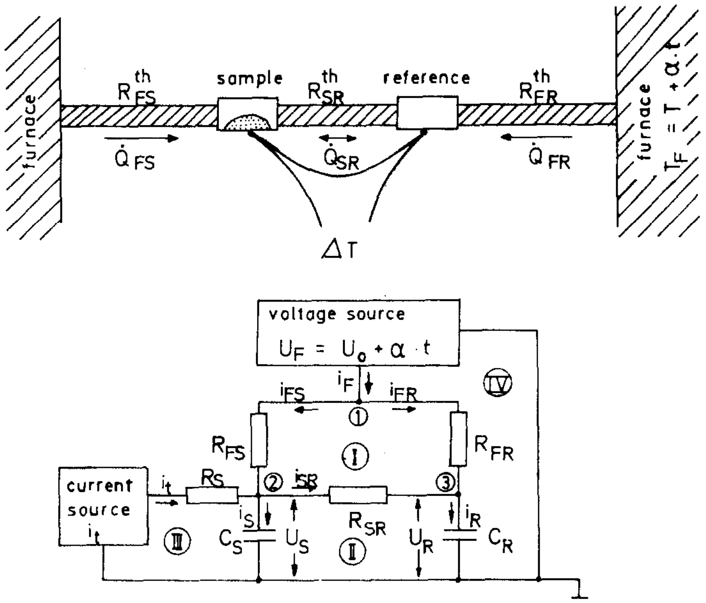


Fig. 1: Heat-flux scanning calorimeter (schematic) and equivalent electric network

R: resistance equiv. to thermal resistance R^{th}

C: capacitance equiv. to heat capacity C_p

i: current equiv.to heat-flux $\dot{Q}$

U: voltage equiv. to temperature T

Kirchhoff's second law states that the sum of all voltages in a closed loop is zero, hence the following equations hold:

(I) : $$\Delta U_{FS} + \Delta U_{SR} = \Delta U_{FR} \tag{6}$$

(II) : $$U_S = \Delta U_{SR} + U_R \tag{7}$$

(III) : $$U_t = \Delta U_S + U_S \tag{8}$$

(IV) : $$U_F = \Delta U_{FR} + U_R \tag{9}$$

With aid of the following fundamental relations

$$i = \frac{U}{R}\,, \quad i = \frac{dq}{dt} = C \cdot \frac{dU}{dt}$$

(R = resistance, q = charge, C = capacitance, t = time)

and equations (6), (7), (9) the equations (4) and (5) read:

$$\frac{U_F}{R_{FS}} - \frac{U_S}{R_{FS}} + \frac{dq_t}{dt} = \frac{\Delta U_{SR}}{R_{SR}} + C_S \cdot \frac{dU_S}{dt} \qquad (10)$$

$$\frac{U_F}{R_{FR}} - \frac{U_R}{R_{FR}} + \frac{\Delta U_{SR}}{R_{SR}} = C_R \cdot \frac{dU_R}{dt} \qquad (11)$$

Usually the calorimeter is built as a very symmetrical twin arrangement, thus the following simplification holds:

$$R_{SR} = R_2$$

$$R_{FS} = R_1 - \Delta R \text{ with } R_1 = R_{FR} \text{ and } \Delta R \ll R_1$$

$$C_S = C + \Delta C \text{ with } C = C_R \text{ and } \Delta C \ll C$$

$$R^{-1}_{FS} = (R_1 - \Delta R)^{-1} \approx \frac{1}{R_1} \cdot \left(1 + \frac{\Delta R}{R_1}\right)$$

As $\Delta U_{SR} = U_S - U_R$ is equivalent to the measured quantity ΔT we are led to subtract equation (11) from (10) getting

$$\frac{dq_t}{dt} = \left(\frac{1}{R_1} + \frac{2}{R_2}\right) \cdot \Delta U_{SR} + C \cdot \frac{d\Delta U_{SR}}{dt} + \frac{\Delta R}{R^2_1} \cdot U_S + \Delta C \frac{dU_S}{dt} - \frac{\Delta R}{R^2_1} \cdot U_F$$

translated into heat conduction language with

R ⟶ R thermal resistance   U ⟶ T temperature

C ⟶ C heat capacity   q ⟶ Q heat

$$\dot{Q}_t = \left(\frac{1}{R_1} + \frac{2}{R_2}\right) \cdot \Delta T + C \cdot \frac{d\Delta T}{dt} + \frac{\Delta R}{R^2_1} \cdot T_S + \Delta C \cdot \frac{dT_s}{dt} - \frac{\Delta R}{R^2_1} \cdot T_F \qquad (12)$$

The differential equation describes the connection between the transition heat-flux $\dot{Q}_t$ and the measured quantity ΔT in case of weak asymmetry. For $\Delta R = 0$ and $\Delta C = 0$ it simplifies to the well known Tian equation:

$$\dot{Q}_t = \left(\frac{1}{R_1} + \frac{2}{R_2}\right) \cdot \Delta T + C \cdot \frac{d\Delta T}{dt} \tag{13}$$

As a result it can be seen that equation (1) only holds for steady state conditions (i.e. $d\Delta T/dt = 0$) and total symmetry.

Solution of the Differential Equation

a) Steady-state case (baseline)

We assume steady-state conditions without any transition in the sample, in other words the temparature of every point changes linear in time and the following relations are valid:

$$T_F = T_o + \alpha \cdot t$$

$$T_S = T_o - \Delta T^{ss}_{FS} + \kappa \cdot t \quad (\kappa: \text{heating rate})$$

$$\frac{dT_S}{dt} = \alpha \ , \ \frac{d\Delta T}{dt} = 0 \text{ and } \dot{Q} = 0$$

Hence from equation (12) follows

$$\left(\frac{1}{R_1} + \frac{2}{R_2}\right) \cdot \Delta T^{ss} - \frac{\frac{\Delta R}{2}}{R_1} \cdot \Delta T^{ss}_{FS} + \Delta C \cdot \alpha = 0 \tag{14}$$

with

$$\Delta T^{ss}_{FS} = \dot{Q}^{ss}_{FS} \cdot (R_1 - \Delta R) \text{ and } \dot{Q}^{ss}_{FS} = \dot{Q}^{ss}_{S} + \dot{Q}^{ss}_{SR} \quad \text{we get:}$$

$$\Delta T^{ss}_{FS} = \left\{(C + \Delta C) \cdot \alpha + \frac{\Delta T^{ss}}{R_2}\right\} \cdot (R_1 - \Delta R) \tag{15}$$

Combination of equations (14) und (15) with the approximations

$\Delta R \cdot \Delta R \approx 0$ and $\Delta R \cdot \Delta C \approx 0$ is leading to the result

$$\Delta T^{ss} = \frac{R_2 \cdot (C \cdot \Delta R - R_1 \cdot \Delta C)}{R_2 + 2R_1 - \Delta R} \cdot \alpha \tag{16}$$

This equation describes the baseline of the heat-flux scanning calorimeter. As can be seen the baseline depends on the heating rate α and the difference of the heat capacity of the sample and reference as well as on the difference of the thermal resistances furnace-sample and furnace-reference.

Usually the steady-state baseline is used to determine the heat capacity of the sample if the reference container is empty and ΔC thus can be taken as the unknown sample heat capacity. From equation (16) follows, however, that ΔT^{ss} is only proportional to ΔC in case of $\Delta R = 0$, in other words if total symmetry in thermal conductivity from furnace to sample and reference is verified. This cannot be fulfilled exactly as sample and reference are necessarily different substances with different heat transfer properties. Especially during transitions the contact between sample and container often changes and causes a step change of the baseline much larger than that caused by the change in heat capacity. (See fig.2). As a result it has to be stated that the change in ΔR cannot be neglected and the determination of heat capacities from baseline signals of heat-flux calorimeters is very problematically in particular as R_1 and R_2 and C in equation (16) depend on temperature.

b) <u>Transition case (peak)</u>

Suppose a transition takes place in the sample within the time-interval (t_1, t_2) with a transition heat flux $\dot{Q}_t$ "switched on" in this period and

$$T_F - T_S = \Delta T_{FS} = \dot{Q}_{FS} \cdot (R_1 - \Delta R) = \left\{ (C+\Delta C) \cdot \frac{dT_S}{dt} + \frac{\Delta T}{R_2} - \dot{Q}_t \right\} \cdot (R_1 - \Delta R)$$

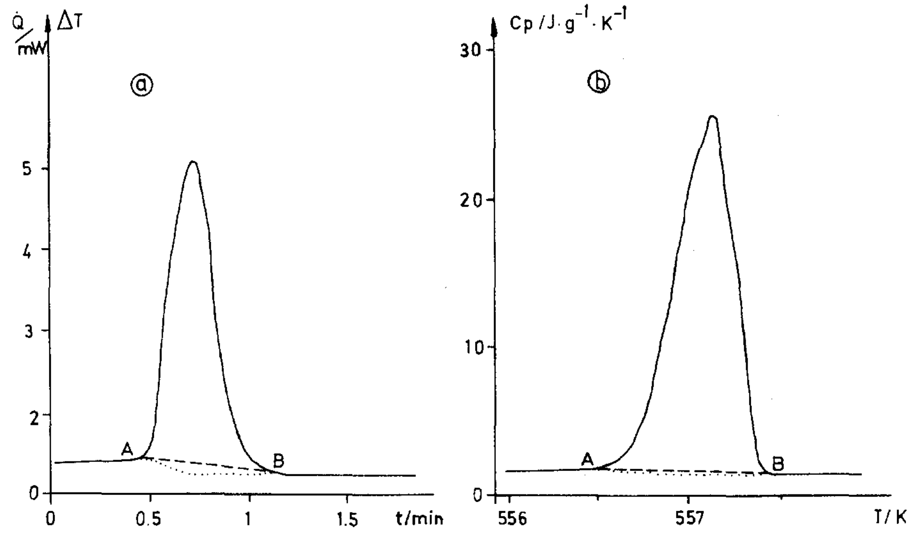


Fig. 2: Plots of transition of $RbNO_3$ at 557 K measured

a) with a heat-flux calorimeter (Du-Pont TA 1090/910) and

b) with a power-compensated scanning calorimeter (Perkin-Elmer DSC-2) of the same sample .

The left curve shows a greater baseline shift than the right one.

which follows with aid of equation (4) translated into heat-flux language and $\dot{Q}_S = C_S \cdot dT_S/dt$, then we get from equation (12) the following differential equation in a good approximation considering $\Delta R \cdot \Delta R \approx 0$ and $\Delta R \cdot \Delta C \approx 0$

$$(1 - \frac{\Delta R}{R_1}) \cdot \dot{Q}_t = (\frac{1}{R_1} + \frac{2}{R_2} - \frac{\Delta R}{R_1 . R_2}) \cdot \Delta T + C \cdot \frac{d \Delta T}{dt} - (\frac{C \cdot \Delta R}{R_1} - \Delta C) \cdot \frac{dT_S}{dt} \qquad (17)$$

This equation must be integrated in the time interval (t_1, t_2):

$$\int_{t_1}^{t_2} (1 - \frac{\Delta R}{R_1}) \cdot \dot{Q}_t dt = \int_{t_1}^{t_2} (\frac{1}{R_1} + \frac{2}{R_2} - \frac{\Delta R}{R_1 . R_2}) \cdot \Delta T dt + \int_{t_1}^{t_2} C \cdot \frac{d \Delta T}{dt} dt$$

$$- \int_{t_1}^{t_2} (\frac{C \cdot \Delta R}{R_1} - \Delta C) \cdot \frac{dT_S}{dt} dt \qquad (18)$$

If we assume R_1, R_2, ΔR, C and ΔC as independent of temperature (a problematic assumption, see last section) and hence of time within the period in question, and the time interval large enough to guarantee steady-state conditions at t_1 and t_2, the following is valid:

$$\Delta T (t_1) = \Delta T (t_2) = \Delta T^{ss}$$

$$\int_{t_1}^{t_2} \frac{d \Delta T}{dt} dt = \int_{T(t_1)}^{T(t_2)} d \Delta T = 0$$

and from equation (16):

$$\frac{C \cdot \Delta R}{R_1} - \Delta C = (\frac{1}{R_1} + \frac{2}{R_2} - \frac{\Delta R}{R_1 . R_2}) \cdot \frac{\Delta T^{ss}}{\alpha}$$

Consequently equation (18) reads

$$(1 - \frac{\Delta R}{R_1}) \cdot \int_{t_1}^{t_2} \dot{Q}_t dt = (\frac{1}{R_1} + \frac{2}{R_2} - \frac{\Delta R}{R_1 . R_2}) \cdot \left(\int_{t_1}^{t_2} \Delta T dt - \frac{\Delta T^{ss}}{\alpha} \cdot \int_{t_1}^{t_2} \frac{dT_S}{dt} dt \right) \qquad (19)$$

The three integrals can be integrated:

$$\int_{t_1}^{t_2} \dot{Q}_t dt = Q_t \qquad \text{(heat of transition)}$$

$$\int_{t_1}^{t_2} \Delta T \, dt = \int_{t_1}^{t_2} (\Delta T^{*} + \Delta T^{ss}) \, dt = \int_{t_1}^{t_2} \Delta T^{*} dt + \Delta T^{ss} \cdot (t_2 - t_1)$$

$$\int_{t_1}^{t_2} \frac{dT_S}{dt} \, dt = T_S \, (t_2) - T_S \, (t_1) = \alpha \cdot (t_2 - t_1)$$

Hence equation (19) reads:

$$Q_t = \frac{R_2 + 2 R_1 - \Delta R}{R_2 \, (R_1 - \Delta R)} \cdot \int_{t_1}^{t_2} \Delta T^{*} \, dt \qquad (20)$$

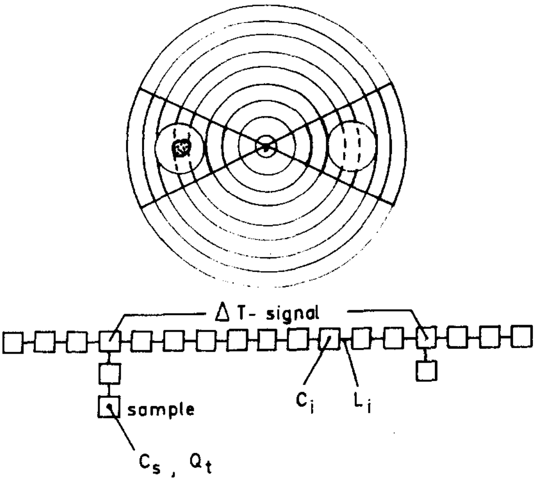
Comparing this with equation (2) yields the calibration factor

$$K = \frac{R_2 + 2 R_1 - \Delta R}{R_2 \, (R_1 - \Delta R)} \qquad (21)$$

It should be emphasized,however,that equation (20) and (21) only holds in case of pure conduction heat transfer and independence of R_1, R_2 and ΔR from temperature. Usually ΔR changes during a transition as the heat transfer to (and trough) the sample changes, this is bringing about a change of the baseline corresponding to $\Delta R(t)$ which must be well known to avoid integration errors. As can be seen in fig. 2 different assumptions relative to the course of the baseline (which cannot be measured) result in large differences in determination of the heat of transition in question. To decrease the influence of this source of error R_1 and R_2 have to be chosen as dominant and ΔR as small as possible, leading to the constructions used by Boersma and Tian-Calvet and applied nowadays in most commercial heat-flux calorimeters.

Numerical Solution of the Heat Conduction Equation

The equation (1) is not valid in case of disturbances of the steady-state conditions as is the matter during transitions in the sample, hence we were interested to study the influence of the magnitude of these disturbances on the calibration factor. Thus we had to solve the heat conduction equation for the geometrical arrangement of the calorimeter in question. This is only possible by numerical methods (Sucec, 1975) as boundery and initial conditions are complicated. In a first approximation the heat conduc-



$C_i = V_i \cdot \rho_i \cdot c_i \qquad L_i = A_i \cdot \lambda_i / d_i$

Fig. 3: Sample support disk of a heat-flux calorimeter and quasilinear cell chain for approximative calculation of heat transfer.

(C_i: heat capacity, V_i: volume, ρ_i: density, c_i: specific heat capacity, A_i: jacket aera, λ_i: thermal conductivity d_i: distance and L_i: coefficient of heat transfer of cell number i) ting disk, used in most of commercial heat-flux calorimeters as a sample and reference support, was considered to be composed of ring-shaped cells with radial heat transfer. Thus the calculation can be done in a quasilinear manner taking a propper sector of the disk as linear chain of cells (with sample and reference container as branches, see fig. 3) and computing the temperature-change with aid of the balance heat transfer and the heat capacity and transition heat of the cell in question. The time interval and the cell size has to be chosen small enough to guarantee a good approximation. The method allows variation of all parameters, the temperature dependence of heat capacity and heat transfer (inclusive radiation and convection) can easily be included into the computer program, which calculates the $\Delta T(t)$-curve and thus allows to determine the calibration factor with aid of equation (2). In the following some results got from a model which meets the real conditions in most commercial heat-flux calorimeters with Boersma principle are presented.

a) Pure conduction heat-transfer

In case of absence of convection and radiation heat transfer and weak temperature dependence of the thermal conductivity the calibration factor is found to be totally independent of the degree of disturbance of the steady-state during transitions within the sample. Variations of parameters such as the coefficient of heat transfer, mass, specific heat of transition within a wide range has no effect on the calibration factor. This can even be shown theoretically with aid of the method of Greens function.
(H. Hoff, Appendix of this paper).
On the other hand the position of the sample on the heat conduc-

ting disk has a great influence on the calibration factor. To reduce this effect different measures were taken in commercial calorimeters to position the sample container exactly and measure the temperature difference beneath the sample and reference not very locally but averaged over a certain area with aid of several thermocouples, a thermodisc or a flat resistance thermometer with a large sensitiv area. Calibration runs (with the sample in different positions within the container) have to show wether the method in question is satisfactory.

b) Radiation and convection heat transfer

For radiation heat transfer the Stefan-Boltzmann law holds

$$\dot{Q}_E = \sigma_B \cdot \; \cdot a \cdot T^4 \tag{22}$$

($\dot{Q}_E$: radiation heat-flux emitted, σ_B: Stefan-Boltzmann constant, ε: emissivity, a: area, T: temperature)

The heat-flux absorbed on the other hand:

$$\dot{Q}_A = \sigma_B \cdot \alpha \cdot a \cdot T^4{}_F$$

(α: absorbtivity, T_F = temperature of surroundings)

The balance heat-flux exchanged of a small body with the surrounding furnace by radiation is (Sucec, 1975)

$$\dot{Q}_r \approx a \cdot \varepsilon \cdot \sigma_B \cdot (T^4 - T^4{}_F) \tag{23}$$

For small temperature differences, as usual in calorimeters, equation (23) reads

$$\dot{Q}_r \approx a \cdot \varepsilon \cdot \sigma_B \cdot 4 \cdot T^3{}_F \cdot \Delta T_F \tag{24}$$

The radiation heat transfer is thus likewise proportional to the temperature difference as conduction heat transfer is, but the coefficient depends strongly on temperature of it's surroundings giving rise to nonlinearity of the device and thus calibration problems (see appendix). This fact can easily be understood by taking in mind that in heatflux calorimeters the temperature of the sample is almost constant during the transition takes place, thus the temperature field around the sample and its change in time depends on sample parameters, more precisely on the magnitude of the effect. Hence the part of heat exchanged by radiation after with the change of sample parameters and thus the calibration factor. To get a quantitative result the quasi-linear model described above was taken for calculation of the $\Delta T(t)$ signal and the calibration factor, the following table shows the results:

temperature	changed parameter	calibration factor $\cdot 10^2$ J/K·s
800 K	transition enthalpie 0,3 J	5.353
	transition enthalpie 3,0	5.445
300 K	transition enthalpie 0,3 J	4.423
	transition enthalpie 3,0	4.464
800 K	sample coeff. of heat transfer 0,005 W/K	5.427
	sample coeff. of heat transfer 0,001	5.460
	sample coeff. of heat transfer 0,0005	5.490
800 K	heating rate 2 K/min	5.445
	heating rate 5	5.456
	heating rate 10	5.468
	heating rate 20	5.507

table 1: Dependence of calibration factor on sample parameters calculated by numerical solution of the heat transfer equations with aid of a model shown in fig. 3

As can be seen the calibration factor changes weakly with variation of characteristic sample parameters in a range of 1 to 1,5 percent. Taking the convection heat transfer into account (which likewise depends on ΔT_F with a temperature dependent coefficient) the results of table 1 must be modified. The convection heat transfer is in the same order of magnitude as the radiation heat transfer is for temperatures and temperature differences in question, but the coefficient of convection heat transfer doesn't change as strongly with temperature as the coefficient of radiation heat transfer do, thus the influence on the calibration factor is more weak. In summa the calibration factor may change by 1,5 to 2 percent for variation of parameters as in table 1.

Conclusions

The model calculations have shown that the calibration factor of heat-flux scanning calorimeters depend principally on sample parameters due to the nonlinearity of convection and radiation heat transfer involved. The magnitude of this effect is about 1 to 5 percent for variations of sample parameters usually common. Thus the uncertainty of the measurements got from heat-flux calorimeters is hardly lower if no special measures were taken, such as doing special calibration runs with sample and calibration standard as equal as possible in all parameters. The dependence of the calibration factor on location of the sample within the sample container has to be proved carefully. The dependence of the baseline on differences in heat capacity and thermal resistance gives rise to problems in its separation from the peak leading to integration errors.

Surely all these effects don't influence the result more than a few percents and may be forgotten for measurements with an uncertainty of about 5 %, but for precision measurements they should be well minded.

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Appendix: PHENOMENA PREVENTING THE PRECISE CALIBRATION OF A HEAT FLOW CALORIMETER

H. Hoff, Sektion für Kalorimetrie, Universität Ulm
7900 Ulm (FRG), Oberer Eselsberg

I. Representation of the signal

Transport of heat is calculated by the balance equation

$$\operatorname{div} \underline{j}\ (\underline{r},t) + \dot{q}\ (\underline{r},t) = c\ (\underline{r}) \frac{\partial T\ (\underline{r},t)}{\partial t} \qquad (I,1)$$

in combination with the phenomenological equation

$$\underline{j}\ (\underline{r},t) = \lambda \cdot \operatorname{grad} T(\underline{r},t) \qquad (I,2)$$

The latter holds for transport by conduction. Inserting into (I,1) yields the well known equation of heat conduction

$$\lambda \cdot \operatorname{div} \operatorname{grad} T\ (\underline{r},t) + \dot{q}\ (\underline{r},t) = c\ (\underline{r}) \cdot \frac{\partial T\ (\underline{r},t)}{\partial t} \qquad (I,3)$$

or

$$\operatorname{grad} \lambda(\underline{r}) \cdot \operatorname{grad} T\ (\underline{r},t) + \lambda \operatorname{div} \operatorname{grad} T\ (\underline{r},t) + \dot{q}\ (r,t) = c\ (\underline{r}) \cdot \frac{\partial T\ (\underline{r},t)}{\partial t} \qquad (I,4)$$

refering to a homogeneous and to an inhomogeneous medium, respectively, where the conductivity $\lambda(\underline{r})$ depends on space. Both partial differential equations are linear with respect to space and time, thus a brief introduction to the theory of linear response is given.

I.1 Theory of linear response

The theory of linear response is based upon linear differential equations. Suppose $\mathcal{L}$ being a linear operator describing the relation between the solution x(t) and the inhomogeneity I(t)

$$\mathcal{L} * x(t) = I(t) \tag{I,5}$$

and the Green function G(t) being the solution with respect to a pulse shaped inhomogeneity $\delta(t)$

$$\mathcal{L} * G(t) = \delta(t) \tag{I,6}$$

The solution with respect to an arbitrary inhomogeneity is found by multiplication and integration

$$\int_{-\infty}^{\infty} \mathcal{L} * G(t-t') \cdot I(t')dt' = \underset{I(t)}{\int_{-\infty}^{\infty} I(t') \cdot \delta(t-t')dt'} \tag{I,7}$$

By consequence of linearity $\mathcal{L}$ can be interchanged with the integration and it is obtained

$$\mathcal{L} * \int_{-\infty}^{\infty} G(t-t') \; I(t')dt' = I(t) \tag{I,8}$$

Comparison with (I,5) yields the solution

$$x(t) = \int_{-\infty}^{\infty} G(t-t') \cdot I(t')dt' \tag{I,9}$$

Now (I,9) is applied to a given physical system: x(t) is considered as the response to a given "force" I(t) acting from outside upon the system. Obviously G(t) represents the dynamical properties of the system itself, thus it does not depend on the strength of the "force" I(t) or its quickness. According to the convolution integral (I,9) the response plays the role of some internal memory with respect to the past time, where the force has acted.

ALL G(t)-functions according to this interpretation of (I,9) which represent the dynamical behaviour of a physical system, have to fulfill certain important criteria, which can be due to fundamental physical laws:

a) law of causality (future cannot act on the actual response)

b) stability (past time will be forgotten; the response to a steady "force" will converge to a steady value)

c) reproducibility (the same response will be observed if the same action I(t) is repeated).

c) is fulfilled automatically by (I,9) as G(t-t') depends on the difference t-t' (it does not depend on both times t,t'),

a) is fulfilled, if

$$G(t<0) \equiv 0 \qquad (I,10)$$

Thus x(t) is written as

$$x(t) = \int_{-\infty}^{t} G(t-t') \cdot I(t')dt' \qquad (I,11)$$

Postulate b) involves that

$$\lim_{t\to\infty} x(t) = x = \lim_{t\to\infty} \int_{-\infty}^{t} G(t-t')\, I_o dt' = I_o \underbrace{\int_{0}^{\infty} G(t')dt'}_{K} = K \cdot I_o \qquad (I,12)$$

converges, i.e. that K is finite.

I.2 Signal of the calorimeter

Evidently, the signal of a calorimeter has to agree with the postulates a), b), c). Furthermore it can be shown by the linearity of (I,3), (I,4) that the signal ΔT (t) is represented as

$$\Delta T(t) = \int_{-\infty}^{t} G(t-t') \cdot \dot{Q}\,(t')dt' \qquad (I,13)$$

$\Delta T(t)$ denotes the difference of temperature between the sample and the reference, $\dot{Q}(t)$ the production of heat due to a thermal event in the sample. For scanning calorimeters (I,13) holds only if the heat capacity of the sample and the reference are equal, otherwise a constant shift of the base line, which depends on the heat capacities and on the heating rate must be added:

$$\Delta T(t) = \underbrace{s \cdot \alpha \cdot \left(\frac{1}{C_{\text{sample}}} - \frac{1}{C_{\text{reference}}}\right)}_{\Delta T_\alpha} + \underbrace{\int_{-\infty}^{t} G(t-t')\,\dot{Q}(t')\,dt'}_{\Delta T_t(t)} \qquad (I,14)$$

By consequence of stability a constant production of heat inside the sample produces a steady signal according to (I,12)

$$\Delta T_t(t) = K \cdot \dot{Q} \qquad (I,15)$$

where K is defined as

$$K = \int_{0}^{\infty} G(t')\,dt' \qquad (I,16)$$

Now we show that

$$\int_{-\infty}^{\infty} \Delta T_t(t)\,dt = K \cdot Q \qquad (I,17)$$

where K is defined as (I,16), i.e. the relation between the total heat and the integrated signal does not depend on the way,how the heat is produced - the relation holds for a fast production of heat as well as for a slow one. Assuming that

$\lim\limits_{t \to -\infty} \dot{Q}(t) = \lim\limits_{t \to \infty} \dot{Q}(t) = 0$ we have

$$\int_{-\infty}^{\infty} \Delta T_t(t)\,dt = \int_{-\infty}^{\infty}\int_{-\infty}^{t} G(t-t')\,\dot{Q}(t')\,dt'dt = \iint_{-\infty}^{\infty} G(t')\,\dot{Q}(t-t')\,dt'dt$$

$$= \int_{-\infty}^{\infty} G(t')\,dt' \cdot \int_{-\infty}^{\infty} \dot{Q}(\tau)\,d\tau = K \cdot Q \qquad (I,18)$$

Calorimeters of this type can be calibrated by measuring a reaction, the enthalpy of which is known.

II. Deviation caused by nonlinearity

Because of Stefan-Boltzmann's law the loss of heat by radiation to the surroundings is not negligeably small at higher temperatures. Taking into account this kind of transport and, that even in the case of heat conduction the local conductivity usually depends on the local value of temperature (this dependence is weak) a pseudolinear phenomenological equation is obtained

$$\underline{j}(\underline{r},t) = \lambda(T(\underline{r},t),\underline{r}) \cdot \operatorname{grad} T(\underline{r},t) \tag{II,1}$$

which leads with the help of (I,1) to the balance equation

$$\frac{\partial\lambda}{\partial T} \operatorname{grad} T(\underline{r},t) \cdot \operatorname{grad} T(\underline{r},t) + \operatorname{grad}_{\underline{r}} \lambda(T(\underline{r},t),\underline{r}) \cdot \operatorname{grad} T(\underline{r},t)$$

$$+\lambda(T(\underline{r},t),r) \cdot \operatorname{div} \operatorname{grad} T(\underline{r},t) + \dot{q}(\underline{r},t) = c(\underline{r}) \cdot \frac{\partial T(\underline{r},t)}{\partial t} \tag{II,2}$$

grad $_{\underline{r}}$ denotes the gradient with respect to the explicit dependence on space. Evidently the first term is nonlinear, thus the theory of linear response cannot be applied.

II.1 Representation of nonlinear response

The general representation (I,11) can be extended to nonlinear relations by considering the linear response as beeing the first term of a series

$$x(t) = \sum_{j=1\ldots} \int_{-\infty}^{t} \ldots \int G^{(j)}(t-t_1,\ldots,t-t_j) \cdot \prod_{l=1}^{j} I(t_l)dt_l \tag{II,3}$$

Evidently this extended representation converges asymptotically for small I(t) to the representation of linear response as it should be. The postulates a), c) require that

$$G^{(k)}\ (t_1\ 0,\ldots,t_j < 0) \equiv 0 \qquad j = 1,\ldots \tag{II,4}$$

and

$$\lim_{t\to\infty} x(t) = x = \sum_{j=1} I_o^j \underbrace{\int_0^\infty\!\!\cdots\!\int G^{(j)}(t_1,\ldots,t_j) \cdot \prod_{l=1}^{j} dt_l}_{K_j} \tag{II,5}$$

$$= \sum_{j=1,\ldots} K_j I_o^j$$

is finite. The postulate of reproducibility will be fulfilled by isoperibol heat-flow calorimeters, thus the response can be written as

$$\Delta T_t(t) = \sum_{j=1,\ldots} \int_{-\infty}^{t}\!\!\cdots\!\int G^{(j)}(t-t_1,\ldots,t-t_j \cdot \prod_{l=1}^{j} \dot{Q}(t_l)dt_l \tag{II,6}$$

A scanning calorimeter, however, may require a more complicated representation, because the dynamical properties will depend on the actual temperature, i.e. on time. Thus the homogeneity with respect to a translation in time can be disturbed. Additionally the deviation of (I,13) is based upon the superposition principle, i.e. the responses with respect to the heat production in the heater and in the sample are superposed. The superposition principle does not hold in the nonlinear case, thus the dynamical behaviour may depend on the heating rate and it should be written

$$\Delta T_t(t) = \sum_{j=1,\ldots} \int_{-\infty}^{t}\!\!\cdots\!\int G^{(j)}(t,t-t_1,\ldots,t-t_j) \prod_{l=1}^{j} \dot{Q}(t_l)dt_l \tag{II,7}$$

II.2 Consequences

We now try to find a relation equivalent to (I,18). In the case of an isoperibol heat flow calorimeter we find

$$\int_{-\infty}^{\infty} \Delta T_t(t)dt = \sum_{j=1} \int_{-\infty}^{\infty} \int_{-\infty}^{t} \dots \int G^{(j)} (t-t_1,\dots, t-t_j) \prod_{l=1}^{j} \dot{Q}(t_l)dt_l dt \qquad (II,8)$$

$$= K_1 \cdot Q + \sum_{j=2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \dots \int G^{(j)} (t_1,\dots,t_j) \cdot \prod_{l=2}^{j} Q(t-t_l)dt_l dt \qquad (II,9)$$

Obviously the integral of (II,9) cannot be related to the total heat because of the product $\prod_{l=2}^{j} Q(t-t_l)$ - it is a functional of the heat production $\dot{Q}$ (t) $(-\infty < t < \infty)$. The case of a scanning calorimeter (II,7) is even worse, because a linear term corresponding to the first one on the r.h.s. of (II,9) cannot be splitted from the total sum (II,8).

Consequently these nonlinear phenomena forbid a precise calibration: the exact heat only can be obtained by simulating $\dot{Q}$ (t) by the Joule heat of an electrical resistor instead of the sample. One has to look for that production of Joule heat, which yields the same signal $\Delta T(t)$ as the original one. The total heat is found by integration of the production of the Joule heat.