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# THE INFLUENCE OF SAMPLE MASS, HEATING RATE AND HEAT TRANSFER COEFFICIENT ON THE FORM OF DSC CURVES

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## ABSTRACT

Several methods of correcting experimental curves in differential scanning calorimetry are in use. A simplified model to which experimental data can be fitted is proposed. From this model it follows that the width of a melting peak of a pure compound depends on the heating rate and on the mass of the sample by a square-root relation

## INTRODUCTION

Recently, several articles [1–5] have been published on the influence of sample mass and heating rate on the form of melting curves in differential scanning calorimetry (DSC) and differential thermal analysis (DTA). The purpose of the studies was to correct the experimental curves for the influence of sample mass and heating rate in order to obtain the actual sample temperature during a phase transition. Such a correction is needed to enable measurement of the impurity of the sample or, in the case of the study of binary phase diagrams, to find the liquidus point (end point of the melting process).

The present authors discuss the ideal curves in power-compensated differential scanning calorimetry, excluding effects which tend to deform the experimental curves, such as sample form (powder, molten or tablet), non-homogeneous temperature in the sample cup, and varying contact between the sample cup and the sample cup holder. Hopefully, these considerations will help to make a framework in which experimental data can be fitted.

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## MODELLING OF THE DSC

The simplified experimental set-up is shown in Fig. 1. In the DSC experiment both holders are heated at the same rate. The surplus in energy needed for the sample is recorded as the measuring signal, usually as a function of the temperature of the sample cup holder. Heating both holders at the same speed can be achieved electronically by using a proportional regulation system with a very high amplification factor, i.e.

$$W = P\mathrm{d}T$$

where $W$ is the measuring signal in W, $P$ is a proportional factor and $\mathrm{d}T$ is the temperature difference between the holders.

The amplification factor of the amplifier used to detect the temperature difference multiplied by $P$ determines the total proportional action of the regulation system. This value can be made so high (before oscillation starts) that the remaining $\mathrm{d}T$ can be neglected compared to the temperature differences which occur between the sample cup holder and the sample cup. For the remainder of this article it is assumed that the sample cup holder and the reference cup holder are always at the same temperature and that the difference in power needed to achieve this is recorded as the measuring signal. Perhaps it is useful to remark here that PI or PID regulation systems cannot be used in this case. It would be perfectly possible to heat both holders at the same speed using these regulation systems, but when a phase transition takes place in the sample cup the integral part of the regulation system increases and should decrease after the phase transition, thus leading to symmetrical (about the base line) curves.

The response of the instrument can be reduced to a simple mathematical model assuming that: (1) the holders are always at the same temperature; (2) the system is symmetrical; (3) the sample cup and the reference cup are equal in mass; and (4) the sample cup and the sample can be considered as one thermal part (in other words, they always have the same temperature). These conditions lead to the model shown in Fig. 2.

The more complicated case which arises when one divides the calorimeter into several regions of the same temperature as is needed in DTA experiments was described by Sarge et al. [1]. They used a numeric method (method of Runge–Kutta) to solve the resulting equations.

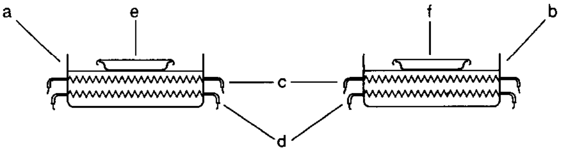

Fig. 1. Schematic drawing of a DSC. a and b, holders; c, heaters; d, thermometers; e, sample cup; f, reference cup.

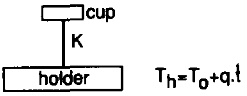

Fig. 2. Simplified model of a DSC.

The temperature of the sample holder can be given by

$$T_h = T_0 + qt \tag{1}$$

where $T_h$ is the temperature of the sample holder, $T_0$ is the starting temperature; $q$ is the heating rate in K s$^{-1}$, and $t$ = time in seconds.

The heat flow to the sample can be given by

$$W = K(T_s - T_h) \tag{2}$$

where $W$ is the heat flow in watts, $K$ is the heat transfer coefficient in W K$^{-1}$, and $T_s$ is the temperature of the sample and the sample cup.

With a heat capacity of the sample of $mC_s$ for $m$ grams of sample, this leads to

$$\frac{dT_s}{dt} mC_s = W \tag{3}$$

Combining eqns. (1), (2) and (3) gives the well known equation

$$\frac{dT_s}{dt} mC_s = K(T_s - T_0 - qt) \tag{4}$$

Assuming at $t = 0$ that $T_s = T_h = T_0$, the solution of this differential equation is

$$T_s = T_0 + qt - \frac{qmC_s}{K}(1 - e^{-Kt/mC_s}) \tag{5}$$

This equation holds for the start of the curve; when $t$ increases the exponential part becomes negligible and

$$T_s = T_0 + qt - \frac{qmC_s}{K} \tag{6}$$

$$W = qmC_s \tag{7}$$

This equation is used for measuring the heat capacity of the sample, assuming that the sample cup and the reference cup are equal in weight. In practice, a run is first made with two empty cups and this run is subtracted from the measurement with the sample.

For a first order phase transition the situation is summarized in Fig. 3. The melting starts at $t_b$ and is completed at $t_e$. During this period the temperature of the sample and the sample cup remains constant. This is an idealization; the temperature of the sample cup may change. The energy supplied to the sample in the period $t_e - t_b$ is given by the integral over the surface ABCD (see Fig. 3). The line AB corresponds to the effect which

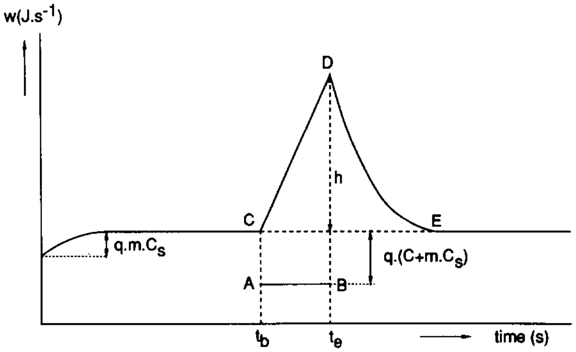

Fig. 3. Curve of a first order phase transition.

would be measured under identical circumstances if the sample holder was empty. The surface ABCD consists of a triangle and a square, and it follows that

$$m\ \mathrm{d}H = 0.5(t_e - t_b)h + (t_e - t_b)q(C + mC_s) \tag{8}$$

in which $\mathrm{d}H$ is the enthalpy of transition, $C$ is the heat capacity of the sample cup, and $h$ is the heat flow to the sample with respect to the base line at $t = t_e$.

At $t_e$, the sample and the sample cup lag behind in temperature to the sample holder. This temperature difference is $q(t_e - t_b)$ and the corresponding surplus in heat flow at $t_e$ is

$$h = Kq(t_e - t_b) \tag{9}$$

Substituting eqn. (9) into eqn. (8) and rearranging, using $\mathrm{d}t = (t_e - t_b)$, leads to

$$0.5qK\ \mathrm{d}t^2 + q(C + mC_s)\ \mathrm{d}t - m\ \mathrm{d}H = 0 \tag{10}$$

This follows closely the derivation given by Gray [6]. Solving this equation leads to

$$\mathrm{d}t = \frac{-q(C + mC_s) + \left[q^2(C + mC_s)^2 + 2Kqm\ \mathrm{d}H\right]^{\frac{1}{2}}}{Kq} \tag{11}$$

Transforming the time scale to a temperature scale by multiplying by $q$ gives

$$T_e - T_b = \frac{-q(C + mC_s) + \left[q^2(C + mC_s)^2 + 2Kqm\ \mathrm{d}H\right]^{\frac{1}{2}}}{K} \tag{12}$$

This equation gave us the opportunity to look at the influence of $q$ (heating rate) and $m$ (sample mass) on the shape of a melting peak. The heat transfer coefficient $K$ cannot be varied freely.

We used a DSC 2 from Perkin–Elmer. From a measurement with indium the constants summarized in Table 1 were found. The heat transfer coefficient $K$ was calculated from the slope of the line CD (Fig. 3) using eqn. (9).

TABLE 1

Measured and calculated values for eq. (12)

| | |
|---|---|
| Sample holder | aluminium |
| Mass sample holder | 0.020 (g) |
| $C$ | 0.0188 (J $K^{-1}$) |
| Mass indium | $4.81\times10^{-3}$ (g) |
| d$H$ | 28.5 (J $g^{-1}$) |
| $mC_s$ | 0.00105 (J $K^{-1}$) |
| $q$ | $5.2\times10^{-3}$ (K $s^{-1}$) |
| $K$ | $1.6\times10^{-2}$ (W $K^{-1}$) |
| $T_e - T_b$ | 0.31 (K) |

A consideration of the relative importance of each term led to the following approximation for eqn. (12)

$$T_e - T_b = \frac{(2Kqm\,\mathrm{d}H)^{\frac{1}{2}}}{K} = \left(\frac{2qm\,\mathrm{d}H}{K}\right)^{\frac{1}{2}} \tag{13}$$

The width of the peak is dependent on the mass of sample and on the heating rate by a square-root relationship. In Table 2, the measured and calculated values of $T_e - T_b$ using 4.81 mg of indium are compared. From this table, it can be seen that with heating rates below $8.33\times10^{-2}$ K $s^{-1}$ (5 K $min^{-1}$) eqn. (13) holds very well.

The return to the base line (line DE in Figure 3 is an exponential curve with the factor $e^{-Kt/(C+mC_s)}$. In this example, this is $e^{-0.806t}$. This is a fast declining function. In about 5 s the heat effect has fallen back to within one per cent of its value at $t_e$. This is one of the merits of the DSC technique; it leads to sharp transitions compared with the DTA method.

In the collaboration between Bordeaux, Barcelona and Utrecht (Courchinoux et al. [2]) a method called shape factor was proposed in order to analyse the melting curves of mixtures.

TABLE 2

Measured and calculated values of $T_e - T_b$ for the DSC 2 using 4.81 g indium

| $q$ (K $s^{-1}$) | $T_e - T_b$ (K) Experimental | $T_e - T_b$ (K) Eqn. (12) | $T_e - T_b$ (K) Eqn. (13) |
|---|---|---|---|
| $5.20\times10^{-3}$ | 0.31 | 0.29 | 0.30 |
| $1.04\times10^{-2}$ | 0.41 | 0.41 | 0.42 |
| $2.08\times10^{-2}$ | 0.57 | 0.57 | 0.60 |
| $4.16\times10^{-2}$ | 0.77 | 0.79 | 0.84 |
| $8.33\times10^{-2}$ | 1.08 | 1.09 | 1.19 |

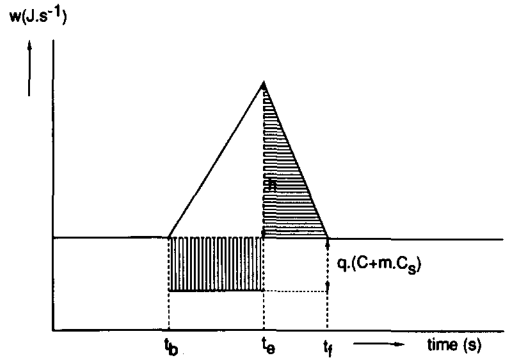

Fig. 4. Curve of a first order phase transition. The return to the base line is approximated by a straight line.

To correct the end point of a transition the factor $\Delta T_f = T_f - T_b$ is calculated from the melting curves of the pure compounds. Therefore, the exponential return to the base line is approximated by a straight line. This situation is given in Fig. 4. The shaded surfaces should be equal, which leads to

$$h \times 0.5(t_f - t_e) = (C + mC_s)q(t_e - t_b) \tag{14}$$

Using eqn. (9) we find

$$(t_f - t_e) = \frac{2(C + mC_s)}{K} \tag{15}$$

$$T_f - T_e = \frac{2q(C + mC_s)}{K} \tag{16}$$

Neglecting $mC_s$ in comparison to $C$ gives

$$T_f - T_e = \frac{2qC}{K} \tag{17}$$

This implies that $T_f - T_e$ does not depend much on the sample mass but mostly on the heating rate. The plot of $T_f - T_e$ and $T_e - T_b$ against sample mass should result in two parallel lines. This is in accordance with the results as given by Courchinoux [7,8].

## DISCUSSION

From Table 2, it follows that the model holds very well in the case of fusion of indium. Organic compounds such as *para*-dichlorobenzene and naphthalene give less ideal curves and lower values for $K$ (about $1 \times 10^{-2}$ W K$^{-1}$), implying that a more sophisticated model might be needed. O'Neill [9] proposed a model which takes into account the changing liquid–solid interface during the melting process. It is questionable, however, that a more complicated model does improve the results. The heat contact between the sample holder and the sample cup does vary considerably; we measured values using indium between $1.6 \times 10^{-2}$ and $2 \times 10^{-2}$ W $K^{-1}$. Therefore, we propose to use eqn. (13) as a function to which experimental data can be fitted. Temperature correction can then be made using eqn. (2).

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