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HEAT TRANSFER IN A DISC-TYPE DSC APPARATUS
IV. Applicability of the coupled cells model to periodic temperature modulation

P. Claudy[1]* *and J. M. Letoffe*[2]

[1]Laboratoire des Matériaux Organiques à Propriétés Spécifiques UPR CNRS 9031, BP 24
69390 Vernaison
[2]ESA 5079 CNRS Energétique et synthèse inorganique INSA, Bat 401, 20 avenue A. Einstein
69621 Villeurbanne Cedex, France

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Abstract

The application of non-linear heating programs to a heat-flux DSC apparatus has attracted much attention. On the basis of thermodynamics, the change in enthalpy of a sample during a temperature change ΔT is due, on the one hand to the true heat capacity of the sample $\Delta T\ C_{p\xi}$ and on the other, to the enthalpy of some transformation occurring in the sample $\Delta_r H\ \Delta\xi$. These contributions can be separated on the basis of the kinetics of the transformation. The coupled cells model of a disc type, heat flux DSC apparatus has been tested, using true heat capacities and a sine modulation of the temperature of the furnace around a constant temperature. In the range from 2 to 60 mHz, the amplitude and phase shift of the calorimetric signal were measured at several frequencies. Theoretical equations, based on the model, and using the thermal Ohm's law explains the results with a reasonable accuracy. A non-linear DSC experiment affords two ways of determination of the heat capacity of a sample making possible a distinction between the enthalpic effect and heat capacity.

Keywords: DSC(temperature modulated DSC), frequency response, modelling of DSC, phase shift response, thermodynamic discussion of DSC

Introduction

Since the original Boersma [1] DSC, the development of electronic devices has made possible a considerable improvement of their performance and a better interpretation of the results. For DSC users, the base line problem is the most difficult one, since it is the basis of the determination of any enthalpy change during the transformation of a sample.

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* Author to whom all correspondence should be addressed.

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For heat flow DSC instruments the calorimetric signal Δ is proportional to the difference between the temperature of the product T_{pr} and reference T_{ref}, often measured with thermocouples.

$$\Delta = g(T_{pr} - T_{ref}) \qquad (1)$$

where g the sensitivity of the thermocouples (in $\mu V\ K^{-1}$).

The calorimetric signal is proportional to the difference in the power absorbed by the product W_{pr} and the reference side W_{ref}, respectively.

$$\Delta = k(W_{pr} - W_{ref}) \qquad (2)$$

where k sensitivity of the DSC apparatus ($\mu V\ mW^{-1}$).

During a temperature scan, at a constant heating rate β, assuming that the thermal power is absorbed by the heat capacities C and C' on the sample and reference side respectively, Δ can be written as:

$$\Delta = k\beta\ (C - C') \qquad (3)$$

The heat capacity C on the sample side is the sum of several heat capacities:

$$C = C_{exp} + C_c + n_{prod}C_{prod} \qquad (4)$$

C_{exp}	heat capacity of the DSC instrument itself on the product side ($J\ K^{-1}$),
C_c	heat capacity of the crucible containing the product ($J\ K^{-1}$),
C_{prod}	molar heat capacity of the product ($J\ K^{-1}mol^{-1}$),
n_{prod}	number of moles of the product.

The total heat capacity of the crucible plus the sample is defined as:

$$C_S = C_c + n_{prod}\ C_{prod}$$

Comparison of (2) and (3) gives the heat capacity C.

$$(W_{pr} - W_{ref}) = \beta(C - C') \qquad (5)$$

Equation (5) was written by assuming no thermal power developed by any transformation in the sample. This hypothesis has to be proved, but it is very difficult to do on an experimental basis. A good example of this is glass transition [2, 3], where the heat effect is still under discussion.

Chemical thermodynamics, kinetics and DSC

The problem of separation of heat capacity and enthalpy change is best understood by going back to the basic thermodynamic equations. The enthalpy of a system, made of one mole of a pure compound, is a function of a number of independent variables, which are usually not known and difficult to even establish.

It was shown by Prigogine [4] that the most general thermodynamic description of a system requires at least three variables. The enthalpy of the system is given by $H(T, P, \xi)$, ξ being the degree of advance of some transformation occurring in the system. DSC experiments are usually done at a constant pressure. Then:

$$C_P = \frac{dH}{dT} = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} + \left(\frac{\partial H}{\partial \xi}\right)_{p,T} \frac{d\xi}{dT} \tag{6}$$

C_p is called the apparent heat capacity[5], and $C_{p,\xi} = \left(\frac{\partial H}{\partial T}\right)_{p,\xi}$ is the true heat capacity [5]. The enthalpy of the transformation is $\Delta_r H_T^P = \left(\frac{\partial H}{\partial \xi}\right)_{p,T}$ and $\Delta_r H_T^P \frac{d\xi}{dT}$ is the conformational heat capacity [4].

In a conventional DSC, the temperature is a linear function of time, and Eq. (6) can be written as:

$$\frac{dH}{dT}\frac{dt}{dT} = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} + \left(\frac{\partial H}{\partial \xi}\right)_{p,T} \frac{d\xi}{dt}\frac{dt}{dT} \tag{7}$$

The power W used to heat the system at β is given by:

$$W = \beta C_{P,\xi} + \Delta_r H_T^P \frac{d\xi}{dt} \tag{8}$$

This power is the sum of two terms: the first one is directly connected to the heating rate, whereas the second one is a complex mathematical expression of time and temperature and (or) composition given by the laws of kinetics [6]. The calorimetric signal given in Eq. (1) is now written as:

$$\Delta = k\left[\beta\left(C_{\mathrm{exp}} + C_c + n_{\mathrm{prod}}\, C_{p\xi} - C'\right) + n_{\mathrm{prod}}\, \Delta_r H_T^P \frac{d\xi}{dt}\right] \tag{9}$$

The base line Δ_l is represented by

$$\Delta_l = k\beta\left(C_{\mathrm{exp}} + C_c + n_{\mathrm{prod}}\, C_{p\xi} - C'\right) \tag{10}$$

and the thermal effect at time t is given by:

$$Q = \int_0^t \frac{1}{k}(\Delta - \Delta_l)dt \tag{11}$$

From Eq. (8) the difference between apparent and true heat capacity depends on the kinetics of the transformation. The first idea was to use step heating so as to wait for the thermal and thermodynamic equilibrium to be established [7–11]. The experiment yielded a set of peaks and it was shown [11] that the slope at the start of each peak and its time constant, gave a separation between the true heat capacity of the sample and its thermal (enthalpic) effect. The area of each peak was proportional to the apparent heat capacity. More recently, an isoperibolic DSC apparatus using a step heating mode has been described [12].

Another possible way was to use another mode of changing the temperature, on adding some periodic function to a constant heating rate so as to modulate the temperature and/or the power in the sample. Periodic heating was described a long time ago [13, 14], and used in AC-calorimetry [15–18] and kinetic experiments [6]. Recently this idea has been utilized in a commercially available DSC apparatus [19].

The model of a coupled cells DSC

A previous study of heat transfer [20, 21] in a disc type heat flow DSC, such as a Mettler TA 2000 or DuPont DSC apparatus, at a constant temperature, has shown that these calorimeters behave as linear systems, they are in fact coupled cells differential heat flow calorimeters. Equations for the correction of the calorimetric signal [22–24] in scanning (linear) mode were published.

The model used

The model used is based on the thermal Ohm's law. The simple electrical model is given in Fig 1. The thermal resistors between the bottom of the crucibles and the thermoelectric disc [20, 21] have been neglected. Heat transfer through the purge gas is contained in the resistors *R* and *r*. The temperatures are represented by electrical quantities and written accordingly.

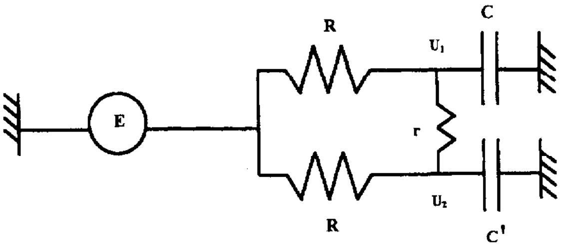

Fig. 1 Representation of a heat flow DSC apparatus, with the meaning of the voltages: E=temperature of the furnace; U_1=temperature of the product; U_2=temperature of the reference; R= furnace-crucible resistor; r=crucible-crucible resistor; C=reference side capacitor; C'=sample side capacitor

Hypothesis

The enthalpy H of the system under study is given by $H=f(T)$, since P is constant. There is no thermal effect.

Equations of the electrical model

The voltage of the generator E is:

$$E = E_o + A_F \sin(\omega t)$$

with:

E_o constant voltage,
A_F amplitude of the modulation,
f frequency (Hz) $\omega=2\pi f$,
p period (s) $p=1/f$

The equation of the calorimetric signal is given by:

$$U_2 - U_1 = A_\Delta \sin(\omega t + \varphi).$$

In the electrical model the ground may be chosen at E_o, and the electrical voltage E of the generator standing for the temperature of the oven is simply $E=A_F\sin(\omega t)$.

The voltage difference U_2–U_1 (analogous to the calorimetric signal Δ) is computed [25] using an equivalent circuit based on Thevenin's theorem: the resistor r is linked to two generators of fem E_1 and E_2 with internal impedance Z_1 and Z_2, respectively.

For sake of simplicity it is assumed that $Z = \dfrac{1}{jC\omega}$ and $Z' = \dfrac{1}{jC'\omega}$ with $j^2 = -1$.

The fem of the generators are $E_1 = E\dfrac{Z'}{R+Z'}$ and $E_2 = E\dfrac{Z}{R+Z}$, respectively.

Their impedances Z_1 and Z_2 are: $Z_1 = \dfrac{RZ'}{R+Z'}$ $Z_2 = \dfrac{RZ}{R+Z}$.

The voltage difference U_2–U_1 is simply given by:

$$U_2 - U_1 = r\frac{\dfrac{EZ'}{R+Z'} - \dfrac{EZ}{R+Z}}{r + \dfrac{RZ'}{R+Z'} + \dfrac{RZ}{R+Z}} = \frac{ErR(Z'-Z)}{r(R+Z')(R+Z) + RZ'(R+Z) + RZ(R+Z')}$$

Upon substitution we get:

$$U_2 - U_1 = -E\frac{jrR\omega\,(C-C')}{r + 2R - rR^2CC'\omega^2 + jR\omega(r+R)(C+C')} \tag{12}$$

It is convenient to use the modules of the gain G of the electrical device given in Fig. 1 as:

$$|G| = \left|\frac{U_2 - U_1}{E}\right| = \frac{rR\omega(C - C')}{\sqrt{\left(r + 2R - rR^2CC'\omega^2\right)^2 + \left(R\omega\,(r + R)(C + C')\right)^2}} \tag{13}$$

The phase shift φ is given by

$$\mathrm{tg}\varphi = \frac{r + 2R - rR^2CC'}{R\omega\,(C + C')(r + R)} \tag{14}$$

These equations are slightly more complex than the equations used by Hatta [26], and Wunderlich [27], because the thermal link between the cells [20, 21, 22] is taken into account.

Discussion

The use of these equations for a real DSC instrument is straightforward. Equations (13) and (14) show that it is possible to measure the values of the resistors and capacitors, and thereby, establish the validity of the model, using temperature modulation.

Experimental

Apparatus

A Mettler TA 2000 B DSC apparatus was used. It was controlled by a computer [20]. Any temperature program of the oven T_F *vs*. time could be achieved since it was possible to send the heating rate $\beta_F=(\mathrm{d}T_F)/\mathrm{d}t$ to the temperature controller of the oven. The experiments were carried out at 298K.

Correction of oven operation

The programmed temperature T_{Fu} of the oven is given by $T_{Fu}=T_0+A_{Fu}\sin(\omega t)$, where A_{Fu} is the amplitude of modulation (in this paper $A_{Fu}=1$ K). This was achieved by sending the heating rate: $\beta_{Fu}=A_{Fu}\omega\cos(\omega t)$ to the temperature controller in every second.

In fact, the temperature T_F of the oven was not the programmed value T_{Fu}, owing to the frequency dependent gain of the PID temperature controller. It was necessary to know and take into account this non-linearity. In order to measure T_F, a thermocouple of a sensitivity of 42.8 μV K^{-1} was tightly attached between the oven and the thermoelectric disc. Measurements were made with a sampling interval Δt of 1 s.

Computation

Since the frequency of temperature modulation is known, the temperature of the oven is fitted by the method of least squares [28] to the equation:

$$T_F = A_1 \sin(\omega t) + A_2 \cos(\omega t) + Bt + T_o. \qquad (15)$$

The amplitude A_F of the temperature modulation is given by

$$A_F = \sqrt{A_1^2 + A_2^2} \qquad (16)$$

and its phase shift φ by:

$$\mathrm{tg}(\varphi_F) = \frac{A_1}{A_2}. \qquad (17)$$

Measurements used for each computation are those done during half of a period $p/2$. The data at t_1, t_2,..t_n are used to compute A_1, A_2, A_F and φ_F at time $(t_n - t_1)/2$ using Eqs (15), (16) and (17), respectively. The values at t_2, t_3....t_{n+1} give A_F and φ_F at time $(t_{n+1} - t_2)/2$ and so on.

From $T=Bt+T_o$, the signal without modulation is obtained.

This method of calculation was found to be very fast and easy to use, even in the scanning mode (β # 0).

Results

The results for the amplitude and phase shift are plotted in Figs 2 and 3.

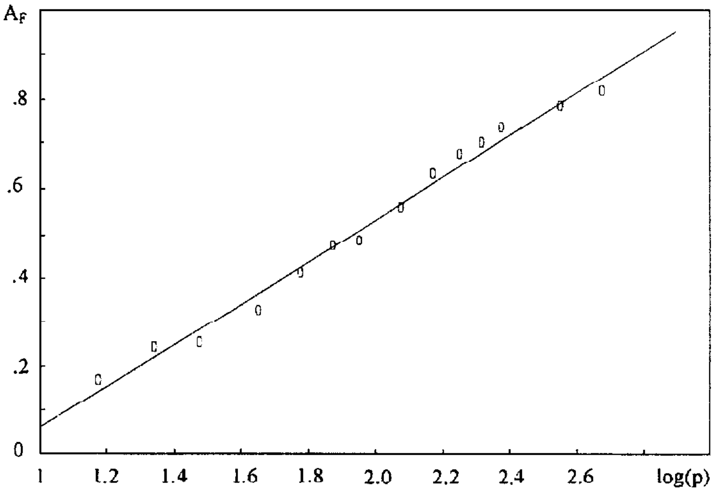

Fig. 2 Amplitude of the modulation of the furnace *vs.* log of period

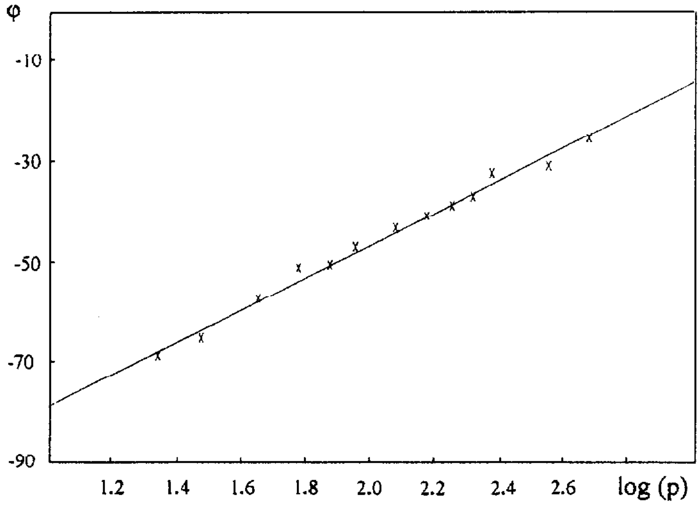

Fig. 3 Phase shift of the furnace *vs.* log of period

As expected, the amplitude decreases when the frequency increases, and the phase shift increases with the frequency. They were fitted by linear equations:

$$A_F = 0.465845 \log(p) - 0.40542 \tag{18}$$

$$\varphi_F = 32.16 \log(p) - 11.114 \tag{19}$$

The cut off frequency of the furnace was found as 2.9 mHz.

Frequency response of the calorimeter

In order to verify the model given in Fig. 1, and Eqs (13) and (14), measurements were made of the calorimetric signal *vs.* frequency and sample heat capacity.

Experiments

The crucibles used were made of aluminium. The sample crucible contained different amounts of aluminium, whose heat capacity is well known [29, 30]. The heat capacity of the sample C_S in the crucible is simply $C_S = n_{Al} C_{Al}$ where n_{Al} is the total number of moles of aluminium and C_{Al} is its molar heat capacity.

The reference crucible contained a small mass of Al_2O_3 and was used for every experiment.

Experiments were made using the same reference crucible i.e. the same value of C', and a variable heat capacity $C=C_{exp}+C_S$ on the sample side.

A set of experiments was made with the same crucible for various periods in the range 30 to 480 s.

Computation

The calorimetric signal $\Delta(\mu V)$, is converted into temperature using the sensivity of the Au/Ni thermocouples given previously [20].

Mathematical analysis of the experiments was carried out as explained in Experimental section (Equations of the electrical model). The gain of the calorimeter G is defined as the ratio of the amplitude of the calorimetric signal to that of the oven A_T given by Eq. (18). G is positive if the temperature of the product increases with that of the oven, and negative in the opposite case.

Results

Four experiments were made with varying amounts of aluminium. Using a multi-variable optimization program, the values for resistors and capacitors were found as:

R	0.1186 mW K^{-1}
r	1.45 mW K^{-1}
C'	120 mJ K^{-1}
C_C	66 mJ K^{-1}

The experimental results of the gain *vs.* C_S are plotted in Fig. 4 together with the theoretical curves computed using Eq. (13).

Discussion

The gain is frequency dependent, which was to be expected. Its maximum is shifted to higher frequencies when the heat capacity of the sample decreases. The same behaviour should occur if the heat capacity of the reference is changed. Heat capacities, thermal conductivities and the sensitivity of thermocouples are temperature dependent. It is expected that the gain is also temperature dependent.

Owing to the very simple model of the calorimeter used, a good correlation was obtained between the observed and theoretical values.

Heat capacity difference response of the calorimeter

Experiments

Experiments were made using different heat capacities. Measurements were performed at two frequencies, close to the maximum of the gain observed in Fig. 4.

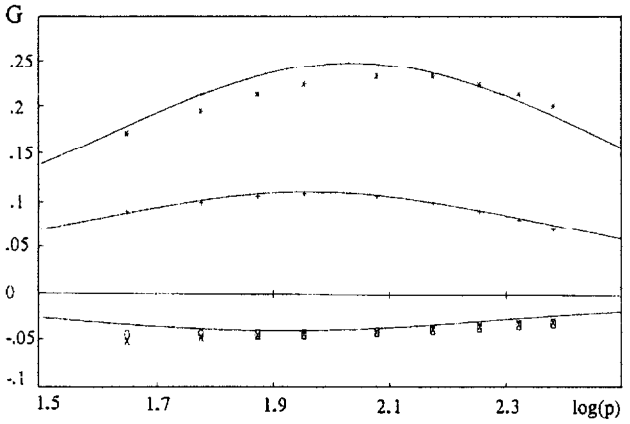

Fig. 4 Gain of the calorimeter vs. log of period, for various samples with different heat capacities product plus crucible and the same reference crucible. * – Gain >0, + – Gain>0, o – and x – Gain<0; C_S=142.2 mJ K^{-1}, C_S=86.4 mJ K^{-1}, C_S=44 mJ K^{-1}

Results

The experimental results of the gain and the theoretical curves calculated using Eq. (13) are plotted in Fig. 5 for two frequencies: $1.11\cdot10^{-2}$ and $5.55\cdot10^{-3}$ Hz, respectively.

The gain *vs.* difference in heat capacity is well represented by the simple model of the calorimeter. The curve is not a straight line, and is valid only with the same reference crucible, i.e. the same total heat capacity C'.

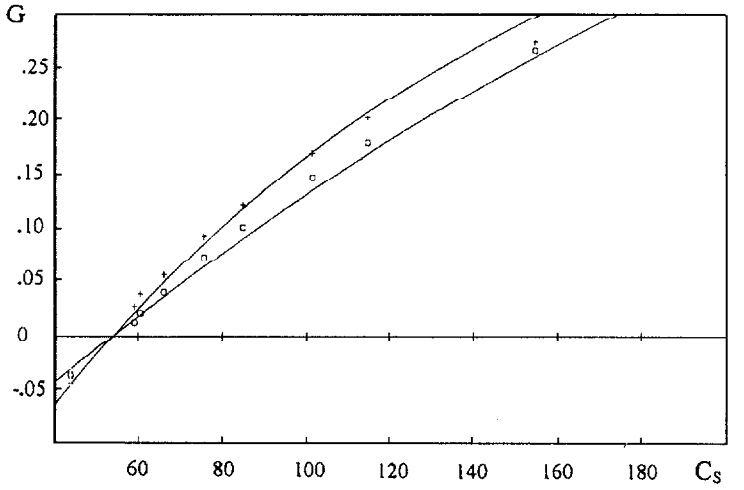

Fig. 5 Gain of the calorimeter *vs.*difference of the heat capacities of the sample and reference crucible. + – period 90 s; o – period 180 s

Phase shift *vs.* frequency

Equation (14) predicts that the phase shift of the calorimetric signal, with respect to the oven modulation should depend on the frequency, and on the difference the heat capacities of the sample and reference side.

Experiments

They were described in 'Experimental' section (Apparatus) 'Frequency response of the calorimeter' section (Experiments), and the results were computed for the phase shift.

Results

In Fig. 6 are plotted the experimental and theoretical phase shift values against the frequency, for the same heat capacity. These measurements are based on the experiments given in Fig. 4 with C_S = 110.0 mJ K^{-1}, and the numerical values of resistors and capacitors given in 'Experimental' section (Computation).

In Fig. 7 are plotted the experimental and theoretical phase shift values against C_S, for two frequencies: $6.66 \cdot 10^{-3}$ and $5.55 \cdot 10^{-3}$ Hz. The theoretical curve is computed with C'=140 mJ K^{-1}, and C_{exp} =86 mJ K^{-1}, appreciably different from the value found in 'Frequency response of the calorimeter' section (Results).

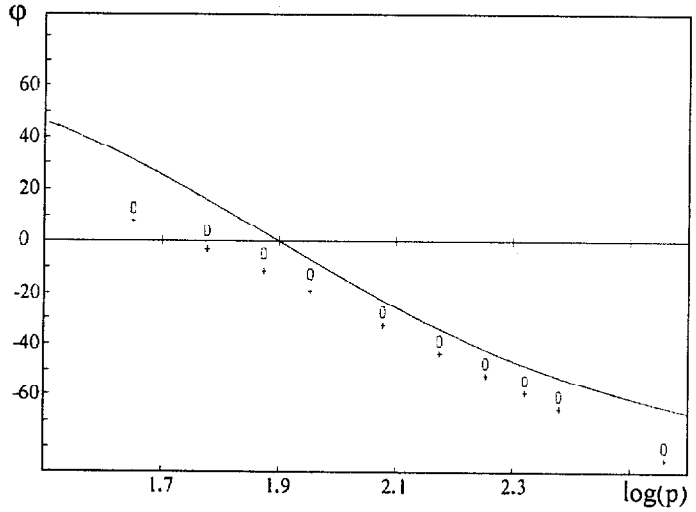

Fig. 6 Phase shift of the calorimeter *vs.* log of period for C_S=44 mJ K^{-1}

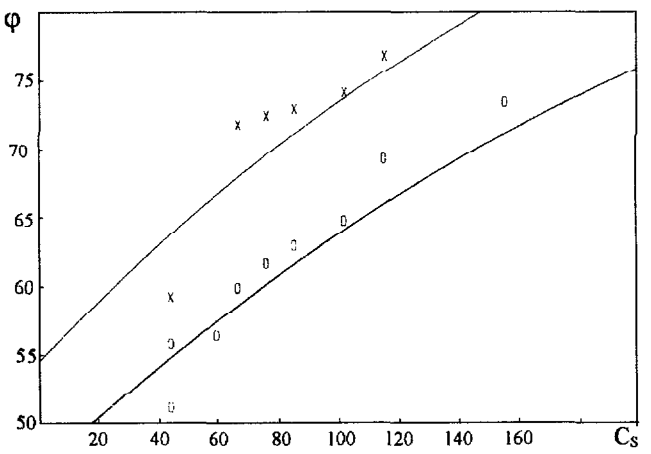

Fig. 7 Phase shift of the calorimeter vs. difference of the heat capacities of the sample and reference crucible, with C'=140 mJ K^{-1} and C_{exp}=86 mJ K^{-1} ; + – period 150 s; o – period 180 s

Discussion

The agreement between computed and experimental data is not as good as expected from the results obtained for the gain. Part of this disagreement is probably due to the high simplicity of the model, which does not take into account the crucible-disc resistor. However, the lack of data for the temperature of the furnace, is an additional source of error.

Conclusions

The experiments reported here show that a simple model of a disc type DSC apparatus describes reasonably well the measurements, and the behaviour of the apparatus at constant temperature.

The ratio of the amplitude of the calorimetric signal to the amplitude of the modulation (gain) depends on the frequency, on the difference of the heat capacities of the sample and reference, on the actual values of the heat capacities on the sample and reference side.

With the same reference crucible, the relationship between the difference of the heat capacities of the sample and reference and the amplitude of the calorimetric signal is not a straight line.

The phase shift of the calorimetric signal provides a possible way to measure the heat capacity. However, the model, or the measurements, do not allow for a good precision.

Nevertheless, as in the DSC step heating mode, around a constant temperature, sine modulation of the temperature of the oven provides two ways for determining the heat capacity, or its change with time or temperature. They are the measurement of the gain of the calorimeter, and that of the phase shift. Of course, they should agree. If there is an appreciable difference it means that the system does not behave as a true heat capacity, i.e. some kind of time dependent transformation occurs in the sample.

References

1 S. L. Boersma, J. Am. Cer. Soc., 38 (1955) 281.
2 S. V. Nemilov, Thermodynamic and kinetic aspects of the vitreous state, CRC Press, Boca Raton, Ann Arbor, London, Tokyo 1995.
3 J. Zarzycki, Les verres et l'état vitreux, Masson Ed., Paris 1982.
4 I. Prigogine and R. Defay, Thermodynamique Chimique. Desoer Ed., Liège 1950.
5 J. P. McCullough and D. W. Scott, Experimental Thermodynamics, Butterworths Ed., London 1968.
6 J. Šesták, V. Sastava and W. W. Wendlandt, Thermochim. Acta, 7 (1974) 333.
7 M. W. Perron, Anal. Chem., 46 (1974) 128.
8 J. Zynger, Anal. Chem., 47 (1975) 1380.
9 G. Kiss, K. Seybold and T. Meisel, J. Thermal Anal., 21 (1981) 57.
10 K. A. Simonsen and M. Zaharescu, J. Thermal Anal., 15 (1979) 25.
11 P. Claudy, J. C. Commerçon and J. M. Létoffé, Thermochim. Acta, 128 (1988) 251.
12 W. Brill and E. Gmelin, J. Thermal Anal., 33 (1988) 365.
13 I. Proks and I. Zlatovsky, Chem. Zvesti, 23 (1969) 620.
14 I. Proks, I. Zlatovsky and K. Adamkovicova, Third Int. Conf. on Thermal Analysis, Davos, August 23-28, 1971 Abstract I-44.
15 Ya. A. Kraftmakher, Zh. Prikl. Mekhan. Tekhn. Fiz., 5 (1967) 176.
16 P. Sullivan and G. Seidel, Phys. Rev., 67a (1968) 173.
17 P. Handler, D. E. Mapother and M. Rayl, Phys. Rev. Lett., 19 (1967) 356.
18 I. Hatta and H. Ikushima, Jpn. J. Appl. Phys., 20 (1981) 1995.
19 M. Reading, B. Crowe and B. K. Hahn, US patent 5224775 6 July 1993.
20 P. Claudy, J. C. Commerçon and J. M. Létoffé, Thermochim. Acta, 65 (1983) 45.
21 P. Claudy, J. C. Commerçon and J. M. Létoffé, Thermochim. Acta, 68 (1983) 305.
22 P. Claudy, J. C. Commerçon and J. M. Létoffé, Thermochim. Acta, 68 (1983) 317.
23 G.-W. Jang and K. Rajeshwar, Anal. Chem., 60 (1986) 1003.
24 G. Höhne, W. Hemminger and H.-J. Flammersheim, Differential Scanning Calorimetry. Springer-Verlag, Berlin–Heidelberg–New York 1996.
25 J. C. Commerçon, Nov. 1986, unpublished results.
26 I. Hatta and S. Muramatsu, Jpn. J. Appl. Phys., 35 (1996) L858.
27 B. Wunderlich, Y. Jin and A. Boller, Thermochim. Acta, 238 (1994) 277.
28 B. J. Frohring, B. E. Peetz, M. A. Unkirch and S. C. Bird, Hewlett Packard Journal, 39 (1988) 39.
29 I. Barin and O. Knacke, Thermodynamical properties of inorganic substances. Springer Verlag, Heidelberg–New York 1971.
30 D. B. Downie and J. F. Martin, J. Chem. Thermodynamics, 12 (1980) 779.