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HEAT TRANSFER IN A DISC-TYPE DSC APPARATUS
Part 5. Theoretical equation of melting with a heat flux coupled cells DSC

K. Alouani[1], *M. Siniti*[2], *F. Schiets*[3] *and P. Claudy*[3*]

[1]Laboratoire de Synthèse Organométallique, Faculté des Sciences, Université El Manar, Tunis
[2]Laboratoire de Chimie Physique, Faculté des Sciences, Université Chouaib Doukkali, 24000 El Jadida, Moroco
[3]Laboratoire des Matériaux Organiques à Propriétés spécifiques. UMR 5041 CNRS-Université de Savoie
BP 24 69390 Vernaison, France

The literature describes models of DSC apparatuses. However, the use of these models require a precise determination of the values of the resistors and the capacitors of the apparatus. Theoretical equations of a first order transition in a coupled cells heat flux DSC at a constant heating rate are given. It is shown that the value of the resistors and capacitors may be obtained. The influence of resistors product - crucible or crucible – detectors is established.

Keywords: *capacitor, DSC, first order transition, resistor*

Introduction

Calorimetric techniques, such as differential scanning calorimetry (DSC) are often used for the study of transitions, the determination of reaction kinetics [1–4] and so on. Most often, these experiments are done on heating, using a constant or a time varying heating rate [5–6]. The result of the experiments should be the enthalpy of the sample *vs.* its temperature and/or time, which is the basis for kinetic and thermodynamic determinations [7–11]. In fact the experiments are smeared, and most often the results are the so-called heat capacity of the sample, *vs.* temperature, at best, at the beginning of the thermal effect.

Desmearing of the calorimetric signal is most often based on a model of the calorimetric apparatus [12–15]. It was shown that disc-type heat flow DSC apparatuses behave as coupled cell calorimeters [16, 17] and not as a Calvet-type [18, 19] microcalorimeters.

A large number of papers [20–23] use thermal Ohm's law. However, the values of the resistors and capacitors of the model are difficult to obtain, which greatly limits the use of this method.

The scope of this paper is to establish the equations in view of a simple method to obtain the most precise values of the resistors and capacitors of the model of the calorimeter.

Theoretical

Chemical thermodynamics and kinetics

To avoid any confusion about heat capacities used in this paper, some thermodynamics considerations have to be made. Prigogine [24] has established that the thermodynamic state of a closed system can always be described using three state variables, namely T, P, ξ. The last variable ξ stands for the degree of advance of some transformation occurring in the system. Then $H=f(T, P, \xi)$. Since H is a state function:

$$\mathrm{d}H=\left(\frac{\partial H}{\partial T}\right)_{\mathrm{P},\xi}+\left(\frac{\partial H}{\partial \xi}\right)_{\mathrm{P,T}}+\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T},\xi} \tag{1}$$

At constant pressure, the 'apparent heat capacity C_p' [25] is defined by:

$$C_\mathrm{p}=\left(\frac{\mathrm{d}H}{\mathrm{d}T}\right)_\mathrm{P}=\left(\frac{\partial H}{\partial T}\right)_{\mathrm{P},\xi}+\left(\frac{\partial H}{\partial \xi}\right)_{\mathrm{P,T}}\left(\frac{\partial \xi}{\partial T}\right)= C_{\mathrm{p}\xi}+\Delta_\mathrm{r}H_\mathrm{T}^\mathrm{P}\left(\frac{\mathrm{d}\xi}{\mathrm{d}T}\right) \tag{2}$$

When the temperature of a sample is changed of dT, the apparent heat capacity is the ratio of the quantity of heat required to heat the sample dQ to its temperature change dT. The apparent heat capacity may be negative (exothermal effect on warming), or infinity (first order transition), positive or negative.

$C_{\mathrm{p}\xi}$ is the heat capacity at constant pressure and composition sometime called [25] the 'true heat capacity' of the system. It has always a positive value.

$$C_{\mathrm{p},\xi}=\left(\frac{\partial H}{\partial T}\right)_\mathrm{P} \tag{3}$$

$\Delta_\mathrm{r}H$ is the enthalpy of the transformation at T and P. If the system is warmed at a heating rate dT/dt, the power absorbed W is:

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[*] Author for correspondence: claudy@lmops.cnrs.fr

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

$$W=C_{\mathrm{p},\xi}\frac{\mathrm{d}T}{\mathrm{d}t}+\Delta_{\mathrm{r}}H\frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad (4)$$

Equation (4) was given much earlier by Vold [26]. It states that the power W required to modify the temperature of a system at heating rate $\mathrm{d}T/\mathrm{d}t$ is the sum of the power absorbed to change the temperature of the true heat capacity $C_{\mathrm{p}\xi}$, plus the power absorbed by the transformation $\Delta_{\mathrm{r}}H\ \mathrm{d}\xi/\mathrm{d}t$, called configurational heat capacity [24]. The rate of the transformation $\mathrm{d}\xi/\mathrm{d}t$ is given by the laws of kinetics.

Of course, if no transformation occurs, $C_{\mathrm{p}\xi}=C_{\mathrm{p}}$ and Eq. (4) states that the heating rate is directly proportional to the power.

A proof has to be given that no thermal effect occurs (i.e. no transformation occurs), and if that information is not available then $C_{\mathrm{p}\xi}\neq C_{\mathrm{p}}$.

Model and equations of the DSC apparatus

Thermal Ohm's law is used in this paper [27–30]. The furnace is seen as a tension generator θ, and the power of the transformation occurring in the sample is an intensity generator φ.

Electrical representation and equations of the DSC

The electrical representation of a coupled cell disc type DSC apparatus, is given in Fig. 1. It was published earlier [17, 31] and is widely accepted.

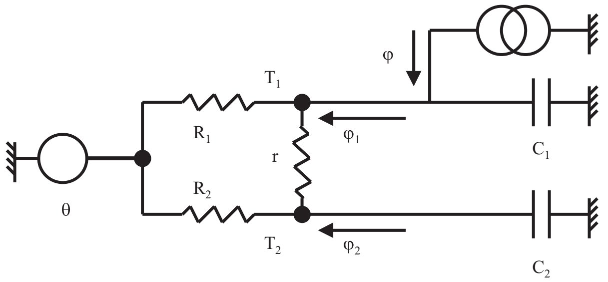

Fig. 1 Electrical model of a coupled cell DSC

C_1 is the sum of the true heat capacity of the sensor and the crucible and the sample. C_2 is the sum of the true heat capacity of the sensor, the crucible and the reference material if any.

The temperature of the furnace is θ. It is usually a linear function of time, but may be any other function. T_1 is the temperature of the sample and its holder; T_2 is the temperature of the reference and its holder. R_1 and R_2 are respectively the thermal resistance between the furnace and the sample and that between the furnace and the reference. The thermal resistance between the sample and the reference sides is represented by the resistor r, the power of the thermal effect φ occurring in the sample is:

$$\varphi=\Delta_{\mathrm{r}}H\frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad (5)$$

Owing to the model, no thermal gradient are taken into account in the sample or the reference. The calorimetric signal $\Delta_{\mathrm{T}}=T_1-T_2$ is expressed in K. It is the difference of the temperature between sample (T_1) and reference (T_2).

The calorimetric signal is an electrical tension Δ_{V} (expressed in μ*V*) given by an electrical device (thermocouples, resistors…), proportional to the difference of temperature Δ_{T}.

Relation between heat flow and calorimetric signal during a transformation

General equation of a coupled cell DSC is given in Eq. (6)

$$\begin{cases} -C_1\dfrac{\mathrm{d}T_1}{\mathrm{d}t}+\dfrac{\theta-T_1}{R_1}+\dfrac{T_2-T_1}{r}+\varphi=0 \\ -C_2\dfrac{\mathrm{d}T_2}{\mathrm{d}t}+\dfrac{\theta-T_2}{R_2}+\dfrac{T_1-T_2}{r}=0 \end{cases} \qquad (6)$$

Equation (6) are written as:

$$\begin{bmatrix}\dot{T}_1\\ \dot{T}_2\end{bmatrix}=\begin{bmatrix}a & b\\ c & d\end{bmatrix}\begin{bmatrix}T_1\\ T_2\end{bmatrix}+\begin{bmatrix}e\\ f\end{bmatrix}\theta+\begin{bmatrix}g\\ 0\end{bmatrix}\varphi \qquad (7)$$

with

$$a=-\frac{1}{C_1}\left(\frac{1}{R_1}+\frac{1}{r}\right),\quad b=\frac{1}{rC_1},\quad c=\frac{1}{rC_2},$$

$$d=-\frac{1}{C_2}\left(\frac{1}{R_2}+\frac{1}{r}\right),\quad e=\frac{1}{R_1C_1},\quad f=\frac{1}{R_2C_2},\quad g=\frac{1}{C_1}$$

and

$$\Delta_{\mathrm{T}}=T_1-T_2,\ \dot{\Delta}_{\mathrm{T}}=\dot{T}_1-\dot{T}_2,\ \ddot{\Delta}_{\mathrm{T}}=\ddot{T}_1-\ddot{T}_2 \qquad (8)$$

where the point stands for a derivation with respect to time. It follows:

$$\dot{\Delta}_{\mathrm{T}}=(a-c)\Delta+(a-c+b-d)T_2+(e-f)\theta+g\varphi \qquad (9)$$

Upon derivation of Eq. (9)

$$\ddot{\Delta}_{\mathrm{T}}=(a-c)\Delta_{\mathrm{T}}+(a-c+b-d)\dot{T}_2+(e-f)\theta+g\dot{\varphi}$$

but

$$\dot{T}_2=cT_1-cT_2+cT_2+dT_2+f\theta$$

by substitution (a) is obtained:

$$\text{(a)}\qquad \ddot{\Delta}_{\mathrm{T}}=(a-c)\Delta_{\mathrm{T}}+(a-c+b-d)c\Delta_{\mathrm{T}}+$$
$$(a-c+b-d)(c+d)T_2+(a-c+b-d)f\theta+(e-f)\theta+g\dot{\varphi}$$

multiplying Eq. (9) by (c+d) gives Eq. (b)

(b)
$$(c+d)\dot{\Delta}_T=(c+f)(a-c)\Delta+$$
$$(c+d)(a-c+b-d)T_2+(c+d)(e-f)\theta+g(c+d)\varphi$$

Subtraction of Eq. (a) to Eq. (b) gives:

$$\ddot{\Delta}_{\mathrm{T}}+(a-c)\Delta_{\mathrm{T}}-(ad-bc)\Delta_{\mathrm{T}}=$$
$$[f(a+b)-e(c+d)]\theta-g(c+d)\varphi+g\dot{\varphi}$$

Since $0=f(a+b)-e(c+d)$ it follows:

$$g(c+d)\varphi-g\dot{\varphi}=$$
$$-\ddot{\Delta}_{\mathrm{T}}+(a+b)\dot{\Delta}_{\mathrm{T}}-(ad-bc)\Delta_{\mathrm{T}}+(e-f)\dot{\theta} \qquad (10)$$

As shown in Fig. 1, if the calorimeter is symmetric $R_1\cong R_2=R$ the power difference Δ_{W} between the heat flux on the product side (φ_1) and the heat flux on the reference side (φ_2) may be written Eq. (10a) as:

$$\Delta_{\mathrm{W}}=\varphi_1-\varphi_2=\left(\frac{1}{R}+\frac{2}{r}\right)\Delta_{\mathrm{T}} \qquad (10a)$$

If the difference of temperature of the DSC is given by differential thermocouple of sensitivity g (expressed in μV K^{-1}), the relation (10b) between Δ_{V} and Δ_{T} is simply:

$$\Delta_{\mathrm{T}}=\frac{\Delta_{\mathrm{V}}}{g} \qquad (10b)$$

The differential power Δ_{W} between sample and reference side is:

$$\Delta_{\mathrm{W}}=\varphi_1-\varphi_2=\frac{1}{g}\left(\frac{1}{R}+\frac{2}{r}\right)\Delta_{\mathrm{V}} \qquad (10c)$$

If the calorimeter is symmetric and $r=\infty$, Eq. (10) simplifies to Eq. (10d):

$$\frac{1}{C_1}\left(\frac{1}{C_2R}\varphi-\dot{\varphi}\right)=-\ddot{\Delta}_{\mathrm{T}}+\left(\frac{1}{C_1}+\frac{1}{C_2}\right)\frac{\dot{\Delta}_{\mathrm{T}}}{R}+$$
$$\frac{\Delta_{\mathrm{T}}}{C_1C_2R^2}-\left(\frac{1}{C_1}+\frac{1}{C_2}\right)\frac{\dot{\theta}}{R} \qquad (10d)$$

This equation gives the thermal power of the transformation, if the values of the components of the calorimeter are known.

Application to a first order transition such as melting

Melting [32–34] was chosen as the model transition studied. Experiments run at a constant heating β, are made of three steps:

- After thermal equilibration at T_{i}, the furnace is heated at β up to a steady state,
- when the temperature of the sample reaches its melting point T_{m}, its temperature remains constant as long as the equilibrium between the phases exists,
- when melting of the sample is complete, a new steady state is reached.

Use of the model gives the theoretical equations of each of these three steps. It leads to a possible way for the determination of the resistors and capacitors.

The equations and the use of the model imply that the heat capacities C_1 and C_2 and the resistors R_1, R_2 and r are constant during each of the three steps.

In sake of simplicity, in the equations given below, the time is reset at zero at each step.

First step. From the initial temperature to a steady state

The different signals are studied, and the equation of the calorimetric signal is established.

- Calorimetric signal up to a steady state

The calorimetric signal Δ_{T} is the solution of Eq. (10), with heat flow $\varphi=0$. The initial condition is $T_1=T_2=\theta$ at $t=0$.

$$0=\ddot{\Delta}_{\mathrm{T}}-(a+d)\dot{\Delta}_{\mathrm{T}}+(ad-bc)\Delta_{\mathrm{T}}-(e-f)\beta \qquad (11)$$

The time constants τ_1 and τ_2 are the roots of:

$$(e-f)\beta=\frac{1}{\tau^2}-(a+d)\frac{1}{\tau}+ad-bc$$

$$-\frac{1}{\tau_1}=\frac{a+d+\sqrt{(a+d)^2-4(ad-bc)}}{2}$$

and

$$-\frac{1}{\tau_2}=\frac{a+d-\sqrt{(a+d)^2-4(ad-bc)}}{2}$$

The calorimetric signal, is the solution of Eq. (11), taking in account the initial conditions:

$$\Delta_{\mathrm{T}}=\frac{\beta}{2}\frac{r}{r+R_1+R_2}(R_2C_2-R_1C_1)\cdot$$
$$\left[2-\left(\exp\left(-\frac{t}{\tau_1}\right)+\exp\left(-\frac{t}{\tau_2}\right)\right)\right] \qquad (12)$$

When the steady state is reached, Eq. (12) gives Eq. (12a). It shows that the calorimetric signal is proportional to the difference of the time constants of each side.

$$\Delta_{\mathrm{T}}=\frac{rR}{r+2R}(C_2-C_1)\beta \qquad (12a)$$

The calorimetric signal is also proportional to the heating rate and to the difference between the heat capacities sample – reference.

If $R_1=R_2=R$ and $r=\infty$, a much simpler equation is obtained:

$$\Delta_T = R(C_2 - C_1)\beta \qquad (12b)$$

- Temperature of the sample

When a steady state is reached, the first line of Eq. (6) can be written as:

$$\frac{\theta - T_1}{R_1} = \beta C_1 - \frac{\Delta_T}{r} \qquad (13)$$

The temperature difference between the furnace and the sample is called the thermal lag δ and using Eq. (11), Eq. (14) is obtained:

$$\delta = \theta - T_1 = \beta\left(R_1 C_1 - \frac{R_1}{r + R_1 + R_2}(R_1 C_1 - R_2 C_2) \right) \qquad (14)$$

For a symmetric calorimeter:

$$\delta = \beta\left(R C_1 - \frac{R^2}{r + 2R}(C_1 - C_2) \right) \qquad (14a)$$

If $r=\infty$, then a very simple and well-known [36] form is obtained:

$$\delta = \beta R_1 C_1 \qquad (14b)$$

The lag is proportional to the sample side time constant.

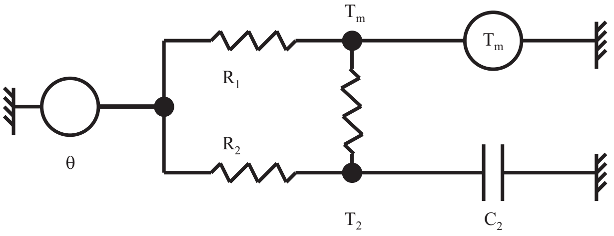

Fig. 2 Electrical model during melting of the sample

θ_0 is the temperature of the furnace when the sample reaches T_m. Then:

$$\theta = \theta_0 + \beta t = \delta + T_m + \beta t$$

It follows:

$$\delta = \beta\left(R_1 C_1 - \frac{R_1}{r + R_1 + R_2}(R_1 C_1 - R_2 C_2) \right) \qquad (16)$$

This equation may be used for the determination of the heat capacity C_1.

- Slope of the peak

The second Eq. (15) is:

$$\frac{dT_2}{dt} = -\frac{T_2}{C_2}\left(\frac{1}{R_2} + \frac{1}{r} \right) + \frac{T_m}{r C_2} + \frac{T_0}{R_2 C_2} + \frac{\beta t}{R_2 C_2} \qquad (17)$$

but since $dT_2/dt = -d\Delta_T/dt$, the derivation of Eq. (16) with respect to time gives:

$$-\frac{d^2\Delta_T}{dt^2} - \frac{d\Delta_T}{dt}\frac{1}{C_2}\left(\frac{1}{R_2} + \frac{1}{r} \right) = \frac{\beta}{R_2 C_2} \qquad (18)$$

At $t=0$, the calorimetric signal is constant, and $d\Delta_T/dt=0$. The solution of the differential Eq. (18) is :

$$\frac{d\Delta_T}{dt} = -\frac{r}{r + R_2}\beta\left[1 - \exp\left(-\frac{1}{C_2}\left(\frac{1}{R_2} + \frac{1}{r} \right) \right) \right] t \qquad (19)$$

The exponential term is negligible for a sufficient duration of the melting. The slope is then:

$$\frac{d\Delta_T}{dt} = -\frac{r}{r + R_2}\beta \qquad (20)$$

The slope of the peak of melting depends on the thermal resistances and on the heating rate. In the case $r=\infty$, the slope of the peak is equal to the heating rate.

$$\Delta_T\left[\left(\frac{r}{r + R_2} \right) t - R_2 C_2 \left(\frac{r}{r + R_2} \right)^2 \cdot \left(1 - \exp\left(-\frac{1}{C_2}\left(\frac{1}{R_2} + \frac{1}{r} \right) t \right) \right) + \frac{r}{r + R_1 + R_2}\left(R_2 C_2 - R_1 C_1 \right) \right] \qquad (21)$$

Second step. Melting of the sample

When the temperature of the sample T_1 reaches the temperature of melting of the sample T_m, the model of the calorimeter switches to the model given in Fig. 2.

Equation (6) are now given by Eq. (15):

$$\begin{cases} \dfrac{\theta - T_m}{R_1} + \dfrac{T_2 - T_m}{r} + \varphi = 0 \\ -C_2 \dfrac{dT_2}{dt} + \dfrac{\theta - T_2}{R_2} + \dfrac{T_m - T_2}{r} = 0 \end{cases} \qquad (15)$$

- Calorimetric signal Δ_T

At $t=0$, the temperature of the furnace is given by Eq. (16). Therefore, during melting Δ_T can be obtained by integration of Eq. (19).

In the case $r=\infty$, the calorimetric signal is:

$$\Delta_T = \beta\left((-t - R_1 C_1) + R_2 C_2 \exp\left(-\frac{t}{R_2 C_2} \right) \right)$$

- Heat flow entering the sample

The first line of Eq. (15) is used. As above, temperature of the furnace θ is given by Eq. (16). Hence, the heat flux entering the sample is:

$$-\varphi=\beta\left[\left(\frac{1}{R_1}+\frac{1}{r+R_2}\right)t-\frac{rR_2C_2}{(r+R_2)^2}\cdot\left(1-\exp\left(-\frac{1}{C_2}\left(\frac{1}{R_2}+\frac{1}{r}\right)t\right)\right)+C_1\right] \tag{22}$$

If the calorimeter is symmetric, and for sufficient duration so as the exponential may be neglected (22) gives Eq. (22a):

$$-\varphi=\beta\left[\left(\frac{1}{R}+\frac{1}{r+R}\right)t-\frac{rRC_2}{(r+R)^2}+C_1\right] \tag{22a}$$

where C_1 is the heat capacity of the sample side at the end of the first step. Of course, the value of the heat capacity during melting does not appear. The heat flux for the melting φ is composed of two terms:

- a time dependent function,
- a constant power βC_1.

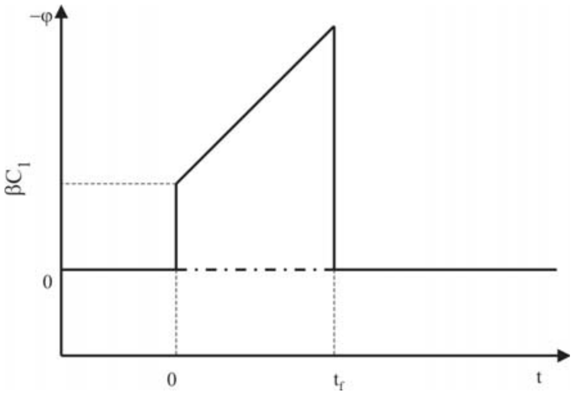

Fig. 3 Heat flow of the transformation in the sample

If $r=\infty$, then a much simpler Eq. (22b), as plotted in Fig. 3, is obtained:

$$-\varphi=\beta\left(\frac{t}{R_1}+C_1\right) \tag{22b}$$

- Duration of the melting of the sample

The heat absorbed q at time t by melting of the sample can be obtained by integration of the heat flow φ entering the sample.

$$q=\int_0^t \varphi\mathrm{d}t$$

Of course, at $t=0$, $q=0$, then:

$$-q=\left[\beta\frac{t^2}{2}\left(\frac{1}{R_1}+\frac{1}{r+R_1}\right)+t\left(C_1-\frac{R_2C_2}{r}\left(\frac{r}{r+R_2}\right)^2\right)+\frac{(rR_2C_2)^2}{(r+R_2)^3}\left(1-\exp\left(-\frac{1}{C_2}\left(\frac{1}{R_2}+\frac{1}{r}\right)t\right)\right)\right] \tag{23}$$

If the calorimeter is symmetric, and for sufficient duration so as the exponential may be neglected (23) gives Eq. (23a):

$$-q=\beta\left[\frac{t^2}{2}\left(\frac{1}{R}+\frac{1}{r+R}\right)+t\left(C_1-\frac{RC_2}{r}\left(\frac{r}{r+R}\right)^2\right)+\frac{(rRC_2)^2}{(r+R)^3}\right] \tag{23a}$$

If $r=\infty$, the heat absorbed by the sample at time t, is:

$$-q=\frac{\beta}{R_1}t^2+\beta C_1t \tag{23b}$$

When melting is finished at time $t=t_\mathrm{m}$, $q=Q$. The duration of melting t_m is the positive solution of Eq. (23a). The height of the peak of melting as given by Eq. (21) is then a function of $\sqrt{t_\mathrm{m}}$ as given earlier [35–37].

Third step. From the end of melting to a new steady state

When the equilibrium between the two phases ceases, the model of the DSC is that of Fig. 1 governed by the Eq. (6), with $\varphi=0$. At $t=0$, the calorimetric signal was $\Delta_\mathrm{T}(t_\mathrm{m})$, the temperature of the sample was T_m, and that of the reference was $T_\mathrm{r}=T_\mathrm{m}-\Delta_\mathrm{T}(t_\mathrm{m})$.

The calorimetric signal Δ_T is the solution of Eq. (11), with these initial conditions. The value of the heat capacity of the sample side is C_1', because it may be different after the transformation. The values of a, b, e, g are changed and are a', b', e', g' respectively, on taking $C_1=C_1'$.

The time constant τ_1' and τ_2' are the roots of:

$$(e'-f)\beta=\frac{1}{\tau_2}-(a'+d)\frac{1}{\tau}+a'd-b'c$$

Finally, the calorimetric signal is given by Eq. (24):

$$\Delta_\mathrm{T}=\Delta_\mathrm{T}(t_\mathrm{f})-\beta\frac{r}{r+R_1+R_2}(R_2C_2-R_1C_1')\cdot\left[1-\left(\exp\left(-\frac{t}{\tau_1'}\right)+\exp\left(-\frac{t}{\tau_2'}\right)\right)\right] \tag{24}$$

An example of an experiment is given in Fig. 4.

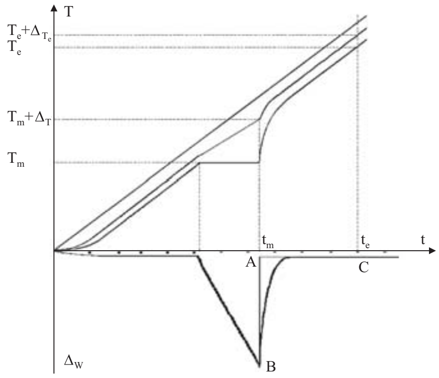

Fig. 4 Temperature of the furnace, reference, product crucibles, and calorimetric signal Δ_W

The quantity of heat Q_P entering the product crucible from the end of melting at time t_m and temperature T_m up to the end of the experiment at temperature T_e and time t_e is:

$$Q_P = \int_{T_m}^{T_e} C_1' \mathrm{d}T$$

On the reference side, the quantity of heat Q_R entering the reference crucible from the end of melting at time t_m and temperature $T_{m+\Delta T}$ up to the end of the experiment at temperature T_e and time t_e is:

$$Q_r = \int_{T_m+\Delta_T}^{T_e+\Delta_{T_e}} C_2 \mathrm{d}T$$

On the DSC curve (Δ_W), the difference $Q_P–Q_r$ is the area B, t_m, t_e, C. Therefore, the DSC curve contains a way to measure the value of C_1', C_1 and C_2.

Influence of the thermal contact between the disc and the crucible

An important question is to know what is the influence on the calorimetric signal of a thermal contact resistor ρ between the sample+crucible+detector represented by C_1, and the thermal detector. It is represented in Fig. 5a.

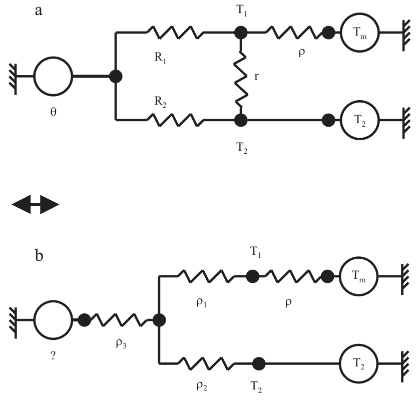

Fig. 5 a – DSC with the resistor ρ, b – star transformation

Using Kennelly's Delta-Star transformation, the Star representation is given in Fig. 5b. The resistors ρ_1, ρ_2, ρ_3 are given by Eq. (25a) and the reverse Star-Delta transformation the resistors are in Eq. (25b):

$$\begin{cases} \rho_1 = \dfrac{rR_1}{r+R_1+R_2} \\ \rho_2 = \dfrac{rR_2}{r+R_1+R_2} \\ \rho_3 = \dfrac{R_1R_2}{r+R_1+R_2} \end{cases} \tag{25a}$$

and

$$\begin{cases} R_1 = \dfrac{\rho_1\rho_2+\rho_2\rho_3+\rho_3\rho_1}{\rho_2} \\ R_2 = \dfrac{\rho_1\rho_2+\rho_2\rho_3+\rho_3\rho_1}{\rho_1} \\ r = \dfrac{\rho_1\rho_2+\rho_2\rho_3+\rho_3\rho_1}{\rho_3} \end{cases} \tag{25b}$$

Finally, the Star-Delta transformation gives in Eq. (26) the values of the resistors R_1', R_2' and r', which takes into account the contact resistor ρ.

$$\begin{cases} R_1' = \dfrac{\rho_1'\rho_2+\rho_2\rho_3+\rho_3\rho_1'}{\rho_2} = \dfrac{\rho_1\rho_2+\rho_2\rho_3+\rho_3\rho_1+\rho(\rho_2+\rho_3)}{\rho_2} \\ R_2' = \dfrac{\rho_1'\rho_2+\rho_2\rho_3+\rho_3\rho_1'}{\rho_1'} = \dfrac{\rho_1\rho_2+\rho_2\rho_3+\rho_3\rho_1'+\rho(\rho_2+\rho_3)}{\rho_1+\rho} \\ r' = \dfrac{\rho_1'\rho_2+\rho_2\rho_3+\rho_3\rho_1'}{\rho_3} = \dfrac{\rho_1\rho_2+\rho_2\rho_3+\rho_3\rho_1'+\rho(\rho_2+\rho_3)}{\rho_3} \end{cases} \tag{26}$$

Equations (22) and (23) giving the heat flux φ′ and the quantity of heat during melting q' are valid using R_1' instead of R_1, R_2' for R_2 and r' for r. The difference of temperature $T_m–T_2$ is given by Δ_T of Eq. (21). The calorimetric signal Δ_T' is easily computed since

$$\Delta_T' = \Delta_T - \rho\varphi$$

The power computed is changed by the thermal contact between the disc and the crucible. It decreases when this resistor increases.

The baseline

This problem was much discussed, but it is felt that a clarification has to be done here. It is expected that DSC gives $\Delta_r H$ and $C_{p\xi}$. But only the differential power Δ_W (Eq. (10a)) is known and, using the suitable corrections, the temperature of the sample (therefore its heating rate) and that of the reference may be obtained.

Heat flux entering the sample side is given by Vold's equation:

$$\varphi_1 = C_1 \frac{\mathrm{d}T_1}{\mathrm{d}t} + \frac{\mathrm{d}\xi}{\mathrm{d}t}\mathrm{d}H$$

and

$$\varphi_2 = C_2 \frac{\mathrm{d}T_2}{\mathrm{d}t}$$

The baseline Δ_{Wb} is:

$$\Delta_{\mathrm{Wb}} = C_1 \frac{\mathrm{d}T_1}{\mathrm{d}t} - C_2 \frac{\mathrm{d}T_2}{\mathrm{d}t}$$

It follows:

$$\frac{\mathrm{d}\xi}{\mathrm{d}t}\mathrm{d}H = \Delta_{\mathrm{W}} - \Delta_{\mathrm{Wb}}$$

The importance of the heating rate of the sample and reference side is notable. In fact $\mathrm{d}T_1/\mathrm{d}t$ may change greatly, from negative to positive values. Heat capacity of the sample and reference side must be known as precisely as possible, if the power of the transformation *vs*. time and its temperature are the goal of the experiment.

Conclusions

These equations were established for a coupled cell heat flux DSC. Of course, they can be used on this type of apparatus only. They should give the values of the components of the apparatus, and may be used to remove the smearing of the heat affect which occurs in the sample.

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