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A theoretical investigation of the preconditions for obtaining the true thermodynamic transition temperature from only one DSC measurement

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Abstract

The true thermodynamic transition temperature can be obtained from one DSC measurement alone. It can be determined by drawing the tangent to the left side of the transition peak in the heat flux versus temperature curve. The intercept of this tangent with the abscissa shows the true thermodynamic transition temperature. This intercept temperature is independent of heat transfer coefficients, heat capacities and the heating rate, provided that (1) the heat capacity of the sample is five or more times higher than that of the sample pan; (2) the heat transfer coefficient between the sample and pan is not smaller than 2×10^{-2} W cm^{-2} K^{-1}.

INTRODUCTION

It has been shown that it is possible to obtain the true thermodynamic transition temperature of a physical phase transition from only one DSC measurement [1].

The true thermodynamic transition temperature is usually obtained by extrapolating the onset temperatures at various heating rates to zero heating rate [2]. This procedure is time-consuming and not sufficiently reliable because the heat transfer coefficients may not be reproducible in different experiments.

In ref. 1 it was shown that in nearly all relevant cases the intercept of the tangent to the left side of the transition peak with the abscissa in the heat flux versus temperature curve represents the true thermodynamic transition temperature. However, for very high ratios between the heat capacities of pan and sample this procedure is not suitable (see Schick and Höhne [3]). It is the purpose of this paper to derive the boundaries which define the scope of applicability for the method proposed in ref. 1.

PHYSICAL MODEL

Figure 1 shows the physical model used in our investigation (see also ref. 4). The temperature T of both the reference holder and the sample holder is $T = T_A + K_1 t$

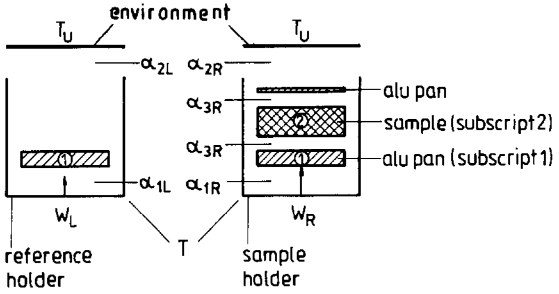

Fig. 1. Physical model of DSC: T is the temperature of the sample holder; T_U is the ambient temperature, α_{1L}, α_{1R} are the heat transfer coefficients between sample holder and pan of the left or right system, respectively; α_{3R} is the heat transfer coefficient between sample and pan of the right system; α_{2L}, α_{2R} are the heat transfer coefficients between the left or right system and ambient conditions, respectively; and W_L, W_R are the heat fluxes into the left and right system, respectively.

where t is time, K_1 the constant heating rate and T_A the constant initial temperature. W_R and W_L in Fig. 1 are heat fluxes into the right and left system, respectively, which are necessary to maintain at any time the temperature T of the sample holder and of the reference holder.

The difference

$$\Delta W = W_R - W_L$$

is recorded during the experiment; it is dependent on the actual temperature (see, below).

The ambient temperature T_U is constant. For the sake of simplicity it is assumed to be zero. The symbols α_{1L} and α_{1R} are the heat transfer coefficients between the sample holder and pan of the left and right systems, respectively; α_{2L} and α_{2R} are the heat transfer coefficients between the left or right systems and ambient conditions; and α_{3R} is the heat transer coefficient between sample and pan of the right system.

MATHEMATICAL SOLUTION AND DISCUSSION

For calculating the heat fluxes, the non-linear parabolical initial boundary problem shown in Fig. 1 has to be solved.

The stationary and quasi-stationary solutions of the physical model used in this investigation are

$$\bar{W}_R(T_A) = \frac{\lambda_2 T_A}{(1/h_{23})(1 + h_{13}/h_1 + D_1 h_{13}) + 1/h_2 + D_2}$$

$$\bar{W}_R(T_E) = \frac{T_E}{T_A} \bar{W}_R(T_A)$$

$$\begin{aligned} W_R(T) = {} & -(\lambda_1 h_1 K_1/A)\{(h_{13}h_{23}c - h_{13}a)z + (1/a_2)[h_{13}h_{23}(e + scD_1^2/2) \\ & - h_{13}b - sd(D_1 + h_{13}D_1^2/2)]\} - (1/\lambda_1)\bar{W}(T_A) \end{aligned} \tag{1}$$

$$\bar{W}_L(T_A)=\frac{T_A h_1 h_2 \lambda_1}{h_2+h_1(1+h_2D_1)}$$

$$\bar{W}_L(T_E)=\frac{T_E}{T_A}\bar{W}_L(T_A)$$

$$W_L(T)=A_L T+W_0$$

$$W_0=\frac{h_1\lambda_1 K_1 D_1(1-h_2D_1/2)}{a_1[h_2+h_1(1+h_2D_1)]} \tag{2}$$

$$W_{FL}(T)=A(T-T_{SP}) \tag{3}$$

$$A=\frac{1}{1/\alpha_{1R}+1/\alpha_{3R}}=\tan\gamma \tag{4}$$

$$A_L=\frac{h_1h_2\lambda_1}{h_2+h_1(1+h_2D_1)}=\tan\delta \tag{5}$$

where the following symbols are used:

$a_1=\lambda_1/(\rho_1c_1)$ $a_2=\lambda_2/(\rho_2c_2)$

$h_1=\alpha_{1R}/\lambda_1$ $h_2=\alpha_{2R}/\lambda_2$

$h_{13}=\alpha_{3R}/\lambda_1$ $h_{23}=\alpha_{3R}/\lambda_2$

$a=h_2h_{23}D_2+h_2+h_{23}$

$b=D_2+h_2h_{23}D_2^3/6+(h_2+h_{23})D_2^2/2$

$c=1+h_2D_2$

$d=h_2h_{23}D_2+h_2+h_{23}$

$e=D_2^2/2+h_2D_2^3/6$

$g=h_1h_{13}D_1+h_1+h_{13}$

$r=D_1+h_1h_{13}D_1^3/6+(h_1+h_{13})D_1^2/2$

$s=a_2/a_1$

$A=ga-h_{13}h_{23}c(1+h_1D_1)$

$E=(1-a_2)[gb-h_{13}h_{23}(1+h_1D_1)e]+(1/a_1)[rd-h_{13}h_{23}c(D_1^2/2+h_1D_1^3/6)]$

$z=(T-T_A)/K_1-E/A$

The symbols D, λ, ρ, c, α_1, α_3 and α_2 stand for thickness, heat conductivity, density, specific heat, and heat transfer coefficient between sample holder and pan, heat transfer coefficient between sample and pan and heat transfer coefficient between the system and the environment. The subscripts 1 and 2 refer to pan and sample, respectively.

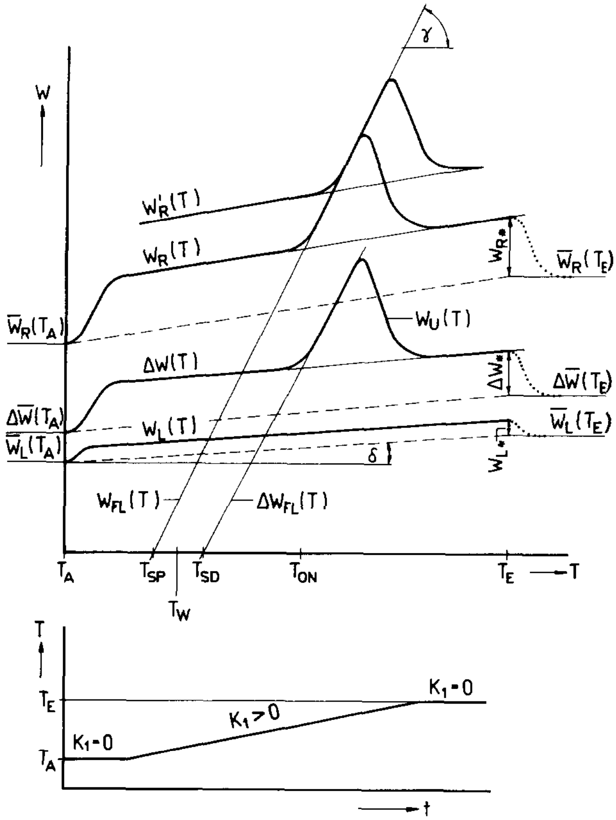

Fig. 2. Graph of the mathematical solution.

The solutions and the temperature program are shown in the graph of Fig. 2.

As with the heat fluxes, the subscripts R and L are used to describe the heat transfer coefficients of the right and left systems.

Before and after heating with the constant heating rate K_1, the temperature is kept constant at T_A and T_E, respectively. The heat fluxes of these constant temperature regimes are $\bar{W}_R(T_A)$, $\bar{W}_L(T_A)$, $\Delta\bar{W}(T_A)$ and $\bar{W}_R(T_E)$, $\bar{W}_L(T_E)$ and $\Delta\bar{W}(T_E)$.

During the regime of increasing temperature, the heat flux into the left (reference) system is $W_L(T)$; the heat flux into the right (sample) system which is consumed by the increasing temperature, but not by a phase transition is $W_R(T)$.

Thus, the heat flux difference ΔW mentioned above has to be interpreted as follows

$T = T_A$: $\quad \Delta W = \bar{W}_R(T_A) - \bar{W}_L(T_A) = \Delta\bar{W}(T_A)$

$T = T_E$: $\quad \Delta W = \bar{W}_R(T_E) - \bar{W}_L(T_E) = \Delta\bar{W}(T_E)$

$T = T_A + K_1 t$: $\quad \Delta W = \Delta\bar{W}(T_A) + W_R(T) - W_L(T) + W_U(T)$

W_U represents the latent heat flux during phase transition. The difference $\Delta W(T) = W_R(T) - W_L(T)$ is the so-called ‘baseline’ of the transition reaction.

The tangent to the left side of the transition peak is $W_{FL}(T)$ and the slopes of $W_{FL}(T)$ and $W_L(T)$ are A and A_L, respectively.

For ideal heat transfer conditions, i.e. $\alpha_{2R}, \alpha_{2L} \rightarrow 0$ and $\alpha_{1L}, \alpha_{1R}, \alpha_{3R} \rightarrow \infty$, eqns. (1) and (2) reduce to the well-known limits

$$\lim\{W_L(T)\} = K_1 D_1 \rho_1 c_1$$

and

$$\lim\{W_R(T)\} = K_1(D_1 \rho_1 c_1 + D_2 \rho_2 c_2)$$

If $\alpha_{2L}, \sigma_{2R} \rightarrow 0$, the heat fluxes at the constant temperatures T_A and T_E are zero.

The initial slope A of the tangent $W_{FL}(T)$ depends only on α_{1R} and α_{3R}, but not on heating rate K_1, heat transfer coefficient α_{2R}, specific heats c_1, c_2 or densities ρ_1 and ρ_2.

From $W_{FL}(T) = 0$, it follows that $T = T_{SP}$, i.e. the intercept of the tangent of the transition peak with the abscissa represents the transition temperature T_{SP} for any heating rate K_1, any heat transfer coefficient α_{2R} and for any slope A of the tangent. However, as shown in Fig. 3, the temperature T_{SP} depends on the heat capacities of the pan and sample.

Figure 3 shows the deviation ΔT_S of T_{SP} from the true thermodynamic temperature T_W for the typical parameters $K_1 = 12\ \mathrm{K\ min^{-1}}$, $\alpha_{1R} = 0.4\ \mathrm{W\ cm^{-2}\ K^{-1}}$, $\alpha_{2R} = 4 \times 10^{-6}\ \mathrm{W\ cm^{-2}\ K^{-1}}$, $c_1 = 0.88\ \mathrm{J\ g^{-1}\ K^{-1}}$, $c_2 = 0.4\ \mathrm{J}$

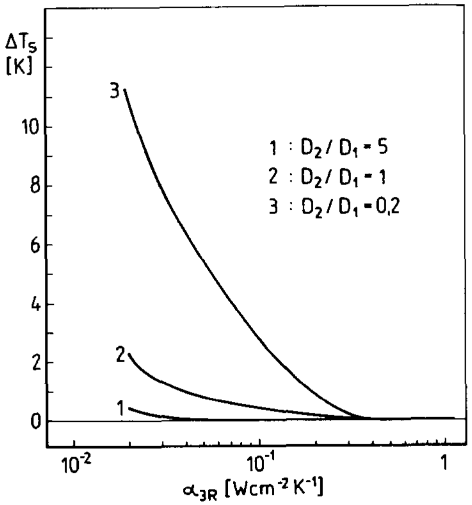

Fig. 3. Deviation $\Delta T_S = T_W - T_{SP}$ versus the heat transfer coefficient α_{3R} between pan and sample.

$g^{-1} K^{-1}$, $\rho_1 = 2.7\ g\ cm^{-3}$, $\rho_2 = 10\ g\ cm^{-3}$, $D_2 = 0.1$ cm, and the specific transition energy $3\ J\ g^{-1}$.

The deviation $\Delta T_S = T_W - T_{SP}$ increases with decreasing α_{3R} and D_2/D_1, i.e. with poor heat contacts between sample and pan and with small D_2/D_1 ratios, the heat flux into the sample system during phase transition is the sum of the latent transition heat flux and of the heat flux which is consumed for increasing the temperature of the sample pan, where the heating rate is smaller than K_1. Therefore, the heat flux $W_R(T)$ increases and, consequently, falsifies the true value T_W by the amount of $\Delta T_S = T_W - T_{SP}$ (see Fig. 3).

Only for high values of D_2/D_1 and with an appropriate heat contact between sample and pan does the deviation ΔT_S tend to zero.

The difference heat flux $\bar{W}(T_A) + W_R(T) - W_L(T) + W_U(T)$ is obtained by subtracting the heat flux of the reference system, $W_L(T_A) + W_L(T)$, from that of the sample system, $\bar{W}_R(T_A) + W_R(T) + W_U(T)$. Consequently, the tangent of the transition peak of the difference flux is shifted to higher temperatures, and the intercept temperature of the difference heat flux is T_{SD} (see Fig. 2). According to eqns. (2)–(5), this difference is

$$W_{FL}(T) - W_L(T) = A(T - T_{SP}) - (A_L T + W_0)$$

With this set to zero, the temperature T_{SD} is obtained as

$$T_{SD} = T_{SP} + \frac{W_0 + A_L T_{SP}}{A - A_L}$$

Figure 4 shows the deviations $\Delta T_{SD} = T_W - T_{SD}$ as a function of α_{3R} at different levels of D_2/D_1. The deviations ΔT_{SD} show the same tendency as the deviations ΔT_S in Fig. 3, but they are much smaller. This is because an

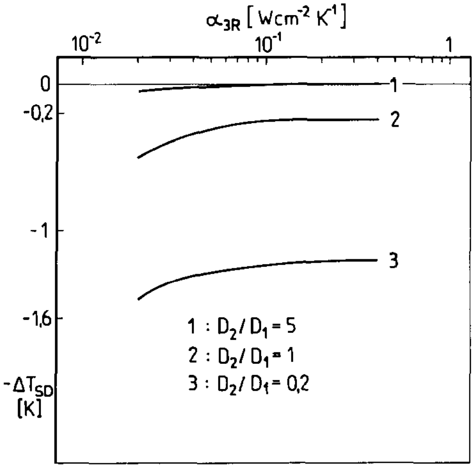

Fig. 4. Deviation $\Delta T_{SD} = T_W - T_{SD}$ versus the heat transfer coefficient α_{3R} between pan and sample.

exact compensation of the deviation ΔT_S by subtraction of the heat flux of the reference system from that of the sample system is not possible: during the phase transition the heating rate of the sample pan is smaller than the heating rate K_1 of the reference pan.

For the set of typical parameters used in our investigation, the deviations ΔT_S and ΔT_{SD} are only zero if $D_2/D_1 \geq 5$. This applies to nearly any heat contact α_{3R} (see curve 1 in Fig. 4).

The point of intersection between $W_R(T)$ and $W_{FL}(T)$ or between $\Delta W(T)$ and $W_{FL}(T)$, represents the so-called onset temperature T_{ON} (see Fig. 2). According to eqns. (1), (3) and Fig. 2, the onset temperature T_{ON} is higher for a lower slope A of the tangent of transition and for a higher $W_R(T)$ and $\Delta W(T)$, respectively, i.e. for higher values of α_{2R}, ρ_1, c_1, ρ_2, c_2 and K_1 (see curve $W'_R(T)$). Whereas, according to eqns. (1) and (2), the onset temperature T_{ON} depends on α_{1L}, α_{2L}, α_{1R}, α_{2R}, α_{3R}, ρ_1, c_1, ρ_2, c_2 and K_1 in a complex manner; the intercept T_{SD} with the tangent $\Delta W_{FL}(T)$ of the differential transition peak is not influenced by these parameters if the deviation ΔT_{SD} is zero, i.e. $T_{SD} = T_W$.

CONCLUSIONS

At present, the true thermodynamic temperature for DSC methods is obtained by time-consuming measurements of the onset temperatures for different heating rates and masses and their extrapolation to a zero heating rate. Closer inspection of this procedure shows that it is possible to obtain the true thermodynamic temperature, for small specific transition energies also, from one DSC measurement only if the following two conditions are met:

1. The heat capacity of the sample is five or more times higher than that of the pan.
2. The following heat transfer coefficients α_{3R} between sample and pan are necessary to limit the deviation ΔT_{SD}.

α_{3R} (W cm^{-2} K^{-1})	ΔT_{SD} (K)
≥0.04	≤0.02
0.02	−0.04

The proposed intercept method is characterised by two advantages:

1. Compared with the onset methods, the proposed procedure is far less time-consuming, because only one measurement with a sufficiently high heating rate is required.

2. It is much more reliable than the onset methods because it does not depend on heat transfer coefficients, heat capacities or the heating rate.

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