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Mathematical studies of modulated differential scanning calorimetry

I. Heat capacity measurements

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Abstract

The mathematical bases for modulated differential scanning calorimetry (MDSC) have been discussed. It is found that the amplitude of heat flow is a non-linear function of the thermal transfer coefficient, λ, the modulation period, p, the heat capacity of reference, C_{pr}, and the heat capacity of a sample, C_{ps}. Therefore, the quantitative determination of the heat capacity of a sample is rather difficult if not impossible. From this point of view, MDSC does not offer any advantage over a conventional DSC. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Temperature modulation; Differential scanning calorimetry; Heat capacity; Amplitude; Phase lag

1. Introduction

Differential scanning calorimetry (DSC) is the most useful and popular technique for thermal analysis of materials. Recently, Reading et al. [5], in conjunction with TA Instruments, have extended the conventional DSC technique to permit a small sinusoidal modulation of temperature superimposed on the linearly programmed temperature changes that are used in the conventional DSC. This new extension is termed modulated differential scanning calorimetry (MDSC) [1–3]. TA Instruments has subsequently developed a commercial instrument. The MDSC technique is drawing increasing attention from researchers in the fields of thermal analysis and materials science [1–3].

MDSC is claimed to have two crucial advantages over conventional DSC. One is that MDSC determines heat capacity of a sample in a single run with higher accuracy than a conventional DSC. The other is its ability to separate reversing and non-reversing components of an endotherm or exotherm, which would have significant impact for thermal analysis of materials. It has been claimed that MDSC has added a new dimension to the conventional approach, and that it may be the greatest advance in DSC since its inception nearly three decades ago [1–6].

To fully understand the capacities of MDSC, its theoretical basis should be examined. This is because of the ability of a mathematical model to disentangle the theoretical principle of an instrument from any possible experimental limitations and from the uncertainties of a test material. Wunderlich et al. [4] have carried out a mathematical study on MDSC. They concluded that the heat capacity can

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be obtained by dividing the amplitude of heat flow by the product of the amplitude of modulation temperature and modulation frequency. The work reported in this, the present, and the accompanying papers will show that the above-mentioned conclusions cannot be justified. This paper dealing with the heat capacity measurements and Part II will discuss the separation of reversing and non-reversing components.

2. Basic equations of MDSC

In principle, both the heat flux and the power compensation types DSC can be modulated to become an MDSC. However, since the MDSC instrument developed by TA Instruments is of the heat-flux type, hereinafter, the mathematical model for the heat-flux type only is addressed. The basic equations for MDSC (conventional DSC can be treated as a special case of MDSC, where the amplitude of modulation is set to zero) consist of the heating program of the MDSC block, the enthalpy equation and the equation expressing the thermal transfer from the MDSC block to the sample or reference;

$$T_{\mathrm{b}}(t) = T_{\mathrm{b0}} + qt + A_{\mathrm{b}} \sin \omega t \tag{1}$$

$$\mathrm{d}Q(t) = C_{\mathrm{p}} \mathrm{d}T(t) \tag{2}$$

$$\frac{\mathrm{d}Q(t)}{\mathrm{d}t} = \lambda[T_{\mathrm{b}}(t) - T(t)] \tag{3}$$

where $T_{\mathrm{b}}(t)$ and T_{b0} are, respectively, the temperature at time t, and the initial temperature of the block; q, A_{b} and ω represent the underlying heating rate, the amplitude and the angular frequency of modulation, respectively ($\omega=2\pi/p$, where p is the modulation period). The symbol $Q(t)$ denotes the total enthalpy taken by a sample or reference up to time, t. C_{p} is the heat capacity. T_0 and $T(t)$ are the initial temperature and the temperature at time, t. $\mathrm{d}Q(t)$, C_{p}, $T(t)$ and T_0 can have subscripts 's' or 'r' to represent a sample or reference. The symbol λ denotes the thermal transfer coefficient, which is determined by the design and construction of a particular instrument, and is also affected by other factors such as the type of sample holder. Here, λ is considered to be identical for sample and reference and to be a constant during a run.

Combining Eqs. (1)–(3), one obtains:

$$\frac{\mathrm{d}T(t)}{\mathrm{d}t} + \frac{\lambda}{C_{\mathrm{p}}} T(t) = \frac{\lambda}{C_{\mathrm{p}}} [T_{\mathrm{b0}} + qt + A_{\mathrm{b}} \sin \omega t] \tag{4}$$

The differential equation for the reference has the same form as that for the sample. Therefore, when a subscript 's' or 'r' is attached to $T(t)$ and C_{p}, Eq. (4) refers to either the sample or reference, accordingly.

Eq. (4) is a first-order linear differential equation and is the basic equation of MDSC. Its solutions for the sample and reference can be written as [7];

$$\begin{aligned} T_{\mathrm{s}}(t) = {} & C_{\mathrm{s}} \exp\left(-\frac{\lambda}{C_{\mathrm{ps}}} t\right) + T_{\mathrm{b0}} + q\left(t - \frac{C_{ps}}{\lambda}\right) \\ & + A_{\mathrm{b}} \frac{\lambda}{C_{\mathrm{ps}}} \frac{(\lambda/C_{\mathrm{ps}}) \sin \omega t - \omega \cos \omega t}{\omega^2 + (\lambda/C_{\mathrm{ps}})^2} \end{aligned} \tag{5}$$

$$\begin{aligned} T_{\mathrm{r}}(t) = {} & C_{\mathrm{r}} \exp\left(-\frac{\lambda}{C_{\mathrm{pr}}} t\right) + T_{\mathrm{b0}} + q\left(t - \frac{C_{\mathrm{pr}}}{\lambda}\right) \\ & + A_{\mathrm{b}} \frac{\lambda}{C_{\mathrm{pr}}} \frac{(\lambda/C_{\mathrm{pr}}) \sin \omega t - \omega \cos \omega t}{\omega^2 + (\lambda/C_{\mathrm{pr}})^2} \end{aligned} \tag{6}$$

where C_{r} and C_{s} are integration constants and can be determined by the initial conditions, $T_{\mathrm{s}}(0)=T_{\mathrm{s0}}$ and $T_{\mathrm{r}}(0)=T_{\mathrm{r0}}$ (usually $T_{\mathrm{s0}}=T_{\mathrm{r0}}=T_{\mathrm{b0}}$).

$$C_{\mathrm{s}} = T_{\mathrm{s0}} - T_{\mathrm{b0}} + q\frac{C_{\mathrm{ps}}}{\lambda} + A_{\mathrm{b}} \frac{\lambda}{C_{\mathrm{ps}}} \frac{\omega}{\omega^2 + (\lambda/C_{\mathrm{ps}})^2} \tag{7}$$

$$C_{\mathrm{r}} = T_{\mathrm{r0}} - T_{\mathrm{b0}} + q\frac{C_{\mathrm{pr}}}{\lambda} + A_{\mathrm{b}} \frac{\lambda}{C_{\mathrm{pr}}} \frac{\omega}{\omega^2 + (\lambda/C_{\mathrm{pr}})^2} \tag{8}$$

A heat flux type DSC measures the temperature difference between the sample and reference as a function of the sample temperature. Therefore, by subtracting Eq. (5) from Eq. (6), one obtains the temperature difference, $\Delta T(t)$, and hence the heat flow, $H_{\mathrm{f}}(t)$, which is proportional to the temperature difference:

$$\begin{aligned} H_{\mathrm{f}}(t) = {} & \lambda[C_{\mathrm{r}} \exp(-\lambda t/C_{\mathrm{pr}}) - C_{\mathrm{s}} \exp(-\lambda t/C_{\mathrm{ps}})] \\ & + q(C_{\mathrm{ps}} - C_{\mathrm{pr}}) + H_{\mathrm{f}}^{\mathrm{m}}(t) \end{aligned} \tag{9}$$

where $H_f^m(t)$ denotes the modulation component, which is written as:

$$H_f^m(t) = A_b\lambda^2\left[\frac{(\lambda/C_{pr})\sin\omega t - \omega\cos\omega t}{C_{pr}[\omega^2+(\lambda/C_{pr})^2]} - \frac{(\lambda/C_{ps})\sin\omega t - \omega\cos\omega t}{C_{ps}[\omega^2+(\lambda/C_{ps})^2]}\right] \qquad (10a)$$

$$H_f^m(t) = \Bigg(A_b(C_{ps}-C_{pr})\lambda^2\omega \times \frac{\sqrt{\lambda^2\omega^2(C_{ps}+C_{pr})^2+(C_{ps}C_{pr}\omega^2-\lambda^2)^2}}{(C_{ps}^2\omega^2+\lambda^2)(C_{pr}^2\omega^2+\lambda^2)}\Bigg) \times \sin(\omega t-\delta) \qquad (10b)$$

where δ is the phase lag, defined by

$$\delta = \tan^{-1}\left(\frac{C_{ps}C_{pr}\omega^2-\lambda^2}{\lambda w(C_{ps}+C_{pr})}\right) \qquad (11)$$

The first term in the right-hand side of Eq. (9) represents the transient effect of an MDSC or DSC, which decays exponentially with time, t. The term included in the bracket of Eq. (10b) represents the amplitude of the modulation component in heat flow.

Eqs. (9), (10a), (10b) and (11) are the complete description for the heat-flow output of an MDSC experiment for a sample with a constant heat capacity. It should be noted that the modulation component in heat flow is the same over the whole period of an experiment, and has a definite form of a sinusoidal wave, independent of the underlying heating rate.

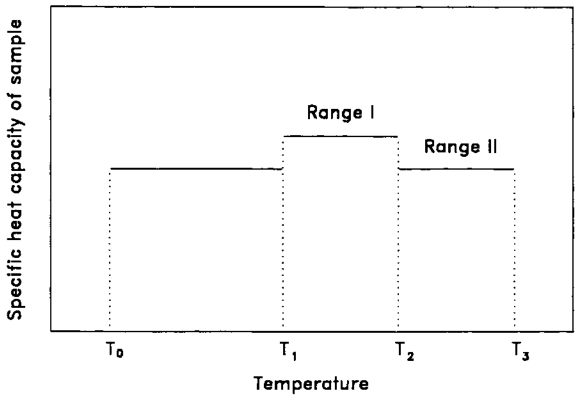

Fig. 1. An assumed relationship of the specific heat capacity of a sample and temperature.

This mathematical treatment can be further extended to include the cases where the heat capacity of the sample has step changes caused, for example, by an ideal glass transition [8], over the interested temperature range, as shown in Fig. 1. Eqs. (9), (10a), (10b) and (11) are no longer applicable to the temperature ranges I and II, since there are discontinuous points for the heat capacity of the sample. However, Eq. (4) remains the same in the temperature ranges I and II. The initial conditions for the sample, over the temperature ranges I and II are written as:

$$T_s(t_1) = T_1;\ T_s(t_2) = T_2 \qquad (12)$$

Applying these initial conditions to Eq. (5) leads to:

$$T_s^i(t) = C_s^i\exp\left(-\frac{\lambda}{C_{ps}^i}(t-t_i)\right) + T_{b0} + q\left(t-\frac{C_{ps}^i}{\lambda}\right) + A_b\frac{\lambda}{C_{ps}^i} \times \frac{(\lambda/C_{ps}^i)\sin\omega t-\omega\cos\omega t}{\omega^2+(\lambda/C_{ps}^i)^2} \qquad (13)$$

and

$$C_s^i = T_i - T_{b0} - q\left[t_i - \frac{C_{ps}^i}{\lambda}\right] - A_b\frac{\lambda}{C_{ps}^i}\frac{(\lambda/C_{ps}^i)\sin\omega t_i-\omega\cos\omega t_i}{\omega^2+(\lambda/C_{ps}^i)^2} \qquad (14)$$

where the superscript or subscript i takes values of 1 or 2, denoting the temperature ranges I and II, respectively.

The heat flow is, therefore, written as:

$$H_f^i(t) = \lambda(C_r\exp(-\lambda t/C_{pr}) - C_s^i\exp(-\lambda(t-t_i)/C_{ps}^i)) + q(C_{ps}^i - C_{pr}) + H_f^{mi}(t) \qquad (15)$$

and

$$H_f^{mi}(t) = \Bigg(A_b(C_{ps}^i - C_{pr})\lambda^2\omega \times \frac{\sqrt{\lambda^2\omega^2(C_{ps}^i+C_{pr})^2+(C_{ps}^iC_{pr}\omega^2-\lambda^2)^2}}{(C_{ps}^{i2}\omega^2+\lambda^2)(C_{pr}^2\omega^2+\lambda^2)}\Bigg) \times \sin(\omega t-\delta) \qquad (16)$$

Eqs. (15) and (16) show that the heat flow for temperature ranges I and II has the same form as Eqs. (9), (10a) and (10b) apart from a different transient effect shown in the first term in the right-hand side of Eq. (15). Thus, the interpretation of MDSC can be concluded by discussing Eqs. (9), (10a) and (10b) only without losing generality.

3. Heat capacity measurements

Eq. (9) consists of three terms, i.e. the transient term associating with the exponential decay function, the underlying heating term associating with the heating rate, q, and the modulation term (Eqs. (10a) and (10b)). The transient term approaches zero as an experiment has been in progress sufficiently long. When the modulation term is absent, Eq. (9) represents the relationship for a conventional DSC. It is clear from Eq. (9) that the heat flow is directly proportional to the product of the heating rate and the heat capacity difference between the sample and reference for a conventional DSC. However, because the absolute baseline of a DSC thermogram is usually unknown, it is a common practice to carry out two experiments at different heating rates for the same sample. The specific heat capacity of the sample, c_{ps}, can thus be obtained according to Eq. (17), which can be derived from Eq. (9):

$$c_{\mathrm{ps}} = \frac{C_{\mathrm{ps}} - C_{\mathrm{pr}}}{m} = \frac{H_{f1} - H_{f2}}{m(q_1 - q_2)} \tag{17}$$

where the symbol m denotes the mass of the sample. This equation shows that the heat capacity measurements are theoretically perfect using a normal DSC. Similar methods based on two runs are also applicable to obtain the specific heat capacity of a sample using the conventional DSC technique [9]. The determination of the specific heat capacity of a sample is independent of the instrumental factor, λ, and the sample holder used for the experiments, C_{pr}. This is the significance of *differential* calorimetry.

The major source of error of the conventional DSC technique is, perhaps, the long-term stability of an instrument and the slow physico-chemical changes of the sample during two runs. The baseline could have slightly shifted during two runs due to low-frequency drifting of the electronics of the instrument. However, most commercial DSC instruments have solved this problem satisfactorily. On the other hand, whether there are slow changes of a sample during two DSC runs is another matter, which must be addressed case-by-case according to the physico-chemical nature of a sample.

In MDSC, the amplitude of the heat flow of a single run is employed to determine the heat capacity of a sample to minimise the experimental errors resulting from the low frequency drifting of baseline and slow changes of a sample during two runs. This has been considered to be one of the major advantages of MDSC over a conventional DSC.

It is, however, clear from Eqs. (10a) and (10b) that the amplitude of heat flow is a complicated non-linear function of ω, C_{ps} and C_{pr} and λ, although the relationship between the amplitude of heat flow and the amplitude of modulation is linear, and the amplitude is independent of the underlying heating rate, q.

To illustrate the complexity arising from the non-linear effects, one can calculate the amplitude of heat flow according to Eqs. (10a) and (10b). Fig. 2 shows the relationship between the amplitude of heat flow and the period of modulation, p, for various λ at a given C_{pr} and C_{ps}. The amplitude of heat flow increases non-linearly with increasing heat transfer coefficient, λ. The amplitude of heat flow increases with increasing modulation period, p, at low modulation period, reaches a maximum then decreases with further increase in p. According to Eqs. (10a) and (10b), the amplitude reaches zero as the modulation period approaches infinity (not shown in Fig. 2). The linearity is seen as changing with different λ.

Fig. 3 shows the relationship between the amplitude of heat flow and the heat capacity of the reference under the condition of a constant difference in the heat capacities between the sample and the reference. The physical meaning of this is to demonstrate how the amplitude depends on the DSC cells used for the reference and sample in an experiment. It is seen that, for a given amount of the sample, the higher the heat capacity of reference, the lower is the amplitude. The non-linearity is obvious. This fact indicates that it would be extremely difficult to use the amplitude to determine the heat capacity of a sample since the amplitude is also dependent on the heat capacity of the reference.

Fig. 4 shows the relationship between the heat capacity of a sample and the amplitude of heat flow.

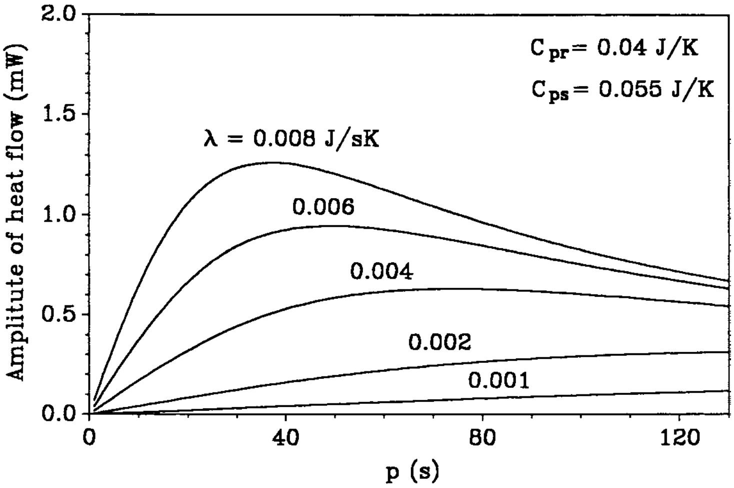

Fig. 2. Amplitude of heat flow vs. modulation period at a given C_{pr} and C_{ps}.

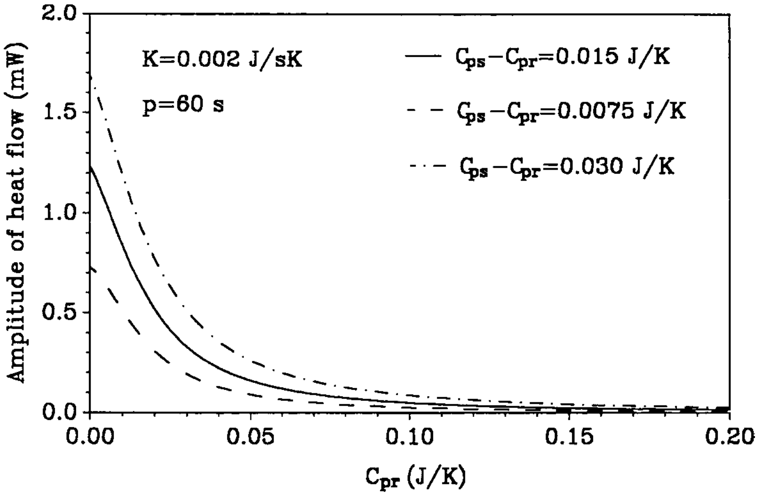

Fig. 3. Reference dependence of the amplitude of heat flow.

This figure illustrates how the amplitude of heat flow depends on the quantity of the sample packed. Nonlinear plots are observed. This is to say that for a set of experiments with identical conditions, except different sample weights, different calibrations are needed to determine the specific heat capacity of the sample.

From Figs. 2, 3 and 4, it is clear that a quantitative determination of the heat capacity of a sample is extremely difficult, if not impossible. Thus, it can be concluded that MDSC does not offer any advantages over a conventional DSC in heat capacity measurements.

4. Numerical experiments

To make further comparison, thermograms of MDSC as well as conventional DSC experiments are computed according to Eqs. (9), (10a) and (10b). The conditions employed for the numerical

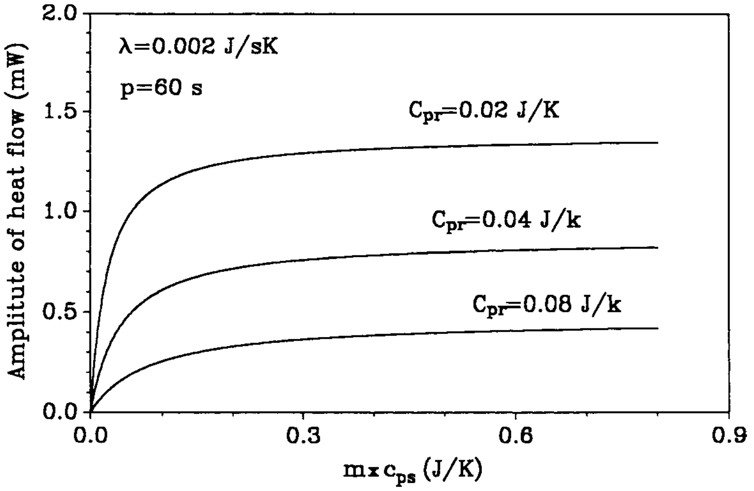

Fig. 4. Sample heat capacity dependence of the amplitude of heat flow.

experiments are displayed in Table 1. Figs. 5 and 6 show the results. An initial transient period can be seen for all the thermograms. The heat capacity of the sample can be definitely determined according to Eq. (17), using the conventional DSC. For MDSC, the amplitude of heat flow is seen to increase with increasing modulation period, p. However, it is important to note that the amplitude represents neither the heat flow difference obtained using a standard DSC at the heating rates $q+A_b$ and $q-A_b$, nor the difference further divided by modulation frequency, ω [4,6].

The computed thermograms of MDSC and conventional DSC for the sample having step changes in its heat capacity over the temperature Range I, shown in Fig. 1, are displayed in Fig. 7. To facilitate the computation for this figure, one has to obtain time t_1 and t_2 corresponding to temperatures T_1 and T_2. This was achieved by solving Eqs. (5) and (13) using the Newtonian interpolation method. Two initial tentative times, $t_i^{(0)}$ and $t_i^{(1)}$, are assumed and the corresponding sample temperatures, $T_i^{(0)}$ and $T_i^{(1)}$ can then be obtained. Assuming that the errors of the calculated temperatures are $e^{(0)}$ and $e^{(1)}$, one obtains new tentative $t_i^{(2)}$ according to the following equation (where k=0,1,2,3...).

$$t_i^{(k+2)} = \frac{\mathrm{e}^{(k+1)} t_i^{(k)} - \mathrm{e}^{(k)} t_i^{(k+1)}}{\mathrm{e}^{(k+1)} - \mathrm{e}^{(k)}} \tag{18}$$

The Newtonian interpolation method can be iterated until the error is <1/100 000 of the real temperature, T_i. The subscript 'i' equals 1 or 2, representing temperature ranges I and II, respectively.

It is clear from Fig. 7, that there are additional transient periods at the discontinuous points of the heat capacity of the sample. Unlike the initial transient period which can be avoided by starting an experiment at a lower temperature, these transient periods are inevitable. Thus, the thermogram of a conventional

Table 1
Numerical parameters employed for the computation of Figs. 5, 6 and 7

Figure	λ/(J/K s)	p/(s), A_b/(°C), q/(°C)	C_{pr}/(J/K)	C_{ps}/(J/K) 20–80°C	C_{ps}/(J/K), Range I, 80–120°C	C_{ps}/(J/K), Range II, 120–160°C
5	0.002	30, 1, 5	0.040	0.055	0.055	0.055
6	0.002	90, 1, 5	0.040	0.055	0.055	0.055
7	0.002	60, 1, 5	0.040	0.055	0.058	0.055

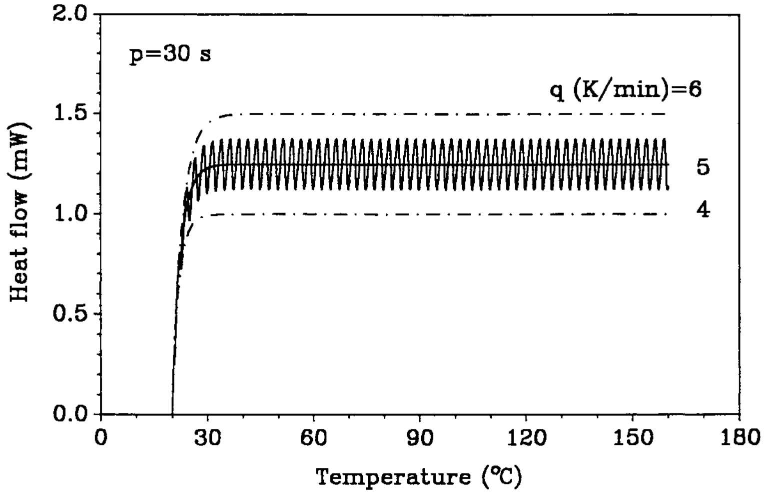

Fig. 5. Numerical results of MDSC and conventional DSC. See Table 1 for the parameters adopted in the computation, modulation period=30 s.

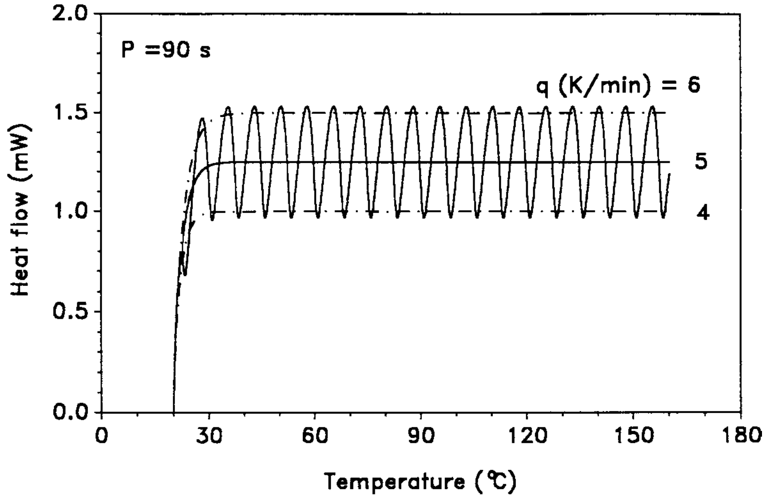

Fig. 6. Numerical results of MDSC and conventional DSC. See Table 1 for the parameters adopted in the computation, modulation period=90 s.

DSC does not reflect the true shape of the change of the specific heat capacity of a sample over its idealised glass transition.

This distortion, which is a result of the transient effect, can be eliminated by subtracting the DSC thermogram from the MDSC thermogram. This is because the amplitude of heat flow for MDSC does not show any transient effect, as elucidated in Eqs. (9), (10a), (10b), (15) and (16). The thermogram of the normal DSC has then been subtracted from the thermogram of MDSC, and the result is shown in Fig. 8. It can be seen that the amplitude of heat flow does show a step-like increment and a step-like decrement over the temperature ranges I and II, indicating that the combination of MDSC and normal DSC probably can capture more accurately the shape of a transition.

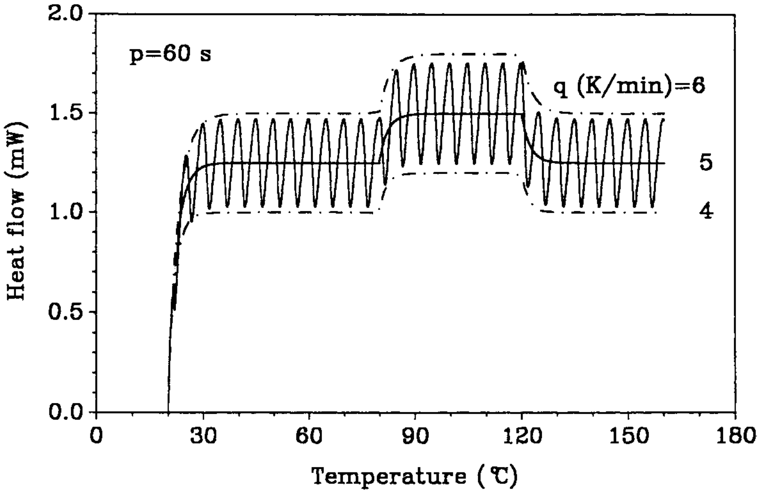

Fig. 7. Numerical results of MDSC and conventional DSC. See Table 1 for the parameters adopted in the computation, modulation period=60 s.

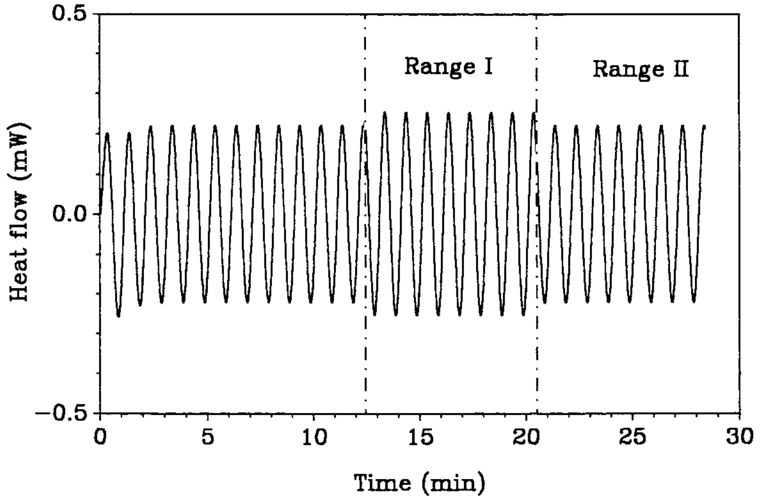

Fig. 8. The amplitudes of heat flow of MDSC for the sample experiencing step changes in its heat capacity.

5. Conclusions

The complete mathematical description for heat capacity measurement using MDSC, including the case where the heat capacity of a sample has step changes, has been established. The expression for heat flow are shown in Eqs. (9), (10a), (10b), (15) and (16). It is found that because the amplitude of heat flow in MDSC is a non-linear function of the thermal transfer coefficient, λ, the modulation period, p, the heat capacity of reference, C_{pr}, and the heat capacity of a sample, C_{ps}, the quantitative determination of the heat capacity of a sample is rather difficult, if not impossible. From this point of view, MDSC does not offer any advantage over a conventional DSC.

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