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THEORETICAL ANALYSIS OF HEAT-FLUX DIFFERENTIAL SCANNING CALORIMETRY BASED ON A GENERAL MODEL

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ABSTRACT

Theoretical analysis is given for heat-flux differential scanning calorimetry, based on a unified model which is applicable also to classical differential thermal analysis and power-compensated differential scanning calorimetry. The equations governing heat flow within the system are solved analytically on the assumption that the values of heat capacity and of thermal conductivity are constant. The temperature-lag of the sample is evaluated, and the method of estimating the actual temperature is given in the case of the first-order phase transition.

INTRODUCTION

Three types of dynamic differential methods have been widely used to study thermal properties of materials: classical differential thermal analysis (DTA), power-compensated differential scanning calorimetry (DSC), and heat-flux DSC. As the instrument for each of these methods is based on a fundamentally different principle, particular attention must be paid to analyze the result (the curve recorded in the chart). In classical DTA, thermocouples are inserted into the sample and the reference material both of which are placed at equivalent positions in the block. Because the small beads of the thermocouple junctions are in direct contact with the sample and the reference material, the temperature of the sample can be derived easily from the experimental result. Under such conditions, however, the peak caused by a phase transition is dependent on the thermal conductivity of the sample and the enthalpy of transition can hardly be estimated quantitatively. In power-compensated DSC, the additional electrical power to keep the sample and the reference at the same temperature is recorded, and the heat capacity and the enthalpy of transition are obtained directly [1].

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In this case, the quantification is guaranteed by the first law of thermodynamics. Since heat-flux DSC [2,3] has been developed from DTA, it is also called "quantitative DTA". The beads of the thermocouple junctions are located on the surfaces of the vessels containing the sample and the reference material. The temperature difference recorded is proportional to the heat-flux difference between the sample and the reference material. Thus, the enthalpy of transition can be estimated if the thermal conductivity governing the heat-flux is known beforehand; the condition for heat-flux is not sample-dependent but is dependent on the instrumental constants. In both the DSC methods, however, the temperature measurement is made outside the sample holder, and the actual sample temperature is different from the recorded temperature.

Recently, Mraw [4] has presented a very simple model which is applicable to heat-flux DSC as well as to classical DTA [5] and power-compensated DSC [6] for a unified theoretical analysis. In this paper, the exact analytical solutions of the equations are given only for heat-flux DSC on his model, as our solutions for classical DTA and power-compensated DSC are identical with those reported already by Gray [6] based on different models. Evaluation of the temperature-lag of the sample is shown in the case of the first-order phase transition in which the actual temperature is obtained from the analysis of the slope of the peak.

MRAW'S MODEL

A sketch of Mraw's model [4] is reproduced in Fig. 1, where the shaded regions are the parts having heat capacity values, while the unshaded regions have no heat capacity, but offer thermal resistance. In Fig. 1, T and C denote temperature and heat capacity, respectively, and the subscripts are defined as follows: h, heater block; s, sample; sm, temperature measuring station of the sample side; r, reference; rm, temperature measuring station of the reference side. R is the thermal resistance between the heater block and the temperature measuring station (denoted by the subscript sm or rm) and R' is that between the temperature measuring station and the sample (or reference material). An important difference between this model and the previous models [5,6] is that there are two thermal resistances separated by the temperature measuring station between the heater block and the sample (or reference material). No temperature gradient is considered in any part of this system. This model is applicable to all three types of instrument: classical DTA, power-compensated DSC, and heat-flux DSC.

Assuming the absence of temperature-dependence in the heat capacities and the thermal resistances on the basis of this model, the heat flows dq/dt between the heater block and the temperature measuring station and dq'/dt between the temperature measuring station and the sample (or reference

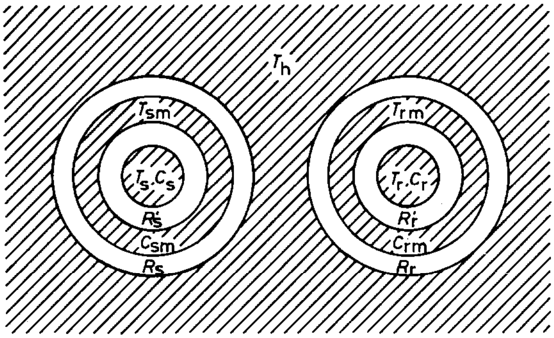

Fig. 1. Sketch of Mraw's model [4]. T_h, temperature of the heater; T_{sm}, temperature of the sample-temperature measuring station; T_s, temperature of the sample; C_{sm}, heat capacity of the sample-temperature measuring station; C_s, heat capacity of the sample; R_s, thermal resistance between the sample-temperature measuring station and the heater; R_s', thermal resistance between the sample and the sample-temperature measuring station. T_{rm}, T_r, C_{rm}, C_r, R_r and R_r' have analogous meanings for the reference side.

material) are represented as follows. For the reference side, the equations are

$$\frac{dq_r}{dt} = C_{rm}\frac{dT_{rm}}{dt} + C_r\frac{dT_r}{dt} \tag{1}$$

$$\frac{dq_r'}{dt} = C_r\frac{dT_r}{dt} \tag{2}$$

Using Newton's law of cooling, these can be written as

$$\frac{1}{R_r}(T_h - T_{rm}) = C_{rm}\frac{dT_{rm}}{dt} + C_r\frac{dT_r}{dt} \tag{3}$$

$$\frac{1}{R_r'}(T_{rm} - T_r) = C_r\frac{dT_r}{dt} \tag{4}$$

For the sample side, the differential equations are

$$\frac{dq_s}{dt} = C_{sm}\frac{dT_{sm}}{dt} + C_s\frac{dT_s}{dt} \tag{5}$$

$$\frac{dq_s'}{dt} = C_s\frac{dT_s}{dt} \tag{6}$$

or

$$\frac{1}{R_s}(T_h - T_{sm}) = C_{sm}\frac{dT_{sm}}{dt} + C_s\frac{dT_s}{dt} \tag{7}$$

$$\frac{1}{R_s'}(T_{sm} - T_s) = C_s\frac{dT_s}{dt} \tag{8}$$

During a first-order phase transition at $T_s = T_{tr}$, the equations are

$$\frac{dq_s}{dt} = C_{sm}\frac{dT_{sm}}{dt} + \Delta H\frac{dx}{dt} \tag{9}$$

$$\frac{\mathrm{d}q_s'}{\mathrm{d}t} = \Delta H \frac{\mathrm{d}x}{\mathrm{d}t} \tag{10}$$

or

$$\frac{1}{R_s}(T_h - T_{sm}) = C_{sm}\frac{\mathrm{d}T_{sm}}{\mathrm{d}t} + \Delta H \frac{\mathrm{d}x}{\mathrm{d}t} \tag{11}$$

$$\frac{1}{R_s'}(T_{sm} - T_{tr}) = \Delta H \frac{\mathrm{d}x}{\mathrm{d}t} \tag{12}$$

where ΔH is the enthalpy of transition and x is the fraction of the transformed part of the sample.

EXACT SOLUTIONS

In this section, we solve the equations of the heat-flux DSC based on Mraw's model. In the idealized system, we can write $R_s = R_r = R$ and $C_{sm} = C_{rm} = C_m$ on the assumption of symmetrical construction of the instrument. The temperature of the heater block, T_h, is assumed to change at a constant rate a, i.e., we can write

$$T_h = T_h^0 + at \tag{13}$$

t_i and t_f are the times at which the transition starts and is completed, respectively; $T_s(t_i) = T_s(t_f) = T_{tr}$, $x(t_i) = 0$ and $x(t_f) = 1$.

Formal solution of eqn. (8) is

$$T_s = \exp\left(-\frac{t}{R_s'C_s}\right)\left\{C' + \frac{1}{R_s'C_s}\int^t T_{sm}(y)\exp\left(\frac{y}{R_s'C_s}\right)\mathrm{d}y\right\} \tag{14}$$

where C' is an integral constant. Differentiation with respect to t after substitution of eqn. (14) into eqn. (7) gives a following second-order differential equation of T_{sm} only

$$\frac{\mathrm{d}^2T_{sm}}{\mathrm{d}t^2} + A\frac{\mathrm{d}T_{sm}}{\mathrm{d}t} + BT_{sm} = Ct + D \tag{15}$$

$$A = \frac{1}{R_s'C_m} + \frac{1}{R_s'C_s} + \frac{1}{RC_m}$$

$$B = \frac{1}{RR_s'C_sC_m}$$

$$C = \frac{a}{RR_s'C_sC_m}$$

$$D = \frac{1}{RC_m}\left(a + \frac{1}{R_s'C_s}T_h^0\right)$$

Solution of eqn. (15) is

$$T_{sm} = \alpha_{s1}\exp(\omega_{s1}t) + \alpha_{s2}\exp(\omega_{s2}t) + at + T_h^0 - aR(C_s + C_m) \tag{16}$$

where α_{s1} and α_{s2} are integral constants determined by boundary conditions, and ω_{s1} and ω_{s2} are roots of the following quadratic equation

$$x^2 + Ax + B = 0 \tag{17}$$

For physical consistency, ω_{s1} and ω_{s2} must be real and smaller than zero. This is confirmed as follows. Explicit forms of ω_{s1} and ω_{s2} are expressed by

$$-\frac{1}{2}\left(\frac{1}{R'_sC_m} + \frac{1}{R'_sC_s} + \frac{1}{RC_m}\right)$$
$$\pm \frac{1}{2RR'_sC_sC_m}\left[(R'_sC_s - RC_m)^2 + RC_s(RC_s + 2R'_sC_s + RC_m)\right]^{1/2}$$

Equation (17) always has two real roots, and one of them always has a negative value. Next, we define f(x)

$$f(x) = x^2 + Ax + B \tag{18}$$

Since $f(0) = B > 0$, we have proved that ω_{s1} and ω_{s2} are real numbers and that they have negative values.

After the substitution of eqn. (16) into eqn. (14), T_s is immediately obtained by integration as

$$T_s = \beta_s \exp\left(-\frac{t}{R'_sC_s}\right) + \frac{\alpha_{s1}}{R'_sC_s + \omega_{s1}}\exp(\omega_{s1}t) + \frac{\alpha_{s2}}{R'_sC_s + \omega_{s2}}\exp(\omega_{s2}t)$$
$$+ at + T_h^0 - a(RC_s + RC_m + R'_sC_s) \tag{19}$$

where β_s is an integral constant determined by a boundary condition.

Since eqns. (3) and (4) are of the same type as eqns. (7) and (8), solutions for eqns. (3) and (4) are obtained in analogous formulae by exchanging the subscript s for r.

Solutions of eqns (11) and (12) are

$$T_{sm} = \gamma \exp\left(-\frac{R + R'_s}{RR'_sC_m}t\right) + \frac{aR'_s}{R + R'_s}t + \frac{1}{R + R'_s}(R'_sT_h^0 + RT_{tr}) - \frac{aRR'^2_sC_m}{(R + R'_s)^2} \tag{20}$$

$$x = \frac{1}{R\Delta H}\left\{\gamma\frac{RR'_sC_m}{R + R'_s}\left[\exp\left(-\frac{R + R'_s}{RR'_sC_m}t_i\right) - \exp\left(-\frac{R + R'_s}{RR'_sC_m}t\right)\right]\right.$$
$$\left. + \frac{aR'_s}{R + R'_s}(t - t_i)^2 + \left[\frac{R'_s}{R + R'_s}(T_h^0 - T_{tr}) - \frac{aRR'^2_sC_m}{(R + R'_s)^2}\right](t - t_i)\right\} \tag{21}$$

where γ is an integral constant determined by a boundary condition.

Since eqns. (7) and (8) show that dT_{sm}/dt must be continuous if T_s and T_{sm} are continuous, the boundary conditions are that T_s, T_{sm} and dT_{sm}/dt

should be continuous at all times. These are written formally as

$$T_s(t') = T_s(t').$$

$$\alpha_{s1} \exp(\omega_{s1}t') + \alpha_{s2} \exp(\omega_{s2}t') = F_1(t') \tag{22}$$

$$\alpha_{s1}\omega_{s1} \exp(\omega_{s1}t') + \alpha_{s2}\omega_{s2} \exp(\omega_{s2}t') = F_2(t')$$

From these equations, α_{s1} and α_{s2} are derived as follows

$$\alpha_{s1} = (\omega_{s2} - \omega_{s1})^{-1} \exp(-\omega_{s1}t')[\omega_{s2}F_1(t') - F_2(t')]$$

$$\alpha_{s2} = (\omega_{s2} - \omega_{s1})^{-1} \exp(-\omega_{s2}t')[F_2(t') - \omega_{s1}F_1(t')] \tag{23}$$

An example of the theoretical signal of the first-order phase transition is shown in Fig. 2. It begins to rise gradually when the transition starts and its slope increases until the transition is completed, and then the slope decreases gradually. The decay of the signal is represented by the sum of the two exponential functions. The characteristic features of the signal in heat-flux DSC are (1) the starting of the transition corresponds to the point at which the curve deviates from the stationary baseline (t_i in Fig. 2), (2) the completion of the transition is given by the first inflection point (t_f in Fig. 2), and (3) therefore, the maximum of the signal comes after the completion of the transition (t_m in Fig. 2).

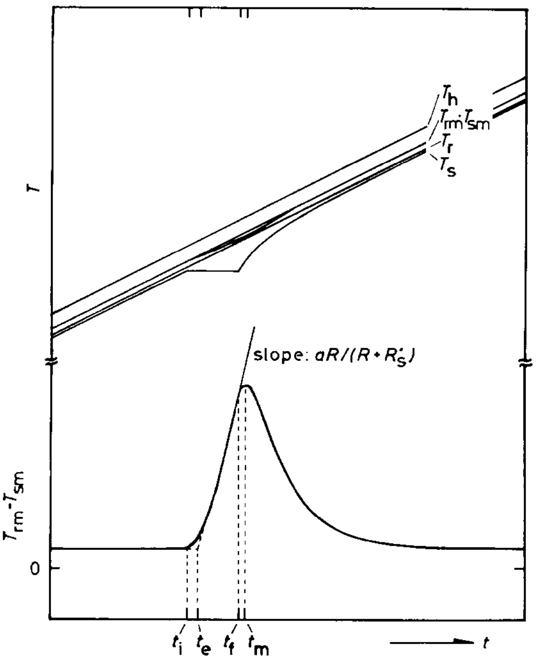

Fig. 2. Calculated signal of the first-order phase transition in heat-flux DSC. The upper is the temperature of each part of the system, and the lower shows the peak in larger scale. The transition starts at t_i and ends at t_f. t_e is extrapolated onset time and t_m is the time at which the peak height is maximum.

The area under the peak is calculated as follows. It is assumed for simplicity that α_{r1}, α_{r2}, β_r, α_{s1}, α_{s2}, and β_s are zero before t_i and $t_i = 0$. From this condition, the following equations are derived

$$T_{rm} = at + T_h^0 - aR(C_r + C_m) \tag{24}$$

$$\left.\begin{aligned} T_{sm} &= at + T_h^0 - aR(C_s + C_m) \quad (25)\\ T_s &= at + T_h^0 - a(RC_s + RC_m + R'_sC_s) \quad (26) \end{aligned}\right\} (t < t_i)$$

The baseline is $aR\ (C_s - C_r)$. At $t = 0$, T_{sm} and $\mathrm{d}T_{sm}/\mathrm{d}t$ must be continuous. Thus, we obtain the equation

$$T_{sm} = \frac{aR^2R'_sC_m}{(R+R'_s)^2}\left[1 - \exp\left(-\frac{R+R'_s}{RR'_sC_m}t\right)\right] + \frac{aR'_s}{R+R'_s}t + T_h^0 - aR(C_s + C_m) \quad (t_i < t < t_f) \tag{27}$$

At $t = t_f$, T_{sm} and $\mathrm{d}T_{sm}/\mathrm{d}t$ must be continuous, i.e.

$$\begin{aligned} \alpha_{s1}\exp(\omega_{s1}t_f) + \alpha_{s2}\exp(\omega_{s2}t_f) &= \frac{aR^2R'_sC_m}{(R+R'_s)^2}\left[1 - \exp\left(-\frac{R+R'_s}{RR'_sC_m}t_f\right)\right] - \frac{aR}{R+R'_s}t_f \\ \alpha_{s1}\omega_{s1}\exp(\omega_{s1}t_f) + \alpha_{s2}\omega_{s2}\exp(\omega_{s2}t_f) &= \frac{aR}{R+R'_s}\left[\exp\left(-\frac{R+R'_s}{RR'_sC_m}t_f\right) - 1\right] \end{aligned} \tag{28}$$

The values of α_{s1} and α_{s2} are given by formulae (23). The area under the peak is

$$\begin{aligned} &\int_0^{\infty}[T_{rm} - T_{sm} - aR(C_s - C_r)]\mathrm{d}t \\ &= \int_0^{t_f}[T_{rm} - T_{sm} - aR(C_s - C_r)]\mathrm{d}t + \int_{t_f}^{\infty}[T_{rm} - T_{sm} - aR(C_s - C_r)]\mathrm{d}t \\ &= \frac{aR}{2(R+R'_s)}t_f^2 - \frac{aR^2R'_sC_m}{(R+R'_s)^2}t_f - \frac{aR'_s}{R+R'_s}\left(\frac{RR'_sC_m}{R+R'_s}\right)^2 \\ &\quad \times\left[\exp\left(-\frac{R+R'_s}{RR'_sC_m}t_f\right) - 1\right] + \frac{\alpha_{s1}}{\omega_{s1}}\exp(\omega_{s1}t_f) + \frac{\alpha_{s2}}{\omega_{s2}}\exp(\omega_{s2}t_f) \\ &= aR\left[C_s + \frac{R^2C_m}{(R+R'_s)^2}\right]t_f + \frac{aR}{2(R+R'_s)}t_f^2 \\ &\quad + \frac{aR^2}{R'_s(R+R'_s)}\left(\frac{RR'_sC_m}{R+R'_s}\right)^2\left[\exp\left(-\frac{R+R'_s}{RR'_sC_m}t_f\right) - 1\right] \end{aligned} \tag{29}$$

The enthalpy of transition is given by

$$
\begin{aligned}
\Delta H &= \frac{1}{R'_{\mathrm{s}}}\int_0^{t_{\mathrm{f}}}(T_{\mathrm{sm}} - T_{\mathrm{tr}})\mathrm{d}t \\
&= a\left[C_{\mathrm{s}} + \frac{R^2 C_{\mathrm{m}}}{(R + R'_{\mathrm{s}})^2}\right]t_{\mathrm{f}} + \frac{a}{2(R + R'_{\mathrm{s}})}t_{\mathrm{f}}^2 \\
&\quad + \frac{aR}{R'_{\mathrm{s}}(R + R'_{\mathrm{s}})}\left(\frac{RR'_{\mathrm{s}}C_{\mathrm{m}}}{R + R'_{\mathrm{s}}}\right)^2\left[\exp\left(-\frac{R + R'_{\mathrm{s}}}{RR'_{\mathrm{s}}C_{\mathrm{m}}}t_{\mathrm{f}}\right) - 1\right] \qquad (30)
\end{aligned}
$$

The area under the peak is $R\Delta H$. Thus, we can estimate the enthalpy of transition (ΔH) from the peak since R is an instrumental constant.

ACTUAL TRANSITION TEMPERATURE

As the temperature measuring station is separated by the thermal resistance from the sample in the two types of DSC, there always is the temperature-lag of the sample in the measurements. The temperature difference ($T_{\mathrm{sm}} - T_{\mathrm{s}}$) in stationary state is given as $aR'_{\mathrm{s}}C_{\mathrm{s}}$ in power-compensated DSC and also in heat-flux DSC. Here, C_{s} and a can be easily estimated. However, the value of R'_{s} must be calculated by analyzing the signal recorded in the measurements. In the case of power-compensated DSC, the evaluation of R'_{s} is straightforward. The slope of the peak due to the first-order phase transition is a/R'_{s}.

On the other hand, the situation is not so simple in heat-flux DSC. From formulae (16) and (19), the peak due to the first-order phase transition is given by subtracting the time-independent terms

$$
\frac{aR}{R + R'_{\mathrm{s}}}t - \gamma\exp\left(-\frac{R + R'_{\mathrm{s}}}{RR'_{\mathrm{s}}C_{\mathrm{m}}}t\right) \qquad (31)
$$

The calculated signals are shown in Fig. 2. The signal deviates from the baseline at t_{i} when the transition starts. If a sufficiently long time is needed for completion of the transition and the second term in formula (31) is negligible, R'_{s} can be evaluated by using the maximum slope of the peak, that is $aR/(R + R'_{\mathrm{s}})$. Thus, we conclude that the actual transition temperature of the sample is evaluated by analyzing the peak. The transition ends at t_{f} which is the inflection point of the curve.

It is important to note that the extrapolated onset time (t_{e} in Fig. 2) does not correspond to the start of phase transition.

SUMMARY

The simple theoretical model presented by Mraw [4], which is applicable to heat-flux DSC as well as classical DTA and power-compensated DSC, has been analytically solved on the assumption that the heat capacity and the thermal conductivity are constant. The results for classical DTA and for power-compensated DSC are identical with those reported by Gray [6]. The equations for heat-flux DSC are solved on the basis of this model. It is shown that the temperature-lag of the sample can be estimated by analyzing the curve. The method of evaluating the actual temperature is given for the first-order phase transition.

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