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"On the Time Lag between Thermal Event and Measuring Signal in a Heat Flux Calorimeter"

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Abstract

The measuring signal of a calorimeter reproduces the original thermal event delayed and in a distorted manner (smeared). The usual methods for correcting this distortion require much effort. Proceeding from a simple equivalent circuit diagram for the calorimeter, an approximate correction for the smearing is shown which eliminates the greatest part of the distortion. Using the example of a differential heat flux calorimeter, it is shown how one can determine the calorimeter's time constants needed for the correction. The constants are derived by means of response functions to electrically generated heat pulses or to melting peaks.

Definition of the Problem

Most caloric measurements are performed in order to determine reaction enthalpies. Beyond that, scanning calorimeters provide the possibility of studying the course of heat release or absorption with time. Thus, calorimeters allow kinetic investigations.

In every calorimeter, the sensor for measuring the caloric signal is not at the site of the sample. For this reason, the sensor reproduces a distorted signal which is delayed compared to the reaction itself. This effect is known as "smearing".

For kinetic investigations it is necessary

- to estimate the size of the smearing and its influence on the measurement results, or, better,
- to determine the smearing quantitatively and correct for it.

Possible Methods of De-smearing

In principle, it is possible to set up and solve the heat conduction equation of the calorimeter. For this, numeric procedures in computers are available nowadays. Thus, it should be possible to determine quantitatively the smearing and hence to correct for it.

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This method has the following disadvantages. Often, some of the data of the calorimeter relevant to heat conduction are not known (the exact size and thermal properties of all the construction elements, the transfer resistances at junction points of the various elements, the radiation characteristics of surfaces, the influence of convection, etc.). The thermal boundary conditions cannot be fully specified. Thus this method is only applicable for relatively simple geometries of the measuring system. In any case the calculations involved are extensive.

But above all, one gets more information than is needed: for de-smearing the temperature field in the calorimeter and its development in time need not be known. Only the relation between the heat production $\dot{Q}(t)$ of the sample and the caloric measurement signal U(t) is of importance:

$$\dot{Q}\,(t) \xleftrightarrow{?} U\,(t).$$

The Test and Response Function Method

The relation between $\dot{Q}(t)$ and U(t) can be determined by the test and response function method. This method is used quite often (for basic data and examples see /1,2/). Here the measuring system is conceived of as a "black box" which transforms the input signal, the rate of heat production $\dot{Q}(t)$, into the caloric measuring signal U(t):

$$\dot{Q}\,(t) \longrightarrow \boxed{\text{Calorimeter}} \longrightarrow U\,(t) \qquad (1)$$

The transfer behavior of this system must be linear, as can be verified, for example, by calibration experiments. Due to the linearity of the heat conduction equation, this requirement is normally fulfilled by isothermally operated calorimeters and well approximated with anisothermal operation.

If one knows the transfer characteristics of such a measuring system, one can calculate backwards from the measured signal U(t) arising from any given reaction to the respective heat dissipation $\dot{Q}(t)$ at the site of the sample. This calculation is referred to as a de-smearing of the measurement curve. The transfer characteristics can be determined by starting a reaction with known time behavior at the sample site (test function) and registering the corresponding measurement curve (response function). It is convenient that the heat-flux calorimeter used here (Type MCB) has at the measuring cell an electric calibration resistance in which a short electric heat pulse can be released. The corresponding measurement signal, the so-called pulse response, is registered.

However, any other physico-chemical reaction is suitable for producing the test function, provided one knows the heat release as a function of time. In the literature several calculation methods are given for de-smearing any measurement signal if the test and response functions are known, for instance conversions using the transfer function of the system in Fourier or Laplace representation, or various recurrence or iteration methods (see /1/ and /2/). The mathematics involved are quite extensive and still do not always lead to satisfactory results. This can arise either from peculiarities of the calculation methods themselves or from the influence of signal noise. It can also be that the calculation prerequisites are only approximately fulfilled.

Therefore, the following shall show a simplified method for de-smearing, parts of which have previously been used in earlier publications, e.g. /3/. The method corrects the smearing of the measurement curve only approximately and permits an estimation of the residual error. For this purpose a simple equivalent circuit diagram will be introduced with which the transfer behavior of a calorimeter can be simulated.

Electric Equivalent Circuit Representing the Calorimeter

A caloric measuring system which shows a linear transfer behavior can be simulated by a series connection of non-retroacting first-order transfer elements plus a time-lag element /4/.

A lag element simply corresponds to a time shift amounting to a dead time t_d. A first order transfer element is most simply respresented by an electric R-C element which is decoupled at input and output by pre- and post-connected amplifiers (Fig.1). Its transfer characteristics are fully described by the definition of the amplification A and the time constant $\tau = R \cdot C$. A pulse-like input signal $\delta(t)$ is followed at the output by a step (A/τ) followed by an exponential decrease to zero:

$$\delta(t) \longrightarrow \boxed{\text{Cal.}} \longrightarrow \begin{cases} 0 & \text{for } t < 0 \\ (A/\tau) \cdot \exp(-t/\tau) & \text{for } t > 0 \end{cases} \qquad (2)$$

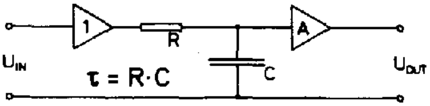


Fig. 1: Non-retroacting first-order transfer element.

The entire equivalent circuit diagram is shown in Fig. 2.

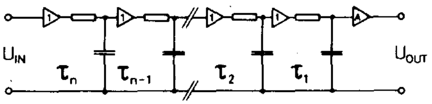


Fig. 2: Electric equivalent circuit representing the calorimeter without time-lag element.

The time behavior is given by the definition of the total amplification A, the dead time t_d and the time constants $\tau_1 \ldots \tau_n$. If enough elements are used and the parameters chosen correctly, any caloric measuring system can be simulated. In practice, two to four such elements are completely sufficient /5/. Since the order of the elements in the circuit is interchangeable /6/, they can be ordered according to the size of their time constants ($\tau_1 > \tau_2 > \tau_3 \ldots$) without limiting the general validity of the method.

The amplifying factor A can be very simply interpreted. If one changes the input signal of the equivalent circuit from zero to U_{in} and waits until the steady state is established, the potential at the output is $U_{out} = A \cdot U_{in}$. Thus, A represents the sensitivity of the calorimeter.

Correction for Smearing

De-smearing consists of two steps. First, the parameters of the equivalent circuit diagram are determined by a pulse response (or another pair of test and response functions). Then, using the parameters one can calculate backwards from any measurement curve to the original heat production.

The amplification A is eliminated by division, that is, the heat output is calculated from the electric signal by means of the sensitivity. The correction for the dead time consists simply of a shift of the scale by t_d. Since the shift amounts to only about 3 seconds for the given calorimeter, this correction can be neglected as apposed to the other lags. Where the dead time cannot be neglected it is quite simple to determine its value: first one applies the correction described hereafter to both the measurement curve in question and the used response function. The best value for the dead time is obtained by shifting the thus corrected response function parallel to the time axis so far that it fits as well as possible to the respective test function. The measurement curve is then shifted by the dead time so determined.

The correction for a single transfer element (Fig. 1) can easily be stated:

$$U_{in}(t) = U_{out}(t) + \tau \cdot \frac{d\,U_{out}(t)}{d\,t} \qquad (3)$$

This can be seen clearly (Fig. 3) in the example of a sudden jump in the input signal U_{in} (step function) to which the transfer element reacts with an exponential increase up to a constant final value. The differential of the output signal reproduces exactly the shape of that part of the step function which was "swallowed" by the system. If this differential, multiplied by τ, is again added, the input step function is reproduced. Since any function can be described as the sum of step functions, this correction is also applicable for any shape of U_{in}.

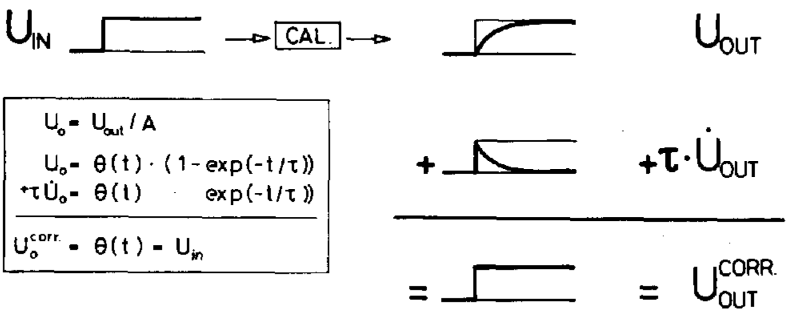


Fig. 3: Correction of smearing for a first-order transfer element. $\Theta(t)$ = Step function.

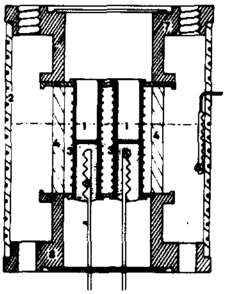
All of the smearing can be corrected successively by the above Equation (3):

$$\begin{aligned} U_o &= U_{out} / A && (4)\\ U_1 &= U_o + \tau_1 \cdot \dot{U}_o \\ U_2 &= U_1 + \tau_2 \cdot \dot{U}_1 && (\dot{U}_i = dU_i/dt) \\ &\text{etc.} \end{aligned}$$

We will now apply this method to a practical example.

Characteristics of the Calorimeter

The calorimeter used at the Institut für Werkstoffe is a differential heat flux calorimeter of the type MCB (made by Thermanalyse of Grenoble, see Fig.4).



1. Sample and reference vessel, resp.
2. Electrically heated furnace
3. Thermopile (70 differential thermocouples)
4. Radiation shield
5. Auxiliary vessels with built-in calibration resistors
6. Platinum resistance thermometer for furnace control
7. upper flange
8. lower flange

Fig. 4: Cross sectional view of the MCB calorimeter.

A special feature of this calorimeter are the built-in calibration resistors. They allow a simple calibration of the calorimeter (more details in Ref. /7/) and the generation of a heat pulse in the measuring cell as a test function. For this purpose a current of 50 mA is sent through the 120 Ω calibration resistor of the measuring cell for approximately 0.3 seconds (Total energy released ≈ 100 mJ). The response to such a short energy release (Fig. 5) does not differ from a real pulse response because of the thermal intertia of the calorimeter.

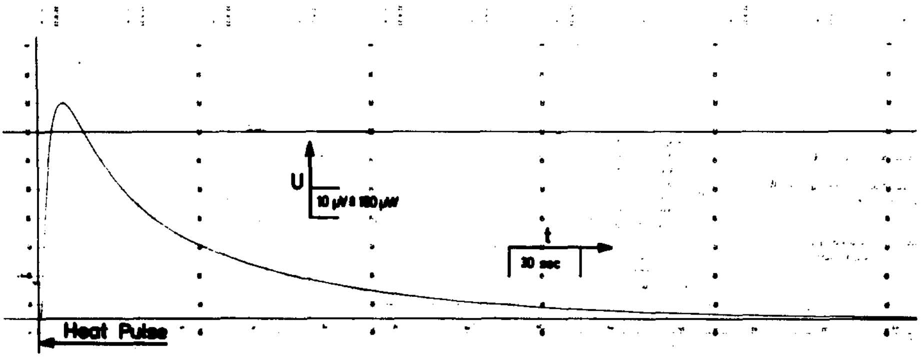


Fig. 5: Example of a pulse response of the MCB. T = 30°C, Sample and Reference each 2.73 g Copper.

A disadvantage of the experimental set-up is that the heat is not released at the site of the sample. For this reason the registered pulse response only approximates that which would be obtained if the heat pulse would be released directly in the sample. From the simple models calculated in /1/ and /2/ it can be seen that the largest time constant τ_1 is caused by the total heat capacity of the cell and sample. For τ_1, these parts act as a whole. This is also shown by our own measurement results (see below). Since both the sample and the calibration resistor release the heat within this entity, τ_1 should be the same in both cases. The next largest time constant τ_2 is determined by the heat capacity of the sample and the heat transfer between sample and cell. Because of this, τ_2 cannot be determined exactly by use of a test function which does not release its heat within the sample. This applies to a greater extent to subsequent time constants. This is another reason why a correction beyond the first transfer element does not seem feasible.

The Time Constants of the Used Calorimeter

In order to determine τ_1 and arrive at an estimate of the size of the subsequent time constants (τ_2, τ_3 ...), responses to electric heat pulses were registered isothermally at 30°C. For this purpose copper samples of various masses were put into the cells. Sample and reference sample were identical in every case. According to the method given in Ref./5/, the time constants were determined. It turned out that three time constants τ_1 ... τ_3 sufficed to describe the pulse responses fully. The largest time constant τ_1 is shown in Fig. 6 as a function of the heat capacity of the samples.

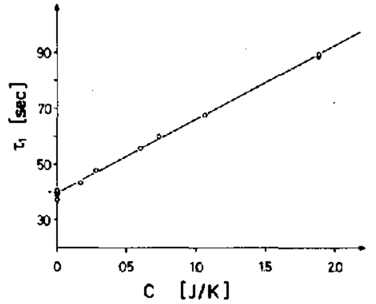


Fig. 6: Time constant τ_1 as a function of the heat capacity C of the specimen.

It satisfies a linear relation according to the equation

$$\tau_1 = R \cdot (C_c + C_s) \tag{4}$$

($C_c = C_{cell}$, $C_s = C_{sample}$), as is usual for a R-C element. The thermal resistance R results from the slope of the extrapolated straight line and the heat capacity of the cell from its point of intersection with the ordinate. The value of 1.64 J/K for C_c is in quite good agreement with the value which can be calculated using the cell dimensions and the specific heat capacity of the material used (Monel, see /8/). This result supports the reasons given above for regarding the largest time constant τ_1 as independent of the site of the heat release.

The calorimeter is usually not run isothermally, but with constant heating rate. Since the heat resistance and heat capacities depend on the temperature, τ_1 also changes with the temperature. Unlike the case of an isothermal calorimeter, the mathematical requirements for the justification of the de-smearing method are only approximately valid, particularly with respect to the linearity of the system. During the small temperature interval of a few degrees usually required for a reaction in the calorimeter, τ_1 changes only slightly, Thus, a correction for de-smearing limited to the first stage is still possible. A value for τ_1 is always used which is valid for the middle of the reaction interval.

No new measurements were performed for determining τ_1 for the anisothermal case and for different temperatures. Instead, electrically generated peaks were taken which had been used for the enthalpy calibration of the calorimeter. For this purpose a constant heating current had been turned on for periods of 5 to 10 minutes, thus producing a step-like input to the calorimeter. From the rising or falling flank of the response the time constant τ_1 was determined by the tangent method (see Fig.7). Here it is necessary to place the tangent far enough behind the point of inflection that a steady value for the time constant results.

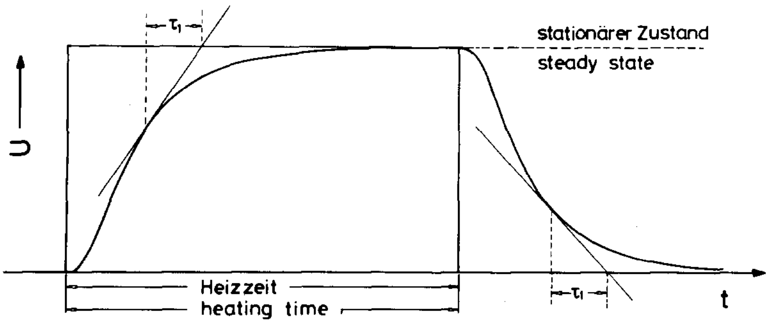


Fig. 7: Tangent method for determining τ_1 from a step response.

The temperature dependence of τ_1 is specified by the temperature influence on the resistance R and on the heat capacities C_c and C_s. The heat capacity of the measuring cell is constant between 80^oC and 600^oC, that is, C_c (T) = const. /8/. The heat resistance R is given primarily by the heat conduction in the cell wall and the cell mounting. Thus, its temperature coefficient α is that of the heat conductivity of the Monel. The temperature coefficients for the heat capacity of the samples (various pure metals) are also known. Therefore, it is valid that

$$\tau_1 (T) = R_0 (1 - \alpha T) \quad (C_c + C_s (T)), \qquad (5)$$

where T is in ^{0}C. A reduced form of the time constant from which R_0 can be determined can be expressed as follows:

$$\tau_1^{\text{red}} = \tau_1 / (1 - \alpha T) = R_0 \cdot (C_c + C_s(T)) \qquad (6)$$

The presentation of all results in this form is shown by Fig. 8. As can be seen, the anisothermally determined points scatter considerably more than those determined isothermally. This is not surprising, since the paper feed was set rather slow in order to achieve good planimetric results. In addition, the base line is not as well established in the anisothermal case as it is in the isothermal.

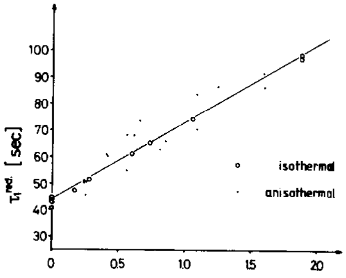


Fig. 8: Reduced time constant τ_1^{red} as a function of the heat capacity of the specimen.

For a correction, therefore, τ_1 is used according to Equation (5), with the parameters R_0 = 26.8 K/W, $\alpha = 1.46 \cdot 10^{-3}$ K^{-1}, C_c = 1.64 J/K. In this way the correction for every measurement curve can be performed with no further effort, as is shown by the example in Fig. 9. In addition to a noticeable shift of the peak toward lower temperatures, the peak maximum is increased.

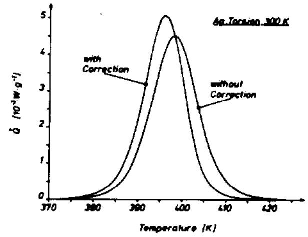


Fig. 9: Recrystallization of Silver deformed in Torsion, Example of a first order correction. Heating rate Ø = 4,45 K/min.

If only the correction of the peak maximum temperature is of interest, such as in kinetic evaluations according to KISSINGER /9/ or OZAWA /10/, a very simple formula can be given. With the bell-shaped measurement curves shown here, the part in the vicinity of the maximum is approximately parabolic. In this case, the corrected temperature of the maximum is expressed by

$$T_{max}^{corr} = T_{max} - \phi \cdot \tau_1, \qquad (7)$$

ϕ being the heating rate. With the given approximation formula (7), which is also valid for the further correction steps using the time constants τ_2 and τ_3 (which were not carried out), it is possible to estimate the error remaining after the correction: the ratio of the time constants is in the case of this calorimeter approximately $\tau_1 : \tau_2 : \tau_3 = 20 : 3 : 1$. Together with the dead time (3 sec), the shift of the maximum according to Equation (5) is about 20 % too low. Since a further correction step is not feasible for the reasons mentioned above, this error remains after the correction.

Determination of the Correction by Means of a Melting Peak

Most calorimeters do not have electric calibration equipment. It is then necessary to use physico-chemical reactions in order to determine the time constant τ_1. An obvious possibility is the use of melting peaks of pure substances, when the calorimeter is anisothermally operated. However, these peaks do not meet the requirements for a test function: the heat release is not set compulsorily, but rather develops of itself according to the heat conduction in the measuring set-up. Nevertheless, the time constant τ_1 can be deduced from a melting peak. For this one uses the tangent construction such as in Fig. 7 for the subsiding flank of the peak. τ is determined beginning at a point shortly behind the apex of the curve, and progressing for various points along the curve. One is far enough from the curve apex when the value for τ no longer changes. This value is used for the correction as τ_1.

An example for such a correction is shown in Fig. 10.

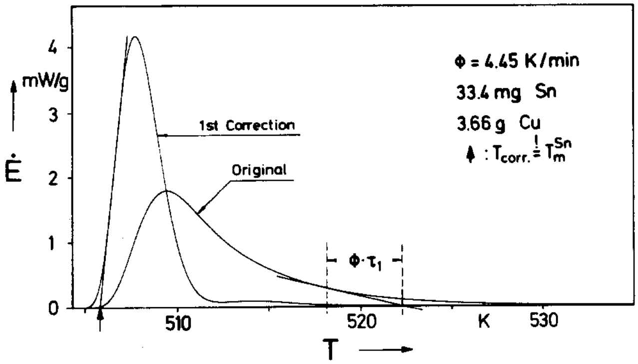


Fig. 10: Melting of Indium within a Copper cylinder of 3.66 g and first order correction. T^{corr} = corrected Temperature Scale.

Here an indium sample was placed in a copper cylinder with a mass of 3.66 g and heated over the melting point at a constant rate ($\phi = 4.45$ K/min). The first correction was calculated with the time constant τ_1.

If the sample is a pure material whose melting point is known exactly, the temperature axis can be calibrated in addition to the above correction. For this purpose the tangent is set up on the left flank of the melting peak through its point of inflection. The melting temperature is assigned to the intersection of that tangent with the base line. This corrected temperature scale is then valid for the peaks de-smeared for the first time constant.

Summary

- The usual methods of de-smearing on the basis of test and response functions involve an extensive amount of calculation.
- In the case of anisothermal measurements, the mathematical presuppositions required for the method are only approximately fulfilled.
- For this reason, it seems opportune not to attempt a complete correction, but to aim at an approximate correction involving relatively little effort.
- The electric equivalent circuit diagram shown here presents the calorimeter simply as a non-reactive series circuit of transfer elements of the first order (R-C elements). Measurements have shown that the calorimeter used here can be completely described using only three time constants.
- If only the first correction is performed, it is possible to calculate by means of a simple formula the time constant τ_1 for every sample mass and peak temperature.
- Without too much effort in calculating, the largest part of the smearing error can be corrected for in this manner.
- The basis for this procedure are the pulse or step response functions of the calorimeter which have been produced by the built-in electric calibration resistors.
- It is also possible to determine the time constant τ_1 by using melting peaks. In the case of pure materials with known melting points, the temperature scale can be calibrated at the same time.
- With relatively simple electronic means (differentiating circuit, sum amplifier), the first correction mentioned above can be performed analogously during the measurement.

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