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A THEORETICAL EVALUATION OF A HEAT-FLOW DIFFERENTIAL SCANNING CALORIMETER

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ABSTRACT

An overview is given of the basic theory of heat-flow differential scanning calorimetry. An alternative definition of the baseline is proposed and an equation for the baseline function is derived. The influence of the heat transfer coefficients on the quality of the DSC curve is thoroughly examined and some recommendations concerning the construction of a heat-flow DSC are given.

INTRODUCTION

In a heat-flow differential scanning calorimeter the temperature of a sample is compared with the temperature of an inert reference, both being placed in a furnace and submitted to a certain temperature-time program.
In a number of articles theories are developed which describe the shape and area of a DSC peak resulting from a thermal transition in a sample (1-6). Analytical equations are derived which give the relation between peak area and transition heat.
In this paper, a description of the basic theory of heat-flow differential scanning calorimetry will be given and a new definition of the thermal baseline will be proposed. Further, the influences of the heat transfer coefficients on the shape of a DSC curve will be made clear and recommendations on the construction of a heat-flow differential scanning calorimeter are given.

THEORY

A schematic description of a heat-flow DSC cell is given in figure 1.

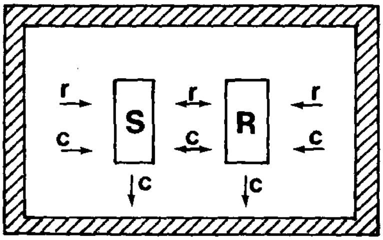

Fig. 1. Heat-flow DSC cell.

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The total heat-flow can be considered as being built up of the following parts:

1. Conductive heat-flow from the furnace wall to the sample (Ψ_{1S}) resp. to the reference (Ψ_{1R}).
   The respective heat transfer coefficients are indicated as K_{1S} resp. K_{1R}.
2. Radiative heat-flow from the furnace wall to the sample (Ψ_{2S}) resp. to the reference (Ψ_{2R}), with heat-transfer coefficients K_{2S} and K_{2R}.
3. Conductive heat-flow through the thermocouple wires (Ψ_{3S} resp. Ψ_{3R}), with heat-transfer coefficients K_{3S} resp. K_{3R}.
4. Conductive heat-flow from the sample to the reference (Ψ_{4SR}), with a heat-transfer coefficient K_{4SR}.
5. Radiative heat-flow from the sample to the reference (Ψ_{5SR}), with heat-transfer coefficient K_{5SR}.

If it is assumed that temperature gradients within sample and reference and between sample and sample holder (resp. reference and reference holder) are zero, the various heat flows are given as:

$$\begin{array}{ll}
\Psi_{1S} = K_{1S}\ (T_f - (T + \Delta T)) & \Psi_{1R} = K_{1R}\ (T_f - T) \\
\Psi_{2S} = K_{2S}\ (T_f^4 - (T + \Delta T)^4) & \Psi_{2R} = K_{2R}\ (T_f^4 - T^4) \\
\Psi_{3S} = K_{3S}\ (T_f - (T + \Delta T)) & \Psi_{3R} = K_{3R}\ (T_f - T) \\
\Psi_{4SR} = K_{4SR}\ ((T + \Delta T) - T) & \Psi_{5SR} = K_{5SR}\ ((T + \Delta T)^4 - T^4)
\end{array} \tag{1}$$

In these equations, T_f denotes the temperature of the furnace, T the reference temperature and $(T + \Delta T)$ the sample temperature.

When performing an experiment with an inert sample, the heat-flow to the reference cell is given as:

$$\Psi_R = \Psi_{1R} + \Psi_{2R} + \Psi_{3R} + \Psi_{4R} + \Psi_{5SR} = C_R \frac{dT}{dt} \tag{2}$$

In eq. (2) C_R denotes the heat capacity of reference + reference holder. From eq. (1) and (2) it follows:

$$\begin{aligned} C_R \frac{dT}{dt} = {} & K_{1R}\ (T_f - T) + K_{2R}\ (T_f^4 - T^4) + K_{3R}\ (T_f - T) + \\ & K_{4SR}\ ((T + \Delta T) - T) + K_{5SR}\ ((T + \Delta T)^4 - T^4) \end{aligned} \tag{3}$$

For the heat-flow to the sample a similar equation can be derived:

$$\begin{aligned} C_s \frac{d\ (T + \Delta T)}{dt} = {} & K_{1S}\ (T_f - (T + \Delta T)) + K_{2S}\ (T_f^4 - (T + \Delta T)^4) + \\ & K_{3S}\ (T_f - (T + \Delta T)) + K_{4SR}\ (T - (T + \Delta T)) + \\ & K_{5SR}\ (T^4 - (T + \Delta T)^4) \end{aligned} \tag{4}$$

The symmetry of the measuring cell can now be represented as:

$$\Delta K_T = (K_{1S} - K_{1R})\,(T_f - T) + (K_{2S} - K_{2R})\,(T_f^4 - T^4) + (K_{3S} - K_{3R})\,(T_f - T) \quad (5)$$

ΔK_T is proportional to the differences in heat-transfer coefficients between sample and reference holder and to the difference in temperature between furnace and reference (if the second term is neglected).
A total heat transfer coefficient is defined as:

$$K_T = K_{1S} + K_{3S} + 2\,K_{4SR} + 4\,(K_{2S} + 2\,K_{5SR})\,T^3 \quad (6)$$

From (6) it follows that K_T is not only a function of the several heat transfer coefficients, but also of the temperature.
Particularly at higher temperatures the last term becomes important.

Subtraction of (3) and (4), using (5) and (6) gives:

$$\Delta T = \frac{\Delta K_T}{K_T} - \left(\frac{C_S - C_R}{K_T}\right)\frac{dT}{dt} - \frac{C_S}{K_T}\frac{d(\Delta T)}{dt} \quad (7)$$

This equation gives the initial transient of a heat-flow DSC curve.
From (7) it can be concluded that $\Delta T = 0$ when $\Delta K_T/K_T = 0$ and $C_S = C_R$.
This illustrates the importance of $\Delta K_T/K_T$ in the construction of a heat-flow differential scanning calorimeter. In order to obtain a small value of $\Delta K_T/K_T$ the symmetry of the construction should be very high, the temperature lag $(T_f - T)$ should be small, the furnace temperature should be homogeneous and K_T should be large.

When the sample shows a transition, the resulting curve is as given in fig. 2.

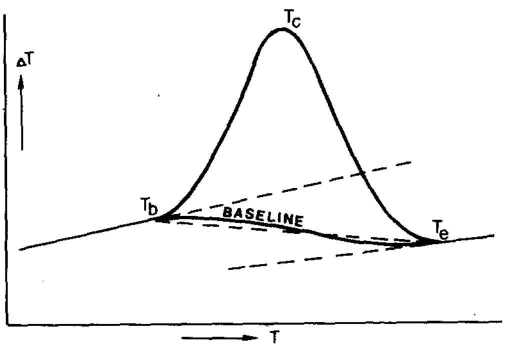

Fig. 2. Schematic diagram of a heat-flow DSC curve.

During the transition the heat capacity of sample plus sample holder changes from C_S via $C_S + \alpha(t) \cdot \Delta C_S$ to $C_S + \Delta C_S$. (α represents the reacted fraction.

At temperatures $T < T_b$, $\alpha = 0$; at temperatures $T_b < T < T_e$, $\alpha = \alpha(t)$ and when $T > T_e$, $\alpha = 1$.

The heat flow during the transition can be given as: $Q \frac{d\alpha}{dt}$, in which Q is the total heat generated or consumed during the reaction.

Now, $$\Psi_S = (C_S + \alpha\,\Delta C_S)\,\frac{d(T + \Delta T)}{dt} + Q\,\frac{d\alpha}{dt} \tag{8}$$

Using eqs. (4) to (7) it follows:

$$\Delta T = \frac{\Delta K_T}{K_T} - \frac{C_S + \alpha\,\Delta C_S - C_R}{K_T}\,\frac{dT}{dt} - \frac{C_S + \alpha\Delta C_S}{K_T}\,\frac{d\Delta T}{dt} - \frac{Q}{K_T}\,\frac{d\alpha}{dt} \tag{9}$$

At temperatures $T_b > T > T_e$, $d\alpha/dt = 0$ and ΔT is given as:

$$\Delta T^b = \frac{\Delta K_T}{K_T} - \frac{C_S - C_R}{K_T}\,\frac{dT}{dt} - \frac{C_S}{K_T}\,\frac{d\Delta T^b}{dt} \qquad T < T_b \tag{10}$$

and

$$\Delta T^e = \frac{\Delta K_T}{K_T} - \frac{C_S + \Delta C_S - C_R}{K_T}\,\frac{dT}{dt} - \frac{C_S}{K_T}\,\frac{d\Delta T^e}{dt} \qquad T > T_e \tag{11}$$

In ref. 4 the first three terms of the right-hand side of (9) are regarded as the baseline function.

We however define the baseline as the shape of the curve when the sample transition proceeds without heat generation or consumption ($Q = 0$). Obviously,

$$\Delta T^n = \frac{\Delta K_T}{K_T} - \frac{C_S + \alpha\Delta C_S - C_R}{K_T}\,\frac{dT}{dt} - \frac{C_S + \alpha\Delta C_S}{K_T}\,\frac{d\Delta T^n}{dt} \tag{12}$$

in which the index n denotes the thermal neutral transition.

We now approximate:

$$\frac{d\Delta T^n}{dt} = (1 - \alpha)\,\frac{d\Delta T^b}{dt} + \alpha\,\frac{d\Delta T^e}{dt} \tag{13}$$

which, combined with (12) gives:

$$\Delta T^n = (1 - \alpha)\left(\frac{\Delta K_T}{K_T} - \frac{C_S - C_R}{K_T}\frac{dT}{dt} - \frac{C_S}{K_T}\frac{d\Delta T^b}{dt}\right) + \alpha\left(\frac{\Delta K_T}{K_T} - \frac{C_S + \Delta C_S - C_R}{K_T}\frac{dT}{dt} - \frac{C_S + \Delta C_S}{K_T}\frac{d\Delta T^e}{dt}\right) - \alpha(1 - \alpha)\left(\frac{d\Delta T^b}{dt} - \frac{d\Delta T^e}{dt}\right) \tag{14}$$

or, if we substitute (10) and (11) and neglect the last term of (14):

$$\Delta T^n = (1 - \alpha)\,\Delta T^b + \alpha\Delta T^e \tag{15}$$

Equation (15) is called the baseline function.

The area of a peak resulting from a thermal transition for which $Q \neq 0$ is given as:

$$\int_{T_b}^{T_e} (\Delta T - \Delta T^n)\, dT \tag{16}$$

If we substitute $\Delta T - \Delta T^n = \Delta T^p$, ΔT^p can be written as:

$$\Delta T^p = \frac{C_S + \alpha\Delta C_S}{K_T}\,\frac{d\Delta T^p}{dt} - \frac{Q}{K_T}\frac{d\alpha}{dt},$$ leading to:

$$\int_{T_b}^{T_c} \Delta T^p dT = -\frac{1}{K_T}\frac{dT}{dt}\int_{T_b}^{T_e} (C_S + \alpha\Delta C_S)\, d\Delta T^p - \frac{Q}{K_T}\frac{dT}{dt} \tag{17}$$

(it is assumed that $K_{T_e} = K_{T_b}$).

The first term of the right-hand side of (17) can be reduced to:

$$\frac{1}{K_T}\frac{dT}{dt}\,\Delta C_S \int_0^1 \Delta T^p\, d\alpha$$

Eq. (17) therefore reads:

$$\int_{T_b}^{T_e} \Delta T^p dT = -\frac{Q}{K_T}\frac{dT}{dt} + \frac{1}{K_T}\frac{dT}{dt}\,\Delta C_S \int_0^1 \Delta T^p\, d\alpha \tag{18}$$

From eq. (18) it follows that the peak area should be corrected by a certain term to give the transition heat Q. This correction term is small and may be neglected when ΔT^p is small, so when K_T is large.

When the reaction is completed, at a temperature T_c, $\frac{d\alpha}{dt} = 0$ and from eq. (9) it follows:

$$\Delta T^c = - \frac{C_S + \Delta C_S}{K_T} \frac{d\Delta T^c}{dt} \qquad (19)$$

(neglecting $\frac{\Delta K_T}{K_T}$ and $- \frac{C_S + \Delta C_S - C_R}{K_T} \frac{dT}{dt}$)

Integration gives:

$$\int_{\Delta T} \frac{d\Delta T^c}{\Delta T^c} = - \int_t \frac{K_T}{C_S + \Delta C_S} dt, \text{ leading to}$$

$$\Delta T = \Delta T^c \exp \left(- \frac{K_T}{C_S + \Delta C_S} \cdot t\right) \qquad (20)$$

Eq. (20) describes the resolving power of a heat-flow differential scanning calorimeter, which is the most important quality determining parameter of this instrument.

Summarizing, in the construction of a heat-flow differential scanning calorimeter a large value of K_T should be aimed at for three reasons. First, a small value of $\Delta K_T/K_T$ is obtained, secondly, the peak area correction term is small and finally, the resolution is high.

CONCLUSIONS

On the basis of eqs. (7), (18) and (20) it is shown that K_T to a large extent controls the performance of a heat-flow differential scanning calorimeter. With large values of K_T the best thermoanalytical curves are obtained. A low thermal lag and a very symmetrical construction give, according to eqs. (5), (6) and (7), a good baseline performance over the whole temperature range. Starting from these theoretical considerations the differential scanning calorimeter DSC model 42 of Maple Instruments has been developed.

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