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HEAT TRANSFER IN A DISC-TYPE DSC APPARATUS. II. THEORETICAL REPRESENTATION

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ABSTRACT

Using an electrical representation, a model of a heat flux DSC apparatus is given. Numerical values of the resistors are computed using experiments done with a Mettler TA 2000 B heat-flow DSC. Theoretical traces of the melting of an Indium sample with inert or melting indium as reference have been computed and compared with experiments: a good accord is obtained thus supporting the validity of the model

INTRODUCTION

In the field of thermal analysis, differential scanning calorimetry (DSC) is a widely used technique. The calorimetric signal, Δ, is usually seen as the representation of the true thermal effect, although several workers [1,2] have shown that this point of view was not realistic.

In previous publications [3,4], it has been shown that the heat-flow DSC apparatus behaves as a conduction coupled cell calorimeter, and not as a Calvet-type microcalorimeter.

Using the thermal form of Ohm's law, Baxter [5] gave an electrical representation of a duPont DSC apparatus. He did not, however, support his view by experiments. In this paper, a simple theoretical model of a heat-flow DSC apparatus is given (Mettler TA 2000). Using the data published previously [4], the validity of the model is tested.

THERMAL OHM'S LAW AND DEVELOPMENT OF A MODEL

There are basically two different approaches to the analysis of the response of a calorimeter: (i) a relation is found between power input, S, and

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calorimetric signal, Δ [6]; (ii) a knowledge model of the calorimeter is established using the thermal Ohm's law. Every resistor or capacitor shown exists in reality [7].

Thermal Ohm's law

We feel it useful for the clarity of the paper to explain in some detail the thermal–electrical analogy.

If temperature and tension are analogous, then heat flow is equivalent to intensity. It follows that thermal and electrical resistors have the same representation as have thermal and electrical capacitors. A constant temperature is seen as an electrical generator of tension. Examples of electrical generators are the temperature of the furnace or a thermal effect at constant temperature (e.g. melting of a pure substance).

Remarks on the model

A disc-type DSC seems to be simple because heat transfer occurs in a very small volume, which can be assimilated to a plane. In some ways this type of calorimeter looks like a section of a Calvet-type microcalorimeter.

The very first goal is to obtain the simplest model which correctly represents the experiments. However, limitations appear immediately because the model is a simplification of the real calorimeter. For example, in place of distributed capacitors and resistors, localized elements are used.

Hypotheses

The assumptions made were as given below.

(a) Resistors and capacitors are localized.

(b) The symmetrical design of the apparatus necessitates a symmetrical model. A real calorimeter is not symmetrical. It is assumed that resistors are symmetrical, but capacitors different.

(c) The gas surrounding the disc is in the conduction mode.

(d) The crucibles and the sample are assimilated to points.

ELECTRICAL MODEL OF A DISC HEAT-FLOW DSC

The essential parts of a heat-flow DSC are a sample crucible, C_1, and a reference crucible, C_2, supported by a disc and heated in a furnace to a temperature, E. The temperature difference between the sample and reference is measured by a thermocouple array of sensitivity g.

Heat flows from the furnace to the crucibles through the disc and the gas. There is a thermal resistor between the bottom of the crucible and the disc,

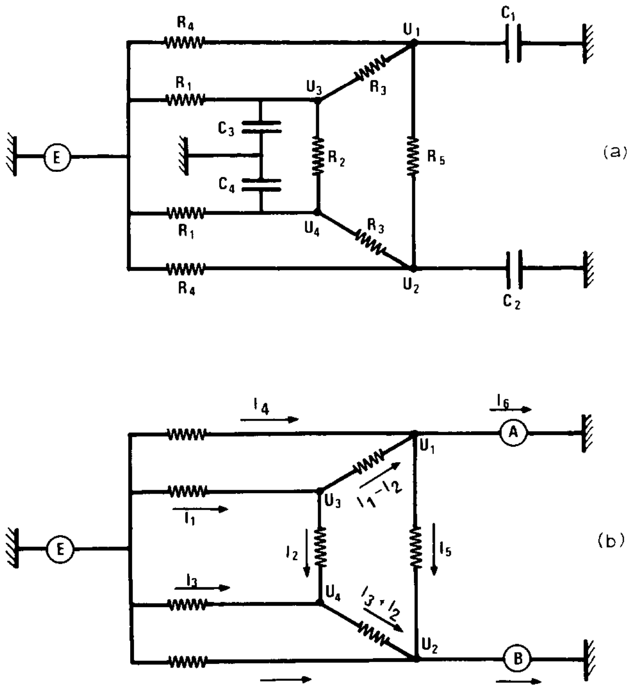

Fig. 1. (a) The electrical circuit of the calorimeter. E, Tension generator (furnace temperature); C_1, C_2, thermal capacitors of sample + crucible and reference + crucible, respectively; C_3, C_4, thermal capacitors of the disc; R_1, furnace–crucible thermal resistor (through the disc); R_2, crucible–crucible thermal resistor (through the disc); R_3, disc–crucible thermal resistor; R_4, furnace–crucible thermal resistor (through the gas); R_5, crucible–crucible thermal resistor (through the gas); U_1, U_2, U_3, U_4, temperatures of the sample crucible, reference crucible, disc below the sample, and the reference, respectively. (b) The heat flow when A and B are at a constant temperature.

as shown by Baxter [5]. Such a thermal resistor may exist between the crucible and the sample (or reference) material.

The crucibles are very close together and the length of the heat path from the furnace to the center of the reference or sample is about half the distance between the centers of the two crucibles. Consequently, a resistor bounding both crucibles has to be taken into consideration. The gas surrounding the crucibles above and below the disc participates in the heat transfer in the same way as the disc. The heat capacity of the part of the disc in the vicinity of each crucible is an important contribution of the solid disc to the dynamic behavior of the calorimeter.

The temperature difference is measured by thermocouples. They are vacuum deposited on the glass disc and it is assumed that the temperature difference reading is that of the disc itself [8].

This simple description is represented in Fig. 1 (a).

The calorimetric signal, Δ, is given by

$$\Delta = g(U_3 - U_4) \tag{1}$$

Equivalent heat paths, in the disc or in the gas, have proportional resistors. Thus

$$\frac{R_1}{R_2} = \frac{R_4}{R_5}$$

The resistance, r, of the furnace sample is given by

$$\frac{1}{r} = \frac{1}{R_4} + \frac{1}{R_1 + R_3} \tag{2}$$

For notational convenience, the disc resistor, R_d, is used, i.e.

$$R_d = R_1 + R_3 \tag{3}$$

COMPUTATION OF THE VALUE OF THE RESISTORS

Equations

The calorimeter is at a constant temperature, E, and has two crucibles containing, respectively, the melting compounds A and B, such that $E > T_m(\text{A}) > T_m(\text{B})$

A steady state has been attained and thermal capacitors can be ignored. For the sake of simplicity $T_m(\text{A})$ and $T_m(\text{B})$ are labelled A and B.

In Fig. 1(b) currents have been represented and the following equations can be formulated

$$E - A = R_1 i_1 + R_3(i_1 - i_3) \tag{4}$$

$$E - B = R_1 i_3 + R_3(i_2 + i_3) \tag{5}$$

$$U_3 = E - R_1 i_1 \tag{6}$$

$$U_4 = E - R_1 i_3 \tag{7}$$

By combining eqns. (6) and (7) and replacing i_1 and i_3 from eqns. (4) and (5) with $U_3 - U_4 = R_2 i_2$, it follows that

$$\frac{\Delta}{g} = U_3 - U_4 = \frac{A - B}{1 + R_3/R_1 + 2R_3/R_2} = \frac{A - B}{D} \tag{8}$$

with

$$D = 1 + \frac{R_3}{R_1} + 2\frac{R_3}{R_2} \tag{9}$$

Equation (8) states that heat flow exchanged between the crucible through the disc does not depend on the temperature of the furnace. This is also true

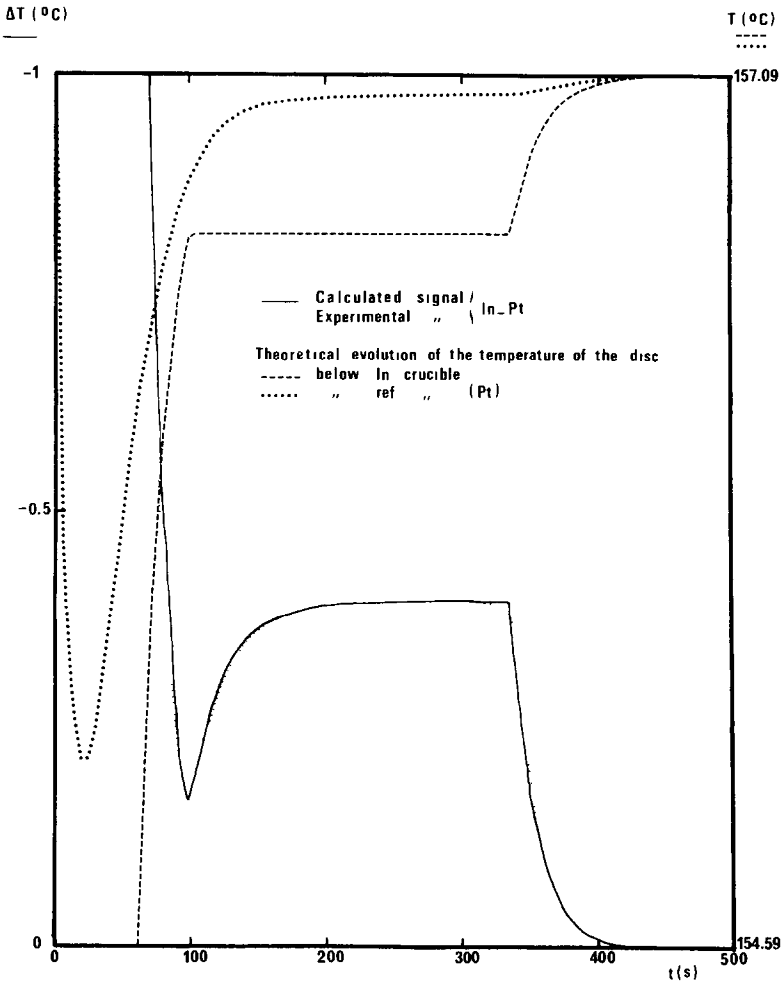

Fig. 2. Theoretical and experimental curves for the melting of In with an inert reference.

for the total heat exchange between sample and reference, and if $A = B$ no heat exchange occurs.

In comparison, the heat flow $\phi = i_6$ entering A is given by

$$\phi = (E - A)\left(\frac{1}{R_4} + \frac{1}{R_1 + R_3}\right) - (A - B)\left[\frac{R_1}{(R_1 + R_3)R_2 D} + \frac{1}{R_5}\right] \tag{10}$$

or, using eqns. (2) and (3)

$$\phi = \frac{E - A}{r} - (A - B)\left[\frac{R_1}{R_d R_2 D} + \frac{1}{R_5}\right] \tag{11}$$

When melting of A is complete, B is still melting, and a new steady state is reached with $\phi = 0$. The temperature U_1 of liquid A is given by

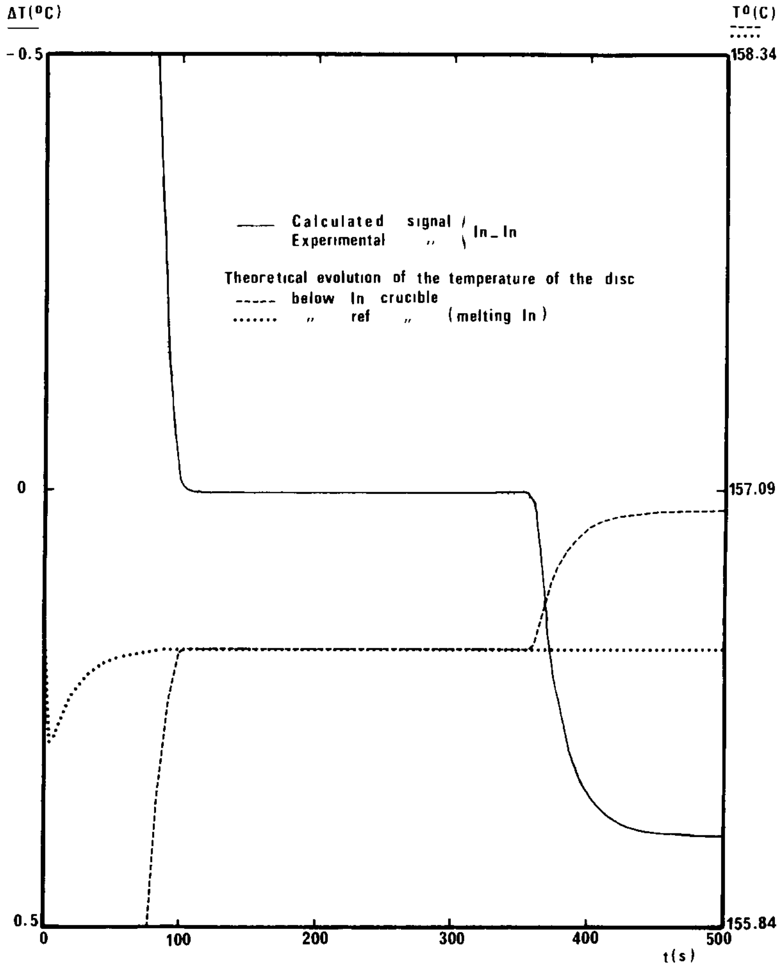

Fig. 3. Theoretical and experimental curves for the melting of In with melting In reference.

$$U_1 = \frac{E + B(R_1 r/R_2 R_d D + r/R_5)}{1 + R_1 r/R_2 R_d D + r/R_5} \tag{12}$$

Replacing A in eqn. (8) with U_1 from eqn. (12) and differentiating with respect to E, we obtain

$$\frac{d\Delta}{dE} = \frac{g}{D + R_1 r/R_2 R_d + Dr/R} \tag{13}$$

Determination of the resistors

In a previous paper [4], the heat flow, ϕ, entering the sample (indium) and the calorimetric signal, Δ, were measured vs. furnace temperature, using melting indium as reference. The equation of the curve $\phi = f(E)$ is given by

$$\phi = \frac{1}{r}[E - T_m(In)]$$

The slope of the curve $\Delta = f(E)$ is given by eqn. (13). The *EMF* of the thermocouple, g, has been measured.

In the scanning mode, melting of the same In sample (heat of melting, Q) with different gases flushing the calorimeter gave a relationship between the thermal conductivity of the gas, λ, and the area of the peak, S. A linear function $\lambda = f(1/S)$ was found. If $\lambda = 0$, the area of the peak, S_0, is given by

$$Q = \frac{g}{R_1 + R_3} S_0$$

For a different value

$$Q = g\left(\frac{1}{R_1 + R_3} + \frac{1}{R_4}\right) S$$

S and S_0 were computed using the relation $\lambda = f(1/S)$. The ratio α is known for argon which was used in the experiments.

$$\alpha = \frac{R_4}{R_1 + R_3} = \frac{S}{S_0 - S} \tag{14}$$

Application to the computation of the resistors

Experimental determinations give numerical values for r, $\mathrm{d}\Delta/\mathrm{d}E$, g and α. x is taken to be

$$x = \frac{R_1}{R_2} = \frac{R_4}{R_5} \tag{15}$$

From eqn. (14), we obtain $R_4 = (1 + \alpha)r$ and with eqn. (2) R_d may be computed. Equation (13) can be rewritten as

$$\frac{g}{\mathrm{d}\Delta/\mathrm{d}E} = D\left(1 + \frac{x}{1 + \alpha}\right) + x\frac{\alpha}{1 + \alpha} \tag{16}$$

leading to a value for D. R_3 is obtained from eqns. (9) and (15).

$$R_3 = R_d \frac{D - 1}{2x + D} \tag{17}$$

The resistor R_1 is given by

$$R_1 = R_d - R_3 \tag{18}$$

and from eqn. (15) it follows that

$$R_2 = \frac{R_1}{x} \text{ and } R_5 = \frac{R_4}{x} \tag{19}$$

It is thus possible for a value of x to compute all the values of the resistors using the experimental relationships.

MATHEMATICAL BACKGROUND

Mathematical tools

The state of the calorimeter at a given time t is defined by four temperatures, $U_1(t)$, $U_2(t)$, $U_3(t)$ and $U_4(t)$, and three inputs, $E_1(t)$, $E_2(t)$ and $E_3(t)$. The equations have the form

$$\dot{U}_i(t) = a_{i1}U_1(t) + a_{i2}U_2(t) + a_{i3}U_3(t) + a_{i4}U_4(t) + b_{i1}E_1(t) + b_{i2}E_2(t) + b_{i3}E_3(t) \text{ for } i\epsilon 1, 4 \tag{20}$$

These equations can be rewritten using matrix notation such that

$$\dot{U}(t) = AU(t) + BE(t) \tag{21}$$

Solution of this system can be done using a numerical integration method or rigorous approach. It seemed more appropriate to use the second method to ensure that no error could occur as a result of the mathematical method, having in mind that the transcription could easily be done on a micro or desk-top computer.

Solution of the system in eqn. (20) at $t > 0$ is given by

$$U(t) = \exp[(t)A]U(0) + \int_0^t \exp[(t-\tau)A]BE(\tau)\mathrm{d}\tau \tag{22}$$

If the solution is desired only at kT, T being the sampling period, the solution is

$$U[(k+1)T] = \exp[(T)A]U(kT) + \int_{kT}^{(k+1)T} \exp\{[(k+1)T - \tau]A\}BE(\tau)\mathrm{d}\tau \tag{23}$$

In the case where the input $E(t)$ is constant in the period kT, $(k+1)T$ [hence $E(kT)$], the integral is calculated exactly and eqn. (23) can be rewritten to give

$$U[(k+1)T] = \exp[(T)A]U(kT) + A^{-1}\{\exp[(T)A] - \dot{I}\}BE(kT) \tag{24}$$

with $\dot{I}$ = identity matrix.

The exponential of the matrix was computed using limited development and the only approximation done is given by

$$\exp Z = \dot{I} + (1/1!)Z + (1/2!)Z^2 + (1/3!)Z^3 + \ldots \tag{25}$$

Application to the melting of In with an inert reference

The calorimeter is at a constant temperature, thus $U_1 = U_2 = U_3 = U_4 = E$. An indium sample at temperature T is put in the calorimeter. The temperature of the In rises to T_m, where it is constant during the whole melting process. When the melting is complete, the temperature of the sample rises to that of the furnace (E). There are three steps to the experiment, described by equations where the inputs are changed.

Heating of the sample

Matrix (26) calculated from the model is given by

$$\begin{bmatrix} U_1 \\ U_2 \\ U_3 \\ U_4 \end{bmatrix} = \begin{bmatrix} -\frac{1}{C_1}\left(\frac{1}{R_3}+\frac{1}{R_4}+\frac{1}{R_5}\right) & \frac{1}{C_1R_5} & \frac{1}{C_1R_3} & 0 \\ \frac{1}{C_2R_5} & -\frac{1}{C_2}\left(\frac{1}{R_3}+\frac{1}{R_4}+\frac{1}{R_5}\right) & 0 & \frac{1}{C_2R_3} \\ \frac{1}{C_3R_3} & 0 & -\frac{1}{C_3}\left(\frac{1}{R_1}+\frac{1}{R_2}+\frac{1}{R_3}\right) & \frac{1}{C_3R_2} \\ 0 & \frac{1}{C_4R_3} & \frac{1}{C_4R_2} & -\frac{1}{C_4}\left(\frac{1}{R_1}+\frac{1}{R_2}+\frac{1}{R_3}\right) \end{bmatrix} \begin{bmatrix} U_1 \\ U_2 \\ U_3 \\ U_4 \end{bmatrix} + \begin{bmatrix} \frac{1}{C_1R_4} \\ \frac{1}{C_2R_4} \\ \frac{1}{C_3R_1} \\ \frac{1}{C_4R_1} \end{bmatrix} E \tag{26}$$

Melting of the sample

When $U_1 = T_m(\mathrm{In})$, the system is reduced by one equation and has two inputs: E nd T_m. The initial conditions are found in matrix (26) at $U_1 = T_m$.

$$\begin{bmatrix} U_2 \\ U_3 \\ U_4 \end{bmatrix} = \begin{bmatrix} -\frac{1}{C_2}\left(\frac{1}{R_3}+\frac{1}{R_4}+\frac{1}{R_5}\right) & 0 & \frac{1}{C_2R_3} \\ 0 & -\frac{1}{C_3}\left(\frac{1}{R_1}+\frac{1}{R_2}+\frac{1}{R_3}\right) & \frac{1}{C_3R_2} \\ \frac{1}{C_4R_3} & \frac{1}{C_4R_2} & -\frac{1}{C_4}\left(\frac{1}{R_1}+\frac{1}{R_2}+\frac{1}{R_3}\right) \end{bmatrix} \begin{bmatrix} U_2 \\ U_3 \\ U_4 \end{bmatrix} + \begin{bmatrix} \frac{1}{C_2R_5} & \frac{1}{C_2R_4} \\ \frac{1}{C_3R_3} & \frac{1}{C_3R_1} \\ 0 & \frac{1}{C_4R_1} \end{bmatrix} \begin{bmatrix} T_m \\ E \end{bmatrix} \tag{27}$$

The heat flow $\phi = \dot{Q}$ is given by

$$\dot{Q} = \left(\frac{1}{R_5}, \frac{1}{R_3}, 0\right) \begin{bmatrix} U_2 \\ U_3 \\ U_4 \end{bmatrix} + \left[-\left(\frac{1}{R_3}+\frac{1}{R_4}+\frac{1}{R_5}\right), \frac{1}{R_4} \right] \begin{bmatrix} T_m \\ E \end{bmatrix} \tag{28}$$

Melting is complete when $\int_0^t \dot{Q}\,\mathrm{d}t = Q_0$. A formal calculation of this integral has been done using the matrix notation

$$\dot{Q} = CU + DE \tag{29}$$

$$\begin{aligned} Q[(k+1)T] = {} & Q(kT) + CA^{-1}\{\exp[A(T)] - \dot{I}\}U(kT) \\ & + CA^{-1}\left[A^{-1}\{\exp[A(T)] - \dot{I}\} - (T)\dot{I}\right]BE(kT) \\ & + (T)DE(kT) \end{aligned} \tag{30}$$

A and B are found in matrix (27).

End of experiment

When melting is complete, matrix (26) describes the current state of the calorimeter, with initial conditions found in matrix (27) when Q is equal to the heat of melting of the In sample, Q_0.

Application to the melting of In with an active reference

In contrast to the foregoing experiment, a reference crucible containing a large amount of In is used. Consequently, since the In reference is in the process of melting during the experiment, its temperature is constant. As previously, the experiment consists of three steps.

Heating of the sample

The system has two inputs: E and T_m. The equations are

$$\begin{bmatrix} U_1 \\ U_3 \\ U_4 \end{bmatrix} = \begin{bmatrix} -\frac{1}{C_1}\left(\frac{1}{R_3}+\frac{1}{R_4}+\frac{1}{R_5}\right) & \frac{1}{C_1R_3} & 0 \\ \frac{1}{C_3R_3} & -\frac{1}{C_3}\left(\frac{1}{R_1}+\frac{1}{R_2}+\frac{1}{R_3}\right) & \frac{1}{C_3R_2} \\ 0 & \frac{1}{C_4R_2} & -\frac{1}{C_4}\left(\frac{1}{R_1}+\frac{1}{R_2}+\frac{1}{R_3}\right) \end{bmatrix} \begin{bmatrix} U_1 \\ U_3 \\ U_4 \end{bmatrix} + \begin{bmatrix} \frac{1}{C_1R_5} & \frac{1}{C_1R_4} \\ 0 & \frac{1}{C_3R_1} \\ \frac{1}{C_4R_3} & \frac{1}{C_4R_1} \end{bmatrix} \begin{bmatrix} T_m \\ E \end{bmatrix} \tag{31}$$

Melting of the sample

There are three inputs: T_m, T_m and E. Thus

$$\begin{bmatrix} \dot{U}_3 \\ \dot{U}_4 \end{bmatrix} = \begin{bmatrix} -\frac{1}{C_3}\left(\frac{1}{R_1}+\frac{1}{R_2}+\frac{1}{R_3}\right) & \frac{1}{C_3R_2} \\ \frac{1}{C_4R_2} & -\frac{1}{C_4}\left(\frac{1}{R_1}+\frac{1}{R_2}+\frac{1}{R_3}\right) \end{bmatrix} \begin{bmatrix} U_3 \\ U_4 \end{bmatrix} + \begin{bmatrix} \frac{1}{C_3R_3} & 0 & \frac{1}{C_3R_1} \\ 0 & \frac{1}{C_4R_3} & \frac{1}{C_4R_1} \end{bmatrix} \begin{bmatrix} T_m \\ T_m \\ E \end{bmatrix} \tag{32}$$

The heat flow entering the sample is given by

$$\dot{Q} = \left(\frac{1}{R_3}, 0\right)\begin{bmatrix} U_3 \\ U_4 \end{bmatrix} + \left[-\left(\frac{1}{R_4}+\frac{1}{R_3}\right), \frac{1}{R_4}\right]\begin{bmatrix} T_m \\ E \end{bmatrix}$$

End of experiment

System (31) was used and the initial conditions were found as for the system described previously.

RESULTS

An HP 85 microcomputer with ROM matrix was used. A complete calculation needed 90 s.

Melting of In with inert reference

It was not possible to calculate directly every value of the resistors of the calorimeter. A trial-and-error method was used. A first value of $x \leqslant 0.21$ was taken and the resistors were computed. A greater value of x gives $R_3 < 0$ which is impossible. Arbitrary values of C_3 and C_4 were given. The heat capacities, C_1 and C_2, the heat of fusion of the indium sample, and the temperature of the furnace were known. The computation of $U_3 - U_4 = f(t)$ was performed and plotted vs. time with the experimental curve and temperature of the disc, U_3 and U_4. This procedure was repeated so as to obtain the best fit of the computed and experimental plots.

Figure 2 shows the experimental and theoretical curves obtained for $x = 0.135$ and with the following numerical values: $C_1 = 57.4$ mJ K^{-1}; $C_2 = 56.4$ mJ K^{-1}; $C_3 = 95$ mJ K^{-1}; $C_4 = 129$ mJ K^{-1}; $R_1 = 0.1878$ K mW^{-1}; $R_2 = 1.391$ K mW^{-1}; $R_3 = 0.010$ K mW^{-1}; $R_4 = 0.784$ K mW^{-1}; $R_5 = 5.807$ K mW^{-1}; $g = 134$ μV K^{-1}; $Q_0 = 791.7$ mJ; $T_m = 156.61$°C; $E = 157.09$°C. The initial conditions were 25°C, E, E and E for U_1, U_2, U_3 and U_4, respectively.

R_3 is a contact resistor between the crucible and the disc. An approximate value of this resistor can be found, assuming that heat transfer occurs mainly through a layer of gas between the bottom of the crucible and the disc [9]. A reasonable value for the thickness of the gas layer is 10^{-2} mm, and the diameter of the crucible is 6 mm. Thus, $R_3 = 0.0149$ K mW^{-1} is in good agreement with the previous determination.

Evolution of the temperature of the disc, U_3 and U_4, clearly explains the shape of the calorimetric signal.

Melting of In with In as reference

The values for the resistors and capacitors found previously were used: the theoretical and experimental calorimetric signals are shown in Fig. 3. The curves are in good agreement.

DISCUSSION

The model correctly represents the experiments and is a reasonable representation of the calorimeter. It is to be noted that a slight difference appears at the end of the melting of the In sample. The sample crucible resistor probably varies during the melting of the sample and is responsible for the change in the calorimetric signal. This resistor was not taken into consideration in this model. A more complex model could most probably give a better fit, but it seems difficult to imagine experiments which would give the values of every resistor or capacitor.

CONCLUSION

The model of a disc heat-flux DSC apparatus correctly represents the experiments described in this paper.

Since the calorimeter has coupled cells, correction of the calorimetric signal in the scanning mode seems to be important for a correct interpretation of the thermal effect.

REFERENCES

1 E. Calvet and F. Camia, J. Chim. Phys., 55 (1958) 818.
2 E. Cesari, V. Torra, J.M. Macqueron, R. Prost, J.P. Dubes and H. Tachoire, Thermochim. Acta, 53 (1982) 17.
3 P. Claudy, J.C. Commercon and J.M. Letoffe, Journée de Calorimetrie et d'Analyse Thermique, Nancy, 14–15 May, 1981.
4 P. Claudy, J.C. Commercon and J.M. Letoffe, Thermochim. Acta, 65 (1983) 245.
5 R.A. Baxter, Proc. 2nd Int. Conf. Therm. Anal., Academic Press, New York, London, Vol. 1, 1969, p. 65.
6 E. Cesari, V. Torra, J.L. Macqueron, R. Prost, J.P. Dubes and H. Tachoire, Thermochim. Acta, 53 (1982) 1.
7 J. Navarro, E. Cesari, V. Torra, J.L. Macqueron, J.P. Dubes and H. Tachoire, Thermochim. Acta, 52 (1982) 175.
8 W.H. King, Jr., C.T. Camilli and A.F. Findeis, Anal. Chem., 40 (1968) 8.
9 G. Sinicki, Thesis No. 7518, Lyon, 1975.