

THEORETICAL ANALYSIS OF PEAK HEIGHT IN CLASSICAL DTA, POWER-COMPENSATED DSC AND HEAT-FLUX DSC

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ABSTRACT

Theoretical analysis of peak height is given for traces, due to a first-order phase transition with substantial latent heat, obtained in classical DTA, power-compensated DSC and heat-flux DSC. Theoretical peak height is represented as a function of the heat capacity, the thermal resistance and the heating (cooling) rate on the basis of a unified model which is applicable to all three types of instruments. The limiting height obtained in the experiment with an infinite rate of heating (cooling) is independent of the amount of sample present. The possibility is discussed of quantitative determination of the enthalpy of transition by using classical DTA.

INTRODUCTION

Although the dynamic differential type of techniques, classical differential thermal analysis (DTA), power-compensated differential scanning calorimetry (DSC) and heat-flux DSC, have been widely used to study the thermal properties of materials, little attention has been paid to the evaluation of the peak height recorded in the trace owing to a thermal anomaly. However, it has been commonly suspected that the peak height due to a phase transition might be a practical measure of the sensitivity of the apparatus. In fact, the peak height increases as the heating (cooling) rate and/or the amount of the sample increases [1,2].

Recently, some efforts have been devoted to the quantitative analysis of the peak height [3–5]. The square-root relationship of the peak height with the heating (cooling) rate is now well known, but the quantitative treatments on the effect of the amount of the sample and those on other problems have not yet been performed.

In this paper, we present a detailed analysis of the peak height due to a first-order phase transition on the basis of the general model presented by Mraw [6], which is applicable to all three types of instruments. The sketch of Mraw's model is reproduced in Fig. 1, where shaded regions are those with

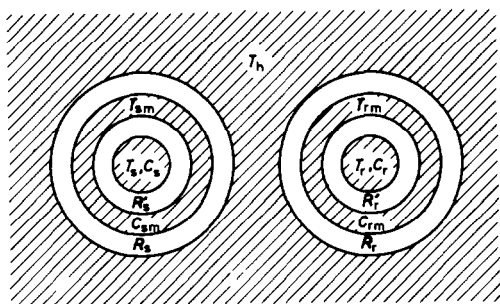


Fig. 1. Sketch of Mraw's model [6]. T_h , temperature of the heater-block; T_{sm} , temperature of the sample-temperature measuring station; T_s , temperature of the sample; C_{sm} , heat capacity of the sample-temperature measuring station; C_s , heat capacity of the sample; R_s , thermal resistance between the sample-temperature measuring station and the heater-block; 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.

heat capacity values. The unshaded regions have no heat capacity, but offer thermal resistance. No temperature gradient is considered in any part of this system. In previous papers [7,8], the equations governing heat flow within the system were solved analytically. It has been shown that the temperature-lag of the sample can be estimated by analyzing the trace recorded in the experiments [7]. The theoretically rigorous drawing of the baseline is given in the case that the posttransition baseline is different from the pretransition baseline [8]. Thus, the present study is an extension of the series of our theoretical investigations on dynamical differential instruments. The expression of the peak height will be given as a function of the heat capacity, the thermal resistance and the heating (cooling) rate. The possibility of quantitative determination of the enthalpy of transition using classical DTA will be also discussed.

PEAK HEIGHT IN MRAW'S MODEL

In this section, we describe the expression of the peak height h as a function of heat capacity, thermal resistance and heating (cooling) rate for classical DTA, power-compensated DSC and heat-flux DSC on the basis of Mraw's model. The temperature of the heater-block is assumed to vary at a constant rate a .

In classical DTA where R'_s and R'_r are omitted (see Fig. 1), the peak height due to the first-order phase transition equals $a\Delta t$. Here, Δt is the time needed for the completion of the transition, and is determined by the equation,

$$\frac{1}{2}a(\Delta t)^2 + aR_sC_s \Delta t = R_s \Delta H \quad (1)$$

where ΔH is the enthalpy of transition. The peak height h is derived as

$$h = -aR_s C_s + (a^2 R_s^2 C_s^2 + 2aR_s \Delta H)^{1/2} \quad (2)$$

In the limit of rapid heating (cooling), i.e. $a \rightarrow \infty$, the peak height approaches the limiting value, $h_{\max} = \Delta H/C_s$. Equation (2) can be rewritten so that the normalized peak height is represented as a function of the dimensionless variable, $y = aR_s C_s^2/\Delta H$, as

$$h/h_{\max} = -y + (y^2 + 2y)^{1/2} \quad (3)$$

This is the master equation of the peak height in classical DTA, which is shown in Fig. 2. As y increases, the normalized peak height increases monotonously and asymptotically approaches the limiting value. In Fig. 2, an approximate formula, $h/h_{\max} = (2y)^{1/2}$, is also shown; this is the exact expression of the well-known square-root dependence of the peak height on the heating (cooling) rate, $h \propto a^{1/2}$ [5]. Thus, it is concluded that the square-root dependence can be considered valid in the range, $y \lesssim 10^{-3}$.

In power-compensated DSC where R_s and R_r are omitted (see Fig. 1), the peak height due to the first-order phase transition equals $a\Delta t/R'_s$. A manipulation similar to that of classical DTA gives the following expression,

$$h = -aC_s + (a^2 C_s^2 + 2a \Delta H/R'_s)^{1/2} \quad (4)$$

In the limit of $a \rightarrow \infty$, the peak height approaches the limiting peak height, $h_{\max} = \Delta H/R'_s C_s$. From eqn. (4), the same master equation as eqn. (3) is obtained, in which the dimensionless variable is $y = aR'_s C_s^2/\Delta H$.

In heat-flux DSC, the peak height due to the first-order phase transition is

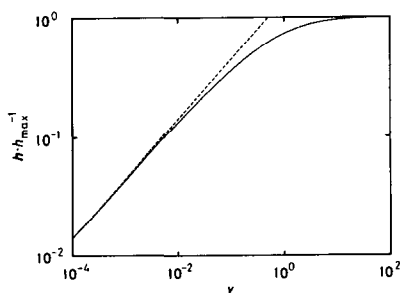


Fig. 2. Peak height h as a function of the heat capacity C_s , the thermal resistance R'_s (R_s), the enthalpy of transition ΔH and the heating (cooling) rate a in classical DTA and power-compensated DSC. y is the dimensionless variable defined as $y = aR_s C_s^2/\Delta H$ in classical DTA and as $y = aR'_s C_s^2/\Delta H$ in power-compensated DSC. The broken line represents the approximate square-root relation, $h/h_{\max} = (2y)^{1/2}$.

expressed as

$$h = \{ \omega_1 (\omega_1 K - L) \}^{\omega_1 / (\omega_1 - \omega_2)} \{ \omega_2 (\omega_2 K - L) \}^{\omega_2 / (\omega_2 - \omega_1)} \quad (5)$$

$$K = \frac{aR_s}{R_s + R'_s} \left\{ \Delta t + \frac{R_s R'_s C_{sm}}{R_s + R'_s} \left[\exp \left(- \frac{R_s + R'_s}{R_s R'_s C_{sm}} \Delta t \right) - 1 \right] \right\}$$

$$L = \frac{aR_s}{R_s + R'_s} \left\{ 1 - \exp \left(- \frac{R_s + R'_s}{R_s R'_s C_{sm}} \Delta t \right) \right\}$$

where ω_1 and ω_2 are constants determined by C_s , C_{sm} , R_s and R'_s [7]. In the limit of slow heating (cooling), i.e. $a \rightarrow 0$, Δt is approximated by $[2(R_s + R'_s) \Delta H / a]^{1/2}$ and h becomes proportional to $a^{1/2}$. On the other hand, in the limit of $a \rightarrow \infty$, Δt is approximated by $R_s \Delta H / a R'_s C_s$ and h approaches the limiting value,

$$h_{\max} = (-\omega_1)^{\omega_1 / (\omega_1 - \omega_2)} (-\omega_2)^{\omega_2 / (\omega_2 - \omega_1)} \frac{R_s \Delta H}{R_s^2 C_s C_{sm}} \quad (6)$$

In the intermediate region, the peak height increases monotonously as the heating (cooling) rate increases. Thus, the general features of formula (5) are very similar to formulae (2) and (4). However, as a number of variables are included in formula (5), it is impossible to obtain a simplified master equation.

In all three types of instrument, as the heating (cooling) rate increases, the peak height increases and approaches the limiting peak height. It is noteworthy that the expression of the limiting peak height is given as

$$h_{\max} = S \Delta H / C_s \quad (7)$$

where S is a constant.

In the case that the posttransition baseline is different from the pretransition baseline, i.e. the heat capacity of the sample after the transition is different from that before the transition assuming a constant thermal resistance, the peak height must be measured from the pretransition baseline and the value of the heat capacity before the transition must be used.

QUANTITATIVE TREATMENTS IN CLASSICAL DTA

In classical DTA, the peak height due to the first-order phase transition increases monotonously according to eqns. (2) or (3) and approaches the limiting value $h_{\max} = \Delta H / C_s$ as y increases; $y = a R_s C_s^2 / \Delta H$. As the thermal resistance R_s , the heat capacity C_s and the enthalpy of transition ΔH are constant, the limiting peak height h_{\max} does not depend on the amount of sample present; $\Delta H / C_s = \text{constant}$. The value of y depends on the

heating (cooling) rate a and on the amount of sample; $C_s C_s / \Delta H$ is proportional to the amount of sample because $C_s / \Delta H$ is constant.

Now, it is interesting to compare two hypothetical peaks due to successive phase transitions with the enthalpies of transition ΔH_1 and ΔH_2 . If it is assumed that there is a large difference between the two values of enthalpy of transition, e.g. $\Delta H_1 = 1$ and $\Delta H_2 = 1000$, and other values are constant, e.g. $aR_s C_s^2 = 1$, the corresponding values of y are 1 and 10^{-3} , respectively. Substituting the two values of y into eqn. (3) yields the normalized peak heights as $h_1/h_{1\max} = 0.73$ and $h_2/h_{2\max} = 0.044$. Hence, actual peak heights are obtained as $h_1 = 0.73/C_s$ and $h_2 = 44/C_s$. A large difference in the enthalpy of transition ($\Delta H_2/\Delta H_1 = 10^3$) results in a rather small difference in the actual peak height ($h_2/h_1 \approx 60$). Thus, a small anomaly may be observed as a rather large peak. This must be the reason why extremely small transitions could be detected in classical DTA [9].

As the limiting peak height ($h_{\max} = \Delta H/C_s$) is independent of the amount of sample and of any instrumental constants, the enthalpy of transition can be determined in classical DTA carried out at an ultimately high heating (cooling) rate. The enthalpy of transition is obtained from the limiting peak height h_{\max} and the heat capacity C_s as $\Delta H = h_{\max} C_s$.

Instead of an experiment at the ultimate rate, several experiments can be done at various heating (cooling) rates on the same sample to calculate the limiting peak height and the parameter $R_s C_s^2 / \Delta H$. By fitting the data to eqn. (3), the enthalpy of transition is also obtainable.

There is another possible way to estimate the enthalpy of transition, in which the sample is diluted with a stable and non-reactive material. The apparent heat capacity C_{sa} and the apparent enthalpy of transition ΔH_a are given as

$$C_{sa} = m_s C_{ss} + m_d C_{sd} \quad (8)$$

$$\Delta H_a = m_s \Delta H_s \quad (9)$$

where m_s is the mass of the sample; m_d the mass of the diluent; C_{ss} the heat capacity of the sample per unit mass; C_{sd} the heat capacity of the diluent per unit mass; ΔH_s the enthalpy of transition per unit mass. As the apparent value of y ($aR_s C_{sa}^2 / \Delta H_a$) is much larger than that of the pure sample ($aR_s C_s^2 / \Delta H$) under the condition of $m_s / (m_s + m_d) \ll 1$, the limiting peak height ($h_{\max} = \Delta H_a / C_{sa}$) is approached more rapidly. Thus the enthalpy of transition is obtained as

$$\Delta H_s = \frac{m_s + m_d}{m_s} C_{sd} h_{\max} \quad (10)$$

PEAK HEIGHT IN GENERAL CASE

Although eqn. (7) is derived on the basis of Mraw's model, the same relation can be obtained in a general case according to dimensional analysis.

The heat flow in the system is represented by the equation of heat flow [10,11],

$$c_s \frac{\partial T}{\partial t} + \Delta H \frac{\partial x}{\partial t} = \lambda_s \nabla^2 T \quad (11)$$

where c_s and ΔH are the sample heat capacity and the enthalpy of transition per unit volume, respectively, λ_s is the thermal conductivity of the sample and x is the fraction of the transformed part of the sample. Here, T and x are functions of time t and position \mathbf{r} ; $T \equiv T(t, \mathbf{r})$ and $x \equiv x(t, \mathbf{r})$. Since $\Delta H/c_s$ is only a parameter having the dimension of temperature, the limiting peak height, if present, should have a form of $S \Delta H/c_s$. The form implies that the limiting peak height is independent of the amount of sample. Therefore, it is concluded that the limiting peak height is independent of the amount of sample in any kind of instrument in which the heat transfer in the system is governed by eqn. (11).

SUMMARY

On the basis of a general model presented by Mraw which was applicable to classical DTA, power-compensated DSC and heat-flux DSC, the peak height was analyzed in the case of a first-order phase transition with substantial latent heat. Theoretical peak height was presented as a function of the heat capacity, the thermal resistance and the heating (cooling) rate. It was shown that the limiting value of experimentally attainable peak height was independent of the amount of sample. Three methods were proposed for quantitative determination of the enthalpy of transition in classical DTA.

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