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On the characteristics of the signal curves of heat flux calorimeters in studies of reaction kinetics. Part 1. A contribution to the desmearing technique

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Abstract

In a chemical reaction or in a phase transition, the heat production or consumption rate is proportional to the rate of conversion. It is well known that the signal curve of a heat flux calorimeter is delayed and deformed. In order to obtain the true heat flow rate generated by the reacting sample, a transformation method is needed. This is often called "desmearing". There are two techniques for performing the transformation. Owing to its simplicity the method based on a linear second-order differential equation is preferred in this paper as a desmearing tool, rather than the method based on the convolution theory. There are two time constants in the transformation formula. The determination of these constants under real conditions is the main subject of this paper. For this, a comprehensive mathematical treatment of the problem is necessary.

INTRODUCTION

In a heat flux calorimeter in its simplest form, a receptacle containing the reactive substance to be investigated is connected to a thermostatically controlled casing by means of a heat conducting resistance. This type of calorimeter can also be called a "heat conduction calorimeter". It is normally operated in an isoperibolic mode. When no heat is flowing from the receptacle to the casing, both ends of the resistance are at the same temperature.

An exothermic reaction in the sample substance generates a heat flow which is exactly proportional to the conversion rate of the reaction. A knowledge of this heat flow rate is therefore of interest in kinetic studies.

At the beginning of heat generation, there is no temperature difference between the ends of the heat resistance. First the substance itself and the receptacle must be heated up by the source to produce an increasing difference in temperature between the ends of the resistance. The rise in the temperature dT/dt at the end of the resistance which is nearest to the receptacle is given by the heat flow rate ϕ_{Sc} from the sources divided by the heat capacity of the reacting substance and the receptacle, i.e.

$dT/d_t = \phi_{sc}/C$. In the first approximation, the effluent heat flow rate through the heat resistance is proportional to the temperature difference between the ends of the resistance. The signal χ displayed by the calorimeter is based on this temperature difference ΔT. Thus it is evident that the signal χ follows the source heat flow rate as a function of time with delay and deformation (smearing).

In order to obtain the source heat flow rate as a reliable basis for kinetic investigation, the signal curve $\chi(t)$ must be desmeared. This task is complicated by the fact that the heat resistance itself has a heat capacity which cannot be wholly neglected and which disturbs the proportionality of the temperature difference at the resistance and the effluent heat flow rate. But it is certain that all the heat generated in the sources flows through the heat resistance. The time integral for the source heat flow rate from $t = 0$ to the end of the reaction is therefore exactly equivalent to the time integral for the effluent heat flow rate from $t = 0$ to ∞.

Twin-type heat flux calorimeters where two equivalent heat conduction calorimeters have the same casing, represent great progress compared with the single type. The receptacle of one calorimetric system contains the reactive substance. An inert reference sample is placed in the receptacle of the other system, so that the heat capacities of the two caloric systems are equivalent. The heat resistances of both systems must also be mutually equivalent. For more details, see Hemminger and Höhne [1].

One of the important advantages of this twin-type calorimeter is that it is possible to raise the temperature of the casing linearly providing a program-controlled furnace. This scanning operation means subjecting a defined heat flow rate from the furnace onto each sample, thus also making the investigation of endothermic reactions possible. From a mathematical point of view, neither the twin-type calorimeter operated in the scanning mode nor the replacement of an exothermic reaction with an endothermic one causes additional difficulties.

The impressed heat flow rate due to the scanning mode can be measured at the resistance of the reference system. It can then be subtracted from the heat flow rate through the resistance of the other system. The heat flow rate from which the impressed flow rate is to be subtracted is the result of the vectorial addition of the heat flow rate from the reacting substance and the heat flow rate from the casing. The subtraction yields the reaction-caused heat flow rate through the heat resistance of this calorimetric system. Thus the problem of the twin-type calorimeter is reduced to that of the single-system type. The replacement of an exothermic reaction with an endothermic one means using heat sinks instead of heat sources. This means only a change in the sign of the corresponding terms in the equation used to describe the physical phenomenon.

Because of the corresponding features of the two types of heat flux calorimeters and because no additional problem arises if the twin-type calorimeter is operated in the isoperibolic mode (Tian–Calvet calorimeter) or in the scanning mode (DSC), all heat flux calorimeters can be treated collectively in order to solve the desmearing problem.

CORRELATION OF THE SOURCE HEAT FLOW RATE WITH THE SIGNAL CURVE

In accordance with Calvet and CAMIA [2], this paper describes the correlation of the source heat flow rate ϕ with the signal χ using a linear differential equation of second order

$$\phi = \chi + (\tau_1 + \tau_2)\, \mathrm{d}\chi/\mathrm{d}t + \tau_1 \tau_2\, \mathrm{d}^2\chi/\mathrm{d}t^2 \tag{1}$$

Depending on the instrument, the signal χ is recorded as an electric potential difference, converted into a temperature difference, or into the effluent heat flow rate; ϕ always has the same dimension as χ. In the following it is assumed that the signal χ represents the effluent heat flow rate. Then ϕ is the source heat flow rate. In the other cases, ϕ is proportional to the source flow rate, e.g. $\chi = \Delta T$, then $R_\lambda \phi_S$, where R_λ is the value of the heat conduction resistance.

In eqn. (1), there are two time constants τ_1 and τ_2. The evaluation of these time constants is the main subject of this paper. When both constants are known, eqn. (1) is the tool used to desmear the signal curve $\chi(t)$ in order to obtain the source heat flow rate $\phi_{Sc}(t)$. For details dealing with reaction kinetics, see ref. 3, especially for handling the base line in kinetic investigations. If the dependence of ϕ_{Sc} on time is low, then it suffices to replace the differential quotients with quotients of differences in eqn. (1), whereby the space of time Δt is chosen to suit the speed of the underlying reaction. The higher the speed, the smaller the Δt.

A higher degree of accuracy is possible when the function $\chi(t)$ is cut into sections and each section then approximated by means of a polynomial of high order which can be exactly differentiated once or twice. The steps of the operation are

(i) $\chi(t) \rightarrow \chi_{\mathrm{poly}}(t)$

(ii) Differentiation: $\mathrm{d}\chi_{\mathrm{poly}}/\mathrm{d}t$, and $\mathrm{d}^2\chi_{\mathrm{poly}}(t)/\mathrm{d}t^2$

(iii) Putting (i) and (ii) into eqn. (1)

$$\chi_{\mathrm{poly}}(t) + (\tau_1 + \tau_2)\, \mathrm{d}\chi_{\mathrm{poly}}/\mathrm{d}t + \tau_1 \tau_2\, \mathrm{d}^2\chi_{\mathrm{poly}}/\mathrm{d}t^2 = \phi_{\mathrm{Poly}}(t)$$

Then $\phi(t)$ can be plotted from $\phi_{\mathrm{poly}}(t)$.

Equation (2) can be applied for the purpose of checking the transformation of χ into ϕ

$$\int_0^{t_e} \phi_{Sc}\, \mathrm{d}t = \int_0^{t_\infty} \chi\, \mathrm{d}t = \int_0^{t_e} \phi\, \mathrm{d}t \tag{2}$$

where t_e is the end of the source heat generation, i.e. the end of the reaction, and t_∞ the time for which χ becomes negligible ($t_\infty > t_e$). In the case of a reaction, the integration of $\chi = \phi_{ex}$ between 0 and t_∞ yields $Q_r = -\Delta_r H$. Equation (2) corresponds to the statement of the preceding paragraph that all the heat generated in the sample will flow out of the calorimetric system. The transformation is correct if the deviation of $\int_0^{t_e} \phi \, dt$ from $\int_0^{t_\infty} \chi \, dt$ is far less than 1%. Theoretically, there should be no deviation at all.

DETERMINATION OF THE TIME CONSTANTS BY MEANS OF THE THEORY OF THE INFINITESIMAL HEAT PULSE

Whereas the integration of eqn. (1) in order to obtain ϕ_{Sc} from χ was not necessary, it is now needed to determine the time constants τ_1 and τ_2. In the case of a heat impulse of infinitesimal duration, this is easily done because $\phi_{Sc} = 0$ for all values of time. Equation (1) therefore becomes homogeneous, i.e.

$$\chi + (\tau_1 + \tau_2)\, d\chi/dt + \tau_1 \tau_2 \, d^2\chi/dt^2 = 0 \qquad (3)$$

Integration of eqn. (3) yields [1]

$$\chi = [Q/(\tau_1 - \tau_2)](e^{-t/\tau_1} - e^{-t/\tau_2}) \qquad (4)$$

In eqn. (4), χ is the response to the heat Q transferred within an infinitesimal space of time. The value of $\chi(t)$ shows a maximum at t_m and a point of inflection at t_{tp}; τ_1 must be greater than τ_2 because a positive Q gives a positive χ. (In order to avoid confusion, it should be mentioned that owing to another way of developing the transformation formula, in the author's earlier papers [4, 5] the numerical order of the indices of the time constants was reversed.) If τ_2 is smaller than τ_1, $\exp(-t/\tau_2)$ fades earlier than $\exp(-t/\tau_1)$ with increasing time t.

DETERMINATION OF THE MAIN TIME CONSTANT τ_1

The larger time constant τ_1 can be determined by means of the subtangent method proposed by Schönborn [6]. Another way to do this is by plotting $\ln \chi$ as a function of t for $t > t_{tp}$. Then τ_1 can be calculated from the slope of the resulting straight line. This method better compensates errors in reading than does drawing a tangent.

It should be borne in mind that the time constant τ_1 is essentially governed by the product of the heat capacity of the reactive substance, including its receptacle, and the resistance R of the heat conductor which connects the receptacle with the casing. The species and the mass of the reactive substance therefore influence the value of τ_1. There is also another aspect: if the substance to be investigated has a low thermal conductivity, this could have an influence on τ_1 by way of influencing the value of R. This influence might even change in the course of the reaction or the phase transition. It should also be mentioned that τ_1 is a function of temperature. All this has to be considered in the calibration procedure, of which the determination of τ_1 is an important part [7].

DETERMINATION OF THE SECOND TIME CONSTANT τ_2

The determination of the second time constant τ_2 is a little more difficult than that of τ_1, and can only be done when the evaluation of τ_1 has been made. To carry it out, we must look for the point of time t_m at which the maximum of $\chi(t)$ appears, and for t_{tp}, at which the turning point occurs. The value of t_m is found by differentiating eqn. (4) once and setting the derivate to zero. To find t_{tp}, eqn. (4) is differentiated twice. The second derivate is set to zero and solved for t.

The first step yields

$$t_m = [\tau_1 \tau_2/(\tau_1 - \tau_2)] \ln(\tau_1/\tau_2) \qquad (5)$$

and the second step

$$t_{tp} = 2[\tau_1 \tau_2/(\tau_1 - \tau_2)] \ln(\tau_1/\tau_2) \qquad (6)$$

Because t_{tp} is twice t_m, it follows that

$$t_{tp} - t_m = t_m \qquad (7)$$

This expression seems extremely trivial but it will gain in importance in further considerations in the more realistic case of a rectangular heat pulse of measurable duration.

Using the abbreviation $\gamma = \tau_1/\tau_2$, we can rewrite eqns. (5) and (7), resulting in

$$(t_{tp} - t_m)/\tau_1 = (\ln \gamma)/(\gamma - 1) \qquad (8)$$

First the right-hand term of eqn. (8), which is a function of the ratio γ of τ_1 and τ_2, will be considered. In Table 1, γ values ranging from 2 to ∞ are given together with the corresponding function values.

The left-hand term of eqn. (8) is known from the analysis of the signal curve $\chi(t)$. Its value corresponds to a particular value of the function $(\ln \gamma)/(\gamma - 1)$ (see Table 1). To determine τ_2, we simply read the corresponding γ in the same row and calculate τ_2 via $\tau_2 = \tau_1/\gamma$; τ_1 and τ_2 are both functions of temperature.

TABLE 1

Values of the function $(\ln \gamma)/(\gamma - 1)$

γ	$(\ln \gamma)/(\gamma - 1)$	γ	$(\ln \gamma)/(\gamma - 1)$
2	0.6931	30	0.1173
5	0.4024	∞	0.0000
10	0.2558		

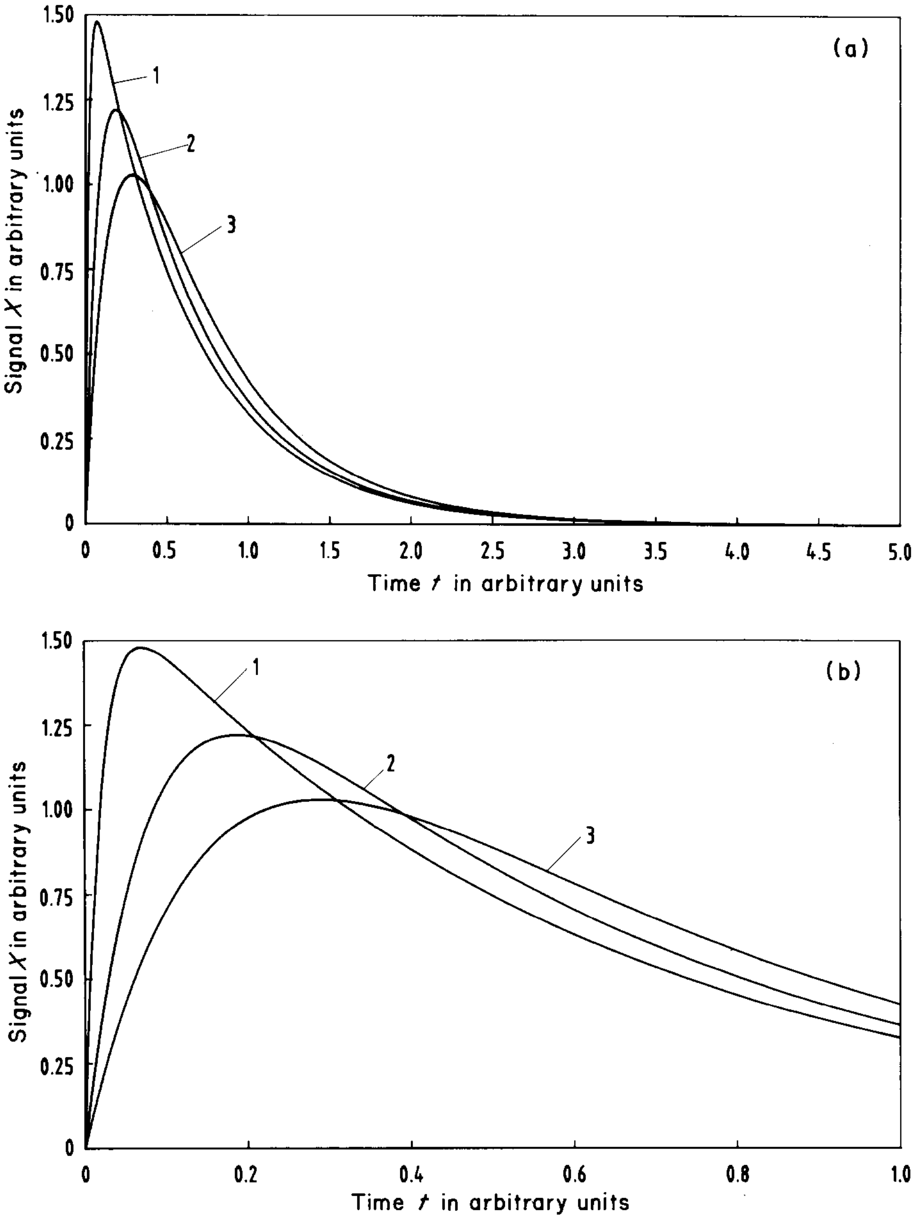

Fig. 1. (a) Influence of γ on the shape of signal curves caused by heat pulses of infinitesimal duration (the transferred heat being the same in each case): (1) $\gamma = 30$; (2) $\gamma = 7.5$; (3) $\gamma = 3.75$. (b) Influence of γ on the shape of signal curves (in comparison with Fig. 1a, the time axis is stretched).

Figure 1 shows the influence of $\gamma = \tau_1/\tau_2$ on the shape of signal curves caused by an infinitesimal heat impulse when τ_1 is given with 0.6 time units. We now have to consider the effect of a rectangular heat pulse of finite length instead of infinitesimal duration. If we formalize this it reads

$Q = \phi_1 \, \mathrm{d}t \rightarrow \chi_{\text{ideal}}$

$Q = \phi_2 \, \Delta t \rightarrow \chi_{\text{real}}$

$\phi_1 \gg \phi_2$, but $\phi_1 \, \mathrm{d}t = \phi_2 \, \Delta t$

The question is whether χ_{real} equals χ_{ideal} for $t \geqslant t_m$.

USE OF A HEAT FLOW OF FINITE DURATION IN THE DETERMINATION OF THE TIME CONSTANTS

Deduction of a formula for the signal curve caused by an expanded heat impulse of rectangular shape

A source heat flow rate which is constant within its duration can be generated, for example, by means of an electric heating element, possibly installed for calibration purposes. In order to answer the question which arose above, a rectangular heat impulse of duration Δt is chopped into short impulses, so that eqn. (4) is at least approximately valid for each of them. A special time measure is now introduced

$$\Delta z = \Delta t / n \tag{9}$$

where z is taken from the initial of the German word for time, "Zeit". The instrument's response to the first partial pulse is analogous to eqn. (4), with Q being replaced by $\phi^* \Delta z$ where ϕ^* is the constant heat flow rate. At $t = 0$, the signal χ is zero.

The signal curve $\chi_i(t)$, the response to the ith partial impulse, is then

$$\chi_i(t) = \frac{\phi^* \Delta z}{\tau_1 - \tau_2} \{ e^{-[t-(i-1)\Delta z]/\tau_1} - e^{-[t-(i-1)\Delta z]/\tau_2} \} \tag{10}$$

where $\chi_i(t)$ must be 0 when $t - (i-1)\Delta z = 0$.

The resultant total signal curve is the superposition of the partial responses, i.e.

$$\chi(t) = \sum_{i=1}^{n} \chi_i(t) = \sum_{i=1}^{n} \frac{\phi^* \Delta z}{\tau_1 - \tau_2} \{ e^{-[t-(i-1)\Delta z]/\tau_1} - e^{-[t-(i-1)\Delta z]/\tau_2} \} \tag{11}$$

Equation (11) is still imperfect because when $\chi(t)$ is taken and inserted into eqn. (1), for all values of t, the incorrect result, $\phi = 0$, is obtained which can only be the case when the source heat flow ϕ^* has ended. This imperfection is due to the fact that the partial responses are not valid for a continuous real source heat flow, but to an artificially chopped one. We must therefore try to overcome this imperfection by transforming eqn. (11) into an integral, which means looking for the limits of $\sum \chi_i(t)$ for n to ∞. According to the definition

$$\lim_{\substack{n \to \infty \\ \Delta x \to 0}} \sum_{i=1}^{n} f(a + i\,\Delta x)\,\Delta x = \int_a^b f(x)\,\mathrm{d}x \qquad \text{with } b = a + n\,\Delta x$$

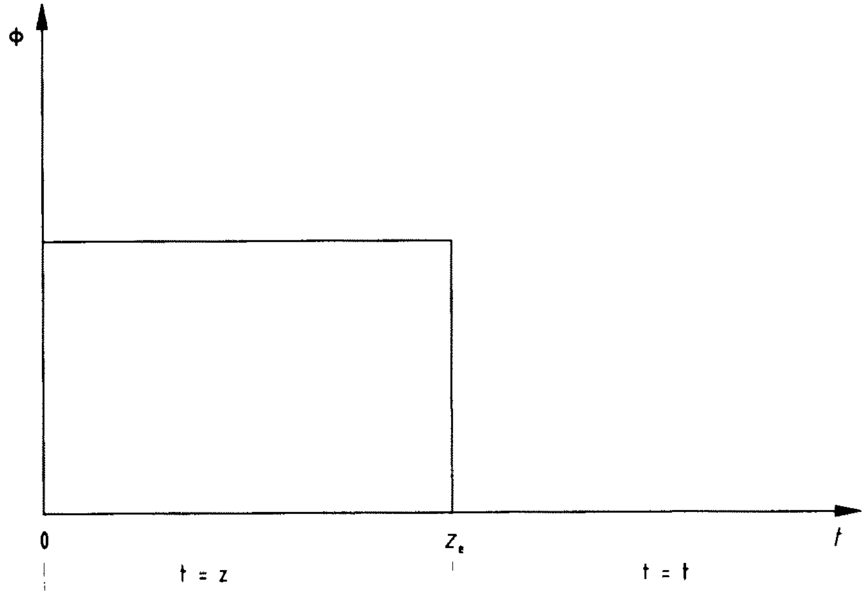

Fig. 2. Sketch of a rectangular heat pulse.

from eqn. (11) we have

$$\chi(t) = \frac{\phi^*}{\tau_1 - \tau_2} \int_{-t}^{-(t-z)} (e^{z/\tau_1} - e^{z/\tau_2})\, dz \tag{12}$$

taking into account that ϕ^* is constant within $\Delta t = n\,\Delta z = z$.

To avoid writing indices with the time constants, in the following h is used instead of τ_1, and k instead of τ_2. Equation (12) then yields

$$\chi(t) = \frac{\phi^*}{h-k} [h e^{-(t-z)/h} - k e^{-(t-z)/k} - (h e^{-t/h} - k e^{-t/k})] \tag{13}$$

where z runs from 0 to z_e, which is the end of the source heat production, i.e. $z \in [0, z_e]$, $t \geqslant z$. Within the range from 0 to z_e, t can neither precede z nor run behind it. This is illustrated in Fig. 2.

If $t < z_e$, then $t = z$; otherwise $t = t$. For $t < z_e$, eqn. (13) reads

$$\chi(z) = \frac{\phi^*}{h-k} [h - k - (h e^{-z/h} - k e^{-z/k})] \tag{14}$$

If $t \geqslant z_e$, then z_e becomes a time constant. Equation (13) now reads

$$\chi(t) = \frac{\phi^*}{h-k} [h e^{-(t-z_e)/h} - k e^{-(t-z_e)/k} - (h e^{-t/h} - k e^{-t/k})] \tag{15}$$

Equations (14) and (15) can be integrated and also differentiated, either once or twice. Taking eqns. (14) and (15) into account, the integration of eqn. (13) yields

$$\int_0^{t_\infty} \chi(t)\,\mathrm{d}t = \int_0^{z_e} \chi(z)\,\mathrm{d}z + \int_{z_e}^{t} \chi(t)\,\mathrm{d}t = \phi^* z_e = Q \tag{16}$$

In order to show that the imperfection inherent in eqn. (11) is eliminated by changing it into an integral (eqn. (12), from which eqns. (13), (14) and (15) follow), the following calculations are made.

The derivations of eqn. (14) are

$$\mathrm{d}\chi/\mathrm{d}z = \frac{\phi^*}{h-k}(\mathrm{e}^{-z/h} - \mathrm{e}^{-z/k}) \tag{17}$$

and

$$\mathrm{d}^2\chi/\mathrm{d}z^2 = \frac{\phi^*}{h-k}[(1/k)\mathrm{e}^{-z/k} - (1/h)\mathrm{e}^{-z/h}] \tag{18}$$

and those of eqn. (15) are

$$\mathrm{d}\chi/\mathrm{d}t = \frac{\phi^*}{h-k}[\mathrm{e}^{-(t-z_e)/k} - \mathrm{e}^{-(t-z_e)/h} - (\mathrm{e}^{-t/k} - \mathrm{e}^{-t/h})] \tag{19}$$

and

$$\mathrm{d}^2\chi/\mathrm{d}t^2 = \frac{\phi^*}{h-k}\{(1/h)\mathrm{e}^{-(t-z_e)/h} - (1/k)\mathrm{e}^{-(t-z_e)/k} - [(1/h)\mathrm{e}^{-t/h} - (1/k)\mathrm{e}^{-t/k}]\} \tag{20}$$

When t is within the range from 0 to z_e, i.e. within the duration of the source heat flow of rectangular shape, where is $t = z$, the substitution of eqns. (14), (17) and (18) into eqn. (1) yields

$$\phi = \chi + (h + k)\,\mathrm{d}\chi/\mathrm{d}z + hk\,\mathrm{d}^2\chi/\mathrm{d}z^2 = \phi^* \tag{21}$$

When $t > z_e$, i.e. the source heat flow has ended, then substituting eqns. (15), (19) and (20) in eqn. (1) results in

$$\phi = \chi + (h + k)\,\mathrm{d}\chi/\mathrm{d}t + hk\,\mathrm{d}^2\chi/\mathrm{d}t^2 = 0 \tag{22}$$

Equations (16), (21) and (22) demonstrate that eqn. (13) is an exact description of the signal curve $\chi(t)$ which is the answer to a constant source heat flow rate ("rectangular heat impulse") of arbitrary duration z_e.

Figure 3 shows the signal curves of a short heat impulse and an infinitesimal heat impulse. Although the duration z_e of the short impulse is only a fifth of the value of the time constant $h = \tau_1$, the signal curve caused by it deviates perceptibly from that which results from an infinitesimal impulse. Only if the value of z_e is smaller than a twenty-fifth of h do the two curves practically coincide, see Fig. 4. The signal curve for a constant source heat flow rate lasting for a prolonged period is shown in Fig. 5.

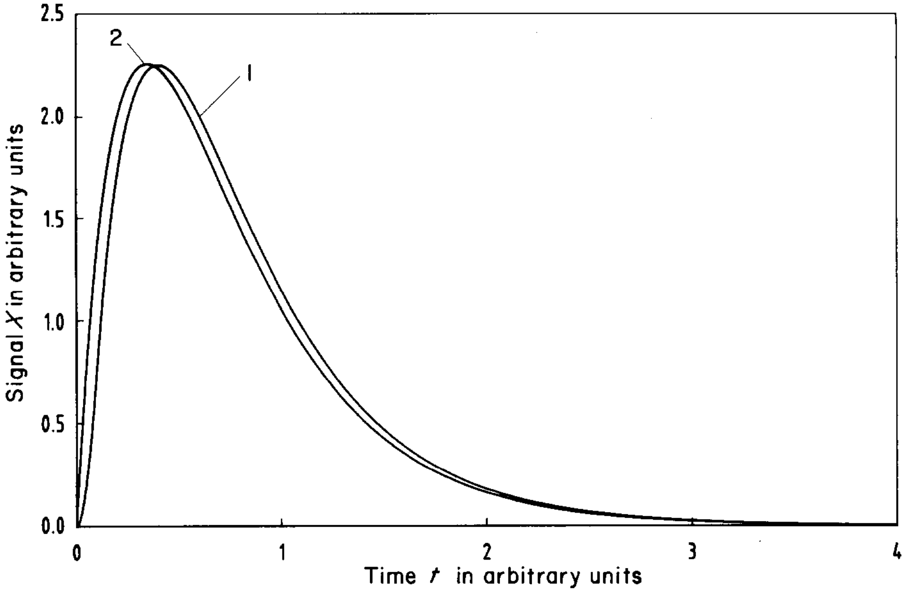

Fig. 3. Comparison of a signal curve caused by a short heat pulse (1) with that of pulse of infinitesimal duration (2). (1) $z_e = 0.1$; (2) $z_e = 0$.

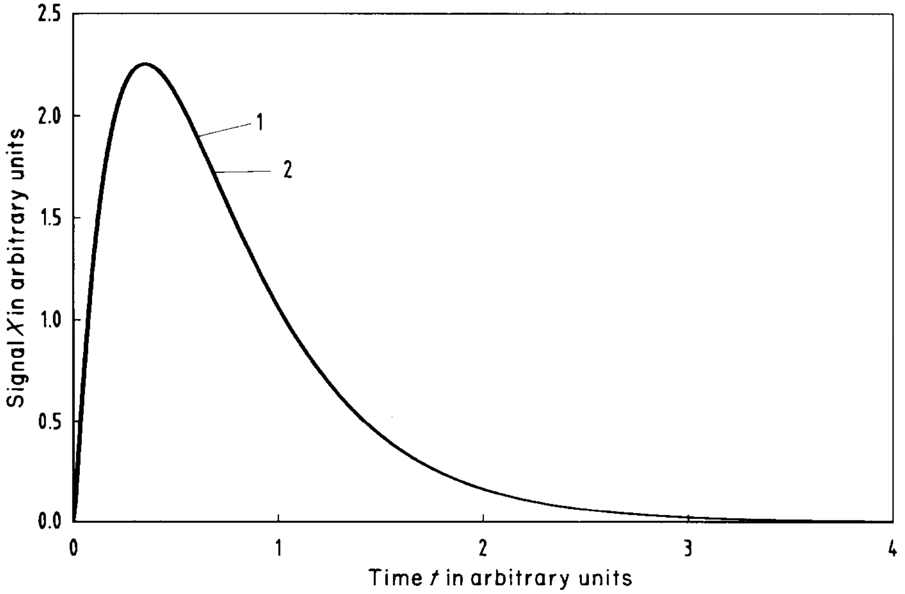

Fig. 4. Comparison of a signal curve caused by a very short heat pulse (1) with that of pulse of infinitesimal duration (2).

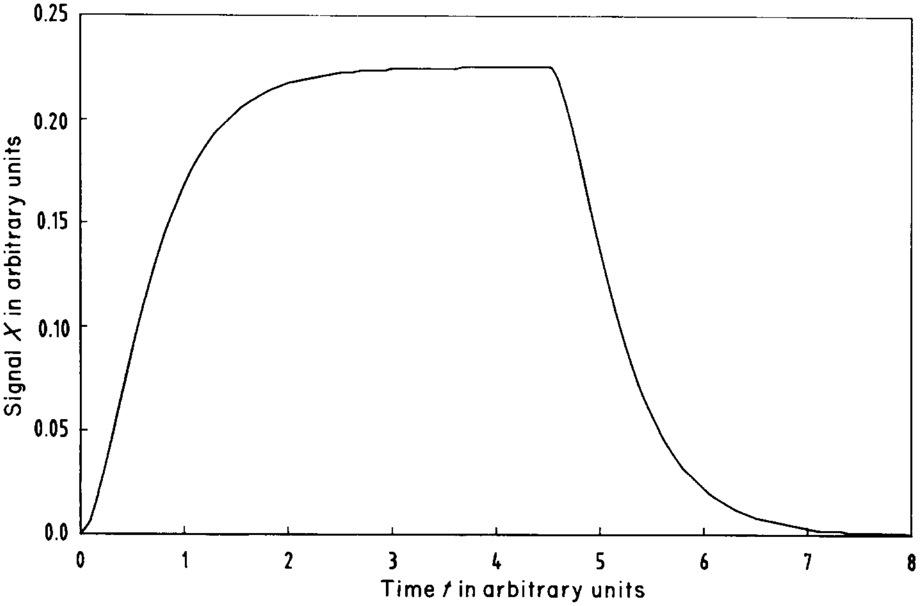

Fig. 5. Signal curve caused by a constant source heat flow rate rectangular in shape lasting for a prolonged period.

Determination of the time constants

As in the idealised case, here too a knowledge of the point in time at which the maximum or the turning point of χ (from eqn. (13)) occurs is essential in order to determine the time constants. If the value of z_e is high, eqn. (14) shows that with increasing z, χ practically reaches the values of ϕ^* but cannot exceed it. Although χ runs for a prolonged period, practically parallel to the time axis, χ does not run exactly parallel to it anywhere. Therefore the maximum can only appear at $t_m = z_e$ or at $t_m > z_e$.

The value of t_m is calculated by setting $d\chi/dt$ (from eqn. (19)) to zero, and by solving it for t. The result is

$$t_m = \frac{hk}{h-k}\ln\left[\frac{e^{z_e/k}-1}{e^{z_e/h}-1}\right] \tag{23}$$

The practical implication of eqn. (23) remains to be discussed. Because

$$\lim_{z_e\to\infty}\ln\left[\frac{e^{z_e/k}-1}{e^{z_e/h}-1}\right] = \frac{h-k}{hk}z_e$$

from eqn. (23), $t_m = z_e$ in the case of a prolonged duration of the rectangular source heat flow.

However, a very short impulse yields

$$t_m = \frac{hk}{h-k}\ln\left[\frac{h}{k}\right] \tag{24}$$

because

$$\lim_{z_e \to 0} \frac{e^{z_e/k} - 1}{e^{z_e/h} - 1} = \frac{h}{k}$$

Consideration of eqn. (23) shows that only in the case of a very short heat impulse is a result obtained (eqn. (24)) that is comparable with that of eqn. (5). Otherwise, t_m corresponds to an expression which is a function of z_e.

As can be seen in Fig. 5, there are two points of inflection in the signal curve of a source heat flow of prolonged duration. In the following, only that turning point which appears after t_m is of interest. This turning point is determined by setting $d^2\chi/dt^2$ from eqn. (20) to zero and by solving the expression for t. This yields

$$t_{tp} = \frac{hk}{h-k}\left[\ln\frac{h}{k} + \ln\frac{e^{z_e/k} - 1}{e^{z_e/h} - 1}\right] \tag{25}$$

Subtracting eqn. (23) from eqn. (25), we have

$$t_{tp} - t_m = \frac{hk}{h-k}\ln\frac{h}{k} \tag{26}$$

where $h = \tau_1$ and $k = \tau_2$.

Equation (26) is identical with eqn. (7), taking into account eqn. (5) as well. This is surprising in so far as the shape of the signal curve caused by a rectangular heat impulse is considerably different from that which would result from an infinitesimal impulse. In contrast to the real heat impulse, an impulse of infinitesimal duration cannot be realised. From this, eqn. (26) gains in importance as it confirms that the method for determining the ratio γ of the two time constants, which was developed on the basis of the hypothetical infinitesimal impulse, applies to the real case.

After the problem of finding the value of the ratio $\gamma = h/k = \tau_1/\tau_2$ has been solved, there remains the question of the determination of the main constant $h = \tau_1$ under real conditions. Schönborn's proposal [6] also indicates the solution in this case. In the ideal case, τ_1 is equal to the length Λ of the subtangent drawn at the signal curve $\chi(t)$ at an arbitrary point far behind t_{tp}. Λ is given by the absolute value of the ratio $\chi(t)/(d\chi/dt)$. It can be calculated from eqns. (15) and (19), resulting in eqn. (27).

$$\Lambda = \left| \frac{-h + k\left[\dfrac{e^{-t/k}(e^{z_e/k} - 1)}{e^{-t/h}(e^{z_e/h} - 1)}\right]}{1 - \left[\dfrac{e^{-t/k}(e^{z_e/k} - 1)}{e^{-t/h}(e^{z_e/h} - 1)}\right]} \right| \tag{27}$$

If z_e is very small, eqn. (27) yields $\Lambda = h = \tau_1$, and if z_e is large, it yields $\Lambda \approx h$. This demonstrates that both the methods described above and proposed to determine τ_1 in the ideal case, can also be used under real conditions.

Because t_m, the point of time at which the maximum of $\chi(t)$ appears, is far behind z_e if z_e is small (see eqn. (24)), there is no need for the source heat flow to be rectangular in shape. This is of some practical interest, especially as regards the experimental technique proposed by Höhne [7]. He recommends the use of a light flash in the absence of an electric heating element for the generation of a heat impulse.

CONCLUSIONS

The intrinsic inertia of a heat flux calorimeter results in a more or less pronounced deviation of the recorded signal from the source of a variable source heat flow rate which is caused by a chemical reaction. This phenomenon is commonly called "smearing". The signal curve must therefore be desmeared in order to obtain the original heat flow rate. Several desmearing methods are known. Of these, the method based on the idea of Calvet and Camia is preferred here because it uses a classical mathematical approach of great lucidity to describe the physical event taking place in the calorimeter. The differential equation established by these authors clearly describes the correlation between the signal curve and the original heat flow rate. The signal is understood as being proportional to the effluent heat flow which passes the heat conduction resistance of the calorimeter, and because of this, the equation of Calvet and Camia (eqn. (1) in this paper) is considered an appropriate tool for transforming the signal curve into the course of the original heat flow rate. As has been shown, it is applicable to all kinds of heat flux calorimeters operated in the isoperibolic or the scanning mode. To apply this equation, the values of the time constants involved in the equation must be determined. This determination is considered to be part of the calibration procedure with the calorimeter.

The determination of the time constants is carried out by analysing the signal curve caused by a heat impulse. Because the equation of Calvet and Camia is easily solved in the case of an impulse of infinitesimal duration, in default of a formula describing the signal due to a real heat impulse, this model has hitherto been used to handle the problem. However, difficulties arose due to the fact that the shape of the signal curve caused by a real heat impulse of short but perceptible duration was considerably different from the hypothetical one, which is considered to be the solution to the unrealisable infinitesimal heat impulse. In both cases the same amount of heat is transferred.

To solve the problem outlined here, a formula has been deduced which exactly describes the signal curve caused by a source heat flow rate, rectangular in shape and of optional duration.

Although the shape of the signal curve caused by a real heat impulse deviates considerably from the signal curve which can be calculated as the answer to the hypothetical impulse of infinitesimal duration, it has been demonstrated that the methods which were proposed to determine the two time constants in the case of the hypothetical impulse, can be used with only little modification to determine the time constants under real conditions.

The mathematical treatment of the problem has contributed to the removal of the uncertainty relating to the determination of the time constants, which are of great importance in the application of the desmearing tool. Some advice has also been given regarding work in practice. It may be hoped that this will help to increase the reliability of the application of thermoanalytical methods to kinetic research problems.

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