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# HEAT TRANSFER IN A DISC-TYPE DSC APPARATUS. III. THEORETICAL AND EXPERIMENTAL CORRECTION OF THE CALORIMETRIC SIGNAL IN SCANNING MODE

P. CLAUDY, J.C. COMMERCON * and J.M LETOFFE

*Laboratoire de Thermochimie Minérale de l'I.N.S.A. Associé au C.N R S. No 116, Institut National des Sciences Appliquées de Lyon, 69621 Villeurbanne Cedex (France)*

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## ABSTRACT

A mathematical treatment of the calorimetric signal for a disc-type DSC apparatus is given. The method relies upon an electrical representation of the DSC instrument. Several applications are given: melting of high purity and less pure indium with determination of purity, determination of the thermal gradient in the crucible.

## INTRODUCTION

It has been shown in previous papers [1,2] that a disc-type DSC apparatus behaves like a coupled cell calorimeter. Heat transfer between the sample and reference crucibles occurs by conduction through the disc and the gas. Using the electrical analogy, a quantitative model has been obtained.

The signal, $\Delta$, given by a calorimeter at time $t_0$ depends on the thermal effect actually occurring in the sample crucible and on the previous state of the calorimeter at $t < t_0$.

Thermochemistry has established relations relating the temperature of the sample with other parameters, e.g. dissociation pressure, composition and melted fraction.

Determination of the purity of a sample by DSC has been the focus of much attention: according to several hypotheses [4], a simple relation exists between the purity of the sample, the fraction melted and temperature. Although many papers have been written on this subject, they mostly deal with a supposed behavior of the sample itself [6] or with empirical corrections of the calorimetric signal [7–9]. It has been pointed out [10] that the purity found depends heavily on the type of apparatus used, and hence, on

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* Laboratoire d'Informatique Appliquée.

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its constitution. To our knowledge, attempts made to take into account the calorimeter itself [11] used the electrical model of a Calvet-type microcalorimeter.

Using the electrical model described in [2], it seemed possible to compute estimates of the true temperature and thermal effect, and to use these data for purity determination.

## DISC-TYPE DSC

### *Model used*

A reasonable model of a Mettler DSC apparatus is given in Fig. 1. *E* is the temperature of the furnace (tension generator) and $\phi$ is the thermal effect occurring in the sample (intensity generator).

In a previous paper [3], the sample crucible contact resistor was not taken into consideration. It was however observed that this resistor could influence the shape of the calorimetric signal. The resistor, $R_6$, is thus taken into account [12,13].

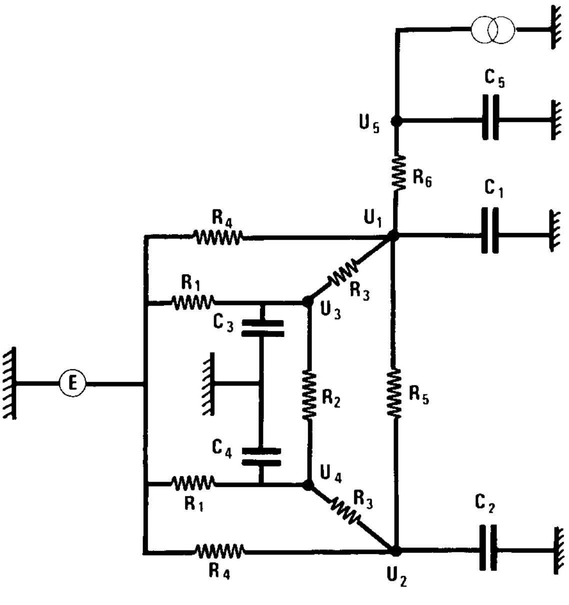

Fig. 1. Electrical representation of the calorimeter in the scanning mode. $R_1$, Furnace–crucible resistor for the heat flowing through the disc; $R_2$, crucible–crucible resistor for the heat flowing through the disc; $R_3$, contact disc–crucible resistor; $R_4$, furnace–crucible resistor through the gas; $R_5$, crucible–crucible resistor through the gas; $R_6$, contact resistor sample crucible; $C_1$,heat capacity of the crucible containing the sample; $C_2$, heat capacity of the reference crucible; $C_3$, heat capacity of the disc below the sample; $C_4$, heat capacity of the disc below reference crucible; $C_5$, heat capacity of the sample. Temperatures: $U_1$, sample crucible; $U_2$, reference crucible; $U_3$, disc below the sample; $U_4$, reference; $U_5$, sample.

### *Hypotheses*

The hypotheses made were as given below.

a Thermal dissymmetry is represented by different disc capacitors.

b Every thermal resistor and capacitor is independent of the temperature in the narrow temperature range studied. Numerical values of the resistors have been found by an isothermal method [3].

## THEORETICAL REPRESENTATION OF A DSC IN SCANNING MODE

### *Equations*

Equations describing the temperature and the calorimetric signal at any temperature with heat evolution $\phi$ in the sample are represented in matrix notation by

$$\dot{U} = AU + BE + C\phi \tag{1}$$

$E$ and $\phi$ are the inputs of the system. From Fig. (1) it follows that

$$U = \begin{bmatrix} U_3 - U_4 \\ U_1 \\ U_2 \\ U_3 \\ U_5 \end{bmatrix} \tag{2}$$

$$B = \begin{bmatrix} \left(\frac{1}{C_3} - \frac{1}{C_4}\right)\frac{1}{R_1} \\ \frac{1}{C_1 R_4} \\ \frac{1}{C_2 R_4} \\ \frac{1}{C_3 R_1} \\ 0 \end{bmatrix} \tag{3}$$

$$C = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ \frac{1}{C_5} \end{bmatrix} \tag{4}$$

$$A = \begin{bmatrix} -\frac{1}{C_4}\left(\frac{1}{R_1}+\frac{1}{R_2}+\frac{1}{R_3}\right)-\frac{1}{C_3R_2} & \frac{1}{C_3R_3} & -\frac{1}{C_4R_3} & \left(\frac{1}{C_4}-\frac{1}{C_3}\right)\left(\frac{1}{R_1}+\frac{1}{R_3}\right) & 0 \\ 0 & -\frac{1}{C_1}\left(\frac{1}{R_3}+\frac{1}{R_4}+\frac{1}{R_5}+\frac{1}{R_6}\right) & \frac{1}{C_1R_5} & \frac{1}{C_1R_3} & \frac{1}{C_1R_6} \\ -\frac{1}{C_2R_3} & \frac{1}{C_2R_5} & -\frac{1}{C_2}\left(\frac{1}{R_3}+\frac{1}{R_4}+\frac{1}{R_5}\right) & \frac{1}{C_2R_3} & 0 \\ -\frac{1}{C_3R_2} & \frac{1}{C_3R_3} & 0 & -\frac{1}{C_3}\left(\frac{1}{R_1}+\frac{1}{R_3}\right) & 0 \\ 0 & \frac{1}{C_5R_6} & 0 & 0 & -\frac{1}{C_5R_6} \end{bmatrix} \tag{5}$$

$$\dot{U} = \begin{bmatrix} \frac{d}{dt}(U_3 - U_4) \\ \frac{d}{dt}U_1 \\ \frac{d}{dt}U_2 \\ \frac{d}{dt}U_3 \\ \frac{d}{dt}U_5 \end{bmatrix} \tag{6}$$

The calorimetric signal $\Delta$ is given by

$$\Delta = g(U_3 - U_4) \tag{7}$$

with $g$ = sensitivity of the thermocouples ($\mu$V K$^{-1}$) [3]

*Equations with discrete measurements*

In the experiments only sampled measurements are available at a period $T$. However, it is possible, with discrete data to reconstitute a continuous signal with particular input. The equation of a system has the form

$$\dot{U} = AU + B'E' \tag{8}$$

and the solution depends on the input $E'$.

*Constant inputs*

If the inputs $E'$ were constant during the sampling period, the solution of eqn. (8) is given by eqn. (9), such that

$$U_{(k+1)T} = \exp[(T)A]U_{kT} + B_1'E_{kT}' \tag{9}$$

with

$$B_1' = A^{-1}\{\exp[(T)A] - I\}B' \tag{10}$$

where $I$ = identity matrix and $U_{kT}$ is the temperature matrix at time $t$.

*E as a linear function of time*

In the scanning mode, the temperature of the furnace is a linear function of time. It is easily shown that the solution of eqn. (8) is now given by

$$U_{(k+1)T} = \exp[(T)A]U_{kT} + B_1E'_{kT} + B_2E'_{(k+1)T} \tag{11}$$

with

$$B_1 = \left[A^{-1}\{\exp[(T)A] - I\} - \left(\frac{1}{T}\right)A^{-1}\{A^{-1}(\exp[(T)A] - I) - T\}\right]B' \tag{12}$$

and

$$B_2 = \frac{1}{T}A^{-1}[A^{-1}\{\exp[(T)A] - I\} - T]B' \tag{13}$$

*General equation*

No information is available on $\phi$ during the sampling period. $\phi$ depends only on the thermal effect occurring in the sample. It is assumed that the sampling period is short enough and it follows that a constant or linear interpolation between two consecutive measurements gives a small error in the solution. It is to be noted that this is the only approximation made. The choice between linear or constant interpolation is made on the basis of the simplicity and stability of the results and is discussed later.

The equation taking into account the thermal effect in the scanning mode is derived from eqn. (1), (9) and (11).

$$U_{(k+1)T} = \exp[(T)A]U_{kT} + B_1E_{kT} + B_2E_{(k+1)T} + C_1\phi_{kT} \tag{14}$$

with

$$C_1 = A^{-1}\{\exp[(T)A] - I\}C \tag{15}$$

## DECONVOLUTION METHOD

With the numerical values of the resistors and capacitors, numerical values of $A$, $B_1$, $B_2$ and $C_1$ can be obtained. The first equation of system (14) is given by

$$(U_3 - U_4)_{(k+1)T} = aU_{kT} + b'_1E_{kT} + b'_2E_{(k+1)T} + c'_1\phi_{kT} \tag{16}$$

where $a$, $b'_1$, $b'_2$ and $c'_1$ are the first line of the matrices $\exp[(T)A]$, $B_1$, $B_2$ and $C_1$, respectively.

$U_3 - U_4$ is obtained directly as experimental data from eqn. (7). $E_{kT}$ and $E_{(k+1)T}$ are the temperatures of the furnace at $kT$ and $(k+1)T$. They are easily obtained since the heating rate, the temperature at the beginning of the experiment, $E_0$, and the time elapsed are experimental quantities. $U_{kt}$ represents the state of the calorimeter at $kT$. At $t < 0$, the calorimeter being at a constant temperature $E_0$, it follows that $U_3 - U_4 = 0$, $U_1 = U_2 = U_3 = U_5$

$= E_0$, and $\phi = 0$. The iterative procedure starts with $k = 0$. The heat flow, $\phi$, is computed from eqn. (17), which is a simple modification of eqn. (18), since $(U_3 - U_4)_{(k+1)T}$, $U_{kT}$, $E_{kT}$, $E_{(k+1)T}$ are known.

$$\phi_{kT} = \frac{1}{c_1'}\left[(U_3 - U_4)_{(k+1)T} - aU_{kT} - b_1' E_{kT} - b_2' E_{(k+1)T}\right] \tag{17}$$

The numerical value of $\phi_{kT}$ and the state $U(kT)$ are then used in eqn. (14) to compute $U_{(k+1)T}$ and the same procedure is repeated with every value of $U_3 - U_4$. With this procedure, $\phi$ and $U_5$ vs. time are obtained. The distortion of the signal, $\Delta$, inherent in the apparatus is then removed on the basis of our hypotheses as stated previously [2].

## DISCUSSION

### *Model*

Figure 1 shows a localized system. It is of course a simplified representation of the real calorimeter, which has distributed resistors and capacitors. However, it has been shown [3] that this model is sufficiently accurate. It is very easy to make the model more complex, but it does not appear to be needed.

### *Heat flow*

No information on the evolution of $\phi$ is available. It seems reasonable to suppose that its change is slow during the sampling period. A linear interpolation could be used with a modified form of eqn. (14), i.e.

$$U_{(k+1)T} = \exp[(T)A]\,U_{kT} + B_1 E_{kT} + B_2 E_{(k+1)T} + C_2\phi_{kT} + C_3\phi_{(k+1)T} \tag{18}$$

$B_1$ and $B_2$ are found in eqns. (12) and (13). $C_2$ and $C_3$ have the same equation as $B_1$ and $B_2$ where $C$ is substituted for $B$. However, the inverse filter [a straightforward modification of eqn. (8)] may be unstable and its stabilization could damage the simplicity of the actual result without giving more useful information on $\phi$.

## EXPERIMENTAL

### *Material*

A Mettler TA 2000 B DSC apparatus was used. The calorimetric signal was read by a H.P. 3455 A digital voltmeter controlled by a H.P. 85 computer. Data were stored and used off-line.

### *Experimental conditions*

Experiments were made in the temperature range 148–163°C with a heating rate of 1°C $\text{min}^{-1}$. The calorimeter was set at a constant temperature (148°C) and when the signal was constant, ten measurements were made and the temperature was increased. The sampling period was 3 s. The indium used was of a high purity grade: 99.9999%, purchased from Preussag.

Experiments have shown that the In sample must be a foil covering the bottom of the crucible. When In wires were used, the curve $\phi$ vs. furnace temperature showed discontinuities. The reference crucible contained platinum wires.

## RESULTS

Several experiments were performed with indium. They were designed to test the practical use and the limits of confidence in the model.

### *Melting of pure indium (Preussag, 99.9999%)*

There is no direct means of evaluating $R_6$, $C_3$ and $C_4$, since $R_6$ depends on the material itself and since $C_3$ and $C_4$ represent, on the basis of our hypotheses, every discrepancy between the model and the real calorimeter. In order to obtain these values, a trial-and-error method was used.

Figure 2 shows plots of: calorimetric signal (100 *μν* full scale) vs. furnace temperature, $E$ (°C); thermal power, $\phi$ (mW), vs. $E$; thermal power, $\phi$, vs. sample temperature, $U_5$; quantity of heat, $q = \Sigma_0^t \phi \mathrm{d}T$, vs. $U_5$; and temperature of the sample, $U_5$, vs. $1/F$. $F$ is the fraction melted: $F = q/Q$ where $Q$ = heat of melting of the sample. The purity of the indium sample is given by the slope of

$$U_5 = x_2 \frac{RT_\mathrm{m}^2}{\Delta H_\mathrm{m}} \frac{1}{F} - T_\mathrm{m}$$

The adjustment process is as described. Resistors $R_1$–$R_5$ and $C_3$, $C_4$ and g are given in ref. (3). An arbitrary value of $R_6$ was taken and a first computation was made. Then, $C_3 - C_4$ was adjusted so as to obtain no shift of the base line in the plot $\phi = \mathrm{f}(E)$. Then $R_6$ was changed: if $R_6$ was too large, then the computed temperature of In decreased during the melting which is of course impossible. If $R_6$ was too small, $U_5 = \mathrm{f}(1/F)$ was not a straight line. Decreasing $C_3$ and $C_4$ created an overshoot of the end of the peak $\phi = \mathrm{f}(U_5)$.

Finally, the correct values are $C_3 = 72$ $\text{mJK}^{-1}$, $C_4 = 57$ $\text{mJK}^{-1}$ and $R_6 = 2 \times 10^{-3}$ K $\text{mW}^{-1}$. As expected, $R_6$ is quite small. The purity was found to be $1.05 \times 10^{-6}$.

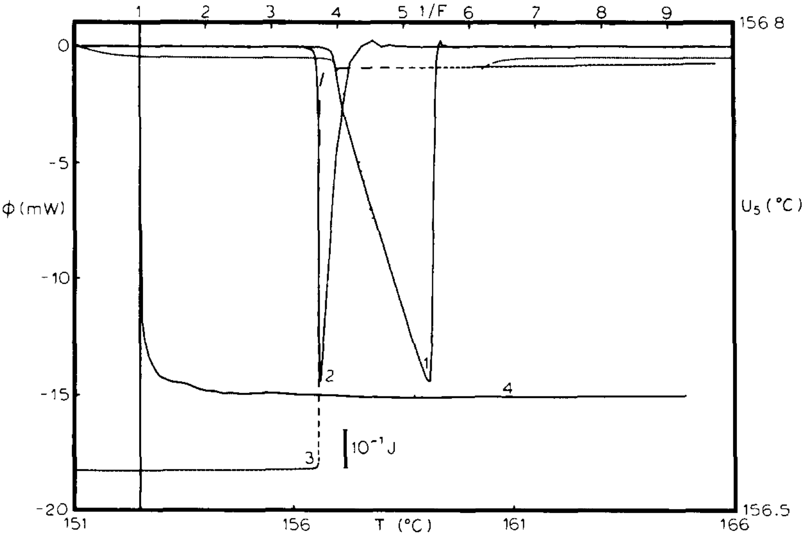

Fig. 2. Deconvolution of the melting of a pure indium sample ($m$ = 40.34 mg). ...., $\Delta = f(E)$; 1, $\phi = f(E)$; 2, $\phi = f(U_5)$; 3, $q = \Sigma_0^t \phi \Delta t$; 4, $1/F = f(U_5)$.

### *Influence of the sample-crucible resistor*

In order to get more information on the influence of this resistor aluminium foil was inserted between the bottom of the crucible and the indium sample foil. The experiment was run as described previously.

The shape of the calorimetric signal was very different: the rising slope of the peak was smaller than in the foregoing experiment and the computed melting temperature with the values of pure In is 0.2°C greater. When deconvolution was carried out using the numerical values used previously, except for $R_6 = 21 \times 10^{-3}$ K mW$^{-1}$, the same melting temperature and the purity $x = 1.7 \times 10^{-6}$ were obtained.

### *Thermal gradient in the crucible*

Two small pieces of indium (about 5 mg each) were placed in the crucible. One was as close as possible to the furnace, and the other as close as possible to the center of the disc.

Figure 3 shows the calorimetric signal vs. furnace temperature and the thermal effect vs. sample temperature. Two sharp peaks are clearly seen which represent the melting of each piece of indium. The thermal gradient in the crucible is then 0.1°C at the heating rate used (1°C min$^{-1}$).

This experiment suggests why indium foil has to be used. Instead of increasing the complexity of the model to represent the thermal gradient in the crucible, it seems more reasonable to use a slightly different sample arrangement.

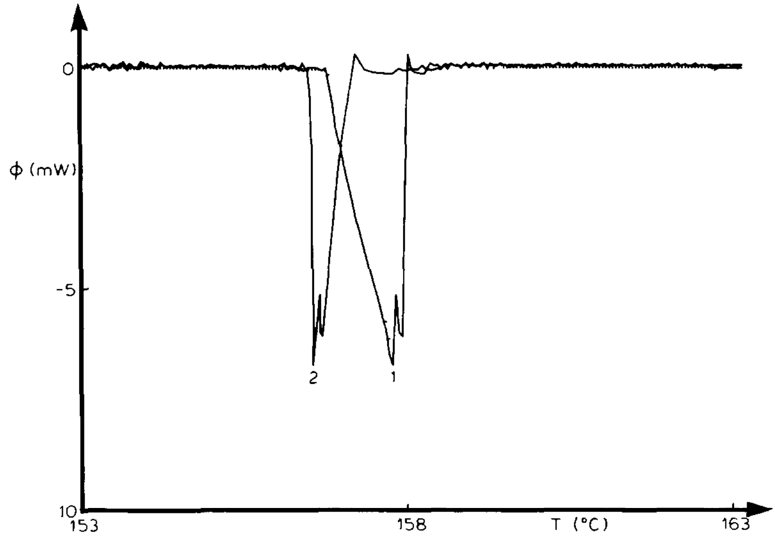

Fig. 3. Determination of the thermal gradient in the crucible. Mass of indium = 9.33 mg. ..., $\Delta = f(E)$; 1, $\phi = f(E)$; 2, $\phi = f(U_5)$.

## *Purity of In sample*

In order to check the deconvolution method, a purity test on common grade indium was carried out. The results are reported in Fig. 4. From the

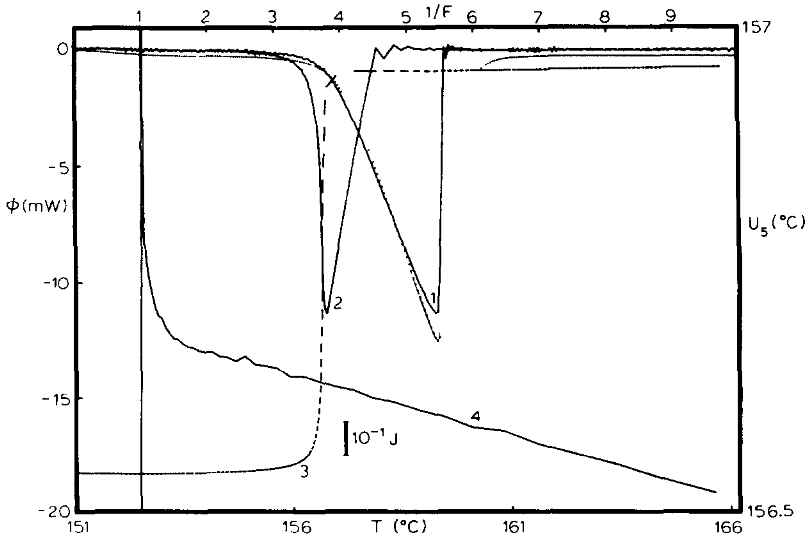

Fig. 4. Purity determination of an In sample ($m = 35.99$ mg). ..., $\Delta = f(E)$; 1, $\phi = f(E)$; 2, $\phi = f(U_5)$; 3, $q = \Sigma_0^t \phi \Delta t$; 4, $1/F = f(U_5)$.

shape of the calorimetric signal, it is clear that this sample is less pure than the sample used in the earlier experiments. Using the same value of $R_6 = 2 \times 10^{-3}$ K mW$^{-1}$, the impurity content was found to be $x = 3.7 \times 10^{-5}$. The curve $T = f(1/F)$ is very close to a straight line.

## DISCUSSION

In these experiments, the computed heat of melting corresponds to the quantity of indium used. It has, however, to be mentioned that the values of $C_3$ and $C_4$ may vary. This can be seen as a consequence of the model chosen since a thermal dissymmetry of the furnace is seen as being due to differences in these capacitors.

Change in the value of $R_3$ ($\pm 50\%$) does not noticeably affect the shape of $\phi = f(U_5)$ but slightly changes the purity found.

The theoretical curve $\phi = f(U_5)$ should be a line and it is seen that the end of the peak is not a straight line. The resultant effect on the heat $q = f(U_5)$ is not visible. The falling part of the peak contains only three points and $U_5$ varies very rapidly.

## CONCLUSION

In this paper, a mathematical treatment of the calorimetric signal in the scanning mode has been given. Examples reported here are limited to a narrow temperature range and to the melting of indium. The technique developed here eliminates most of the apparatus response in spite of the simplicity of the model: (i) a discrete and simple model is used to represent a continuous system; (ii) a quite straightforward deconvolution method is used.

A compromise between model complexity and experimental requirements has been made and seems to be satisfactory.

Application of these results to the widely used purity method gives straight lines for the plot $T = f(1/F)$ and allows the determination of impurities as traces.

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