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AN ANALYSIS OF THE FACTORS AFFECTING THE PEAK SHAPE AND THE QUANTITATIVE RELIABILITY OF A HEAT FLUX DSC CELL

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ABSTRACT

In a previous work it was shown that unexpected problems may arise in the calibration of a heat flux DSC cell. To understand the origin of these problems an analysis has been undertaken of what happens in the cell before, during and after the peak. Here the first part of this analysis is reported dealing with the baseline and with the dependence of the recorded signal on time. Analytical expressions are obtained connecting the measured signal with experimental variables and instrument constants. Completely independent on sample related properties, a maximum measurable ΔT is introduced as limiting factor for quantitative reliability.

INTRODUCTION

The ability to give reliable quantitative results on reaction enthalpies is probably the most appreciated feature of differential scanning calorimetry and explains why this technique has nowadays been widely substituted for DTA whose chief limit was just a poor quantitative reliability.

In a previous work (ref.1) it was shown that unexpected problems may arise in the calibration of a heat flux DSC cell and that contrary to the manufacturer statements and to that is generally believed, different calibration constant values can be obtained by different standards. This is obviously not a desirable situation and a full understanding of the reasons by which it is determined is necessary if full advantage of heat flux differential scanning calorimetry has to be taken. Notwithstanding models have been proposed (ref.s 2,3) based on electrical analogue representations of the cell, this understanding has not yet been reached. As the problem is a very important one in the field of thermal analysis, a detailed study has been undertaken by our group of what happens, from a calorimetric point of view, during a DSC run. The final aim of such a study is to show if and in which way experimental variables and sample properties can affect the quantitative response of the apparatus. Here the first part of the analysis is reported dealing with the baseline and with the dependence of the recorded signal on time.

BASELINE ANALYSIS

Figure 1 shows a cross section of a Du Pont heat flux DSC cell. Hearth of the cell is a constantan disc which serves as the major path for heat transfer and as a part of the differential thermocouple. The disc is attached to a silver programmed temperature block and two raised, symmetrically positioned platforms

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act as sample and reference holders.This is the cell by which our calibration measurements were performed. Cells by other manufacturers differ with respect to the materials by which they are constituted and to the way by which the differential thermocouple is realized. As however our analysis is concerned only with the operating principle of a heat flux DSC cell, its conclusions are of general validity, no matter of cell manufacturer.

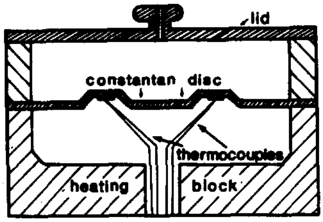

Fig.1. Du Pont DSC cell:cross section.

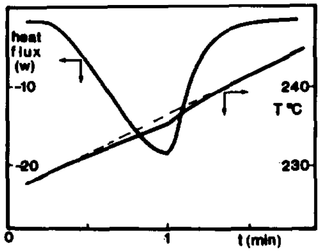

Fig.2. W and T vs.t for a tin sample.

It may be at this point useful to explicitly assess the basic assumptions on which the following analysis is carried out . They are:

1) the cell is perfectly symmetrical;
2) the temperature dependence of thermal capacities and thermal resistances can be neglected.

The first point does not need any comment.

For what concerns the second one it is to note that an electronic compensation exists in the recorder signal for the temperature dependence of the thermal resistances and that, as a consequence, these last ones can really be considered temperature independent.

Let Cp_S and Cp_R be the thermal capacities of the sample and reference systems respectively, i.e. of sample pan plus sample and reference pan plus reference.

Even in the case no physico-chemical phenomenon takes place on the sample, the heat fluxes on the sample and reference systems will be identical during a DSC run only for $Cp_S=Cp_R$.

If $Cp_S \neq Cp_R$ (for example $Cp_S>Cp_R$), at the beginning of the cell heating the sample holder temperature (T_{Sh}) will be lower than the reference holder temperature (T_{Rh}) and as a consequence a differential heat flux will be supplied to the sample holder. This differential heat flux must be thought as supplied both by the furnace and the reference holder; as however it is due to a temperature difference and acts in such a way to oppose to this temperature difference, an equilibrium condition will be reached characterized by a stationary temperature difference. The heat fluxes from the furnace to the sample and reference holders can be written as (see symbols table for the definition of each term of this and following equations)

$$(dQ/dt)_{Sh} = (T_F - T_{Sh})/R_1 \quad (1) \quad ; \quad (dQ/dt)_{Rh} = (T_F - T_{Rh})/R_1 \quad (1')$$

the differential heat flux from the furnace to the sample holder is:

$$(dQ/dt)_{ShdF} = (T_{Rh} - T_{Sh})/R_1 \qquad (2)$$

On the other hand the differential heat flux from the reference to the sample holder is:

$$(dQ/dt)_{ShdR} = (T_{Rh} - T_{Sh})/R_2 \qquad (3)$$

the total differential heat flux on the sample holder is then given by the sum of eq.s (2) and (3), i.e. :

$$(dQ/dt)_{Shd} = (T_{Rh} - T_{Sh}) (1/R_1 + 1/R_2) \qquad (4)$$

and making $1/R = 1/R_1 + 1/R_2$ we obtain $(dQ/dt)_{Shd} = (T_{Rh} - T_{Sh})/R$ (4′)

On this basis the total heat flux on the sample holder will be

$$(dQ/dt)_{Sh} = (dQ/dt)_{Rh} + (T_{Rh} - T_{Sh})/R \qquad (5)$$

Now if we take into account that, as a consequence of the sample and reference holder thermal capacities, part of the heat flux on each holder must be utilized for its own temperature increase, we can write for the heat fluxes on the sample and reference systems

$$\begin{aligned} (dQ/dt)_S &= (dQ/dt)_{Sh} Cp_S/(Cp_S + Cp_{Sh}) \\ (dQ/dt)_R &= (dQ/dt)_{Rh} Cp_R/(Cp_R + Cp_{Rh}) \end{aligned} \qquad (6)$$

and by substituting equations (6) in (5)

$$\begin{aligned} (dQ/dt)_S = {} & (dQ/dt)_R [(Cp_R + Cp_{Rh})/Cp_R] [(Cp_S/(Cp_{Sh} + Cp_S)] + \qquad (7) \\ & + [Cp_S/(Cp_S + Cp_{Sh})] [(T_{Rh} - T_{Sh})/R] \end{aligned}$$

Equation (7) relates the heat flux on the sample system to the heat flux on the reference system. By it and taking into account that $dQ/dt = Cp(dT/dt)$, the temperature difference between the sample and reference systems can easily be obtained:

$$\begin{aligned} T_S - T_R = {} & [(Cp_R + Cp_{Rh} - Cp_S - Cp_{Sh})/Cp_R(Cp_S + Cp_{Sh})] \int_0^t (dQ/dt)_R dt + \\ & + [1/ (Cp_S + Cp_{Sh})R] \int_0^t (T_{Rh} - T_{Sh}) dt \end{aligned} \qquad (8)$$

When a stationary condition is reached it must be $d(T_S - T_R)/dt = 0$; differentiating equation (8) with respect to time and solving for $T_{Rh} - T_{Sh}$ we obtain $[Cp_{Rh} = Cp_{Sh}$; $(dQ/dt)_R / Cp_R = dT_R/dt = \beta]$

$$T_{Rh} - T_{Sh} = \beta R (Cp_S - Cp_R) \qquad (9)$$

Equation (9) is the baseline equation and represents the level of the measured signal when no physico-chemical phenomenon on the sample occurs. As the measured signal must start from zero level, it can be argued from eq.(9)

there is an early jump at the beginning of a DSC run whose magnitude, once sample and reference have been fixed, is proportional to the heating rate β .

PEAK ANALYSIS

Suppose now melting of a metal is taking place.The total heat flux on the sample holder during melting will be

$$\begin{aligned}(dQ/dt)_{Shf}&=(dQ/dt)_{Rhf}+\beta(Cp_S-Cp_R)+(T_{Rhf}-T_{Shf})/R=\\&=[(T_{Shf}-T_{Sf})/(R_3+R_4)]\ [(Cp_S+Cp_{Sh})/Cp_S]\end{aligned}\tag{10}$$

and, taking into account eq. (6)

$$\begin{aligned}&[(dQ/dt)_{Rf}](Cp_R+Cp_{Rh})/Cp_R+\beta(Cp_S-Cp_R)+(T_{Rhf}-T_{Shf})/R=\\&\qquad=[(T_{Shf}-T_{Sf})/(R_3+R_4)]\ [(Cp_S+Cp_{Sh})/Cp_S]\end{aligned}\tag{11}$$

A brief discussion is now necessary on the term $(dQ/dt)_{Rf}$. Due to the melting a heat flux arises from the reference to the sample holder; as a consequence the heat flux on the reference system during melting will be lower than it was before melting. As the differential heat flux from the reference to the sample holder is given by $(T_{Rhf}-T_{Shf})/R_2$, it must be

$$(dQ/dt)_{Rhf}=(dQ/dt)_{Rh}-(T_{Rhf}-T_{Shf})/R_2\tag{12}$$

From equation (12) by simple considerations eq.(13) can be obtained

$$[(dQ/dt)_{Rf}](Cp_R+Cp_{Rh})/Cp_R=[(dQ/dt)_R](Cp_R+Cp_{Rh})/Cp_R-(T_{Rhf}-T_{Shf})/R_2\tag{13}$$

On the other hand,owing to the fact that ,as noted, only a part of the heat flux on the reference holder can arrive to the reference system, the other part being utilized by the reference holder for its own temperature increase, it must also be

$$\begin{aligned}(dQ/dt)_{Rhf}&=Cp_{Rh}\,(dT_{Rhf}/dt)+(dQ/dt)_{Rf}\\(dQ/dt)_{Rh}&=Cp_{Rh}\,(dT_{Rh}/dt)+(dQ/dt)_R\end{aligned}\tag{14}$$

The heating rate of the reference holder during melting can then be obtained by eq.s (12),(13),(14):

$$(dT_{Rhf}/dt)=\beta-(T_{Rhf}-T_{Shf})/[R_2(Cp_R+Cp_{Rh})]\tag{15}$$

It can be seen from equation (15) that as a consequence of the heat flux from the reference to the sample holder, the heating rate of the reference holder during melting is lower than it was before melting. From eq.s (11) and (13) and taking into account that $(dQ/dt)_R=Cp_R(dT_R/dt)$, equation (16) is obtained

$$\begin{aligned}&(Cp_R+Cp_{Rh})(dT_R/dt)-(T_{Rhf}-T_{Shf})/R_2+\beta(Cp_S-Cp_R)+(T_{Rhf}-T_{Shf})/R=\\&\qquad=[(T_{Shf}-T_{Sf})/(R_3+R_4)][(Cp_S+Cp_{Sh})/Cp_S]\end{aligned}\tag{16}$$

By differentiating equation (16)with respect to time $[(d/dt)(dT_R/dt)=d\beta/dt=0; (dT_{Sf}/dt)=0]$ the relationship between the rate of change of the sample and reference holder temperatures can be obtained :

$$(dT_{Shf}/dt)\{(Cp_S+Cp_{Sh})/[(R_3+R_4)Cp_S]+1/R-1/R_2\} = (dT_{Rhf}/dt)\ (1/R - 1/R_2) \qquad (17)$$

Now from equations (15) and (17) the dependence of the measured signal on time is easily obtained

$$\begin{gathered} d(T_{Rhf}-T_{Shf})/dt = d\,\Delta T/dt = \beta\,[R_1(Cp_S+Cp_{Sh})]/[R_1(Cp_S+Cp_{Sh})+(R_3+R_4)Cp_S]- \\ -[\,\Delta T/\ R_2(Cp_R+Cp_{Rh})]\ \{[R_1(Cp_S+Cp_{Sh})]/[R_1(Cp_S+Cp_{Sh}) + (R_3+R_4)Cp_S]\} \end{gathered} \qquad (18)$$

A basic requirement of a heat flux DSC cell is that R_1>>(R_3+R_4). If, in fact, this would not be true, the cell would have a too low sensitivity and precision and could not be used for reaction enthalpy measurements. It follows that equation (18) can be easily simplified to

$$d\,\Delta T/dt \;=\; \beta \;-\; \Delta T/[R_2(Cp_R+Cp_{Rh})] \qquad (19)$$

Equation (19) expresses in a simplified form the slope of the measured signal during a melting peak. The second term of the right hand side of this equation could in principle be neglected only if R_2 was infinitely large. In this case no heat exchange would take place between the sample and reference holders and the slope of the measured signal would be a constant over the entire melting process. R_2 cannot however be handled as an independent variable in the manufacture of a heat flux DSC cell and its value in a real cell cannot be made as large as is necessary to make the second term of the right hand side of equation (19) negligible with respect to the first one. As however the temperature difference between the reference and the sample holders increases from the beginning to the end of the melting process, the relative weight of the second term increases approaching the peak maximum. The result is that while at the beginning of the melting peak the recorded signal looks as a straight line (ΔT is small), a lowering of the signal slope becomes evident approaching the peak maximum.

Figure 2 reports, as an example, the melting peak for a tin sample. It can be seen that the baseline,the sample holder temperature during melting and the temperature difference between the sample and the reference holders vary with respect to time as predicted by equations (9), (17) and (19) respectively.

To fully understand the very important role the heat transfer between the sample and reference holders plays on the performances of a heat flux DSC cell, some other comment on equation (19) is however necessary.

It was seen in the upper discussion that a lowering of the measured signal slope near to the peak maximum occurs as a consequence of the ΔT value increase.

The magnitude of the lowering obviously depends on the ΔT value. Suppose now a sufficiently large ΔT value is reached during a peak as to make the second term of the right hand side of equation (19) equal to the first one. In this case it would be $d\,\Delta T/dt=0$ and no further increase of the ΔT value would be possible no matter of the fact that part of the sample has not yet undergone melting. By putting $d\,\Delta T/dt=0$ in equation (19) and solving for ΔT we obtain

$$(\,\Delta T)_{lim} = \beta R_2(Cp_R+Cp_{Rh}) \qquad (20)$$

Equation (20) indicates there is a limit to the maximum ΔT value which can be generated in a heat flux DSC cell and that this limit is completely independent on sample related properties depending on instrumental constants (R_2, Cp_{Rh}) and on experimental variables (β , Cp_R) only.

It will be shown in a next work (4) that this concept is of fundamental importance in the discussion of the factors affecting the accuracy of quantitative data obtained by heat flux differential scanning calorimetry.

SYMBOLS TABLE

$\underline{Cp_S}$= thermal capacity of sample system (sample plus sample pan);$\underline{Cp_R}$ = idem for reference system;$\underline{Cp_{Sh}}$ = thermal capacity of sample holder; $\underline{Cp_{Rh}}$ = thermal capacity of reference holder ; $\underline{T_{Sh}}$ = sample holder temperature; $\underline{T_{Rh}}$ = reference holder temperature; $\underline{T_F}$ =furnace temperature; $\underline{T_S}$ = sample system temperature ; $\underline{T_R}$ = reference system temperature; $\underline{T_{Rhf}}$ = reference holder temperature during melting; $\underline{T_{Shf}}$ = sample holder temperature during melting ; $\underline{T_{Sf}}$ = sample temperature during melting ; $\underline{R_1}$ = furnace-holder thermal resistance; $\underline{R_2}$ = holder-holder thermal resistance ; $\underline{R_3}$ = holder-pan thermal resistance ; $\underline{R_4}$ = pan-sample thermal resistance ; $\underline{(dQ/dt)_{Sh}}$ = heat flux from the furnace to the sample holder when no melting is taking place ; $\underline{(dQ/dt)_{Rh}}$ = heat flux from the furnace to the reference holder when no melting is taking place ; $\underline{(dQ/dt)_{ShdF}}$ = differential heat flux from the furnace to the sample holder ;$\underline{(dQ/dt)_{ShdR}}$ = differential heat flux from the reference holder to the sample holder.

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