HEAT TRANSFER IN A DISC-TYPE DSC APPARATUS
Part 6. Determination of the resistors and capacitors of a heat flux coupled cell DSC

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Several models of DSC apparatuses are given in literature. However, use of these models requires a determination of the values of the components of the apparatus. Based on the theoretical equations of a first order transition in a coupled-cells heat flow DSC, two methods of determination of the values of the resistors and two methods of determination of the heat capacities are given. It seems possible to use these values for desmearing of the DSC experiments.

Keywords: determination of capacitors, determination of resistor, heat flow DSC, standardization

Introduction

The theoretical equations giving the calorimetric signal of a coupled cell heat flux DSC during a first order transition were given in previous papers [1]. The behavior of disc type coupled cells heat flux DSC is described [2–6] by the equations:

$$\begin{cases} -C_1 \dfrac{dT_1}{dt} + \dfrac{\theta - T_1}{R_1} + \dfrac{T_2 - T_1}{r} + \varphi = 0 \\ -C_2 \dfrac{dT_2}{dt} + \dfrac{\theta - T_2}{R_2} + \dfrac{T_1 - T_2}{r} = 0 \end{cases} \quad (1)$$

where

- θ – temperature of the furnace,
- T_1, T_2 – temperature of the crucible side, sample and reference respectively,
- R_1, R_2 – furnace–crucible side resistors, sample and reference respectively,
- C_1, C_2 – crucible side heat capacity, sample and reference respectively,
- r – crucible–crucible resistor,
- φ – heat flux of the transformation in the sample.

The equations describing a first order transition were established. In this paper, these equations are used on real experiments of the melting of three pure metals, so as to establish a method giving the values of the resistors and capacitors of a disc type coupled cell heat flux DSC apparatus.

Experimental

A heat flux DSC apparatus gives a differential signal Δ_V measured with a differential thermocouple array between the product and reference crucibles [7–9]. As explained previously [1] this signal gives the temperature difference $\Delta_T = T_1 - T_2$, and the power difference Δ_W.

Materials

The closest approximation of a first order transition is the melting of high purity metal [10, 11]. Indium, gallium and mercury (purity 99.999%) were purchased from Aldrich. The samples were sealed in aluminum crucibles (40 µL), previously dried at 180°C for three days. Masses were in the 20–100 mg range. Experiments were done as follows.

The sample was put into the DSC, at an initial temperature T_{init} below the melting temperature of the metal. It was heated at a temperature T_{end} above its melting temperature with a heating rate of 2 K min^{-1}. The liquid was then cooled to T_{init} with a cooling rate of 2 K min^{-1}. The DSC curve of crystallized compound was then recorded from T_{init} up to the end of the melting process T_{end} at a heating rate β. The next experiment was done with another heating rate β and new values for T_{init} and T_{end}.

For each metal, a series of experiments was done at several heating rates from 0.1 up to 2.4 K mn^{-1}. For some series the place of the product and reference crucibles were exchanged (to test the symmetry of the apparatus). Other series were done after removing and

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replacing one or both crucibles (to test the repro-ducibility of the thermal resistors crucible – thermo-couples).

Apparatus

A Mettler TA 2000 B DSC apparatus described elsewhere [12] was used. It was flushed with dry argon, chosen on the basis of its chemical inertia, low thermal conductivity and density.

The apparatus was controlled by a computer. Experiments were carried out under the control of programs, written for this purpose.
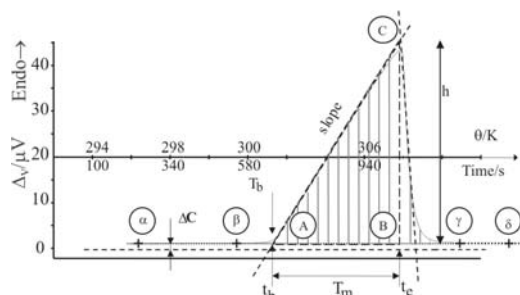

Fig. 1 Melting of In at β=1 K min^{-1}

Measurements

A typical experiment is given in Fig. 1.

In order to improve the reproducibility of the measurements, a specific computation program was written. The computation are done as follows:

• Time at the onset of the melting t_b:

It is taken as the time of the intersection of the extrapolation of the leading edge of the peak and the baseline. The temperature of the furnace at this time is easily obtained.

• Time at the maximum of the peak t_e:

It is the intersection of the leading edge of the peak fitted as a straight line, and the tangent at the inflexion point of its falling edge. Another method is to find the change of the sign of $d(\Delta_T)/dt$ between the beginning and the end of the peak.

• Transformation of Δ_V into Δ_T:

It is simply computed using the fem g of the thermocouples Au/Ni measured previously [3].

$$\Delta_T = \frac{\Delta_v}{g} \qquad (2)$$

• Slope of the peak p:

The derivative of the calorimetric signal Δ_T [1], at the leading part of the peak, is fitted as

$$p = \frac{d(\Delta_T)}{dt} = at + b = -\beta \frac{r}{r+R} \qquad (3)$$

where p is the value of the fit of $d(\Delta_T)/dt$ at $t=t_e$.

• Determination of the height of the peak h:

It is represented by BC: it is measured between the extrapolation of the baseline and the extrapolation of the peak at t_e,

• S_{tot} is the area ACγ expressed in K s, (hatched area)
• S_{tr} is the area ABC expressed in K s
• S_c is the area BCγ expressed in K s

The baseline is made of two straight lines: the first one is the extrapolation of the line $\alpha\beta$ up to the maximum of the peak t_e. The second one is the extrapolation of the line $\gamma\delta$. The duration of the melting t_m is readily obtained as $t_m=t_e-t_b$.

Results and discussion

Experimental verification of the model

The very first question is to establish whether or not, the model is adequately represented by the model given in Eq. (1) i.e. a heat flux coupled cells calorimeter. Furthermore, it is important to verify $R_1=R_2$.

Area of the peak

The area of the peak of melting of a sample must not depend on the heating rate, and the same area of the peak of melting should be found when the sample and the reference crucibles have been exchanged.

Results are plotted in Fig. 2. A fit using the series of measurements for the crucibles in a position, or after exchange, shows a difference. It amounts to 1/360. The difference between the resistors furnace crucible on product or reference side is not significant. The calorimeter is then symmetrical, so in this paper, $R_1=R_2=R$.
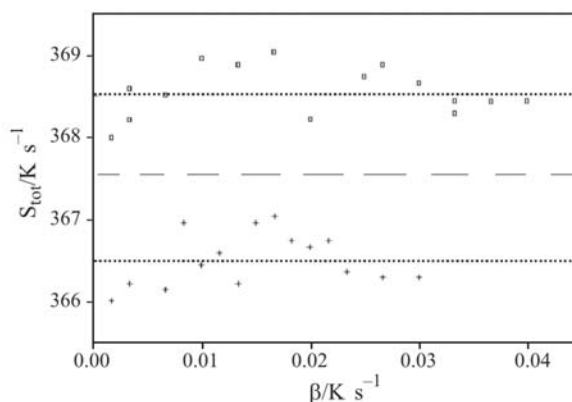

Fig. 2 Melting of In. $S_{tot}=f(\beta)$. □ – material and reference crucible arranged in a position, + – the position of the crucibles were exchanged. ··· – line for each series of measurements, --- – line for the series

Height of the peak of melting h

Duration of melting t_m is the solution of Eq. (4), as found in [1]:

$$-\frac{Q}{\beta} = \frac{t_m^2}{2}\left(\frac{1}{R} + \frac{1}{r+R}\right) +$$
$$+ t_m\left[C_1 - \frac{RC_2}{r}\left(\frac{r}{r+R}\right)^2\right] + \frac{(rRC_2)^2}{(r+R)^3} \quad (4)$$

Height of the peak of melting at his maximum h is given by Eq. (5),

$$h = \beta\left[\left(\frac{r}{r+R_2}\right)t_m - R_2C_2\left(\frac{r}{r+R_2}\right)^2\right] +$$
$$+ \left[\frac{r}{r+R_1+R_2}(R_2C_2 - R_1C_1)\right] \quad (5)$$

Plot of h vs. β is given in Fig. 3. It is well represented by a fit $h = f(\beta^{1/2})$ [13–15].

Agreement of the data with theoretical equation based on a heat flux coupled cells DSC, support this model. Furthermore, the measurements do not depend on the position of the crucibles, showing that the resistors furnace-product or reference crucibles are nearly identical.
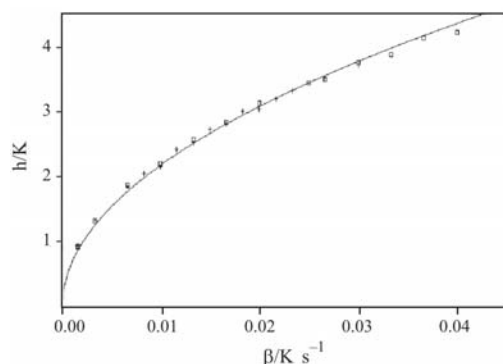
Fig. 3 h vs. heating rate β of In. □ – material and reference crucible arranged in a position, + – the position of the crucibles were exchanged
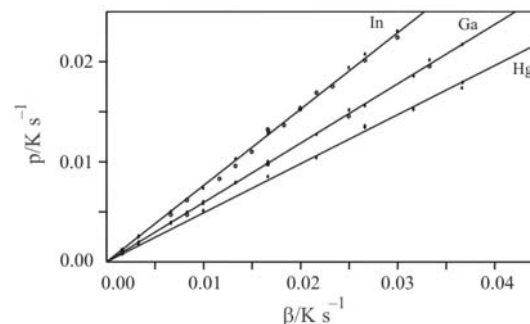
Determination of the resistors r, R

The equations established previously [1] requires that the ratio of the resistors r/R has to be first determined.

In a second step, the resistors may be obtained. From the experiments, two methods, based on two different equations may be used:

Determination of the ratio of the resistors

The slope p of the peak of melting is given by:

$$p = -\frac{r}{r+R}\beta \quad (6)$$

Fig. 4 Slope of the peak p vs. heating rate. □ – material and reference crucible arranged in a position, + – the position of the crucibles are exchanged

Table 1 Ratio of the resistors r/R

Metal	$T_m/°C$	$\Delta H/J\ g^{-1}$	$r/(r+R)$	r/R
In	156.61	28.42	0.7623	3.22
Ga	29.76	79.88	0.5924	1.45
Hg	–38.85	11.469	0.4899	0.960

Measurements are plotted in Fig. 4. The ratio R/r is easily obtained. It is given in Table 1. It decreases with the temperature, from about 3 at 156°C (In), down to 0.9 at –39°C (Hg).

Determination of the resistors r, R

As explained above, two methods were used.

Using the total area S_{tot}

The relation between the area of the peak of melting and the quantity of heat of the first order transition is simply:

$$Q = \left(\frac{1}{R} + \frac{2}{r}\right)S_{tot} = \frac{1}{R_e}S_{tot} \quad (7)$$

The determination of S_{tot}, is done as explained in I-3. In Fig. 5 S_{tot} vs. heating rate is plotted. As expected and as is widely known, this area does not depend on heating rate β.

As explained using other sets of data, the apparatus is symmetric since S_{tot} does not depend on the position of the crucibles.

Using the duration of melting t_m

Equation (4) gives the relation between duration of melting, quantity of heat and heating rate. The results are plotted in Fig. 6.

The results for r, R are reported in Table 2. Both methods give a good agreement.

This method does not require a baseline. It is thought that its accuracy is better.
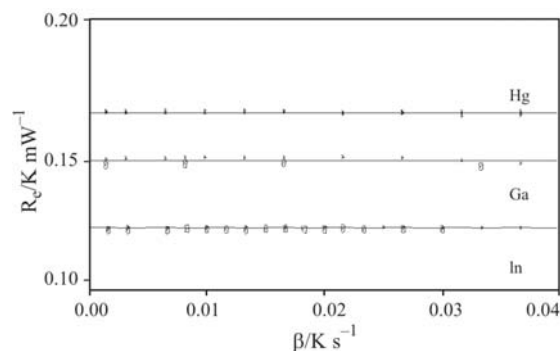
Fig. 5 $R_e=S/Q=f(\beta)$ for In, Ga, Hg. □ – material and reference crucible arranged in a position, + – the position of the crucibles were exchanged
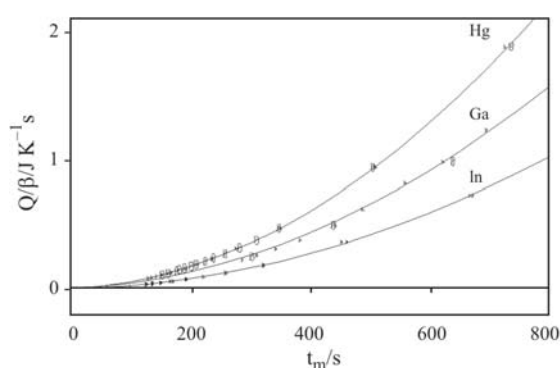
Fig. 6 $Q/\beta=f(t_m)$. For In, Ga, Hg (bottom to top). □ – material and reference crucible arranged in a position, + – the position of the crucibles were exchanged

Table 2 Computed values for r and R

$T_m/$ °C	$\dfrac{R^a}{R+r}$	$R^a/$ mW K^{-1}	$r^a/$ mW K^{-1}	$R^b/$ mW K^{-1}	$r^b/$ mW K^{-1}
156.61	0.7624	0.199	0.650	0.206	0.669
29.76	0.5924	0.365	0.499	0.372	0.509
−38.85	0.4899	0.537	0.48	0.564	0.504

^{a}Method using Q/S_{tot} *vs.* heating rate β, ^{b}method using Q/β *vs.* t_m

An equation $R=f(T)$ is computed as $R=a_1+b_1T$ and $r=a_2+b_2T$.

Determination of the heat capacity

Two equations may be used for the determination of the heat capacity on product (C_1 or C_1') (C_1' is the heat capacity of the product side) and reference (C_2) sides. The area of the falling part of the peak of melting S_C and the thermal lag δ may be used.

Area of the falling part of the peak S_C

When melting is terminated at t_m, the sample is at T_m. If no melting had occurred the temperature of the sample T_P should be

$$T_P=T_m+\beta t_m \tag{8}$$

The quantity of heat Q_P to warm the product crucible from T_m up to T_P is

$$Q_P = \int_{T_m}^{T_P} C_1 dT \tag{9}$$

When melting began, the reference crucible was at T_m'. At the end of the melting, its temperature T_R is:

$$T_R = T_m' + \beta \frac{r}{r+R} t_m \tag{10}$$

The difference of the quantity of heat entering each crucible is:

$$Q_P - Q_R = \int_{T_m}^{T_P} C_1' dT - \int_{T_m'}^{T_R} C_2 dT \tag{11}$$

Assuming that the values of C_1' and C_2 do not change on the temperature interval of the falling part of the peak:

$$Q_P - Q_R = C_1'\beta t_m - C_2\beta t_m \frac{r}{r+R} \tag{12}$$

On the DSC curve, the area of the falling part S_C of the DSC curve Δ_W is Q_P–Q_R. Hence:

$$\frac{S_C}{t_m R_e} = \beta\left(C_1' - C_2 \frac{r}{r+R}\right) \tag{13}$$

Use of this last equation requires the determination of the difference C_1–C_2 (Fig. 1). It is given by Eq. (14):

$$C_1' - C_2 = \beta \frac{\Delta_C}{R_e} \tag{14}$$

Three series of experiments were done using different references and product crucibles. Results are plotted in Fig. 7. The values are given in Table 3.

As expected, curves 1 and 3 are symmetric proving that the measuring device itself has a very small asymmetry.

A plot of $S_C/(R_e t_m)$ *vs.* β is given in Fig. 8. The slope gives the value of C_1' and C_2 because d$C=C_1'$–C_2 and R_e were measured previously.

For some series of experiments, the position of the crucibles were exchanged. However, only the sign of the signal is changed. It shows that the apparatus is symmetric.

The computation is done using Eq. (13). It gives the values of C_1' and C_2. The heat capacity [16–18] of the product and of the crucible or only that of the reference crucible can be easily computed. Then the heat capacity of the disc C_S can be obtained.

Results are given in Table 4.

An equation $C_S=f(T)$ is computed as $C_S=a+bT+cT^{-1}$.

Table 3 Mass of metal, reference material and crucibles

Curve number	Product side		Reference side	
1	In=104.1 mg	crucible=49.2 mg	Al_2O_3=186.09 mg	crucible=48.6 mg
2	In=104.1 mg	crucible=49.2 mg	Al_2O_3=0 mg	crucible=49.5 mg
3	Al_2O_3=186.09 mg	crucible=48.6 mg	In=104.1 mg	crucible=49.2 mg
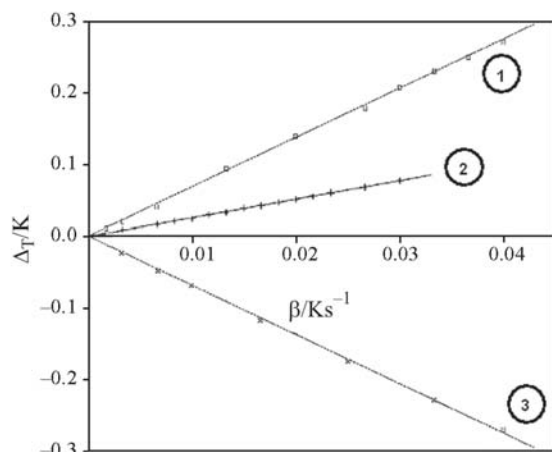
Fig. 7 $\Delta_T = f(\beta)$ for several product crucibles (Table 3)
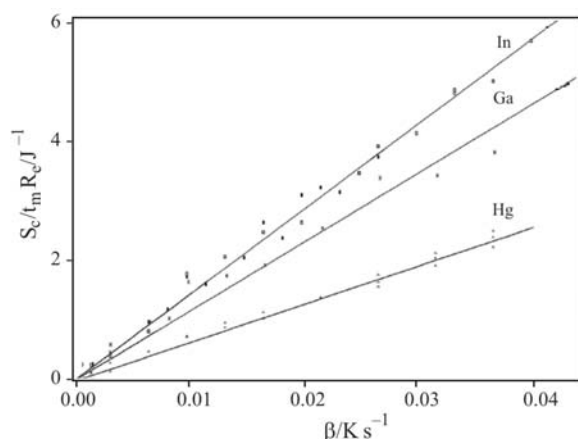
Fig. 8 $S_c/(t_m R_e) = f(\beta)$; □ – material and reference crucible arranged in a position, ■ – the position of the crucibles were exchanged

Thermal lag δ

The temperature of the sample is lower than that of the furnace on heating, and greater on warming [19, 20]. That difference of temperature is called the thermal lag δ. For a symmetric heat flux coupled cells DSC, it is given by:
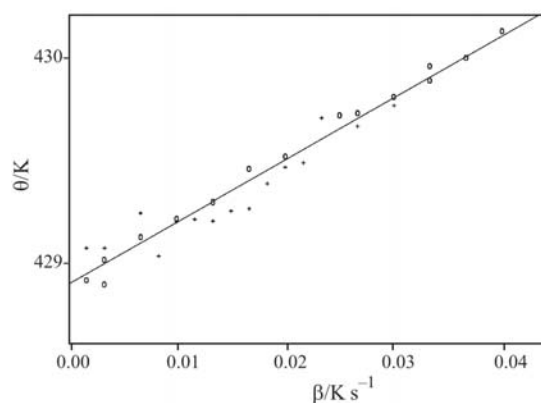
$$\delta = \beta \left[RC_1 - \frac{R^2}{r+2R}(C_1 - C_2) \right] \quad (15)$$

A plot of $\delta = f(\beta)$ is given in Fig. 9 and the results are reported in Table 4.

The agreement between both methods is excellent.

Table 4 Heat capacity product and reference sides using both methods, heat capacity of the disc based on method 2

T_m/°C	Method 1		Method 2		
	C_1'/	C_2/	C_1'/	C_2/	C_s/
	mJ K^{-1}				
156.61	158	144	157	143	97
29.76	128	93	124	89	78
−38.85	89	77	89	76	42

Fig. 9 $\theta = f(\beta)$ at the temperature of melting of In; □ – material and reference crucible arranged in a position, + – the position of the crucibles were exchanged

Simulation and comparison with the experiments

The simulation of an experiment is easy, and it was interesting to compare an experiment with its theoretical representation. The melting of indium was chosen. The computation uses Eq. (1), with three steps:

- from the initial temperature to the temperature of melting of the sample
- melting of the sample
- reinstallation of a stationary state

An experiment and its simulation are given in Fig. 10. The difference between the experiment and the computation shows that the shape of the peak is well represented. Differences are mostly at the beginning and the maximum of the peak. The error on the quantity of heat is very low.

The same computation done with gallium or mercury gives a good fit between the real and the simulated experiments.
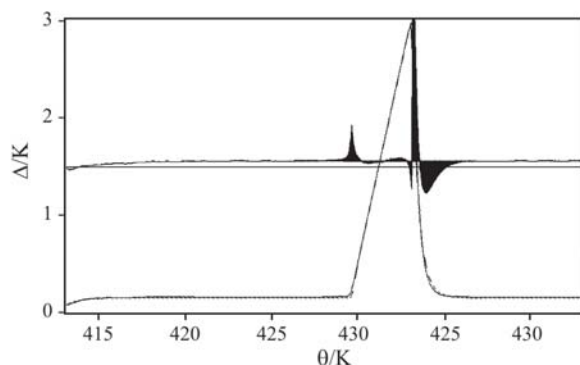
Fig. 10 Melting of In at 1 K mn^{-1}. Continuous line:
experiment, dotted line: simulation, the difference
between the two curves is in full line, the scale is ×10

Conclusions

The DSC apparatus used is well represented by the
simple model of a couple cells heat flux calorimeter.
The values of the resistors are obtained using two
methods which give close values. The determination
of the heat capacities is much more difficult, but the
values found agree.

The simulation of the melting of the metals used
shows that the model is a good representation of the
apparatus, and support the validity of the methods of
determination of the values of resistors and capacitors.

References

1 K. Alouani, M. Siniti, F. Schiets and P. Claudy,
  J. Therm. Anal. Cal., (2007), in press.
2 P. Claudy, J.-C. Commerçon and J.-M. Létoffé,
  Thermochim Acta, 68 (1983) 305.
3 P. Claudy, J.-C. Commerçon and J.-M. Létoffé,
  Thermochim Acta, 68 (1983) 317.
4 A. Lindemann and J. Schmidt, Thermochim. Acta,
  337 (1999) 219.
5 Y. L. Shishkin, J. Thermal Anal., 27 (1983) 301.
6 H. B. Dong and J. D. Hunt, J. Therm. Anal. Cal.,
  64 (2001) 167.
7 P. Claudy, J.-C. Commerçon and J.-M. Létoffé,
  Thermochim. Acta, 65 (1983) 245.
8 P. Roura and J. Farjas, Thermochim. Acta, 430 (2005) 115.
9 V. A. Drebushchak, J. Therm. Anal. Cal., 76 (2004) 941.
10 Y. Boling and J. Jiaodong, Thermochim. Acta,
   137 (1989) 307.
11 R. L. Danley, Thermochim. Acta, 409 (2004) 111.
12 P. Claudy, B. Bonnetot, G. Chahine and J.-M. Létoffé,
   Thermochim. Acta, 38 (1980) 75.
13 P. Navard and J. M. Haudin, J. Thermal Anal., 29 (1984) 405.
14 P. Navard and J. M. Haudin, J. Thermal Anal., 30 (1985) 61.
15 Y. Saito, K. Saito and T. Ataké, Thermochim. Acta,
   107 (1986) 277.
16 D. B. Downie and J. F. Martin, J. Chem. Thermodyn.,
   12 (1980) 779.
17 Y. Takahashi, T. Azumi and Y. Sekine, Thermochim. Acta,
   139 (1989) 133.
18 K. H. Schönborn, Thermochim Acta, 69 (1983) 103.
19 J. M. Barton, Thermochim. Acta, 20 (1977) 249.
20 M. E. Patt, B. E. White, B. Stein and E. J. Cotts,
   Thermochim. Acta, 197 (1992) 413.