Thermochimica Acta, 215 (1993) 15–23
Elsevier Science Publishers B.V., Amsterdam

Thermokinetics in conduction calorimetry: the lower limits in dynamic heat-power resolution

Eugeniusz Margas [a], Vicenç Torra [b] and Wojciech Zielenkiewicz [a]

[a] *Institute of Physical Chemistry of the Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw (Poland)*
[b] *Dep. Fisica Aplicada, ETSECCIP-UPC, Jordi Girona Salgado 31, E-08034 Barcelona (Spain)*

(Received 24 April 1992)

Abstract

This paper gives the necessary conditions for determining the minimal heat power W_0 on the basis of the minimal increase in the output function in conduction calorimetry. It is shown that W_0 depends on the duration of the constant heat effect, the sensitivity of the dynamic calorimeter, the noise level, the signal/noise ratio and the time constants of the instrument. The results of the calculation of the static and dynamic heat-power resolution are presented.

INTRODUCTION

The application of dynamic calorimetry in the determination of the evolution of heat power with time, e.g. thermogenesis and thermokinetics [1, 2], is increasing. For this purpose, many sophisticated devices are used to study, for example, the kinetic rates of reaction in the hardening of cement and cement minerals [3], the phase transition phenomena in memory alloys [4] and the processes occurring in inclusion compounds [5, 6].

As a result of calorimetric determinations, we have obtained thermograms corresponding to temperature changes with time; however, these do not correspond to the thermokinetics. It is well known that a calorimeter is an inertial object that is a transducer of the input function (heat power) into an output function (thermogram). The thermogram represents a sum of partial, to some extent degraded, information about the process studied. Nevertheless it can be elaborated to obtain the input function — the thermokinetics [7]. The distortion of the output function

Correspondence to: W. Zielenkiewicz, Institute of Physical Chemistry of the Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland.

0040-6031/93/$06.00

depends on the dynamic properties of the device and the signal-to-noise ratio.

DYNAMIC RESOLUTION LIMITS

For determination of the heat-power evolution with time, it is necessary to know the change in the output signal of the calorimeter. Let us then try to answer the question: what is the minimal heat power W_0 sufficient to provide a perceptible increase in the output signal? To solve this problem, we must consider the set of basic data characterizing the static and dynamic parameters of the calorimeter, the sampling period γ and the noise level of the output signal.

Having these data, let us try to determine the approximated general relationship between W_0 and the parameters characterizing the calorimeter and the process under study.

We assume that the calorimeter is calibrated by a constant heat pulse over a short time interval γ, corresponding to [8–11]

$$\gamma = \Delta t \approx \tau_1/300 \tag{1}$$

where τ_1 is the time constant. Then, the change in the output signal (the thermogram) corresponds to the pulse response $h(t)$, which has the form

$$h(t) = \sum_{i=1}^{N} a_i e^{-t/\tau_i} \tag{2}$$

where N is the order of the system and a_i is the pre-exponential coefficient.

The area A of the thermogram is given by

$$A = \int_0^\infty h(t)\,dt = \sum_{i=1}^{N} a_i\tau_i \tag{3}$$

In the simplest case, eqns. (2) and (3) can be approximated by

$$h(t) \approx a_1^* e^{-t/\tau_1} \qquad A \approx a_1^* \tau_1 \tag{4}$$

where a_1^* corresponds to the maximal increase in temperature Θ_{max}.

The sensitivity S, the static parameter of the calorimeter, is given by the relationship

$$S = \Theta_{max}\tau_1/W_0\gamma \tag{5}$$

In order to observe W_0, let us assume that Θ_{max} is k times greater than the noise level b

$$\Theta_{max} \geqslant kb \tag{6}$$

Taking into account eqns. (5) and (6)

$$SW_0\gamma/\tau_1 \geqslant kb \tag{7}$$

Thus

$$W_0 \geqslant kb\tau_1/S_\gamma \tag{8}$$

The condition (8) seems to be sufficient to determine the value W_0, from which determination of the $W(t)$ function is possible. In the condition it was assumed that the dynamic properties of the calorimeter can be expressed by only one time constant. Nevertheless, Θ_{max} and S values were obtained experimentally, thereby characterizing uniquely a given calorimeter.

Let us treat this relationship as a general, approximated dependence and proceed to more particular considerations, so as to confirm the degree to which it is in accord with the particular relationships for calorimeters, which can be described by different mathematical models, see for example ref. 12, the simple body model [13], the two-body model [14] and the N-body model [15–19].

DETERMINATION OF W_0 BY CALORIMETRIC MODELS

For a calorimeter treated as a simple body, its properties can be described by the equation

$$\tau_1 \frac{d\Theta_1(t)}{dt} + \Theta_1(t) = SW(t) \tag{9}$$

Let us assume that a constant heat effect of amplitude W_0 and time duration time γ is associated with the calorimeter. Then $W(t)$ can be expressed in the form

$$W(t) = W_0[u(t) - u(t-\gamma)] \tag{10}$$

where $u(t)$ is a step function. Taking into account relationship (10), at zero initial condition the solution of eqn. (9) has the form

$$\Theta_1(t) = \begin{cases} SW_0[1-\exp(-t/\tau_1)] & \delta t \in \langle 0, \gamma) \\ \Theta_1(\gamma)\exp[-(t-\gamma)/\tau_1] & \delta t \in \langle \gamma, \infty) \end{cases} \tag{11}$$

From condition (1) $\gamma \ll \tau_1$, the value of the expression $[1-\exp(-t/\tau_1)]$ for $t=\gamma$ can be approximated by

$$1-\exp(-\gamma/\tau_1) \approx \gamma/\tau_1 \tag{12}$$

Thus

$$\Theta_1(\gamma) \approx SW_0\gamma/\tau_1 = y_1 \tag{13}$$

The plot of function (11) is shown in Fig. 1. From Fig. 1, $\Theta_1(\gamma)$ is the highest value for the response of the calorimetric system. If

$$y_1 > b \tag{14}$$

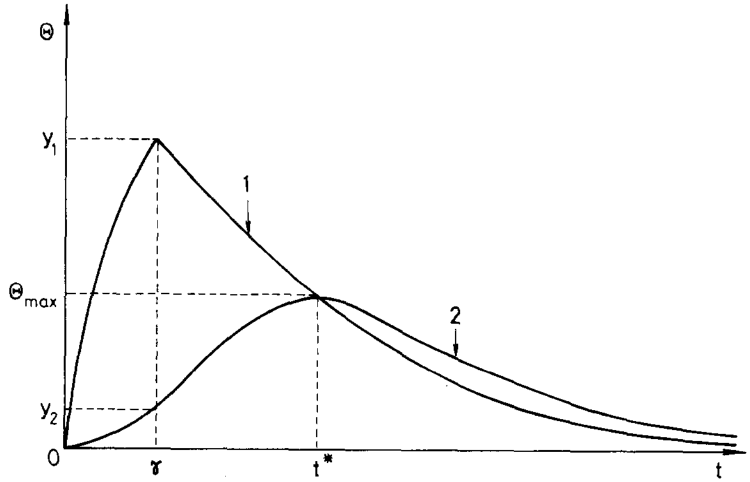

Fig. 1. The plots of the functions: 1, eqn. (11); 2, eqns (18) and (19).

we obtain

$$SW_0\gamma/\tau_1 > b \tag{15}$$

and

$$W_0 > b\tau_1/S\gamma \tag{16}$$

Thus, for a calorimeter treated as a simple body we obtain a relationship identical to the experimental one.

A calorimeter treated as a two-body system of concentric configuration [14] can be described by a set of equations

$$C_1\frac{d\Theta_1(t)}{dt} + G_{12}[\Theta_1(t) - \Theta_2(t)] + G_{01}\Theta_1(t) = W(t) \tag{17}$$

$$C_2\frac{d\Theta_2(t)}{dt} + G_{12}[\Theta_2(t) - \Theta_1(t)] = 0 \tag{18}$$

where C_1 and C_2 are the heat capacities of particular bodies, and G_{01} and G_{12} are heat loss coefficients. The solution of eqns. (17) and (18) with respect to $\Theta_2(t)$ at zero initial conditions, has the form

for $t \in \langle 0, \gamma)$

$$\Theta_2(t) = SW_0\left(1 - \frac{\tau_1}{\tau_1 - \tau_2}e^{-t/\tau_1} + \frac{\tau_2}{\tau_1 - \tau_2}e^{-t/\tau_2}\right) \tag{19}$$

for $t \in \langle \gamma, \infty)$

$$\Theta_2(t) = A_1e^{-(t-\gamma)/\tau_1} + A_2e^{-(t-\gamma)/\tau_2} \tag{20}$$

where τ_1 and τ_2 are time constants of the system, and coefficients A_1 and A_2 have the form

$$A_1 = \tau_1[\Theta_2(\gamma) + \tau_2\Theta_2'(\gamma)]/(\tau_1 - \tau_2) \tag{21}$$

$$A_2 = -\tau_2[\Theta_2(\gamma) + \tau_1\Theta_2'(\gamma)]/(\tau_1 - \tau_2) \tag{22}$$

and $\Theta_2'(\gamma)$ denotes the value of the derivative of the function $\Theta_2(t)$ for $t = \gamma$. The plot of the function $\Theta_2(t)$ is shown in Fig. 1.

Applying the approximation of the function e^{-x} for small values of x

$$e^{-x} \approx 1 - x + 0.5x^2 \tag{23}$$

the value of the function $\Theta_2(t)$, eqn. (20), for $t = \gamma$ when $\gamma \ll \min\{\tau_1, \tau_2\}$, can be expressed as

$$y_2 = \Theta_2(\gamma) \approx SW_0\left[1 - \frac{\tau_1}{\tau_1 - \tau_2}(1 - \gamma/\tau_1 + 0.5\gamma^2/\tau_1^2) + \frac{\tau_2}{\tau_1 - \tau_2}(1 - \gamma/\tau_2 + 0.5\gamma^2/\tau_2^2)\right] \tag{24}$$

or

$$y_2 \approx SW_0\gamma^2/2\tau_1\tau_2 \tag{25}$$

As presented in Fig. 1, the value of $\Theta_2(\gamma)$ is smaller than the highest value of the response $\Theta_2(t)$ of the calorimeter. The upper value of $\Theta_2(t)$ is reached in time t^*, longer than $\gamma(t^* > \gamma)$, and is lower than that previously obtained if we assume that the time constant τ_1 is the same in both cases. It can be calculated from the relationship obtained from the following considerations. If we compare y_2 and y_1 from relationships (13) and (25), we have

$$\Theta_2(\gamma) = \Theta_1(\gamma)\gamma/2\tau_2 \tag{26}$$

Then the ratio $\Theta_1(\gamma)$ to $\Theta_2(\gamma)$ depends upon the values of γ and τ_2.

The derivative of $\Theta_2(t)$ at point t^* is equal to zero

$$\left.\frac{d\Theta_2(t)}{dt}\right|_{t=t^*} = 0 \tag{27}$$

Differentiating the function (20) with respect to time t and taking into account condition (27), we obtain

$$(A_1/\tau_1)e^{-(t^*-\gamma)/\tau_1} + (A_2/\tau_2)e^{-(t^*-\gamma)/\tau_1} = 0 \tag{28}$$

Putting

$$\alpha = e^{-(t^*-\gamma)/\tau_1} \tag{29}$$

condition (28) can be written in the form

$$(A_1/\tau_1)\alpha + (A_2/\tau_2)\alpha^{\tau_1/\tau_2} = 0 \tag{30}$$

Dividing it by α ($\alpha \neq 0$)

$$A_1/\tau_1 + (A_2/\tau_2)\alpha^{(\tau_1-\tau_2)/\tau_2} = 0 \tag{31}$$

Thus

$$\alpha = (-A_1\tau_2/A_2\tau_1)^{\tau_2/(\tau_1-\tau_2)} \tag{32}$$

From relationship (29)

$$e^{-(t^*-\gamma)/\tau_1} = (-A_1\tau_2/A_2\tau_1)^{\tau_2/(\tau_1-\tau_2)} \tag{33}$$

Then

$$t^* = \gamma + [\tau_1\tau_2/(\tau_1-\tau_2)]\ln(-A_2\tau_1/A_1\tau_2) \tag{34}$$

Using eqns (21) and (22), we finally get

$$t^* = \gamma + \frac{\tau_1\tau_2}{\tau_1-\tau_2}\ln\left[\frac{\Theta_2(g)+\tau_1\Theta_2'(\gamma)}{\Theta_2(\gamma)+\tau_2\Theta_2'(\gamma)}\right] \tag{35}$$

Substituting the value t^* in function (20), we can calculate $\Theta_2(t^*)$

$$\Theta_{\max} = \Theta_2(t^*) = A_1 e^{-(t^*-\gamma)/\tau_1} + A_2 e^{-(t^*-\gamma)/\tau_2} \tag{36}$$

if we know the time constants of the calorimeter.

We consider also the calorimetric system which can be treated as an N-body system of concentric configuration (thermal coupling with next-neighbours), which is described by a set of equations

$$C_1\frac{d\Theta_1(t)}{dt} + G_{01}\Theta_1(t) + G_{12}[\Theta_1(t)-\Theta_2(t)] = 0$$

$$C_k\frac{d\Theta_k(t)}{dt} + G_{k-1,k}[\Theta_k(t)-\Theta_{k-1}(t)]$$

$$+ G_{k,k+1}[\Theta_k(t)-\Theta_{k+1}(t)] = 0 \qquad k = 2, 3, \ldots, N-1$$

$$C_N\frac{d\Theta_N(t)}{dt} + G_{N-1,N}[\Theta_n(t)-\Theta_{N-1}(t)] = W(t) \tag{37}$$

where the calorimeter is the inertial N-order system with time constants $\tau_1, \tau_2, \ldots, \tau_N$. Its response $\Theta_N(t)$ to a heat pulse of constant power W_0 and time duration γ, at zero initial conditions, can be expressed in the form

for $t \in \langle 0, \gamma)$

$$\Theta_N(t) = SW_0\left(1 - \sum_{i=1}^{N} B_i e^{-t/\tau_i}\right) \tag{38}$$

where the coefficients B_i satisfy the conditions

$$\sum_{i=1}^{N} B_i = 1 \tag{39}$$

$$\sum_{i=1}^{N} B_i/\tau_i^k = 0 \qquad k = 1, 2, \ldots, N-1$$

for $t \in \langle \gamma, \infty)$

$$\Theta_N(t) = \sum_{i=1}^{N} A_i e^{-(t-\gamma)/\tau_i} \tag{40}$$

and the coefficients A_i are calculated from the final conditions of function (38) for $t = \gamma$.

Using the approximation

$$e^{-x} = \sum_{k=0}^{N} \frac{1}{k!} x^k \tag{41}$$

the value of function (38) for $t = \gamma$ can be expressed as

$$\Theta_N(\gamma) \approx SW_0\left[1 - \sum_{i=1}^{N} B_i \sum_{k=0}^{N} \frac{1}{k!} (\gamma/\tau_i)^k\right] \tag{42}$$

Using conditions (39) and after the transformation, relationship (42) can be presented as

$$\Theta_N(\gamma) \approx SW_0\gamma^N/N! \prod_{i=1}^{N} \tau_i \tag{43}$$

The sequence of values $\{\Theta_n(\gamma)\}$ satisfy the condition

$$\Theta_n(\gamma) = \Theta_{n-1}(\gamma)\gamma/n\tau_n; \qquad n = 2, 3, \ldots, N \tag{44}$$

Assuming that Θ_{max}^N is proportional to $\Theta_N(\gamma)$

$$\Theta_{max}^N \approx \Theta_N(\gamma)N! \prod_{i=2}^{N} \tau_i/\gamma^{N-1} \tag{45}$$

Then, using the relationships (39) and (29), we obtain the equation which must be satisfied in the maximal point

$$\sum_{i=1}^{N} (A_i/\tau_i)\alpha^{\tau_i/\tau_1} = 0 \tag{46}$$

This equation can only be solved by iteration methods for the given values of the parameters of the system.

The evaluation of the maximal value Θ_{max} suggests that formula (6) can be applied with good approximation for any order systems. Knowing the values of the dynamic parameters of the system, the maximal value of the

TABLE 1

Heat-power resolution of several calorimeters: S, sensitivity; τ_1, first time constant; γ, sampling period; b, noise level; k, signal/noise used; W_0, heat-power resolution (dynamic); W_S, heat-power resolution (static or standard)

Calorimeter [a]	S (mV W^{-1})	τ_1 (s)	γ (s)	b (μV)	k	W_0 (μW)	W_S (μW)
HRC*	400	10	1	1	2	50	5
HRC	400	10	1	0.1	2	5	0.5
Calvet	60	200	1	0.01	2	70	0.3
EU	120	180	1	0.05	2	15	0.8
EUTC	270	64	1	0.1	2	5	0.07
EUM	205	205	1	0.05	2	10	0.05
LKB	100	115	1	0.05	2	11.5	0.1
MAM	20	40	1	0.06	2	24	0.6

[a] HRC*, high-resolution calorimeter with programmed Peltier cooling/heating [4]; HRC, high-resolution calorimeter (spontaneous heating/cooling) [2]; Calvet; Tian–Calvet type calorimeter [20]; EU, conduction calorimeter [21]; EUTC, conduction calorimeter [21]; EUM, conduction calorimeter [21]; LKB, batch calorimeter [6, 22]; MAM, modified adsorption microcalorimeter [23].

impulse response can be calculated. The way to calculate the maximal value is demonstrated in the examples above.

Table 1 gives the values of the parameters and the values of the minimal power for a number of calorimeters of varying dynamic properties. From data given in the table, it can be seen that the dynamic resolution limit W_0 is different from the static resolution W_S ($W_S = Kb/S$) which is the standard resolution used for the steady-state estimation of the limits of each calorimetric device.

CONCLUSIONS

The dynamic criterion obtained makes it possible to reconstruct the smallest heat effects liberated during the heat reaction in a calorimeter. The relationship we propose has a general character and does not depend on the calorimetric system under investigation. A valuable advantage of this relationship is that, to a better degree than the static resolution given in previous works, it characterizes the suitability of the calorimeter for thermokinetics studies.

REFERENCES

1 W. Zielenkiewicz (Ed.), Thermokinetics. Signal Processing in Calorimetric System, Ossolineum, Wrocław, 1990.
2 H. Tachoire, J.L. Macqueron and V. Torra, Thermogenesis by Heat Conduction Calorimetry, in M.A.V. Riberio da Silva (Ed.), Thermochemistry and Its Applications to Chemical and Biochemical Systems, NATO ASI Series C 119, D. Reidel, Dordrecht, p. 77.

3 M. Kamiński and W. Zielenkiewicz, Cem. Concr. Res., 12 (1982) 549.
4 A. Amengual and V. Torra, J. Phys. E: Sci. Instrum., 22 (1989) 433.
5 J. Lipkowski, A. Zielenkiewicz, J. Hatt and W. Zielenkiewicz, J. Inclusion Phenomena, 7 (1989) 511.
6 W. Kibalczyc, A. Zielenkiewicz and W. Zielenkiewicz, Thermochim. Acta, 131 (1988) 47.
7 J. Ortin, A. Ramos, J. Vinals, E. Margas and W. Zielenkiewicz, Thermochim. Acta, 76 (1984) 325.
8 E Cesari, J. Ortin, V. Torra, J. Vinals, J.L. Macqueron, J.P. Dubes and H. Tachoire, Thermochim. Acta, 53 (1982) 29.
9 J. Hatt, E. Margas and W. Zielenkiewicz, Thermochim. Acta, 64 (1983) 305.
10 W. Zielenkiewicz, J. Therm. Anal., 29 (1984) 179.
11 W. Zielenkiewicz, E. Margas and J. Hatt, Thermochim. Acta, 88 (1985) 387.
12 W. Zielenkiewicz and E. Margas, Podstawy teoretyczne kalorymetrii dynamicznej, Ossolineum, Wrocław, 1990.
13 W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 14 (1966) 583.
14 E. Margas and W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 28 (1980) 89.
15 E. Margas and W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 26 (1978) 503.
16 J.L. Macqueron, J. Navarro and V. Torra, Proc. 3rd Meeting on Calorimetry and DTA, 3–4 February 1977, Dep. Termologia and RSEFyQ, Univ. Barcelona (Spain), 1977, pp. 90–101 (in Spanish).
17 E. Margas, A. Tabaka and W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 20 (1972) 323.
18 E. Margas, A. Tabaka and W. Zielenkiewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 20 (1972) 329.
19 W. Zielenkiewicz and E. Margas, Proc. VIIth Union Conf. Cal., Moscow State University, Moscow, 1977 (in Russian).
20 E. Calvet and H. Prat, Microcalorimetre, Masson, Paris, 1956.
21 W. Zielenkiewicz and E. Utzig, Raport, IChF PAN, 1990.
22 LKB 10700-2 Batch Microcalorimeter, Operation Manual, LKB Produkter AB, Bromma, Sweden.
23 L. Zommer, R. Duś and S.L. Randzio, Appl. Surf. Sci., 45 (1990) 93.