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BASE LINE DRAWING FOR THE DETERMINATION OF THE ENTHALPY OF TRANSITION IN CLASSICAL DTA, POWER-COMPENSATED DSC AND HEAT-FLUX DSC

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ABSTRACT

A principle for drawing the base line is given when determining the enthalpy of the first-order phase transition by experiments with classical differential thermal analysis, power-compensated differential scanning calorimetry and heat-flux differential scanning calorimetry. When the principle is applied to Mraw's model which is applicable to the three types of instruments, theoretically rigorous drawing of the base line is shown in the case when the heat capacity of the sample before and after transition is different. The enthalpy of transition is obtained from the area enclosed by the base line and the recorded trace.

INTRODUCTION

Dynamic differential methods have been extensively used to study thermal properties of materials. Three types of instruments have been developed; classical differential thermal analysis (DTA), power-compensated differential scanning calorimetry (DSC) and heat-flux DSC. In any application of these instruments to enthalpic events, it is especially important to draw the base line when determining the excess enthalpy value due to the thermal anomaly. In classical DTA, the quantitative estimation is poorly established for the enthalpy of transition since the trace obtained by experiment depends on the thermal conductivity of the sample. However, quantitative treatments have been attempted using simplified models for classical DTA [1–5] after a theoretical analysis by Vold [6], and these manipulations have been extended and applied to heat-flux DSC [7–10]. The problem of base line has been also discussed with respect to rough and/or inconsistent assumptions for power-compensated DSC [11–13]. Theoretically rigorous treatments of the base line were given by Adam and Müller

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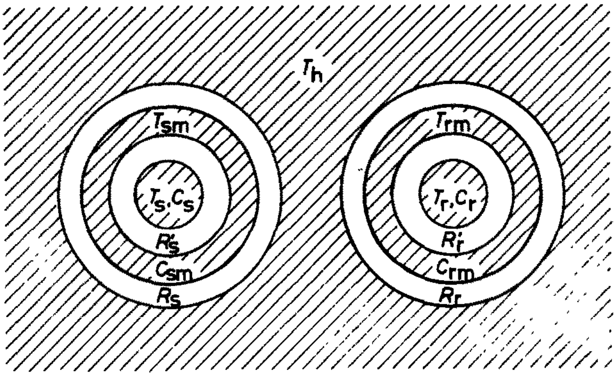

Fig. 1. Sketch of Mraw's model [14]. T_h, temperature of the heater; T_{sm}, temperature of the sample-temperature measuring station; T_s, temperature of the sample; C_{sm}, heat capacity of the sample-temperature measuring station; C_s, heat capacity of the sample; R_s, thermal resistance between the 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 similar meanings for the reference side.

[5], and Ozawa [10], but these treatments are complicated and rather impractical.

In this paper, we put forward a fundamental principle for drawing the base line and apply it to the general model presented by Mraw [14] which is applicable to all three types of instruments. The sketch of Mraw's model 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. No temperature gradient is considered in any part of this system. In a previous paper [15], we solved analytically the equations governing heat flow within the system on the assumption that the values of heat capacity and of thermal conductivity were constant. It was shown that the temperature-lag of the sample could be estimated by analyzing the trace recorded in the experiments. The method of evaluating the actual temperature was given in the case of the first-order phase transition. In the present study, we extend the series of our theoretical investigations on dynamical thermal instruments. The theoretically rigorous drawing of the base line will be given for the case when the post-transition base line is different from the pre-transition base line, i.e., the heat capacity of the sample after the transition is different from that before, assuming the constant thermal conductivity of the sample.

FUNDAMENTAL PRINCIPLE

The principle for drawing the base line is proposed as shown in Fig. 2, where the hypothetical traces are schematically drawn for classical DTA as

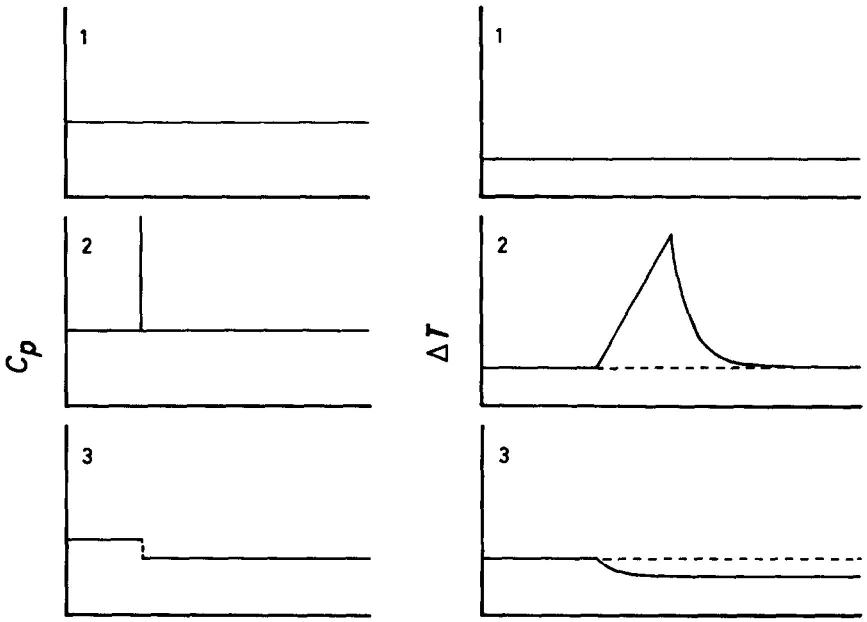

Fig. 2. Fundamental principle of drawing the base line in classical DTA. The hypothetical traces are given on the right-hand side, and the corresponding heat capacities and other thermal events are shown on the left-hand side. 1, stationary state of condition; 2, the first-order phase transition with substantial amount of latent heat; 3, heat capacity changes abruptly at the transition point.

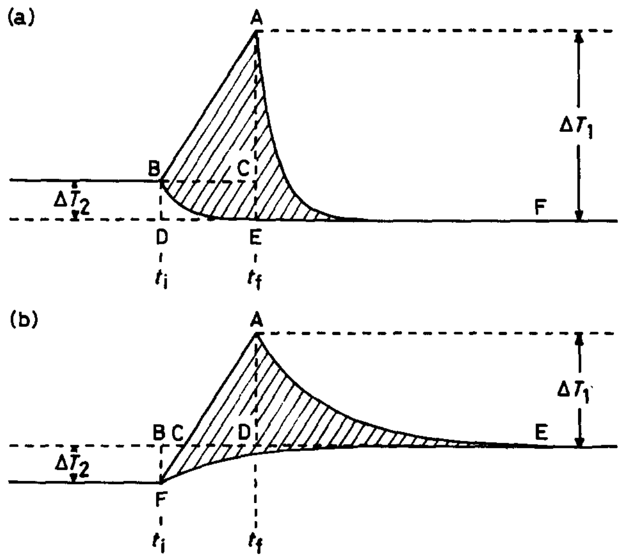

Fig. 3. Theoretically rigorous drawing of the base line in classical DTA. The shaded area corresponds to the enthalpy of transition: (a) the heat capacity after the transition (C_{sa}) is smaller than that before the transition (C_{sb}); (b) $C_{sa} > C_{sb}$.

an example on the right-hand side, and the corresponding heat capacities and other thermal events of the sample are shown on the left-hand side. In case 1, the trace is a straight line as the heat capacity of the sample is constant. In case 2, the first-order phase transition occurs with a substantial amount of latent heat. The trace begins to deviate from the pre-transition base line at the time the transition starts, and after completion it returns asymptotically to the extrapolated pre-transition base line since the heat capacity value before and after the transition is the same. The area enclosed by the trace and the base line is $R\,\Delta H$, where R is the thermal resistance between the sample and the heater and ΔH is the enthalpy of transition. In case 3, the heat capacity value changes abruptly at the transition point, where the trace begins to deviate from the pre-transition base line and becomes the new base line asymptotically.

In a general case where the value of heat capacity after the first-order phase transition accompanying a substantial amount of the latent heat is different from that before the transition, the base line is drawn as shown in Fig. 3, and the area of the shaded region is proportional to the enthalpy of transition. In other words, the base line corresponds to the hypothetical trace which would be obtained by assuming no thermal anomaly.

THEORETICALLY RIGOROUS TREATMENT OF MRAW'S MODEL

In this section, the theoretically rigorous drawing of the base line is described for classical DTA, power-compensated DSC and heat-flux DSC, based on Mraw's model. The temperature of the heater block is assumed to vary at a constant rate a; $T_h = T_h^0 + at$ (the constant, T_h^0, is the temperature of the heater block at the start). The transition starts at the time t_i, and it is completed at t_f. The subscripts a and b are used to designate "after" and "before" the transition, respectively.

In classical DTA, based on Mraw's model, R'_s and R'_r are omitted (Fig. 1), and T_s is represented as [6,15]

$$T_s = C_1 \exp\left(-\frac{t}{R_s C_s}\right) - aR_s C_s + at + T_h^0 \tag{1}$$

where C_1 is an integral constant determined by a boundary condition. From eqn. (1), the trace after the transition, $D_1(t - t_f)$, is derived as

$$D_1(t - t_f) = \Delta T_1 \exp\left(-\frac{t - t_f}{R_s C_{sa}}\right) \tag{2}$$

where ΔT_1 is the maximum deviation from the stationary base line after the transition. The theoretical trace is shown in Fig. 4(a). On the other hand, the base line during the excess thermal events due to the phase transition should

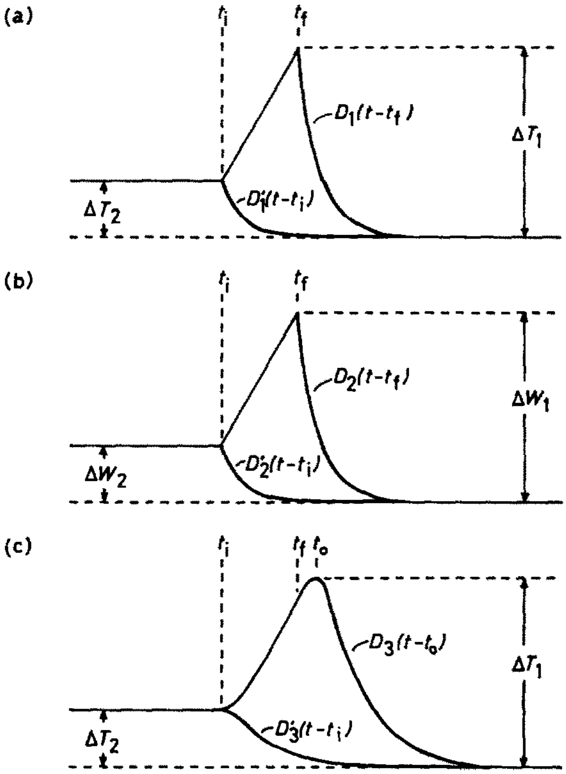

Fig. 4. Methods of drawing the base line in (a) classical DTA, (b) power-compensated DSC and (c) heat-flux DSC. Functions D and D' represent the trace and the base line, respectively. The first-order phase transition starts at time t_i and is completed at t_f. t_0 is the time at which the trace reaches maximum in heat-flux DSC.

be drawn by assuming that the heat capacity value changes abruptly at the transition point without latent heat as shown in Figs. 2 and 3. Its function is represented as $D_1'(t-t_i)$, which decays exponentially with the time constant of $R_s C_{sa}$

$$D_1'(t-t_i) = \Delta T_2 \exp\left(-\frac{t-t_i}{R_s C_{sa}}\right) \tag{3}$$

where ΔT_2 is the temperature difference between the two stationary base lines before and after the transition. From eqns. (2) and (3), we obtain the base line function

$$D_1'(t-t_i) = \frac{\Delta T_2}{\Delta T_1} D_1(t-t_i) \tag{4}$$

The area enclosed by the base line and the trace corresponds to the enthalpy of transition. This is verified as follows. The enthalpy of transition is represented as

$$
\begin{aligned}
\Delta H &= \frac{1}{R_s}\int_{t_i}^{t_f}(T_h - T_{trs})\,dt \\
&= \frac{1}{R_s}\int_{0}^{\Delta t}(aR_sC_{sb} + at)\,dt \\
&= \frac{a}{2R_s}(\Delta t)^2 + aC_{sb}\,\Delta t
\end{aligned}
\tag{5}
$$

where $\Delta t = t_f - t_i$. When the heat capacity after the transition is smaller than that before the transition, ΔT_1 equals $a\,\Delta t + \Delta T_2$ and ΔT_2 equals $aR_s(C_{sb} - C_{sa})$. The shaded area in Fig. 3(a) is given as

$$
\begin{aligned}
&Area(\mathrm{ABC}) + Area(\mathrm{AEF}) + Area(\mathrm{BCED}) - Area(\mathrm{BDF}) \\
&= \frac{a}{2}(\Delta t)^2 + \Delta T_1 R_sC_{sa} + \Delta T_2\,\Delta t - \Delta T_2 R_sC_{sa} \\
&= \frac{a}{2}(\Delta t)^2 + R_sC_{sa}(\Delta T_1 - \Delta T_2) + \Delta T_2\,\Delta t \\
&= \frac{a}{2}(\Delta t)^2 + a\,\Delta t R_sC_{sa} + aR_s(C_{sb} - C_{sa})\,\Delta t \\
&= \frac{a}{2}(\Delta t)^2 + a\Delta t R_sC_{sb} \\
&= R_s\,\Delta H.
\end{aligned}
\tag{6}
$$

When $C_{sa} > C_{sb}$, which is shown in Fig. 3(b), ΔT_1i equals $a\Delta t - \Delta T_2$ and ΔT_2 equals $aR_s(C_{sa} - C_{sb})$. The shaded area in Fig. 3(b) is given as

$$
\begin{aligned}
&Area(\mathrm{ACD}) + Area(\mathrm{ADE}) + Area(\mathrm{BEF}) - Area(\mathrm{BCF}) \\
&= \frac{a}{2}\left(\frac{\Delta T_1}{a}\right)^2 + \Delta T_1 R_sC_{sa} + \Delta T_2 R_sC_{sa} - \frac{a}{2}\left(\frac{\Delta T_2}{a}\right)^2 \\
&= \frac{1}{2a}(\Delta T_1)^2 + R_sC_{sa}(\Delta T_1 + \Delta T_2) - \frac{1}{2a}(\Delta T_2)^2 \\
&= \frac{1}{2a}\left[(\Delta T_1)^2 - (\Delta T_2)^2\right] + a\,\Delta t R_sC_{sa} \\
&= \frac{1}{2a}(\Delta T_1 - \Delta T_2)(\Delta T_1 + \Delta T_2) + a\,\Delta t R_sC_{sa} \\
&= \frac{\Delta t}{2}(a\,\Delta t - 2aR_sC_{sa} + 2aR_sC_{sb}) + a\,\Delta t R_sC_{sa} \\
&= \frac{a}{2}(\Delta t)^2 + a\,\Delta t R_sC_{sb} \\
&= R_s\,\Delta H.
\end{aligned}
\tag{7}
$$

Therefore, in both cases, $C_{sa} < C_{sb}$, and $C_{sa} > C_{sb}$, we can estimate the enthalpy of the first-order phase transition from the base line drawn as described above and the trace recorded in the experiments.

In power-compensated DSC, based on Mraw's model, R_s and R_r are omitted (see Fig. 1) and dq_s/dt is represented as [15,16]

$$\frac{dq_s}{dt} + C_2 \exp\left(-\frac{t}{R_s'C_s}\right) + a(C_s + C_{sm}) \tag{8}$$

where C_2 is an integral constant determined by a boundary condition. Since eqn. (8) is similar to eqn. (1), the method of drawing the base line is also similar to the case of classical DTA. The theoretical trace is shown in Fig. 4(b). From eqn. (8), the trace after the transition, $D_2(t - t_f)$, is derived as

$$D_2(t - t_f) = \Delta W_1 \exp\left(-\frac{t - t_f}{R_s'C_{sa}}\right) \tag{9}$$

where ΔW_1 is the maximum deviation from the stationary base line after the transition. On the other hand, the base line during the excess thermal events, $D_2'(t - t_i)$, is given as

$$D_2'(t - t_i) = \Delta W_2 \exp\left(-\frac{t - t_i}{R_s'C_{sa}}\right) \tag{10}$$

where ΔW_2 is the difference between the two stationary base lines before and after the transition. From eqns. (9) and (10), we obtain the base line fucntion as

$$D_2'(t - t_i) = \left(\frac{\Delta W_2}{\Delta W_1}\right) D_2(t - t_i) \tag{11}$$

In heat-flux DSC, the situation is rather complicated. The temperature of the sample-temperature measuring station, T_{sm}, is represented as

$$T_{sm} = \alpha_{s1} \exp(\omega_{s1} t) + \alpha_{s2} \exp(\omega_{s2} t) + at + T_h^0 - aR_s(C_s + C_{sm}) \tag{12}$$

which has been derived from the basic equations in our previous report [15]. In eqn. (12), α_{s1} and α_{s2} are integral constants determined by boundary conditions, and ω_{s1} and ω_{s2} are constants determined by the values of R_s, R_s', C_s and C_{sm}. The boundary conditions are represented as

$$\begin{aligned} &\alpha_{s1} \exp(\omega_{s1} t) + \alpha_{s2} \exp(\omega_{s2} t) = F_1(t) \\ &\alpha_{s1}\omega_{s1} \exp(\omega_{s1} t) + \alpha_{s2}\omega_{s2} \exp(\omega_{s2} t) = F_2(t) \end{aligned} \tag{13}$$

where $F_1(t)$ is a deviation from the stationary base line and $F_2(t)$ is a slope of the trace at the time t. The theoretical trace is shown in Fig. 4(c). The base line function $D_3'(t - t_i)$ must satisfy the boundary conditions

$$\begin{aligned} &F_1(t_i) = \Delta T_2 \\ &F_2(t_i) = 0 \end{aligned} \tag{14}$$

where ΔT_2 is the temperature difference between the two stationary base lines before and after the transition. From eqns. (12)–(14), $D_3'(t - t_i)$ is represented as

$$D_3'(t - t_i) = \left(\frac{\Delta T_2}{\omega_{sa2} - \omega_{sa1}}\right)\{\omega_{sa2} \exp[\omega_{sa}(t - t_i)] - \omega_{sa1} \exp[\omega_{sa2}(t - t_i)]\} \tag{15}$$

On the other hand, the trace after t_f satisfies the boundary conditions

$$F_1(t_0) = \Delta T_1$$
$$F_2(t_0) = 0 \tag{16}$$

where t_0 is the time at which the trace reaches the maximum and ΔT_1 is its value measured from the stationary base line after the transition. Thus, the trace after t_f is represented as

$$D_3(t - t_0) = \left(\frac{\Delta T_1}{\omega_{sa2} - \omega_{sa1}}\right)\{\omega_{sa2} \exp[\omega_{sa1}(t - t_0)] - \omega_{sa} \exp[\omega_{sa2}(t - t_0)]\} \tag{17}$$

From eqns. (15) and (17), we obtain the base line function as

$$D_3'(t - t_i) = \left(\frac{\Delta T_2}{\Delta T_1}\right) D_3(t - t_i) \tag{18}$$

The method described above is also applicable to the case of $C_{sa} > C_{sb}$, in which the sign of ΔT_2 should be taken to be minus.

In practical use for the three types of instruments, the curve of the trace after the maximum (ΔT_1 or ΔW_1) recorded in the experiments should be reduced to the scale of the difference between the two stationary base lines before and after the transition (ΔT_2 or ΔW_2). The reduced curve should then be shifted to the time t_i and connected to the pre-transition stationary base line. The enthalpy of transition can be estimated from the area enclosed by the base line and the trace recorded in the experiments.

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