On the characteristics of the signal curves of heat flux calorimeters in studies of reaction kinetics. Part 2. The response to an inconstant heat flux

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Abstract

Part 1 of this investigation describes a formula with two time constants and the methods used to determine these. The formula is used to transform the signal curve of a heat flux calorimeter into the curve of a reaction-induced source heat flux. Because a mathematically exact procedure must be reversible, Part 2 deals with the calculation of the signal curve as a response to an inconstant source heat flux. A mathematically exact solution is derived for the case of a source heat flux that is linearly variable with time. It is then shown how reaction-kinetic models can be verified by thermal analysis.

INTRODUCTION

Equation (1), which is widely known and which describes the signal curve as the response of a heat flux calorimeter to an infinitesimal heat impulse [1]

$$\chi(t) = [Q/(\tau_1 - \tau_2)](e^{-t/\tau_1} - e^{-t/\tau_2}) \tag{1}$$

can be taken as the solution of the linear second-order differential equation

$$\Phi(t) = \chi(t) + (\tau_1 + \tau_2)\,d\chi/dt + \tau_1\tau_2\,d^2\chi/dt^2 \tag{2}$$

in the case when the source heat flux Φ is zero for all finite times. Equation (2) can also be derived by analysis of the physical events in heat flux calorimeters [2–4]; therefore, eqn. (2) can be used to transform the signal curve $\chi(t)$ into the source flux curve $\Phi(t)$, where $\Phi(t)$ is proportional to the conversion rate of a chemical reaction.

It is not necessary to use a differential equation of a higher order in place of the second-order differential equation because practice has shown that its n time constants represent a rapidly decreasing sequence. Due to multiplication by ever decreasing factors derived from time constants, after the first factor and with increasing degrees of derivation, the higher differential quotients become increasingly less significant so that only the second differential quotient will be considered.

In Part 1 of this investigation [5], eqn. (2) was integrated for the case of a source heat flux constant of between $t = 0$ and $t = z_e$, so that it is possible to calculate the response curve to a rectangular impulse of finite duration. The calculation can be verified experimentally if the calorimeter has a controllable electric heating element for calibration purposes.

An attempt is now made to calculate the signal curve $\chi(t)$ as a response to a heat flux which is inconstant between the times $t = 0$ and $t = z_e$. If this problem is solved, it would be possible to predetermine the signal curve for a chemical reaction, provided the time constants for the heat conduction calorimeter used and for the mean reaction temperature are known.

When complex reactions are concerned, DSC experiments alone are not considered sufficient to find the reaction mechanism. It is advisable to use additional methods to obtain a model which reliably describes the kinetics in question [6]. This model could be verified by DSC by comparing the signal curve calculated on the basis of the model with the signal curve obtained by experiment.

The mathematical basis of this will be developed. First, the signal curve $\chi(t)$ from a source heat flux that is linearly variable with time will be considered.

THE SIGNAL CURVE FROM A SOURCE HEAT FLUX THAT VARIES LINEARLY WITH TIME

The case $\Phi(z) = q + az$ is considered. In this case, z is the measure of time of Φ and q is the initial value of Φ for $z = 0$ (q has the dimension of heat/time). The coefficient a is the rate of increase of Φ with z, i.e. $d\Phi/dz$. To avoid writing indices, h is set for τ_1 and k for τ_2. Integrating

$$\Phi(z) = q + az = \chi(t) + (h + k)\, d\chi/dt + hk\, d^2\chi/dt^2 \tag{3}$$

with $t \geq z$ and $z \in [0, z_e]$

$$\Phi(z) = q + az \tag{4}$$

the time z is subdivided into n sections Δz. For the ith section, eqn. (4) becomes

$$\Phi(z) = q + ai\Delta z \tag{5}$$

Following eqn. (10) in Part 1, the following response to the ith partial impulse is obtained

$$\chi_i = [(q + ai\Delta z)\Delta z/(h - k)]\{\exp\{-[t - (i - 1)\Delta z]/h\}$$
$$- \exp\{-[t - (i - 1)\Delta z]/k\}\} \tag{6}$$

As

$$\lim_{n \to \infty} \sum_{i=1}^{n} f(c + i\Delta x)\Delta x = \int_c^d f(x)\, dx \qquad \Delta x \to 0 \tag{7}$$

with $d = c + n\Delta x$, where $c = -t$, $d = -(t - n\Delta z)$, $d = -(t - z)$. Then

$$an\Delta z = a(-t + t + n\Delta z) = at - a(t - n\Delta z) = at - ax \tag{8}$$

Because of eqn. (7), the integral

$$\chi(t) = [(q + at)/(h - k)] \int_{-t}^{-(t-z)} (e^{x/h} - e^{x/k})\, dx$$

$$- [a/(h-k)] \int_{-t}^{-(t-z)} x(e^{x/h} - e^{x/k})\, dx \tag{9}$$

is obtained from eqns. (6) and (8).

As a result, it follows from eqn. (9) that

$$\chi(t) = [1/(h-k)]\{h(q + az - ah)\exp[-(t-z)/h]$$
$$- k(q + az - ak)\exp[-(t-z)/k] - h(q - ah)\exp(-t/h)$$
$$+ k(q - ak)\exp(-t/k)\} \tag{10}$$

In eqn. (10), the time z of the source heat flux runs from 0 to z_e. Furthermore, $t \geq z$ is valid, i.e. in the range from $z = 0$ to $z = z_e$, t can neither precede not fall behind z.

Equation (10) is valid for both the case $\Phi(z) = q + az$ and the case $\Phi(z) =$ constant, because for $a = 0$, it becomes identical with eqn. (13) of Part 1. The coefficient a can also, of course, be negative; $\Phi(z)$ is then a linearly decreasing source heat flux.

For $t \leq z_e$, $t = z$. For this time interval, eqn. (10) becomes

$$\chi(z) = [1/(h-k)][h(q + az - ah) - k(q + az - ak) - h(q - ah)e^{-z/h}$$
$$+ k(q - ak)e^{-z/k}] \tag{11}$$

For $t > z_e$, eqn. (10) becomes

$$\chi(t) = [1/(h-k)]\{h(q + az - ah)\exp[-(t-z_e)/h]$$
$$- k(q + az - ak)\exp[-(t-z_e)/k] - h(q - ah)\exp(-t/h)$$
$$+ k(q - ak)\exp(-t/k)\} \tag{12}$$

As expected, when eqn. (11) is differentiated once and then again, and when $\chi(z)$, $d\chi/dz$ and $d^2\chi/dz^2$ are introduced into eqn. (2), $\Phi(z) = q + az$ is obtained at any time t within the time interval from $t = 0$ to $t = z_e$ in which $t = z$.

When the same operation is carried out with eqn. (12) and when $\chi(t)$, $d\chi/dt$ and $d^2\chi/dt^2$ are introduced into eqn. (2), the result $\Phi(t) = 0$ is obtained for $t > z_e$. These two results are proof that eqn. (10) is the exact integration of eqn. (2) (in the form of eqn. (3)).

Figure 1 shows the signal curve calculated as the response to a source heat flux lasting 4.5 units of time and increasing from 0 to 50 units ($\Phi(z) = 11.111z$ with $z \in [0, 4.5]$, q here being 0). The time constants were assumed to have the values $h = 0.5$ and $k = 0.25$ units of time.
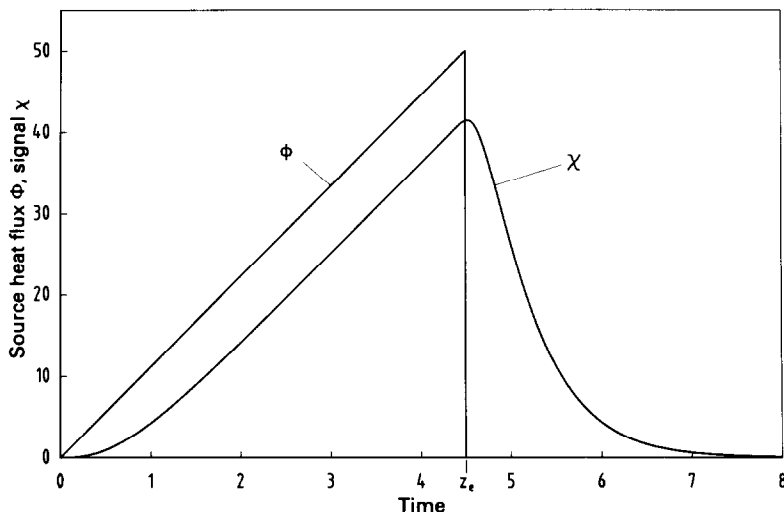
Fig. 1. The signal curve $\chi(t)$ in response to the source heat flux $\Phi(z) = 11.111z$ of duration $t = z_e$. In this example, the time constants are $h = 0.5$ and $k = 0.25$ units of time.

Figure 2 shows the signal curve as a response to a source heat flux $\Phi = 50 - 11.111z$, linearly decreasing within 4.5 units of time from $q = 50$ units to 0; q has the dimension heat/time, i.e. Q/t. Figure 2 shows that in this case the values of the two time constants h and k cannot be concluded as easily from this curve as was described in Part 1; this is, however, possible in the case represented in Fig. 1.
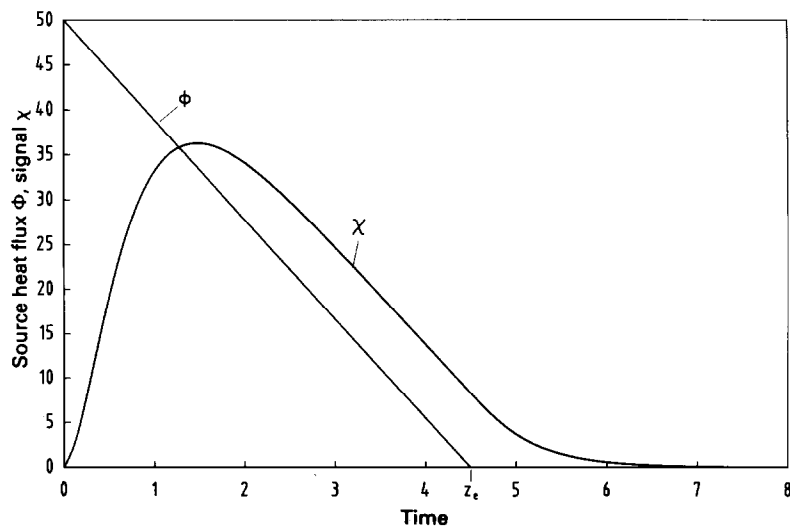

Fig. 2. The signal curve $\chi(t)$ in response to the source heat flux $\Phi(z) = 50 - 11.111z$ of duration $t = z_e$. Here again, $h = 0.5$ and $k = 0.25$.

In the case of a linearly increasing source heat flux, limited in time and of duration z_e units of time (for example, according to Fig. 1), the maximum of the signal curve $\chi(t)$ is situated in or beyond z_e. As a result, $t_m \geq z_e$. By differentiation of eqn. (12) and setting the derivative to zero

$$t_m = [hk/(h-k)]\{\ln[(q-ak)-(q+az_e-ak)\exp(z_e/k)]$$

$$-\ln[(q-ah)-(q+az_e-ah)\exp(z_e/h)]\} \tag{13}$$

is obtained. The point of inflection is found by zeroing the second derivative of eqn. (12)

$$t_p = [hk/(h-k)]\{\ln\{[(q+az_e-ak)\exp(z_e/k)-(q-ak)]/k\}$$

$$-\ln\{[(q+az_e-ah)\exp(z_e/h)-(q-ah)]/h\} \tag{14}$$

For the difference $t_p - t_m$ the relation known from Part 1 results

$$t_p - t_m = [hk/(h-k)]\ln(h/k) \tag{15}$$

Equation (15) confirms the information furnished by both Fig. 1 and Part 1; in the latter, it was demonstrated that under certain conditions the impulse-like source heat flux need not have an absolutely "rectangular" shape in order that the time constants h and k be determined from the signal curve. Caution is, however, to be exercised if the source heat flux decreases slowly, as in Fig. 2.

Equations (13) and (14) will also be valid if a assumes a negative value, i.e. if $a = -m$. The information furnished by eqn. (15) will then only be valid if the duration z_e of the decreasing heat flux is small compared with the greater time constant h. In the case of Fig. 2, however, z_e is a multiple of h. When the data valid for this case are introduced into eqn. (13), this furnishes the result $t_m < z_e$. As t can never, however, be smaller than z, the result is an unreal one and does not describe the temporal position of the maximum of $\chi(t)$. The true position is z_m which is found by zeroing the first derivative of eqn. (11) and resolution with respect to z. This can also be seen directly in Fig. 2. Whether the methods to determine the time constants can be applied to a curve $\chi(t)$ can also be checked by plotting $\ln[\chi(t)]$ against t for $t > t_m$. If a straight line is obtained for only the smallest section of the descending branch of the signal curve, the curve will be unsuitable for determining h and k.

THE COMPLEXLY VARIABLE HEAT FLUX

In the preceding section, it was shown that it is possible to integrate exactly eqn. (2) or (3) for the linearly variable source heat flux in order to calculate the associated signal curve. The task of transforming the signal curve into the underlying source flux curve is, therefore, basically reversible. In the case of a source heat flux that is completely variable with time, the integration of eqn. (2) must, however, be replaced by a summation.

Any source heat flux Φ that is complexly variable with time can be sub-divided into temporal sections so that, in such a section Δz, a linear variation of the heat flux can be assumed to a good approximation. The total duration z_e of the complex event is thus subdivided into n sections Δz, the number n being greater, the greater the variation of Φ with the time z

$$\Delta z = z_e/n \tag{16}$$

Within the time interval Δz, the measure of time ζ is introduced for which

$$\zeta \in [0, \Delta z] \quad \text{and} \quad \zeta_e = \Delta z \tag{17}$$

are valid. Thus, according to eqn. (10) and on account of eqn. (4), $\Phi = q_1 + a_1\zeta$, the following is valid for the first section

$$
\begin{aligned}
\chi_1 = [1/(h-k)]\{ & h(q_1 + a_1\zeta - a_1h) \exp[-(t-\zeta)/h] \\
& - k(q_1 + a_1\zeta - a_1k) \exp[-(t-\zeta)/k] \\
& - h(q_1 - a_1h) \exp(-t/h) + k(q_1 - a_1k) \exp(-t/k)\}
\end{aligned}
$$

For the ith section, the following applies

$$
\begin{aligned}
\chi_i = [1/(h-k)]\{ & h(q_i + a_i\zeta - a_ih) \exp\{-[t-(i-1)\Delta z - \zeta]/h\} \\
& - k(q_i + a_i\zeta - a_ik) \exp\{-[t-(i-1)\Delta z - \zeta]/k\} \\
& - h(q_i - a_ih) \exp\{-[t-(i-1)\Delta z]/h\} \\
& + k(q_i - a_ik) \exp\{-[t-(i-1)\Delta z]/k\}\}
\end{aligned}
\tag{18}
$$

with $t - (i-1)\Delta z \geq \zeta$.

As a result by summing all the component curves

$$\chi(t) = \sum_{i=1}^{n} \chi_i(t) \tag{19}$$

is obtained as a response $\chi(t)$ to a source heat flux that varies complexly with time and of duration z_e.

Figure 3 shows the retransformation of the source flux curve $\Phi(z)$ obtained from the signal curve $\chi(t)$ for the thermal decomposition of magnesium hydroxide into the signal curve, as an example of the application of the method given by eqns. (18) and (19). In this case, the source heat flux is directed into the decomposing sample, which constitutes a heat sink. Figure 3 illustrates that the reversal by subdivision of $\Phi(z)$ into $n = 35$ temporal sections and application of the method to these has yielded satisfactory results. The accuracy can be arbitrarily increased by increasing n.

USE OF THE SIGNAL CURVE CALCULATION FOR CHECKING A REACTION-KINETIC MODEL

Heat flux calorimeters, particularly the DSC type, have, in many cases, been used successfully for reaction-kinetic investigations of relatively slow
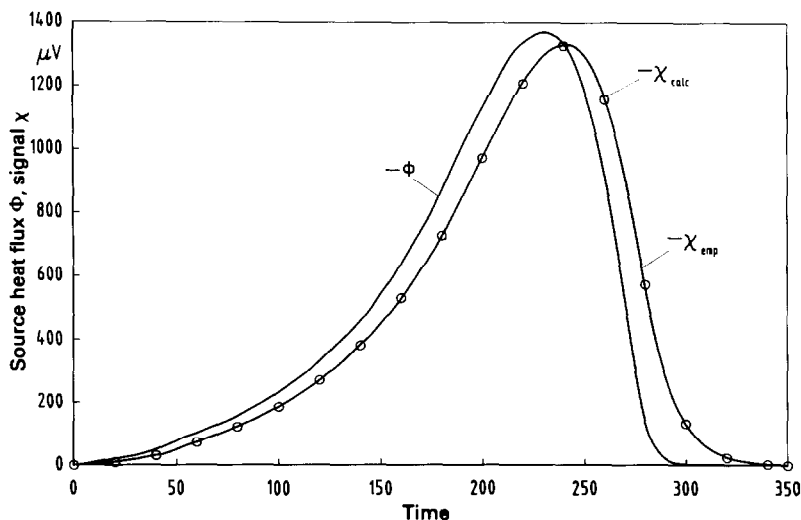
Fig. 3. Retransformation of Φ into χ_{calc} with eqns. (18) and (19). Φ had been obtained by transformation of χ_{emp} with eqn. (2). The signal curve $\chi_{emp}(t)$ had been plotted during the thermal decomposition of 7.33 mg $Mg(OH)_2$ in the Netzsch DSC444 at a heating rate of 20 K min^{-1}. The time constants were $h = 12.13$ s and $k = 0.483$ s. The caloric sensitivity was $E = 14.47$ μV mW^{-1}, the thermopile gradient $\sigma = 970$ μV K^{-1} and the thermal conductivity resistance $R_\lambda = 0.01492$ K mW^{-1}. In this case, χ/E is thus the effluent heat flux.

reactions proceeding according to a simple pattern. But errors are possible, all the same, when the equivocal concept of "slow" is defined too widely. As shown in Fig. 3, it will already be necessary to de-smear the signal curve (transform it into the source flux curve) if the half-time of the reaction is approximately 17 times greater than time constant $h = \tau_1$. Not χ but Φ describes the reaction course correctly. A simple method for carrying out the transformation has been described in Part 1. But an analysis of the exactly determined source flux curve in order to clarify the reaction mechanism, can be very difficult or even impossible with complex reactions because too many quantities that vary in the course of the reaction are covered by a single curve.

In the case of reactions with a complex course, other methods in addition to thermal analysis must be used to investigate the mechanism [6]. For this, classical chemical procedures and physical methods such as spectrometry are suitable. When the investigation results ultimately allow a reaction-kinetic model of the reaction course to be established, this can be checked by a test in the heat flux calorimeter; the model and eqns. (18) and (19) are used to calculate the signal curve which is compared with the curve found by experiment. This checking procedure is represented below. For the sake of simplicity, it will be assumed that the calorimeter emits χ as the effluent heat flux.

As soon as a reaction-kinetic model is available, it is used to represent the reaction rate in the form of the rate of conversion in a formula. As a generalization, the rate of conversion $r = d\alpha/dt$ can be written

$$r = K(\Theta)f(\alpha) \tag{20}$$

The particular form of $f(\alpha)$ is given by the mechanism. The so-called rate constant $K(\Theta)$ is a function of the temperature T which can, in turn, be a function of time due to the gradual heating by reaction heat and/or due to a superimposed variation in T with t, for example, when the calorimeter is used in the scanning mode, i.e. $\Theta = T(t)$. As α is also a function of the time t, the following is obtained for the variation of r with time

$$\frac{dr}{dt} = \frac{d[K(\Theta)]}{dt}f(\alpha) + K(\Theta)\frac{d[f(\alpha)]}{d\alpha}\frac{d\alpha}{dt} = \left\{\frac{d[K(\Theta)]}{dt} + [K(\Theta)]^2\frac{d[f(\alpha)]}{d\alpha}\right\}f(\alpha) \tag{21}$$

To adapt eqns. (20) and (21) to eqns. (18) and (19), t in eqns. (20) and (21) is replaced by z and ζ, respectively. As in the preceding sections, z is the measure of time for the source heat flux, and, hence, also for the reaction, ζ is the measure of time within a time section Δz, and t is the time of observation which is identical with z during the reaction time but then extends beyond the latter.

At the instant z, the reaction-induced source heat flux is

$$\Phi(z) = -r(z)\Delta_r H \tag{22}$$

where $\Delta_r H$ is the reaction enthalpy for the used mass which reacts until equilibrium is reached. To achieve a good fit of the calculated curve $\chi(t)$ to the experimental curve $\chi_{emp}(t)$, $-\Delta_r H$ is taken from the graphical or numerical integration of $\chi_{emp}(t)$. It is necessary here to carry out the baseline correction which must also be considered in this investigation.

The duration of the reaction is z_e. Regarding the reaction rate $r(z)$, the variable z is subdivided into n sections of duration $\Delta z = z_e/n$, so that linearity in such a time section may be assumed, to a good approximation, for both $r(z)$ and $\phi(z)$ within these sections. In Δz, the measure of time ζ is introduced, which runs from 0 to $\zeta_e = \Delta z$.

At the instant when the reaction starts, $t = z = 0$ and $\alpha = 0$; this does not, however, apply to $r = d\alpha/dz$ and dr/dz. The degree of conversion $\alpha(z)$ to be entered into $r(z)$ can be determined as follows

$$\Delta_i\alpha = [r_{i-1} + (dr/dz)_{i-1}(\Delta z/2)]\Delta z \tag{23}$$

and

$$\alpha(z) = \sum_{i=1}^{v} \Delta_i\alpha \tag{24}$$

where v are the steps selected between 0 and the instant z, i.e. $v\Delta z = z$. The Δz selected must be so small that any additional reduction yields a result for $\alpha(z)$ that is practically identical with the result first calculated.

When the Arrhenius formulation is used for the coefficient $K(\Theta)$ in eqn. (20), $K(\Theta) = K_T \exp(-E_A/R\Theta)$, where

$$\Theta_{i-1} = T_{i-1} + \beta\zeta \tag{25}$$

is set for Θ, to a first approximation, and β is the heating rate in the scanning operation. For $i = 1$, $T_0 = T(0)$, i.e. the temperature at the beginning of the reaction. With these specifications, the following is to be entered into eqn. (21) for $d[K(\Theta)]/dt$

$$\frac{d[K(\Theta)]}{dt} = K_T \frac{E_A \beta}{R\Theta^2} e^{-E_A/R\Theta} \tag{26}$$

As T_{i-1} is very great compared with $\beta\zeta$, it is possible to consider Θ to be constant and to set $\Theta = T_{i-1} + \beta\Delta z/2$ when Δz is small enough. This allows eqn. (21) to be evaluated from eqns. (23)–(26).

With the specifications selected, $\phi(z)$ is also subdivided into n sections of duration Δz such that during Δz a linear development with the time ζ may be assumed. In the ith section, $\phi_i(\zeta) = q_i + a_i\zeta$.

According to eqn. (22)

$$q_i = -r_{i-1}\Delta_r H \tag{27}$$

and according to eqn. (21)

$$a_i = -(dr/dz)_{i-1}\Delta_r H \tag{28}$$

Equation (27) is valid for the beginning of every time section Δz, where the temperature always has a fixed value. This value is T_{i-1} (because of $\zeta = 0$) and is to be introduced into the Arrhenius formulation for the evaluation of eqn. (27). With the values calculated from eqns. (27) and (28), eqn. (18) is used to calculate χ_i.

The first steps will be described briefly. First the component curve χ_1, which starts at the beginning of the reaction is obtained. At the point $t = \Delta z$, the ordinate of this point is read off from χ_1. This allows the difference ΔT between the temperature of the reacting sample and the temperature T_0 imposed by the scanning to be determined, as χ corresponds, or is proportional, to this temperature difference, i.e. $A\chi = \Delta T$. Provided that the calorimeter outputs χ as the temperature, the proportionality factor A is 1. If, however, χ is output as effluent heat flux, as in this case, A is the thermal conductivity resistance R_λ which is also a function of temperature and must be known as such. Now the temperature of the reacting sample at $t = \Delta z$ can be estimated from

$$T_1 = T_0 + \beta\Delta z + A\chi_1(t = \Delta z)$$

for the calculation of r_1 with $K(T)$ and

$$\Theta_1 = T_1 + \beta \Delta z/2 \tag{29}$$

for the calculation of dr/dz.

For the second section, i.e. $i = 2$, T_1, or rather Θ_1, is introduced into eqns. (26), (27) and (28), and with these, χ_2 is calculated using eqn. (18). Then χ_1 and χ_2 are added

$$\chi_{S_2} = \chi_1 + \chi_2$$

Now the ordinate is read off on χ_{S_2} at the point $t = 2\Delta z$ to estimate T_2 for the calculation of χ_3

$$T_2 = T_0 + 2\beta \Delta z + A\chi_{S_2}(t = 2\Delta z)$$

$$\Theta_2 = T_2 + \beta \Delta z/2$$

This pattern is followed further until the following intermediate stage is reached by summing the component curves χ_1 to χ_v:

$$\chi_{S_v} = \sum_{i=1}^{v} \chi_i \tag{30}$$

The ordinate is picked off from χ_{S_v} at the point $t = v\Delta z$ in order to estimate T_v according to

$$T_v = T_0 + v\beta \Delta z + A\chi_{S_v}(t = v\Delta z) \tag{31}$$

The mean temperature within each interval Δz is larger by the term $\beta \Delta z/2$, i.e. here $\Theta_v = T_v + \beta \Delta z/2$. The result serves to calculate χ_{v+1}, etc. At the end, the final result is obtained

$$\chi(t) = \sum_{i=1}^{n} \chi_i \tag{32}$$

When the signal curve $\chi(t)$ calculated according to eqn. (32) agrees satisfactorily with the $\chi_{emp}(t)$ found by experiment, the model being checked can be considered confirmed.

CONCLUSION AND OUTLOOK

The matematical handling of the events in heat flux calorimeters shows how the signal from the calorimeter $\chi(t)$ is associated with the source heat flux $\Phi(t)$. The relation between $\Phi(t)$ and $\chi(t)$ is described with sufficient accuracy by eqn. (2). The application of a differential equation of an order higher than second is therefore not required here, because the time constants represent a sequence which decreases so rapidly that the products of the higher differential quotients and the coefficients formed from the time constants would become practically insignificant.

Equation (2) contains two time constants. Part 1 of this investigation deals with the mathematical bases of the experimental determination of these constants. It is obvious that the more accurate the determination of the time constants, the more accurate the transformation of the signal curve $\chi(t)$ into the source heat flux curve $\Phi(t)$. $\Phi(t)$ reflects the reaction event to be investigated, whereas $\chi(t)$ is a "smeared" reflection.

The time constants represent products of heat capacities and thermal conductivity resistances and are, therefore, temperature-dependent. To determine the dependence of the time constants on the temperature, these must be determined at several temperatures. There is also, however, an influence exerted by the kind and mass of the reactive substance to be examined in the heat conduction calorimeter, which chiefly affects the greater of the two time constants. Provided that this substance is very similar to the inert substance used for calibration in terms of thermal properties and mass, no problems arise. Otherwise, a correction must be applied to the greater of the two time constants. The higher the share of the calorimeter-specific heat conduction resistance and of the heat capacity in the total heat conduction resistance and in the total heat capacity, the smaller the correction necessary. Furthermore, the time constants will be influenced if flowing gases are used. The use of auxiliary gases must therefore be taken into account when the calibration is carried out.

In the course of the reaction or of a phase transition, the thermal conductivity resistance in the substance being examined often changes. The influence of this phenomenon can be kept small when small layer thicknesses are used.

A mathematically exact procedure to transform $\chi(t)$ into $\Phi(t)$ should be reversible, i.e. when $\Phi(t)$ is given, it should be possible to calculate $\chi(t)$. The reversion would offer the possibility of checking kinetic models for their correctness by using thermoanalytical measurements.

For a source heat flux $\Phi(z)$ that is linearly variable in the time interval from $t = 0$ to $t = z_e$, the exact integration of eqn. (2) is possible in the form of eqn. (3). When the time constants h and k are known, this allows the signal curve $\chi(t)$ as a response to $\Phi(z)$ to be calculated. The integration result is given by eqn. (10).

If the source heat flux $\Phi(z)$ is a complex time function, the integration of eqn. (2) is replaced by the sum of a great number of partial integrals of the type of eqn. (10). By increasing the number n of the terms in the sum, the accuracy can be arbitrarily improved. The procedure is described by eqns. (18) and (19). Figure 3 shows an example of the retransformation of the curve $\Phi(t)$, obtained by transformation of $\chi(t)$, into the original curve $\chi(t)$ which was plotted for the thermal decomposition of magnesium hydroxide in the Netzsch-DSC 444. Here, n is 35.

Finally, the application of the procedure defined by eqns. (18) and (19) to the examination of reaction-kinetic models is presented. These models

can be obtained by investigation of the reaction using several methods. Whether such a model describes the mechanism of a reaction formally and correctly can be checked thermoanalytically according to the pattern described above. The necessary experiment is carried out in a heat flux calorimeter in isoperibolic or scanning operation. The scanning mode allows a temperature variation to be increased in the course of the reaction. The principle of the model test consists of a comparison between the signal curve $\chi(t)$, calculated on the basis of the model, and the curve $\chi_{emp}(t)$, obtained by experiment. The procedure for the calculation is based on the set of equations, eqns. (18)–(32).

It remains to examine the extent to which the calculation procedures developed for heat flux calorimeters can be applied to power-compensated differential scanning calorimeters. In these instruments, the calorimeter-specific thermal conductivity resistances and heat capacities are generally substantially smaller than those of heat flux calorimeters. As a result, the time constants are smaller than in heat flux calorimeters; therefore the influence of the mass and of the thermal properties of the substance under examination on the greater time constant, $h = \tau_1$, is much more appreciable.

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