Thermochimica Acta, 25 (1978) 269–275

TRANSFORM OF A THERMOGRAM INTO A THERMOGENESIS CURVE BY THE USE OF THE FREQUENCY TRANSFER FUNCTION OF A CALORIMETER

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(Received 7 October 1977)

ABSTRACT

In calorimeter experiments, we obtain the thermogram $y = y(t)$, temperature variation $y(t)$ as a function of time t, when thermal reaction occurs in the calorimeter reaction cell. For thermokinetic studies, we need to know the calorific power generated in the cell, due to the thermal reaction, as a function of time. By use of the frequency transfer function of the calorimeter, we can calculate numerically the calorific power at any time from numerical analysis of the thermogram without any assumption of analytical form of the transfer function.

The method is composed of three steps. (1) Experimental determination of the frequency transfer function G of the calorimeter from numerical analysis of the thermogram which is obtained by applying a constant calorific power in the calorimeter cell. (2) Numerical Laplace transform $L[y] = Y$ of the thermogram which is recorded when the thermal reaction under investigation occurs in the cell. (3) Numerical determination of the calorific power, evolved by the thermal reaction in the cell, by numerical inverse Laplace transform of Y/G.

This method is examined in two ways. First, simulation by numerical calculation on a mathematical model calorimeter is done and the accuracy of the method is assured. Second, experiments and numerical analysis on the heat-flow (conduction) type of calorimeter are performed to test the availability of the method.

INTRODUCTION

In calorimeter experiments we obtain the thermogram which is a record of some quantity as a function of time. The value is usually given by the position of a pen on an electronic recorder, or out-put signal from a measuring device of the calorimeter. In some cases, the output is proportional to the calorimeter temperature change and in others, such as in DSC experiments, it is proportional to the electronic heat power produced in the heater of the calorimeter cell. In all cases, the measured quantity is neither equal to nor strictly proportional to the calorific power produced by a thermal reaction to be investigated in the calorimeter cell. But it is often more necessary to obtain the calorific power rather than the thermogram especially in the case of thermokinetic study. Therefore, our problem is how to obtain the calorific power produced within the calorimeter cell starting from the measured thermogram.

For this problem, several authors have presented some methods of analysis of the thermogram. Calvet expressed the thermogram curve by a series of exponentials and tried to solve the equation by an analytical or graphical method[1]. Tateno and Tachoire[2,3] treated the thermogram by the Laplace transform, and expressed the transfer function (TF) of the calorimeter in a simple analytical expression. However, for more precise treatments, we must use a more complex form of the expression and determine a larger number of calorimeter constants in the expression. As this is very complicated and difficult work, we have used the frequency transfer function (FTF) of the calorimeter and calculated the calorific power from an analysis of the thermograms without any assumption of analytical form of the TF.

THEORETICAL

We assume the following properties of the calorimeter system:

(1) a linear relationship between the calorific power $x(t)$ and output signal $y(t)$ at time t;

(2) time-invariant thermal properties of the system; that is, the heat capacity, the heat conduction constant and other thermal properties of the calorimeter system do not change throughout the experiment;

(3) zero initial conditions of the system.

Then we have[4]

$$Y(s) = G(s)X(s) \tag{1}$$

where $X(s) = \mathrm{L}[x(t)]$ and $Y(s) = \mathrm{L}[y(t)]$ are the Laplace transforms of $x(t)$ and $y(t)$, respectively, $G(s)$ the transfer function (TF) of the calorimeter system and s the parameter in the Laplace transform. If the TF $G(s)$ of the calorimeter and the Laplace transform of the thermogram $Y(s) = \mathrm{L}[y(t)]$ are known, we can obtain the desired calorific power $x(t)$ by the inverse Laplace transform of $Y(s)/G(s)$. To carry out the transform numerically, Tateno and Tachoire assumed a simple analytical form of $G(s)$. For a more precise treatment by their method, we must assume a more complicated form of $G(s)$. To avoid the complicated problems of determining a larger number of the coefficients in the expression of $G(s)$, we used the frequency transfer function (FTF)[5] of the calorimeter and could calculate the transform numerically in a general scheme without any assumption of the analytical form of the TF $G(s)$.

Determination of the FTF of a calorimeter

The FTF of a calorimeter system is determined by the analysis of output response $y(t)$ when a constant heat power $x(t) = x_0$ for $t \geqq 0$ and $x(t) = 0$ for $t < 0$ is generated in the calorimeter cell. From the formula of the Laplace transform

$X(s) = \mathrm{L}[x(t)] = x_0/s$ and $\mathrm{L}[\mathrm{d}y(t)/\mathrm{d}t] = sY(s) - y(+0) = sY(s)$, we have $G(s) = Y(s)/X(s) = sY(s)/x_0 = \mathrm{L}[\mathrm{d}y(t)/\mathrm{d}t]/x_0$

$$= \frac{1}{x_0}\int_0^\infty \frac{\mathrm{d}y(t)}{\mathrm{d}t}\,\mathrm{e}^{-st}\,\mathrm{d}t$$

$$= \frac{1}{x_0}\int_0^\infty \mathrm{e}^{-st}\,\mathrm{d}y(t) \tag{2}$$

Setting $s = jw$, we obtain the FTF as follows[5]

$$G(jw) = \frac{1}{x_0}\int_0^\infty \mathrm{e}^{-jwt}\,\mathrm{d}y(t) \tag{3}$$

where $j = \sqrt{-1}$, w is the frequency in radians per unit time and $G(jw)$ is the FTF. To perform the integration (3) numerically, we divide the range of the integration into intervals $[t_n, t_{n+1}]$ and approximate $y(t)$ as linear with t in $[t_n, t_{n+1}]$ as follows

$$y(t) \doteqdot (y_{n+1} - y_n)(t - t_n)/(t_{n+1} - t_n) + y_n, \quad (t_n \leqq t \leqq t_{n+1}) \tag{4}$$

where $y_n = y(t_n)$ and $y_{n+1} = y(t_{n+1})$.

Equation (3) then becomes

$$G(jw) = \frac{1}{x_0}\sum_{n=1}^{\infty}\int_{t_n}^{t_{n+1}} \mathrm{e}^{-jwt}\,\mathrm{d}y(t)$$

$$\doteqdot \frac{1}{x_0}\sum_{n=1}^{N}\frac{(y_{n+1} - y_n)}{w(t_{n+1} - t_n)}[(\sin wt_{n+1} - \sin wt_n) + j(\cos wt_{n+1} - \cos wt_n)] \tag{5}$$

Transform of the thermogram $y(t)$ into $Y(jw)$

A thermal reaction which we wish to investigate is then carried out and the thermogram $y(t)$ is obtained. The method of transforming the thermogram $y(t)$ into the frequency response $Y(jw)$ is similar to that of obtaining the FTF illustrated above. Setting $s = jw$ in $Y(s)$, we have

$$Y(jw) = \int_0^\infty y(t)\,\mathrm{e}^{-jwt}\,\mathrm{d}t \doteqdot \sum_{n=1}^{N}\int_{t_n}^{t_{n+1}} y(t)\,\mathrm{e}^{-jwt}\,\mathrm{d}t$$

$$= Y_r(w) + jY_i(w) \tag{6}$$

where

$$Y_r(w) = \frac{1}{w} \sum_{n=1}^{N} \left[(y_{n+1}\sin wt_{n+1} - y_n \sin wt_n) + \frac{(y_{n+1} - y_n)(\sin wt_{n+1} - \sin wt_n)}{(wt_{n+1} - wt_n)} \right] \quad (7)$$

$$Y_i(w) = \frac{1}{w} \sum_{n=1}^{N} \left[(y_{n+1}\cos wt_{n+1} - y_n \cos wt_n) - \frac{(y_{n+1} - y_n)(\sin wt_{n+1} - \sin wt_n)}{(wt_{n+1} - wt_n)} \right] \quad (8)$$

Here we again divided the range of the integration into intervals $[t_n, t_{n+1}]$ and approximated $y(t)$ to be linear with t in $[t_n, t_{n+1}]$.

Determination of calorific power $x(t)$ for $t > 0$

We can then determine the desired calorific power $x(t)$ from the inverse Laplace transform of $Y(jw)/G(jw) = Y(jw)F(jw)$, where $1/G(jw) = F(jw)$. From the formula we have

$$x(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} Y(jw)F(jw)\, e^{jwt}\, dw$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} [(A\cos wt - B\sin wt) + j(A\sin wt + B\cos wt)]\, dw \quad (9)$$

where

$$\begin{aligned} 1/G(jw) &= F(jw) = F_r(w) + jF_i(w) \\ A &= Y_r(w)F_r(w) - Y_i(w)F_i(w) \\ B &= Y_r(w)F_i(w) + Y_i(w)F_r(w) \end{aligned} \quad (10)$$

and the suffixes r, i refer to the real and imaginary parts, respectively.

The Laplace transform of the sectionally continuous function gives an analytical function, so that we can have[6] $Y(\bar{s}) = \overline{Y(s)}$ and $F(\bar{s}) = \overline{F(s)}$. Therefore, A and B are even and odd functions of w, respectively, and eqn. (9) becomes

$$x(t) = \frac{1}{\pi} \int_{0}^{\infty} (A\cos wt - B\sin wt)\, dw \quad (11)$$

Considering $x(t) = 0$ for $t < 0$ and using the same approximation in (4) and (5), we have

$$x(t) = \frac{2}{\pi} \int_{0}^{\infty} A\cos wt\, dw \quad (12)$$

$$\doteq \frac{2}{\pi t} \sum_{n=1}^{N} \left[(A_{n+1}\sin w_{n+1}t - A_n \sin w_n t) + \frac{(A_{n+1} - A_n)(\cos w_{n+1}t - \cos w_n t)}{(w_{n+1}t - w_n t)} \right] \quad (13)$$

Here we have divided the integral range into intervals $[w_n, w_{n+1}]$ and $A_n = A(w_n)$, $A_{n+1} = A(w_{n+1})$.

Determination of $x(+0)$

From the initial value theorem of the Laplace transform

$$x(+0) = \lim_{t \to +0} x(t) = \lim_{s \to \infty} sX(s),$$

and setting $s = jw$, we have

$$x(+0) = -\lim_{w \to \infty} w(Y_r F_i + Y_i F_r) \tag{14}$$

MATHEMATICAL SIMULATION BY A MODEL CALORIMETER

In order to test the accuracy of our method, we examined it in two ways. First, we carried out a mathematical simulation by use of a mathematical model calorimeter. Second, we carried out a test experiment with a commercially available calorimeter which is widely used in Japan.

The mathematical model calorimeter is a one-dimensional model of a heat conduction calorimeter which is composed of a reaction cell, thermal bath and a solid thermal conductor connecting the cell with the thermal bath, as shown[7] in Fig. 1. The dimensions and thermal properties of the model calorimeter were set to be nearly equal to those of the available calorimeter as follows: the solid thermal conductor has

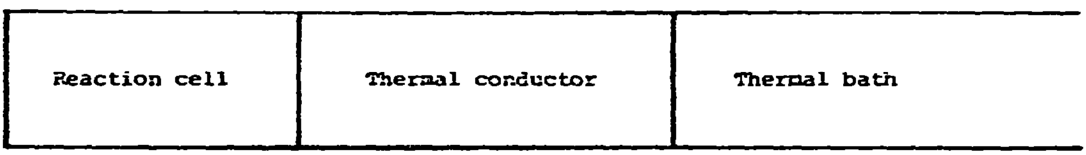

Fig. 1. One-dimensional model of a heat conduction calorimeter.

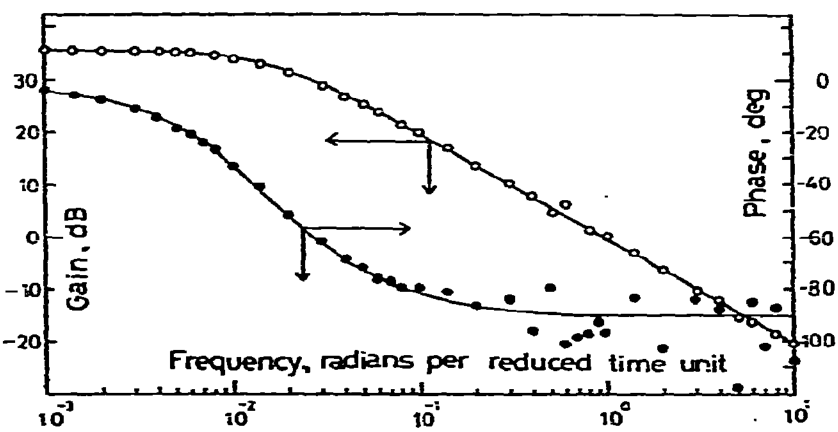

Fig. 2. Bode plots of a model calorimeter.

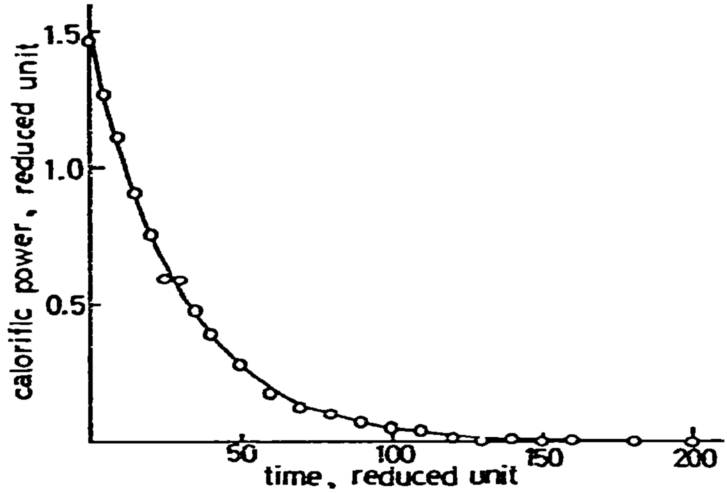

Fig. 3. Results of the transform of the thermogram into a thermogenesis curve on a model calorimeter.

the length $L = 1.45 \times 10^{-2}$ m, the area of its cross-section $S = 1.23 \times 10^{-3}$ m^2, the thermal conductivity $\Lambda = 1.4$ W mK^{-1}, and the thermal diffusivity $K = 1.17 \times 10^{-6}$ m^2 s^{-1}. The temperature of the thermal bath is $\Theta_0 = 298.15$ K. the thermal capacity of the cell is $C_0 = 212$ J K^{-1}. Using this model, we can know precisely the FTF of the calorimeter and output response for any thermal input from the theory of a one-dimensional heat conduction calorimeter[7].

First, we drew a thermogram curve for a constant heat input of unit power from a numerical calculation by our model and its theory. Remembering that data is usually obtained from a curve on an electronic recorder chart in a real experiment, we made a series of output response data for the constant heat from the thermogram curve in order to simulate a real experiment. We analysed the data thus obtained and obtained the FTF of the model calorimeter by our method. Figure 2 shows the Bode plots of the FTF, where the circles are calculated from an analysis of the thermogram curve for the constant heat input and the lines are theoretical which we can know precisely from the theory of a one-dimensional heat conduction calorimeter[7].

We then drew a thermogram curve for time vs. heat input

$$x(t) = 1.5 \exp(-t/30) \tag{15}$$

The shape of the heat input was chosen because it would take place for a first-order chemical reaction. We obtained a series of data by reading the curve, analysed the data using the FTF calculated previously, and obtained the heat input at any time. Figure 3 shows the results thus obtained and a comparison with the theoretical line, eqn. (15).

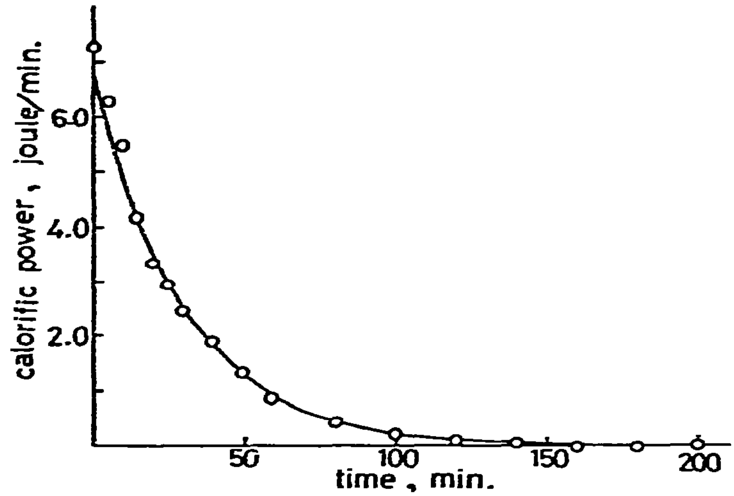

Fig. 4. Results of the transform of a thermogram into a thermogenesis curve on a TCC-2 calorimeter.

EXPERIMENT WITH THE AVAILABLE CALORIMETER

A Tokyo Rikō TCC-2 heat conduction type calorimeter was used to examine our method for test heat input. Experiments were carried out at 25°C and 50 ml of water were continuously stirred in the reaction cell. The heat was generated by applying a voltage across an electrical resistance inside the cell. A constant or varying voltage was supplied from a variable source. The output of the calorimeter is the thermogram curve on chart paper of the electronic recorder and we obtained numerical data from reading of the curve. Figure 4 shows the comparison between the heat generated in the cell and the calculated power from analysis of the thermogram by our method.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. T. Nishikawa and Dr. I. Takeda for their assistance with computer techniques.

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