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DIAGNOSIS OF PHASE SHIFT IN A TEMPERATURE-MODULATED CALORIMETRIC METHOD

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Abstract

In a temperature-modulated calorimetric method using the same apparatus as a standard differential scanning calorimeter, we have to pay attention to the thermophysical parameters of the apparatus, which cause phase shift in ac temperatures, such as heat capacity of base plate, heat capacity of a pan, thermal conductance between a heater and base plate, and thermal conductance between a pan and base plate. We performed the analysis of the thermal system of the apparatus with these parameters. Beside the theoretical consideration, we carried out heat capacity measurement in a wide range of modulation periods. We found that the experimental results were well-expressed in terms of these thermophysical parameters.

Keywords: ac calorimetry, heat capacity measurement, periodic temperature, temperature-modulated calorimetry

Introduction

Temperature-modulated calorimetry is a technique which has potentiality to measure heat capacity with high accuracy using the same apparatus as in standard differential scanning calorimetry. Contrary to differential scanning calorimetry, in temperature-modulated calorimetry heat capacity measurement can be performed under the steady-state condition without scanning temperature. In this measurement, we should take into account the contribution of heat capacity of base plate, heat capacity of a pan, thermal conductance between a pan and base plate, etc. [1], in addition to thermal conductance K between base plate and a heater, which is a leading parameter in conventional differential scanning calorimetry. Taking into account the principal parameters, we have proposed a method to measure heat capacity with high accuracy by a temperature-modulated calorimeter [2]. In the present study, we first put a pan only on base plate of the sample side so as to exclude the contribution of an another uncontrollable parameter, that is, thermal conductance between a reference pan and base plate.

In the present paper, we will report the detailed results of the experimental test performed under the above conditions with special attention to the phase of ac temperatures caused by the dynamic characteristic of an apparatus and as a re-

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sult, will propose a guiding principle to the heat capacity measurement with high accuracy.

Theory

Consider the thermal system of an apparatus as shown in Fig. 1. At a stationary state, ac heat with angular frequency ω is applied to both sample and reference sides through thermal conductance K by a heater, whose ac temperature is shown by T_h. A sample pan is put only on base plate of the sample side. Effective heat capacity of the base plate is given by C_o, and whole heat capacity of a sample and its pan and the ac temperature are given by C_s and T_s, respectively. In such a situation, we have to take into account thermal conductance K' between the sample pan and the base plate. The ac temperatures of the sample and reference sides at the base plate are defined by T_{so} and T_{ro}, respectively. In the present measurement, we observe both T_{so} and $T_{ro}-T_{so}$ ($=\Delta T$). They are given by

$$T_{so} = A_s \exp[i(\omega t + \varepsilon)], \tag{1}$$

$$\Delta T = A_\Delta \exp[i(\omega t + \delta)], \tag{2}$$

where A_s and A_Δ are their amplitudes, and ε and δ are phases, respectively. In our consideration, we only need the phase difference, $\delta-\varepsilon(=\Phi)$, which can be obtained from T_{so} and ΔT.

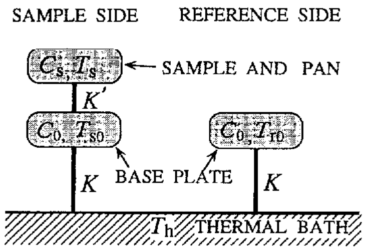

Fig. 1 Model of a temperature-modulated calorimeter for the high accurate heat capacity measurement. A pan containing a sample is placed on base plate of the sample side and no pan on base plate of the reference side due to the reason mentioned in text. C_s indicates whole heat capacity composed of that of the sample and also the pan in the present analysis. K' is thermal conductance between the sample pan and the base plate of the calorimeter

We can get the following relations [2]:

$$R = \frac{\frac{KA_\Delta}{\omega A_s}}{C_s} = \frac{1}{\sqrt{(1+\omega^2\tau_s^2)(1+\omega^2\tau_o^2)}}, \tag{3}$$

$$\sin\Phi=\frac{1-\omega^2\tau_s\tau_o}{\sqrt{(1+\omega^2\tau_s^2)(1+\omega^2\tau_o^2)}},\tag{4}$$

where

$$\tau_s=\frac{C_s}{K'},\tag{5}$$

$$\tau_o=\frac{C_o}{K}.\tag{6}$$

Using a standard sample we can determine the phase difference in various conditions.

We point out that the right side of both Eqs (3) and (4) is given by a function of ω, τ_o and τ_s. At a certain angular frequency ω, τ_o is constant and then, both Eqs (3) and (4) connected by a common variable τ_s. Therefore, the R *vs.* $\sin\Phi$ relation given by Eqs (3) and (4) is expressed by a single curve, that is, a calibration curve. Furthermore, it is worth to point out that the contribution of heat capacity C_s of a sample and thermal conductance K' between a sample pan and base plate is always coupled as given by τ_s in Eq. (5). For this characteristic, it is not necessary to distinguish the contribution of the two parameters, C_s and K', in the calibration of heat capacity of the unknown sample as discussed in the next section in detail.

When $\omega\tau_s<<1$, Eqs (3) and (4) tend, respectively, to

$$R=\frac{\dfrac{KA_\Delta}{\omega A_s}}{C_s}=\frac{1}{\sqrt{1+\omega^2\tau_o^2}},\tag{7}$$

$$\sin\Phi=\frac{1}{\sqrt{1+\omega^2\tau_o^2}}.\tag{8}$$

The above condition is satisfied when the thermal conductance K' between the sample pan and the base place is large enough and/or the measuring angular frequency ω is small enough. As seen from Eqs (7) and (8), $R=\sin\Phi$, then,

$$C_s=\left(\frac{K}{\sin\Phi}\right)\frac{A_\Delta}{\omega A_s}.\tag{9}$$

Therefore, from the measurement of the phase difference, we can directly determine the heat capacity, C_s.

As can be easily deduced, in the case when K' is large enough, we can ignore the contribution of K' in the analysis. This means that there is no difference between the systems; one is a system in which only a sample pan is put on the base plate of the sample side and the other is a system in which both a sample pan and a reference pan (an empty pan in the present case) are put on the base plate of the sample side and the reference side, respectively. In the latter C_o in Eq. (6) is composed of the heat capacities of the base plate and the pan and then C_s results in the heat capacity of a sample itself.

Furthermore, when $\omega\tau_o$<<1, Eqs (7) and (8) tends, respectively, to

$$R = \frac{\frac{KA_\Delta}{\omega A_s}}{C_s} = 1, \tag{10}$$

$$\sin\Phi = 1. \tag{11}$$

Therefore, Φ should be $\pi/2$ and R=1. Finally we obtain the relation

$$C_s = \frac{KA_\Delta}{\omega A_s}. \tag{12}$$

When the measuring angular frequency ω is small enough, the above condition might be satisfied.

In the study of kinetics mechanism in materials, it is of interest to measure complex heat capacity $C_s^*(=C_s'-iC_s'')$. Under the last condition, we can easily obtain C_s' and C_s'' from the measurement of the amplitude and the phase in Eqs (1) and (2). Furthermore, in the second case of $\omega\tau_s$<<1, we can also obtain C_s' and C_s'' from the measurement of the amplitude and the phase in Eqs (1) and (2). However, in the first case, it is not easy to obtain C_s' and C_s'' in temperature-modulated calorimetry.

Experimental

First, using standard samples, we obtained the calibration curve of R *vs.* $\sin\Phi$. We used a commercial modulated differential scanning calorimeter, Type 2920 of TA Instruments, for the present experimental test. Dry N_2 gas with a flow rate of 40 ml min^{-1} was purged. Sample pans used were hermetically sealed. These two choice might be generally unfavourable for the accurate heat capacity measurement. In fact, it gives rise to finite thermal conductance between the sample pan and the base plate because N_2 gas has much smaller thermal conductivity than He gas and by sealing a sample pan the bottom of the pan might be deformed. However, to reveal the notable points which play an important role in the precise heat capacity measurement, we tested expressly under such a circumstance.

As a standard material, we used water. We used sample pans of TA Instruments. The measurement was done at 25°C. The modulation period was ranged from 40 to 100 s and the modulation amplitude was 0.1°C throughout the measurements. The sample mass were 3.50, 11.04, 12.60, 22.29, and 23.90 mg. The results were shown in Figs 2(a) to (d). By fitting the results to the relation of R *vs.* sinΦ derived from Eqs (3) and (4), we obtained the fitting curves as shown in Figs 2(a) to (d). Therefore, the results are well-expressed in terms of the thermophysical parameters which will be given later. Within the framework of the model shown in Fig. 1, it results in a single curve independent of C_s and K', that is, when C_s or K' changes independently, the data point moves along the same calibration curve. Then, as expected from Eqs (3) and (4) the calibration curve itself is not affected by C_s and K'. In the experiment for an unknown sample, we observe the phase difference Φ and then, according to the calibration curve of R *vs.* sinΦ we can determine the factor R. Based upon this calibration, we can finally obtain the heat capacity of a sample. Using this method curve, we can obtain heat capacity within the accuracy of 1%.

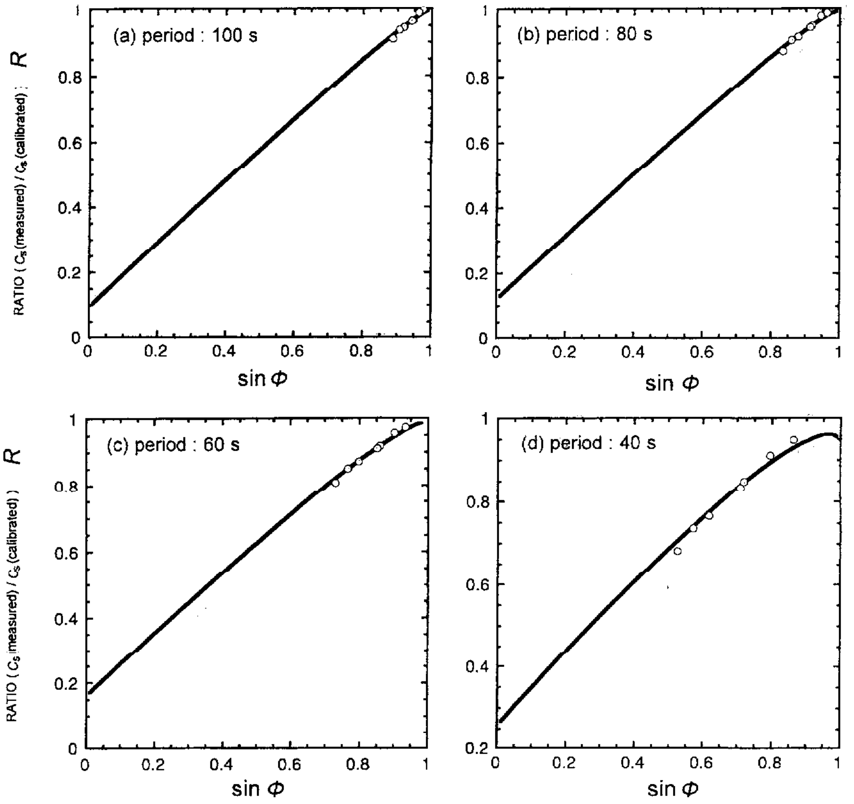

Fig. 2 Relations of R *vs.* sinΦ at the period of (a) 100 s, (b) 80 s, (c) 60 s and (d) 40 s. The ratio R is given by $C_{\text{uncalibrated}}/C_{\text{calibrated}}$, that is, $C_{\text{measured}}/C_{\text{calibrated}}$. The phase difference Φ is given by $\delta-\varepsilon$, which is the phase difference between T_{so} of Eq. (1) and ΔT of Eq. (2). The open circle indicates the date obtained experimentally. The thick solid line is the fitting curve to Eqs (3) and (4)

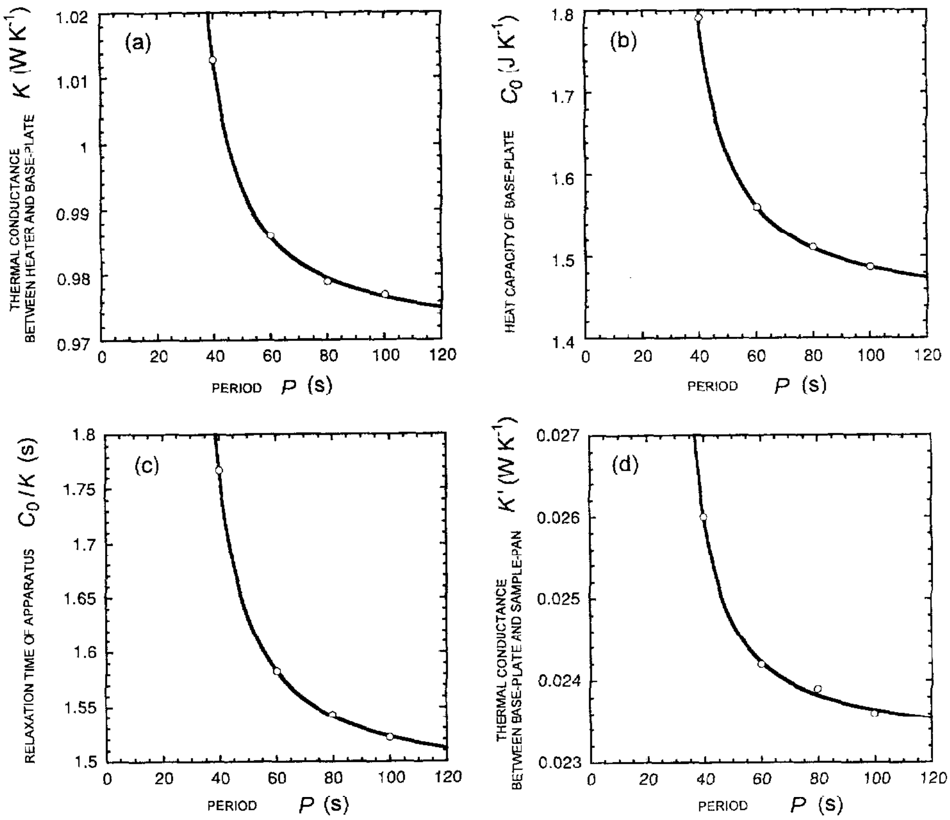

Fig. 3 (a) Thermal conductance K between the base plate and the heater, (b) Effective heat capacity C_0 of the base plate, (c) Relaxation time of the apparatus $\tau_0(=C_0/K)$ and (d) Thermal conductance K' between the base plate and the pan. These thermophysical parameters were obtained from the fitting analysis. The thick solid lines are only to guide eyes

In a conventional temperature-modulated calorimeter, we can define uncalibrated heat capacity $C_{\mathrm{uncalibrated}}$ which corresponds to measured heat capacity C_{measured} as

$$C_{\mathrm{uncalibrated}}=\frac{KA_{\Delta}}{\omega A_{\mathrm{s}}}. \tag{13}$$

However, from this expression in the strict sense we cannot obtain the correct heat capacity as deduced from Eqs (3) and (4) and also Eq. (9) and then generally, the calibration should be done. Based upon the factor R obtained from $\sin\Phi$ in the relation of R *vs.* $\sin\Phi$, we can calculate the calibrated heat capacity $C_{\mathrm{calibrated}}$ in such a way as

$$C_{\mathrm{calibrated}} = \frac{C_{\mathrm{uncalibrated}}}{R}. \tag{14}$$

For the accurate heat capacity measurement, it is important to establish the calibration curve of R *vs.* sinΦ in an individual temperature-modulated calorimeter. In Eq. (14), it should be stressed that the calibration factor R depends on frequency, temperature, heat capacity of a sample, thermal conductance between the sample pan and the base plate and therefore, the calibration should be performed in principle at each of the above conditions although all of them are not always so sensitive to R.

Finally, the thermophysical parameters obtained from the fitting analysis are shown as a function of the modulation period in Figs 3(a) to (d). As seen in Figs 3(b), (c) and (d), the effective heat capacity C_o of the base plate, the relaxation time τ_o ($=C_o/K$) and the thermal conductance K' between the base plate and the pan are markedly dependent on the modulation period. On the other hand, as expected, the thermal conductance K between the base plate and the heater is close to 1 W K^{-1} independent of modulation period as shown in Fig. 3(a).

Results and discussion

We propose a method to measure heat capacity with high accuracy using a temperature-modulated calorimeter, where not only the amplitude of ac temperatures but also the phases are important. A calibration curve in which the phase is important factor can be expressed by Eqs (3) and (4), even though there is uncontrollable thermal conductance between the sample pan and the base plate. To get a much simple calibration curve, as inferred from Eqs (3) and (4) easily, we have to choose longer modulation period and/or smaller τ_s. The latter situation is achieved in the following ways: Using a smaller sample, τ_s becomes smaller. If we use He gas instead of N_2 gas, τ_s becomes considerably small. Using a sample pan which has bottom tightly matching to the surface of base plate, τ_s becomes also small. These trials are promising to construct an ideal temperature-modulated calorimeter.

Based upon the present results, we can solve some pending problems. Boller *et al.* [3] have pointed out that the apparent heat capacity measured decreases with increasing the sample mass of sapphire due to the insufficient thermal diffusion. This might be not always the case because under their experimental conditions the thermal diffusion length of sapphire is as long as 1.7 cm which is far longer than the thickness of the sample. On the other hand, the above decrease of the apparent heat capacity is well-expressed by Eq. (3). Namely, this behaviour is caused by τ_s, where thermal conductance between the sample pan and the base plate is not large enough. Ozawa and Kanari [1] have claimed that, for instance, since R is due to heat capacity of a sample, the strict calibration is impossible. However, it is not always serious because in such a linear system the calibration should be done at each heat capacity where the comparison between the measured heat capacity and the calibrated heat capacity will be made for the calibration which results in a single curve, although this is quite different from the calibration method in standard differential scanning calorimetry.

References

1 T. Ozawa and K. Kanari, Thermochim. Acta, 288 (1996) 39.
2 I. Hatta and S. Muramatsu, Jpn. J. Appl. Phys., 35 (1996) L858.
3 A. Boller, Y. Jin and B. Wunderlich, J. Thermal Anal., 42 (1994) 307.