

## ON DE-SMEARING OF HEAT-FLOW CURVES IN CALORIMETRY\*

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### ABSTRACT

The calorimetrically measured heat-flow curves of physical, chemical or biological processes are recorded with an intrinsic error, due to the slow heat conduction phenomenon. Mathematical calculations have shown that the size and type of "smearing" is a function of the size, geometry and heat the conductivity of the sample. Under certain conditions, it is possible to mathematically eliminate the "smearing" by employing the Convolution-Integral equation. It is necessary, that one is familiar with the apparatus function. It is demonstrated how one can obtain the apparatus function and steps required for the calculation of "de-smearing".

### INTRODUCTION

One of the most significant purposes of calorimetry is the study of the measurement of heat evolved or absorbed in physical, biological and chemical reactions. The flow of heat or other analogous quantities are usually graphically shown against time or temperature. An example is illustrated in Fig. 1 of a first-order phase transition (e.g., melting of a substance), which could also be substituted by a sudden chemical (e.g., an explosion) or biological (e.g., muscle contraction of a test animal) event. Ideally, the corresponding heat flow at the moment of the reaction should be infinitely large or constant (Dirac-function). However, the calorimeter supplies a finite "smeared" heat-flow peak, whose size and form are dependent upon the calorimeter, time and many others factors. The measured peak does not coincide with the true event, because the calorimeter falsifies the physical reactions. Even the pioneers of calorimetry have been occupied with the search for a method to correct this intrinsic error<sup>1</sup>. I do not wish to dwell upon the literary aspects, but rather to supply the practical man with a summary to aid him in evaluating the significance, need and possibility of obtaining a correction. Also to make him aware to procure the "apparatus function" and, with the help of this "desmear", the measured heat-flow-curve in a computer.

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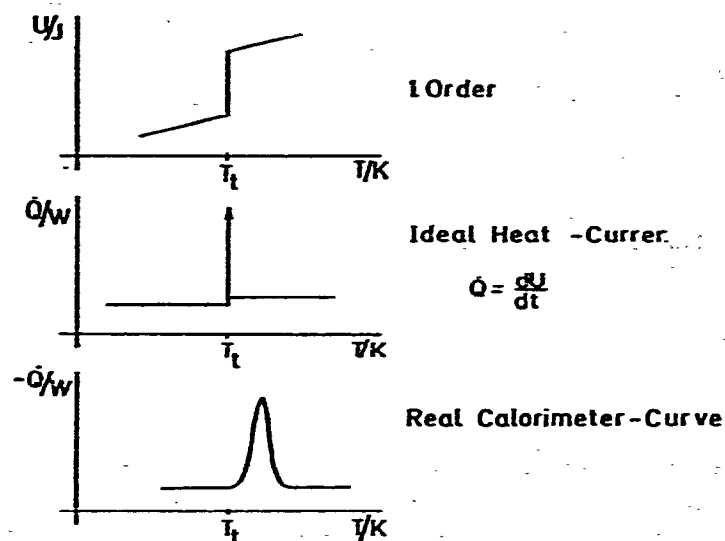


Fig. 1. Connection between a thermodynamical step-function and calorimeter-recording.

#### ORIGINS OF SMEARING

First of all, it is necessary to clarify the origins of "smearing" of the ideal heat flow due to the apparatus. The transportation of heat by molecular compensation effects requires much more time than needed in other balance processes. The heat conduction equation describes the relation:

$$\text{div grad } T = \frac{\rho \cdot c_p}{\lambda} \cdot \frac{\partial T}{\partial t} \quad (\text{A})$$

One dimensionally simplified:

$$\frac{\partial^2 T}{\partial x^2} = \frac{\rho \cdot c_p}{\lambda} \cdot \frac{\partial T}{\partial t} \quad (\text{A}_1)$$

$T(x,t)$  is the temperature at time  $t$  and place  $x$ ,  $\rho$  the density,  $c_p$  the specific heat capacity,  $\lambda$  the heat conduction coefficient.

The flow of heat per unit in isotropic media is:

$$\frac{\vec{Q}}{F} = -\lambda \cdot \text{grad } T \quad (\text{B})$$

One dimensionally simplified:

$$\dot{Q} = -\lambda \cdot F \frac{dT}{dx} \quad (\text{B}_1)$$

For media which are not isotropic (i.e., crystals)  $\lambda$  is not a number, but a tensor.

The correct solution of the heat conduction equation is applicable only in a few special cases, since every solution is subject to initial and boundary conditions. In

other words, the temperature field and the geometry at the beginning of the balance process must be taken into account.

#### SOLUTION OF THE HEAT-CONDUCTION PROBLEM

Figure 2 illustrates the solution for a simple problem. A rod with temperature  $T_e$  is brought into contact with a block with temperature  $T_u$  at time  $t_0$ , heat flows into the rod at a distinct rate until it has reached the temperature of the block. Figure 3 shows the time-dependent flow of heat through two cross-sections of a rod. This example gives an explanation for the "smeared" heat flow curves obtained for a quick event (heat contact). In order to obtain a more precise statement of the calorimetric processes, one must first solve the heat conduction equation for the initial and boundary conditions. There are many different methods that can be employed, for example to calculate the heat flow phenomena in reactor technology<sup>2-4</sup>. The following is an approximation developed at the atomic research center in Karlsruhe<sup>5</sup>. Any given body composed of various substances can be reduced into its sub-particles (e.g., cubes). A

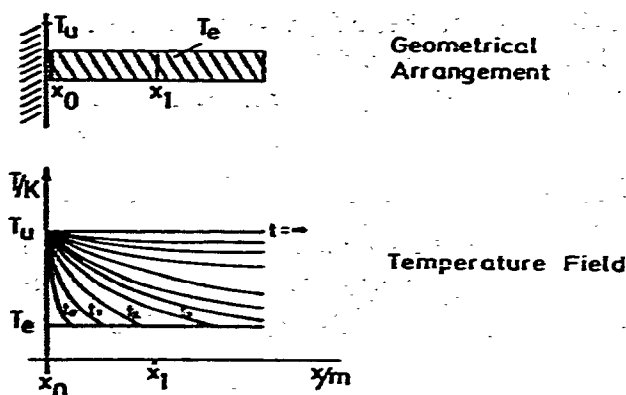


Fig. 2. Time-dependent change of the temperature field in a rod which is in contact with a heating-block.

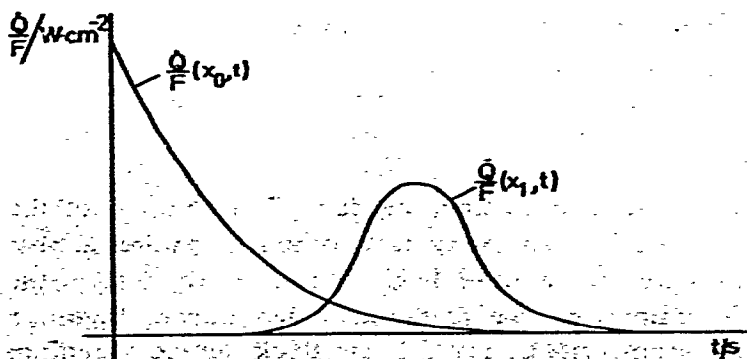
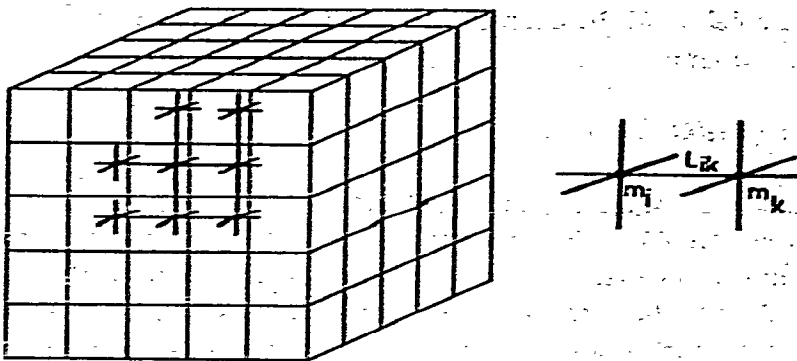


Fig. 3. Time-dependent change of heat-flow through two cross-sections of a rod which is in contact with a heating-block.



Coefficient of Heat Conductivity:  $L_{ik} = \lambda_{ik} \cdot \frac{F_{ik}}{\Delta x_{ik}}$

Fig. 4. Decomposition of a body in a heat-conducting network.

cube is then substituted by a massless, ideal conductive rod to the next neighboring site. The thermal conductivity coefficient of the rod can be calculated from the contact point, the distance between the cubes and the thermal conductivity coefficient of the corresponding substances (Fig. 4). One then obtains a network of thermal conductivity, whereby an energy-balance at each distinct point can be calculated as follows:

$$\sum \dot{Q} \cdot \Delta t = c_p \cdot \rho \cdot V \cdot (T' - T) + Q_m \cdot \rho \cdot V$$

$\dot{Q}$  is the heat flow,  $c_p$  the specific heat capacity,  $V$  the volume,  $\rho$  the density,  $T'$  the final temperature,  $T$  the initial temperature,  $Q_m$  the specific heat of transformation of the distinct point and  $\Delta t$  the change in time. The following equation system is for an entire network of points:

$$\sum_{k=1}^6 L_{ik} \cdot (T_i - T_k) \cdot \Delta t = c_{pik} \cdot \rho_{ik} \cdot V_i (T'_i - T_i) + Q_{mi} \quad (i = 1, 2, 3, \dots, n)$$

$T_i$  is the initial temperature field,  $T'_i$  the final temperature field. The change in time  $\Delta t$  must be lower than a critical coefficient to avoid fluctuations.

$$\Delta t < \text{Min} \frac{c_{pik} \cdot \rho_{ik} \cdot V_i}{2 \cdot \sum_k L_{ik}}$$

When the subdivision of the body is sufficiently fine, one can get a solution of the heat-conduction problem to a very good approximation. A computer requires almost one hour to calculate a steady-state temperature field. We have calculated the theoretical heat-flow curves, by employing the equation stated above. Figure 5 illustrates the results of a phase transformation of a 1 mm thick sample of indium (In) and polyethylene (PE), which were heated at one side at  $1 \text{ K min}^{-1}$ . The heat flow peaks are not all similar, which is due to the 100 time greater temperature distri-

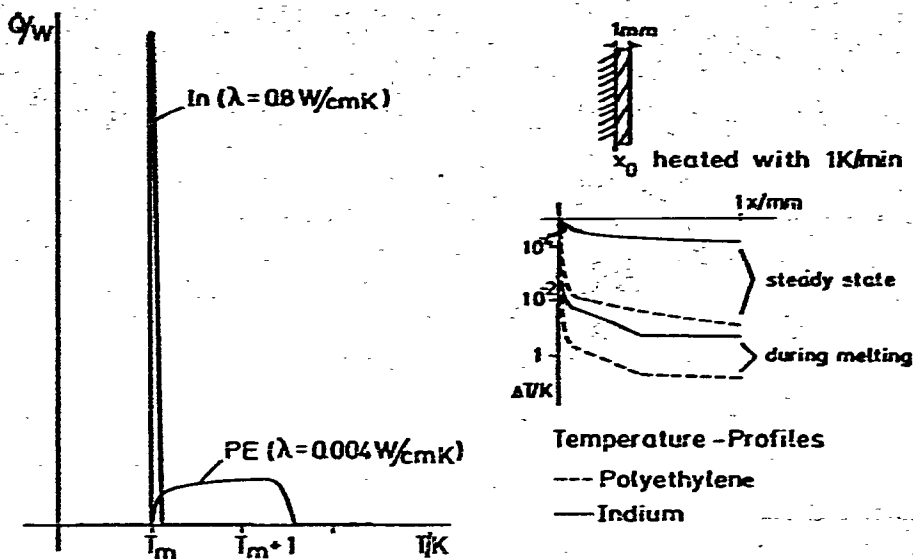


Fig. 5. Computed temperature-fields and heat-flow curves of constant heated plates. Normalized to one melting point.

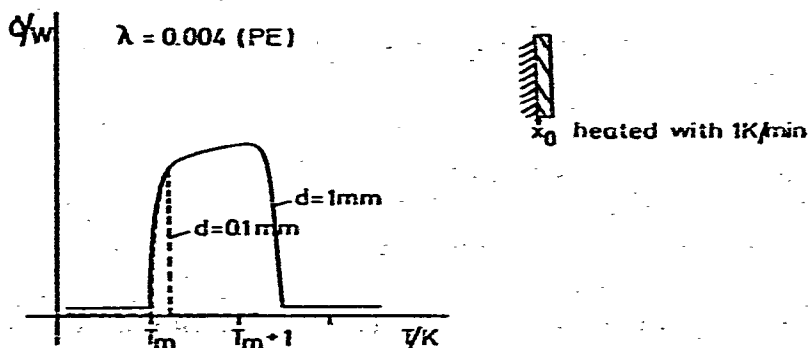


Fig. 6. Computed heat-flow curves into constant heated plates of different thickness.

bution inside the PE- and In-samples as well as in the steady-state and during the melting stages. Figure 6 shows that the thickness of the sample is a very important factor for the resulting melting curve.

The melting peak can be drastically changed by placing a thin sheet of aluminum between the In sample and the heating element, whereby the aluminum is a resistor to the heat flow (Fig. 7).

The geometry of each sample is also responsible for any changes in the heat-flow profiles of the melting point. This is illustrated in Fig. 8 by two samples of a poorly conductive material; one flat and the other a symmetrical cylinder. The form and size of the "smearing" of the heat-flow curve is dependent upon many factors; the pathway of heat conduction, the geometry and size of the sample, the conductivity and the specific heat.

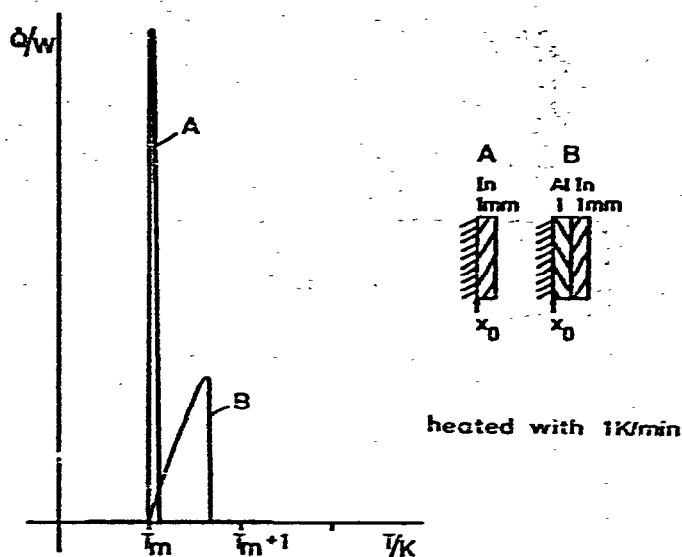


Fig. 7. Computed heat-flow curves into In-plates heated directly or through an Al-layer.

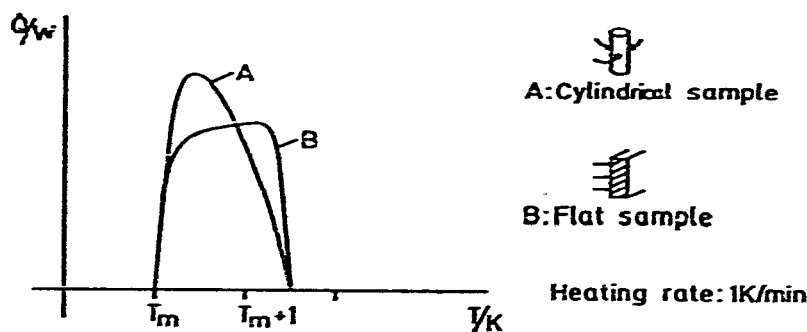


Fig. 8. Computed heat-flow curves for a bad heat-conducting material. A = a flat plate; B = a cylindrical sample.

#### CONSTRUCTION OF CALORIMETERS

Figure 9 shows the principal construction of calorimeters, which record temperature-dependent heat flow curves (DTA or DSC principle). This type of calorimeter records a specific curve (see Fig. 10), when an endothermic or exothermic reaction occurs in the sample at a temperature  $T_c$ . The temperature of the sample increases very quickly in an exothermic reaction, whereas during an endothermic reaction it remains constant until the required heat for a transition is gained. Therefore, it can be stated that the size of the distortion (see segments a and b in Fig. 10) is dependent upon the size and efficiency of the heat-conduction within the given path (2 in Fig. 9). The transition of heat from section 2 to the container and from the container to the sample are also determining factors.

The size of the distortion according to the DSC-principle can be reduced

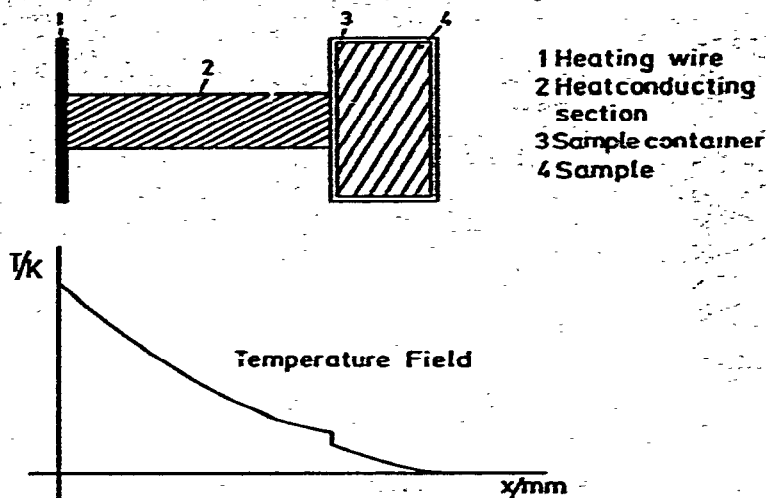


Fig. 9. Principle construction of calorimeters heating samples with constant heating-rates.

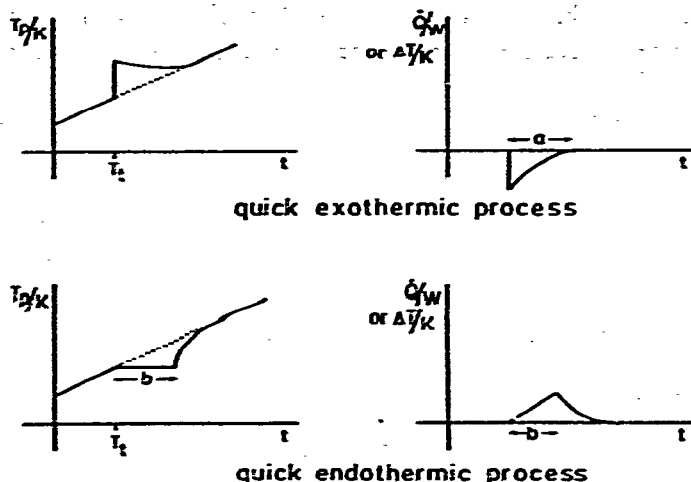


Fig. 10. Time-dependent temperature (or difference-temperature) curves of samples undergoing a phase-transition in calorimeters.

without changing the distance of the heat conduction pathway. This is made possible because the heater counteracts the tendency towards temperature variation within the sample and therefore creates a more rapid heat balance.

An isoperibole calorimeter which follows the Calvet-principle is usually employed when measuring time-dependent processes at almost isothermic conditions (see Fig. 11). The sample is in a container, which is connected to an isothermic block by thermoelements, which are thermally conductive. The heat flow through the thermoelements is therefore proportional to the recorded temperature difference within the thermoelements.

$$\frac{dQ}{dt} \sim (T_B - T_D) \quad (\text{see B 1})$$

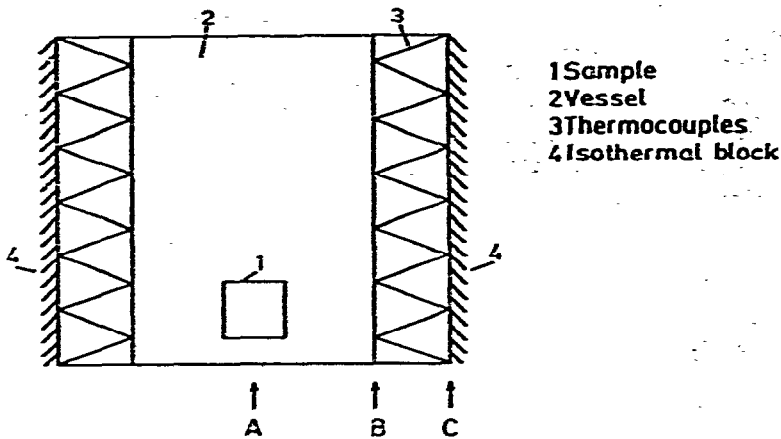


Fig. 11. Construction of isoperibol calorimeters according to Calvet.

The heat flow also creates a temperature balance between the isothermic block and the container, because the conducted heat is related to the temperature of the container via its heat capacity  $C$ .

$$\frac{dQ}{dt} = C \cdot \frac{dT_B}{dt}$$

Since  $T_c$  is constant:

$$\frac{dT_B}{dt} \sim T_B$$

with  $T = T_B - T_c$  it follows:

$$\frac{dT}{dt} \sim T$$

integrated:

$$T \sim e^{-\alpha t}$$

When the calorimetric container undergoes a sudden change in temperature a curve is obtained as illustrated in Fig. 12. The recorded curve in Fig. 13 is the sum of two exponential functions with different time constants. Because the length of the heat conductive pathway from the sample to jacket B must be taken into consideration, the time constants of the exponential curves are usually very different. The first constant is usually much smaller and therefore an important factor for the "de-smearing", which is to be described later. But this constant is dependent upon the size and location of the sample.

In all instruments available for calorimetric measurement, the biological, physical or chemical events get "smeared" recordings in time direction, which are



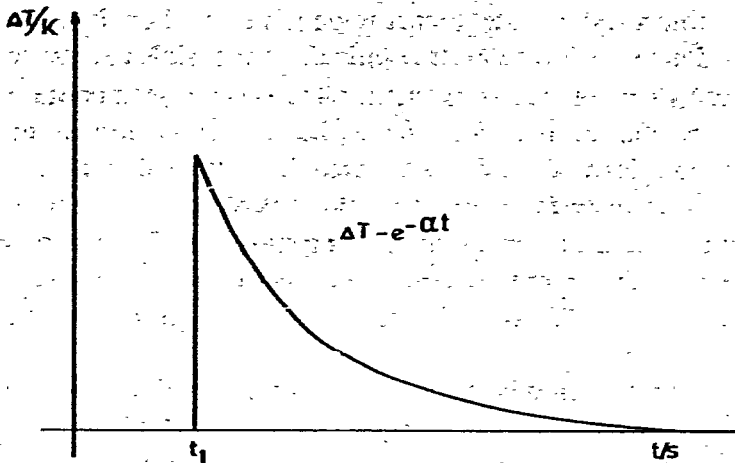


Fig. 12. Temperature compensation in a Calvet-calorimeter after quick temperature increase in the sample-vessel.

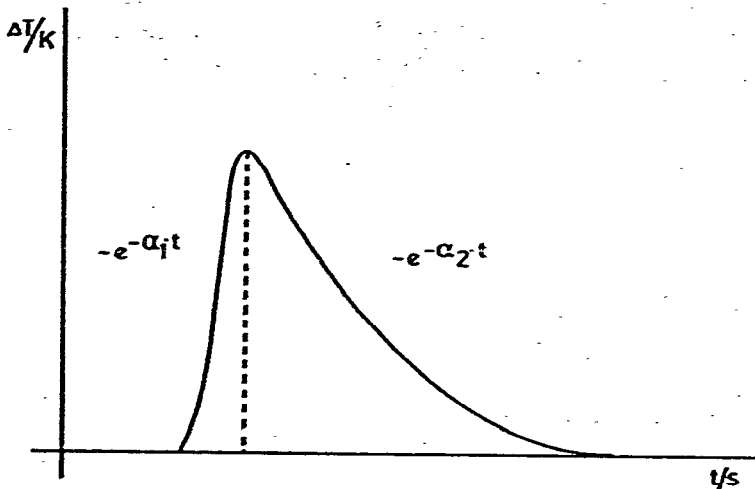


Fig. 13. Temperature compensation in a Calvet-calorimeter after quick temperature increase in the sample.

caused by the heat conduction phenomena. The degree of "smearing" varies and therefore also the falsification of the results. This will be discussed below.

Let us suppose a fly is placed in the calorimeter container. Can we measure the heat produced by the action of the fly's wing muscles at a specific moment? This is not possible, since the time constant of a few milliseconds would require an immensely small heat-conductive pathway between the heat source and the measuring probe. Principally, the heat conduction equation (A) can be solved for negative time, with the aid of known boundary and initial values. It is possible to measure the values at the end of the heat-conductive pathway and to employ them to reconstruct the initial conditions. But this cannot be done without restriction, since the transmission of heat is a statistical process. When the signal becomes smaller than the statistical noise

(i.e., Brownian motion of air molecules) or the measurement error, then it is no longer distinct enough to be recorded and it is also mathematically impossible to retrace it to its origin. The flapping of the fly's wings produces heat, which comes into contact with moving air molecules. This oscillating heat flow from the fly can no longer be distinguished, since it has been transformed into a balanced heat flow due to the presence of the motion of the air molecules. Therefore, the entire information of reaction is lost and there are no possible means to obtain it. The statistical fluctuations of the measured values should be included in the heat conduction equation, they cause fluctuations at the point of measurement for negative times much greater than the measured event.

Also signals obtained at the measuring probe that have a greater value than the statistical error can hardly be retraced back to their origin, with the aid of the heat conduction equation. A simplified mathematical method has been adopted in other fields of physics (i.e., optics). This method utilizes the entire knowledge of the apparatus in order to calculate unknown complex processes from measured curves.

The following gives a summary of the conditions under which this "de-smearing" method can be employed. Let us assume that at  $x$ , a rapid reactions  $g(x)$  takes place, which can be described with the aid of the Dirac function  $\delta(x)$ :

$$\delta(x) = \begin{cases} \infty & \text{for } x = 0 \\ 0 & \text{else} \end{cases} \quad \text{and} \quad \int_{-\infty}^{\infty} \delta(x) dx = 1$$

$$g(x) = Q_1 \cdot \delta(x - x_1) \quad \text{and} \quad \int_0^{\infty} g(x) dx = Q_1$$

$Q_1$  is total heat of the reaction.

The instrument gives the function  $h(x)$  where:

$$\int h(x) dx = Q_1$$

From  $h(x)$  one obtains the "apparatus function"  $f(x)$  also known as "slit-function" in optics, by normalizing the initial values and the area:

$$f(x) = \frac{h(x - x_1)}{Q_1} \quad \text{and} \quad \int_0^{\infty} f(x') dx' = 1$$

This correlation is shown graphically in Fig. 14. When one is dealing with two independent sudden reactions, then  $h(x)$  is equal to the sum of the measured curves of each reaction, when the principle of superposition applies to the physical circumstances (Fig. 15).

The function of  $n$  sudden reactions:

$$h(x) = \sum_{i=1}^n Q_i \cdot f(x - x_i) \quad (C)$$

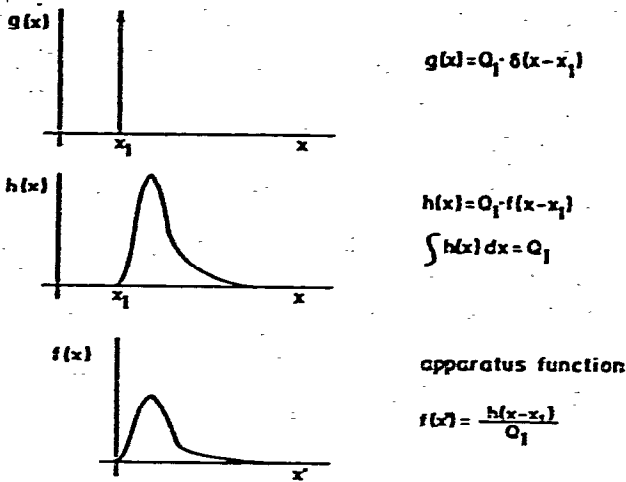


Fig. 14. Relation between quick event and apparatus function (see text).

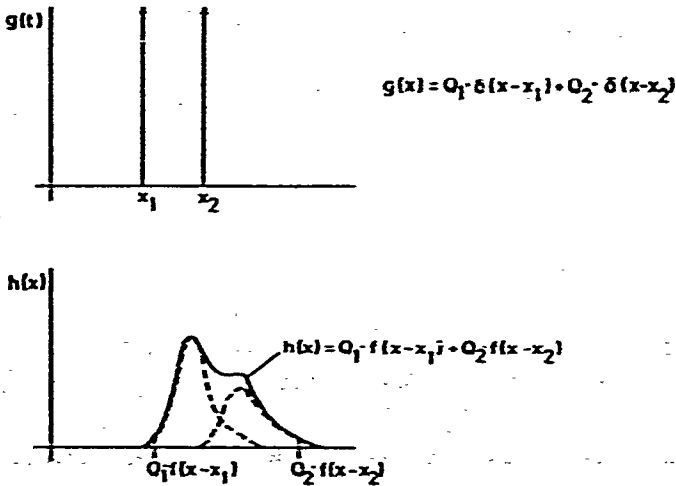


Fig. 15. Superposition of the answers of the apparatus to two quick events.

One can approximate a continuous function  $g(x)$  with the aid of a multitude of rapid reactions, in which the function is composed of many strips with a width  $\Delta x_i$  and height  $g(x_i)$  (Fig. 16).

Then the area of one strip is  $Q_i = \Delta x_i \cdot g(x_i)$ . And we can write:

$$g(x) = \lim_{\substack{\Delta x_i \rightarrow 0 \\ n \rightarrow \infty}} \sum_{i=1}^n \Delta x_i \cdot g(x_i) \cdot \delta(x - x_i)$$

The value recorded by the apparatus:

$$h(x) = \lim_{\substack{\Delta x_i \rightarrow 0 \\ n \rightarrow \infty}} \sum_{i=1}^n \Delta x_i \cdot g(x_i) \cdot f(x - x_i)$$

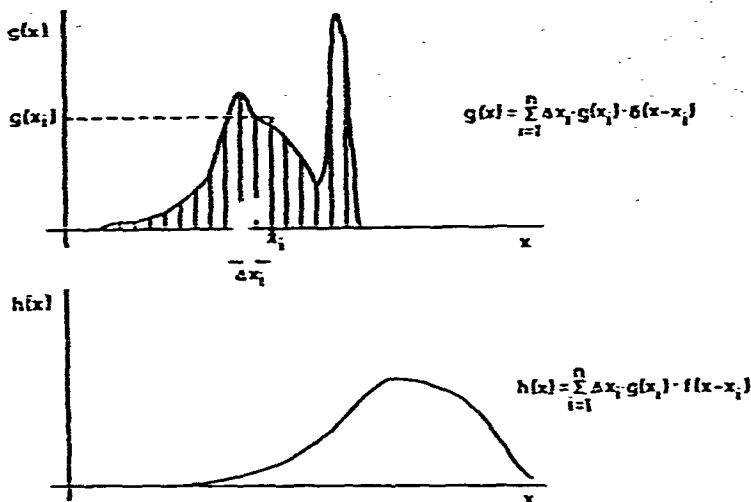


Fig. 16. Answer of the apparatus to a time-dependent event.

this is the definition of the following integral:

$$h(x) = \int_{-\infty}^{\infty} g(x') \cdot f(x - x') dx' \quad (D)$$

This is the so-called Convolution Theorem which can also be stated in a familiar abbreviated form:

$$h(x) = \overbrace{g(x) f(x)}$$

This integral equation reveals the mathematical relationship between the measured function  $h(x)$ , the true result  $g(x)$  and the apparatus function  $f(x)$ , under the following assumptions:

- (1) The apparatusive result of a sudden event must be reproducible and normalizable relative to all other experimental factors (i.e., initial value and area).
- (2) The apparatus must be capable to superpose the results of many rapid reactions (linear behavior).

#### FOURIER TRANSFORM AND RECURSION METHOD

If the apparatus function is known, then it can be substituted in the integral equation above. It is then possible with the function of the measurement  $h(x)$  to obtain the unknown true result  $g(x)$ . Both the Fourier-transformation and the recursion method require the mathematical calculation of a computer. The Fourier-transformation is an integral operation:

$$\mathcal{F}(f(x)) = \sqrt{\left(\frac{1}{2\pi}\right)} \cdot \int_{-\infty}^{\infty} f(y) \cdot e^{i\omega y} dy$$

applied to the convolution theorem:

$$\mathcal{F}(h(x)) = \mathcal{F}(g(x)) \cdot \mathcal{F}(f(x))$$

The convolution product transforms into a simple product and it becomes possible to solve the required function in Fourier space:

$$\mathcal{F}(g(x)) = \frac{\mathcal{F}(h(x))}{\mathcal{F}(f(x))}$$

The required function is produced in the Fourier-retransformation:

$$g(x) = \mathcal{F}^{-1} \mathcal{F}(g(x)) = \mathcal{F}^{-1} \frac{\mathcal{F}(h(x))}{\mathcal{F}(f(x))}$$

This method is always applicable, since Fourier transformation has become commonplace in all computers. The main drawback is the lengthy calculations and the general unclarity because of computation in Fourier space. Those who have no experience with Fourier-transformation should be aware of the "breaking-off-effect" and the "sampling theorem", which tend to register periodicity and fluctuations that do not exist. More extensive information can be found in the literature<sup>6, 8</sup>.

The following shows the Recursion method employed to solve the Convolution Theorem:

$$g_0(x) = h(x)$$

$$g_n(x) = g_{n-1}(x) + (h(x) - \widehat{f(x)g_{n-1}(x)}) \quad (E)$$

The difference between the "refolded" approximation  $g_{n-1}(x)$ :

$$h_n(x) = \widehat{f(x)g_{n-1}(x)}$$

and the measured function  $h(x)$  are simply added to correct the approximation. The Recursion formula does not converge in the case of angular functions of an event (In-Out-Effect). Angles or unsteady functions create oscillations of the approximation function, which quickly diverge. The smooth curves obtained in calorimetry converge quickly and easily. Usually after 20 steps, the square-sum of the error between the measured and fabricated function:  $(\Delta h(x))^2$  is less than 5 percent. It is very easy to program the Recursion formula, since it contains only the Convolution product which is a simple integration-procedure. In order to "desmear" the measured curves, the assumptions stated above must be checked and the apparatus-function procured. As was shown in the deduction of the formulas, it is necessary to employ rapid reactions. One can make use of the following effects:

*DTA and DSC apparatus: ( $\Delta T$  or  $\dot{Q}$  as a function of the temperature).*

*Exothermic processes: mini-explosions (rapid disintegration) Joules heat (current impulses according to resistance).*

*Endothermic processes: first-order phase transition of pure substances.*

*Isoperibol apparatus:*

Exothermic processes: Joules heat (current impulses according to resistance or electrolyses).

Endothermic processes: Peltier effect in thermoelements.

One varies the size of the heat impulses but maintains the conditions identical to the measurements to be desmeared. This is a very crucial factor because, as we have seen, the measured curve is dependent upon the size and geometry of the sample as well as the heat-conduction coefficients. The measured curves obtained are normalized with respect to the area and initial position. If there is a fairly good correlation, then it can be employed as the apparatus function. If the fluctuations are not systematical or of a large size, then the mean curve can be employed with caution to try "desmearing". It is also advisable to compare the measured curves of two or more rapid reactions with the calculated curve, in order to check the superposition. If the apparatus works in linear behavior and is reproducible, then the convolution integral gives a precise method to "desmear" heat-flow curves and an astonishing high resolution. This is shown in Fig. 17 for the melting-curve of octadecane. A normalized melting curve of the same amount of benzoic acid was employed to give the apparatus function. Indium, a common standard substance was not used in this case, because it has an entirely different heat-conduction coefficient than the organic substance. The extent of the "de-smearing" efficiency is shown by the relationship between the

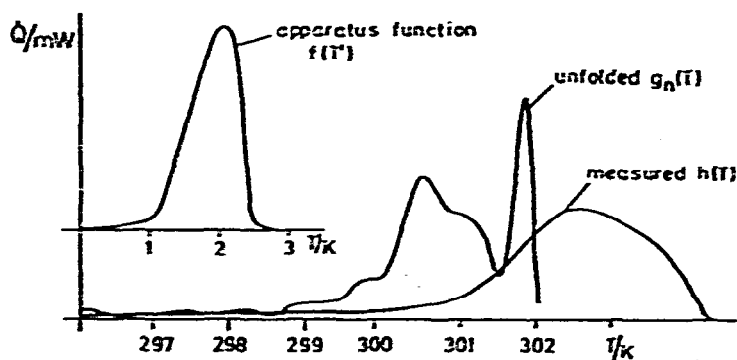


Fig. 17. Original and "desmeared" DSC-melting-curve of octadecane.

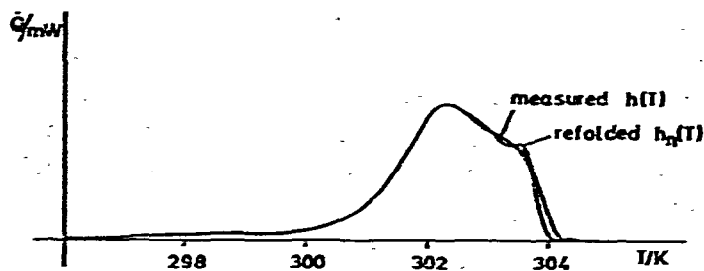


Fig. 18. Comparison of original measurement with desmeared and then refolded melting curve of octadecane.

refolded function  $h_r(x)$  and the measured function. This is illustrated in Fig. 18 for octadecane. When the change of the measured heat flow as a function of time is comparable in size to the resolution of the apparatus, characterized as the halfwidth of the apparatus function, then desmearing is advisable. When the changes of the measured heat flow occur at a very slow rate, then it is not necessary to "de-smear", since the measured function is a good approximation of the truth.

**ERRORS**

In conclusion, I would like to discuss errors. The preciseness of the results is dependent upon the preciseness of the measured function  $h(x)$  and the apparatus function  $f(x)$ . Here, this relationship cannot be derived exactly but only hinted<sup>7</sup>.

According to all rules, the preciseness in the  $x$ -direction (temperature or time scale) is much greater and we can write:

$$f(x)_{\text{measured}} = f(x)_{\text{true}} \pm \Delta f$$

$$h(x)_{\text{measured}} = h(x)_{\text{true}} \pm \Delta h$$

$$g(x)_{\text{calculated}} = g(x)_{\text{true}} \pm \Delta g$$

with fluctuations independent of  $x$  and approximated by the mean value, which is assumed to be constant.

Substitution in equation (D) gives an approximation of the error:

$$|\Delta g| \leq |\Delta h| + Q \cdot |\Delta f| \text{ and } Q = \int g(x) \, dx$$

This formula only holds, if we can solve the integral equation for the convolution exactly. By employing an approximation such as the Recursion formula, the resulting errors must be taken into account separately:

$$|\Delta g_{\text{Rec}}(x)| = |h(x) - h_r(x)| + Q \cdot |\Delta f|$$

As shown in Fig. 18,  $|h(x) - h_r(x)|$  is a function of the abscissa and the error also.

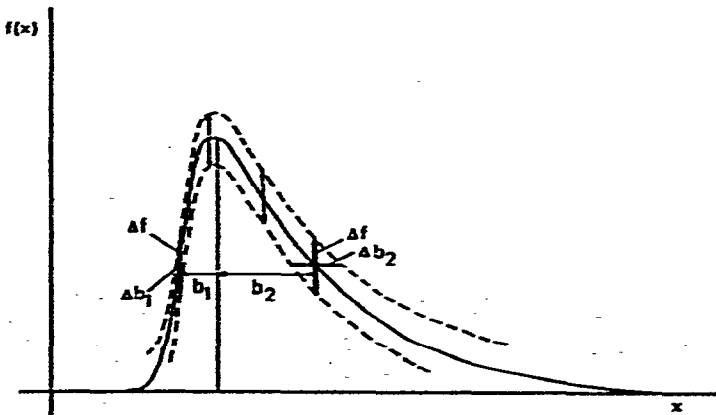


Fig. 19. Apparatus function with fluctuation and hence following width-fluctuation.

Any fluctuations of the "de-smearred" measured curve which are smaller than  $|\Delta g| + |\Delta g_{rec}|$  are merely statistical and not important. Fluctuations of the apparatus function  $\Delta f$  cause fluctuations of the half-width value  $\Delta b$  (see Fig. 19). One can show that the half-width value of the steep flank of the apparatus function is a measure of the resolution of the apparatus in the abscissa direction. Therefore, its fluctuation is a measure of the resolution of the "de-smearred" measured curve in the abscissa direction. The improvement of the resolution is contiguous to the difference between the half-width value and its fluctuation. As a rule of thumb, one can say that for apparatus functions similar to the one shown in Fig. 13, the resolution in the abscissa direction after "de-smearing" is better than half of the steep flank width  $b_1$  (Fig. 19).

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