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Application of dynamic differential scanning calorimetry to study of phase transitions¹

Ichiro Hatta^{a,*}, Hiroaki Ichikawa^b, Minoru Todoki^b

^a*Department of Applied Physics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan*

^b*Toray Research Center, Inc., 3-3-7 Sonoyama, Otsu 520, Japan*

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Abstract

A dynamic differential scanning calorimeter (dynamic DSC) works simultaneously as a differential scanning calorimeter and an AC calorimeter, using the same apparatus with AC temperature modulation superposed on a linear temperature ramp. From AC calorimetric (ACC) operation in which the part responding to AC temperature modulation is taken into account, we can determine the absolute value of heat capacity by making the best of the twin-type apparatus, although the temperature resolution is a little lower than in high precision AC calorimetry. Therefore, at a second order phase transition, ACC operation is useful for obtaining temperature dependence of linear heat capacity and furthermore, the frequency dispersion of the linear heat capacity is obtainable. On the other hand, at a first order phase transition, the situation is complicated. Nevertheless, latent heat at a first order phase transition can be estimated precisely from the both results of DSC operation and ACC operation. For further study, we have to pay attention to non-linear heat capacity. When a first order transition takes place over a certain temperature range, the analysis of the waveform of AC temperature observed at a steady temperature in this range gives evidence for a kinetic mechanism. The experimental test is performed for sodium nitrite, which undergoes both first and second order phase transitions.

Keywords: AC calorimetry; DSC; Linear heat capacity; Non-linear heat capacity; Latent heat; Phase transition

1. Introduction

Differential scanning calorimetry (DSC) is widely accepted as a useful analytical tool in the study of phase transitions. Recently, dynamic DSC has been proposed, in which

* Corresponding author.

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AC temperature modulation is superposed on a linear temperature ramp [1]. In such a method, we can measure the temperature difference between the sample and the reference sides, which is composed of the responses to the linear temperature ramp and to AC temperature modulation. In the present paper, the heat capacity of a sample derived from the former response is called the DSC component and from the latter response the AC calorimetric (ACC) component. As discussed in detail in Section 3, even when we use a common apparatus, thermophysical quantities such as effective heat capacity and effective coefficient of heat transfer treated in the theoretical analysis are different between the cases for obtaining the DSC component and the ACC component and therefore, owing to the difference in their operation mechanism, we distinguish the two cases as DSC operation and ACC operation throughout this paper. The DSC component can be obtained from DSC operation as usual DSC. On the other hand, the ACC component obtained by ACC operation is similar to heat capacity obtained by usual ACC [2]. In this study, we exhibit the usefulness of a dynamic DSC experiment at phase transitions.

2. Thermodynamics at phase transitions

There are two types of phase transitions, first and second order. For a first order phase transition, the curves for Gibbs function, G_1 and G_2 , in the two phases at a given pressure cut each other at a temperature as shown in Fig. 1. Therefore, phase 1 is stable below and phase 2 above the first order transition temperature denoted by T_0 . There appears heat capacity or latent heat. Below and above T_0 , we only observe heat capacity. This is given by

$$C_{p1} = -T \left(\frac{\partial^2 G_1}{\partial T^2} \right)_p \quad (1)$$

below T_0 and

$$C_{p2} = -T \left(\frac{\partial^2 G_2}{\partial T^2} \right)_p \quad (2)$$

above T_0 . On the other hand, at T_0 we observe latent heat, which is given by

$$\begin{aligned} L &= T_0 (S_2 - S_1) \\ &= H_2 - H_1 \end{aligned} \quad (3a,b)$$

where S_1 and S_2 are entropy and H_1 and H_2 are enthalpy at T_0 for the limits of low and high temperature sides, respectively. In a one component system, when two phases coexist, the temperature is unchanged from Gibbs' phase rule, that is, a first order transition temperature lies at a point on temperature axis. For a second order phase transition, the differential coefficients of the curves for Gibbs function with respect to temperature in the two phases at a given temperature are the same at the second order transition tempera-

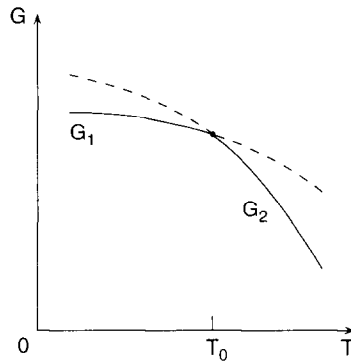


Fig. 1. Gibbs free energy function at a first order phase transition.

ture, T_c . Then, the entropy is continuous below and above T_c and as a result there is no latent heat at T_c . From the thermal measurement, we obtain only linear heat capacity which is given by a similar expressions to Eqs. (1) and (2).

In practical cases, thermal behavior at a first order phase transition seems to be complicated. The first order transition region frequently has a certain temperature width. This is due to non-ideal conditions such as temperature gradient, imperfections, internal stress, particle size, etc. In connection with this fact, sometimes it is difficult to distinguish between the two parts, latent heat and linear heat capacity, since the lower slopes of the latent heat merge with the increases in the linear heat capacity from both lower and higher temperatures. Furthermore, we have to pay attention to the fact that the observed anomalous enthalpy includes not only the intrinsic latent heat gained from the degree of freedom but also the additional contributions. The origins of the latter contributions are the energy required for overcoming barriers during the course of phase boundary movement, the pinning energy due to imperfections and others.

3. Theoretical consideration

In a system composed of the components which are associated with linear response in a thermal event, we can apply the principle of superposition and therefore, we discuss DSC operation and ACC operation separately. However, in a case when we can no longer exclude the non-linear response, we cannot extend the principle to such a case and then we discuss each operation independently for convenience, especially in ACC operation. We point out later that, for instance, in a first-order region, the analysis of non-linear events with respect to AC temperature modulation at a certain temperature in the region gives much clearer evidence for the kinetic mechanism.

Let us discuss firstly heat-flux DSC operation in dynamic DSC, where the temperature of a reference cell is scanned. Heat balance on the reference side is given by

$$C_r \frac{dT_r}{dt} = K(T_h - T_r) \quad (4)$$

where C_r is the effective heat capacity of the reference material and its cell including the contribution of the surrounding materials, t is time, K is the effective coefficient of heat transfer between the reference material and a heater, and T_r and T_h are the temperatures of the reference material and the heater, respectively.

On the other hand, heat balance on the sample side is given by

$$C_s \frac{dT_s}{dt} + \Delta H_s \frac{dx}{dt} = K(T_h - T_s) \quad (5)$$

where C_s is the effective heat capacity of a sample and its cell including the contribution of the surrounding materials. In principle, except for the heat capacity of the sample, the heat capacity of the cell including surrounding materials is the same as that on the reference side. K is the effective coefficient of heat transfer between the sample and the heater, which is also equivalent to that on the reference side. T_s is the temperature of the sample, ΔH_s is the enthalpy due to kinetic mechanism and x is the fraction of the part of the sample transformed by the kinetic mechanism.

Latent heat at a first order phase transition, L , is obtained from the relation

$$L = \int_0^1 \Delta H_s dx \quad (6)$$

Next, let us consider ACC operation done by the same twin-type calorimeter [3]. In the following, AC temperature \tilde{T} , AC heat flux \tilde{Q} and the AC part \tilde{x} of the fraction at x include implicitly the factor of $\exp(i\omega t)$ and then, $d\tilde{T}/dt = i\omega\tilde{T}$, \tilde{T}/\tilde{Q} , etc. are independent of t . Heat balance on the reference side is given by

$$\tilde{C}_r \frac{d\tilde{T}_r}{dt} + \tilde{K}\tilde{T}_r = \tilde{Q} \quad (7)$$

where \tilde{C}_r is the effective heat capacity of the sample and its cell including the contribution of surrounding materials. \tilde{T}_r is the AC temperature of the reference. \tilde{K} and \tilde{Q} are the effective coefficient of heat transfer from the reference material to the surroundings and AC heat flux supplied to the reference material, respectively.

Heat balance on the sample side is given by

$$\tilde{C}_s \frac{d\tilde{T}_s}{dt} + \tilde{K}\tilde{T}_s + \Delta\tilde{H}_s \frac{d\tilde{x}}{dt} = \tilde{Q} \quad (8)$$

where \tilde{C}_s is the effective heat capacity of the sample and its cell including the contribution of the surrounding materials. The latter heat capacity is almost the same as that on the reference side. \tilde{T}_s is the AC temperature of the sample. In this consideration, for simplicity it is assumed that \tilde{K} and \tilde{Q} are the same as those on the reference side. This means that we consider the case when the constitution of an apparatus is perfectly symmetric with respect to the center between the sample and the reference sides and furthermore, the applied AC heat flux is the same between the both sides. $\Delta\tilde{H}_s$ is related to the

periodic change of enthalpy due to the kinetic process. For instance, in a two state change, according to the temperature modulation, the boundary of the two states might oscillate with some phase lag and deviate from the sine waveform due to a non-linear mechanism, in which \tilde{x} indicates the AC part at the fraction of x .

It is important to notice the difference between both effective heat capacities of the cell including the contribution of surrounding materials in DSC and ACC operations. The effective heat capacity in ACC operation is smaller than that in DSC operation, because the characteristic thermal length in ACC operation is shorter than that in DSC operation. Furthermore, in ACC operation, as the modulation frequency is lower, the characteristic thermal length is shorter, that is, the effective heat capacity is smaller. Although the dependence of the scanning rate on the effective heat capacity has not been considered in usual DSC so far, similar behavior occurs. Then, as the scanning rate is larger, the effective heat capacity is smaller. Similarly \tilde{K} is also different from the corresponding coefficient K in DSC operation.

First, we consider linear heat capacity due to thermal fluctuation. In this analysis, the terms related to ΔH_s and $\Delta \tilde{H}_s$ should be excluded in Eqs. (5) and (8), respectively and the principle of superposition of T and \tilde{T} can be applied, that is, the two sets of differential equations are solved separately and the solutions for T and \tilde{T} can be added finally. From Eqs. (4) and (5) without the second term on the left-hand side of Eq. (5), we obtain

$$\Delta T = \left(-\frac{dT_r/dt}{K} \right) \cdot \Delta C_s \quad (9)$$

where $\Delta T = T_s - T_r$ and $\Delta C_s = C_s - C_r$. In ideal heat-flux DSC, the temperature scan rate, dT_r/dt , is constant. Then, from the measurement of ΔT as a function of time, in principle we can obtain the temperature dependence of $\Delta C_s = C_s - C_r$, i.e. the temperature dependence of the linear heat capacity of the sample. It is worth noticing that the linear heat capacity anomaly due to thermal fluctuation at a second-order phase transition is included in ΔC_s , i.e. it shows critical behavior generally. This means that such linear heat capacity in a sample is not always temperature independent.

From Eqs. (7) and (8), we can derive at an angular frequency ω under a condition that $\Delta \tilde{C}_s \ll \tilde{C}_r$, where \tilde{C}_r is composed of the heat capacities of not only the cell but also its surroundings, as

$$\Delta \tilde{T} = \left[-\frac{i\omega \tilde{Q}}{(i\omega \tilde{C}_r + \tilde{K})^2} \right] \cdot \Delta \tilde{C}_s \quad (10)$$

where $\Delta \tilde{T} = \tilde{T}_s - \tilde{T}_r$ and $\Delta \tilde{C}_s = \tilde{C}_s - \tilde{C}_r$. As seen in Eq. (10), $\Delta \tilde{T}$ is proportional to $\Delta \tilde{C}_s$. Then we can determine the absolute value of linear heat capacity, $\Delta \tilde{C}_s$. This is in fact linear heat capacity at an angular frequency ω . Generally, at a second order phase transition we might expect frequency dispersion of linear heat capacity due to thermal fluctuation.

In the practical measurement to obtain $\Delta \tilde{C}_s$, we have to calibrate firstly the factor in the square brackets in Eq. (10). Since \tilde{Q} , \tilde{C}_r and \tilde{K} are generally frequency dependent, the factor should be determined at a measuring frequency. In the above theoretical con-

sideration, we assumed that the temperature oscillated uniformly over the sample, i.e. the angular frequency should be lower than a certain frequency given by the inverse of the internal relaxation time [2]. Furthermore, the calibration should be done in the temperature range where the measurement will be performed, because \bar{C}_T and \bar{K} are temperature dependent.

At a first order phase transition, in the analysis the terms concerned with ΔH_s and $\Delta \bar{H}_s$ should be taken into account. As discussed at the beginning of this section, both enthalpy terms associated with the linear temperature ramp and AC temperature modulation are caused by a common origin. In such a case, the application of dynamic DSC results in a complicated response. When we wish to express the kinetic mechanism in a simple form, ACC operation should be carried out at a proper steady temperature. On the other hand, to obtain latent heat at first order phase transition from the DSC component, we have to pay attention to the estimation of the part which should be excluded from the DSC component as discussed below.

4. Experimental test

We carried out dynamic DSC experiments in the phase transitions of a single crystal of sodium nitrite with thickness of 0.5 mm, using Type 2920 apparatus from TA Instruments. Sodium nitrite is a convenient material for such a test, because there are two typical phase transitions, a first order ferroelectric to antiferroelectric phase transition at 163.6°C and a second order antiferroelectric to paraelectric phase transition at 164.8°C and furthermore, the precise ACC experiment has been performed in a previous study [4].

The dynamic DSC experiments were made under various conditions indicated in Table 1 for experiments 1–5. In Fig. 2, the results for the ACC and DSC components and the difference between them (DSC component minus ACC component) are shown for Expt. 1. The origin of the ordinate is arbitrary in Fig. 2 except for the ACC component. Outside the first order transition region around 163.6°C, the DSC component coincides with the ACC component (to make this easy to see, move the origin of the ordinate for the DSC component to overlap the ACC component), that is, there is no difference between them.

Table 1

The experimental conditions for experiments 1–5 and the latent heat at the first order phase transition of sodium nitrite (NaNO₂)

No.	Amp. (°C)	Period (s)	Ramp (°C/min)	Latent heat (cal/mol)
1	0.1	100	0.1	59.4
2	0.05	60	0.05	57.4
3	0.05	60	0.1	56.6
4	0.1	60	0.1	57.8
5	0.1	30	0.1	57.8

Amp. indicates the amplitude of AC temperature, period indicates the time for a cycle in ACC operation, and ramp is the temperature scanning rate in DSC operation.

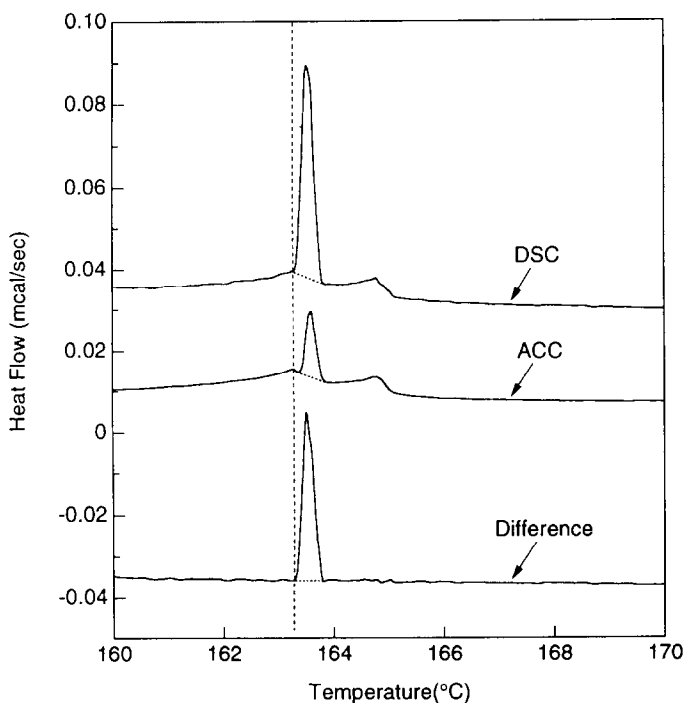


Fig. 2. DSC and ACC components and the difference between them (DSC component minus ACC component) at the first and second order phase transitions of sodium nitrite (NaNO_2). This is the result for experiment 1. The vertical dotted line indicates the onset temperature of the first order transition region. The dotted line in the curve of the ACC component is the mean linear heat capacity in the first order transition region. Note that there is no anomaly in the difference at the second order transition temperature of 164.8°C .

This fact means that the heat capacity associated only with thermal fluctuation takes place outside the first order transition region. Furthermore, the heat capacity generally exhibits critical behavior at the second order phase transition, as discussed below.

It is of interest to compare the critical behavior in the present experiment with the result obtained from former ACC [4]. From the former ACC results, the heat capacity was analyzed by a critical exponent expression. In Fig. 3 the present result is shown with the curve drawn by the critical exponent expression in the former ACC, where the origin of the ordinate was shifted to coincide. This is due procedure, because in the former ACC we could not exclude the additional heat capacity due to a thermocouple and some glue. Thus, the coincidence of the present result with that for the former ACC is satisfactory.

Let us consider the first order transition region fenced by two vertical lines in Fig. 4. We should point out that the concept of the ACC component is no longer meaningless, because a non-linear response is significant in this region as seen in the AC heat flow of Fig. 4. Therefore, we use the term ACC component as an expedient. There are two distinct thermal properties at the first order phase transition: one is latent heat and the other is related to the kinetic mechanism of the phase boundary. For estimation of the latent heat, we define the linear heat capacity, C_{p1} , in the first order transition region as

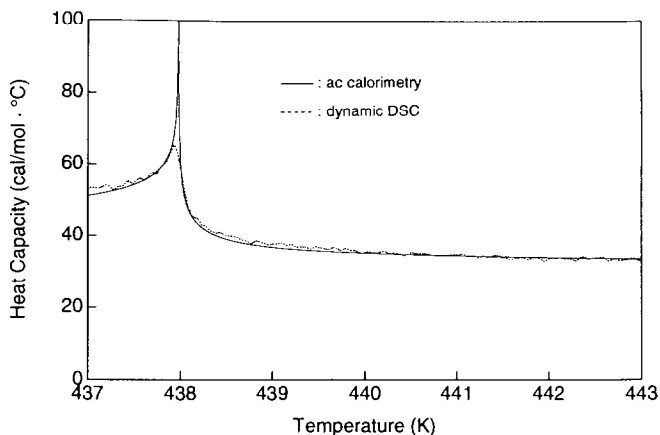


Fig. 3. Comparison between the present linear heat capacity (dotted curve) and the former result which is drawn based upon the analyzed critical exponent expression obtained from the former ACC (thin solid curve) at the second order phase transition. The agreement of the both curves is satisfactory.

$$C_{pt} = C_{p1}(1-x) + C_{p2}x \quad (11)$$

Roughly we can assume that it changes linearly against temperature in the first order transition region, since phase 1 is replaced by phase 2 gradually and therefore, the mean heat capacity is given by the quota allotment of the heat capacities of the two phases.

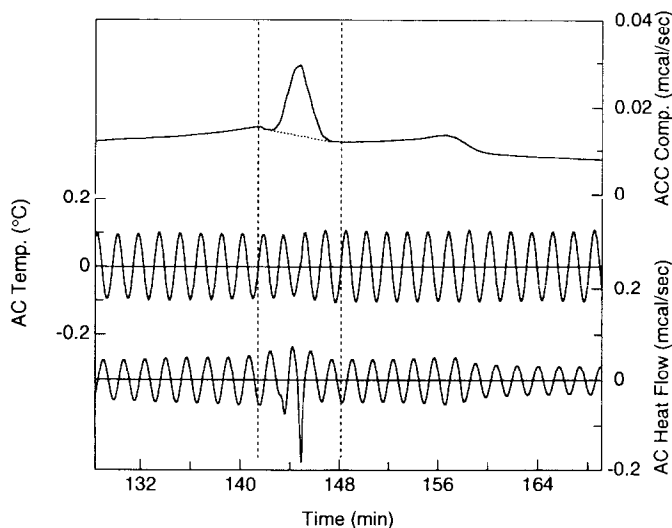


Fig. 4. The ACC component of experiment 1 in the corresponding temperature region from 162 to 166°C, together with the waveform of the AC temperature at the sample side (AC Temp.) and the waveform of the AC difference temperature ΔT (AC Heat Flow). Especially in the latter waveform, the non-linear response is remarkable.

This is shown by the dotted curve of the ACC component in Fig. 4. In Fig. 5(1)–(5), the ACC component and the DSC component minus the ACC component are shown, where the dotted curves in the ACC component are connected between the onset heat capacity and the final heat capacity in the first order transition region as expected from Eq. (11). It

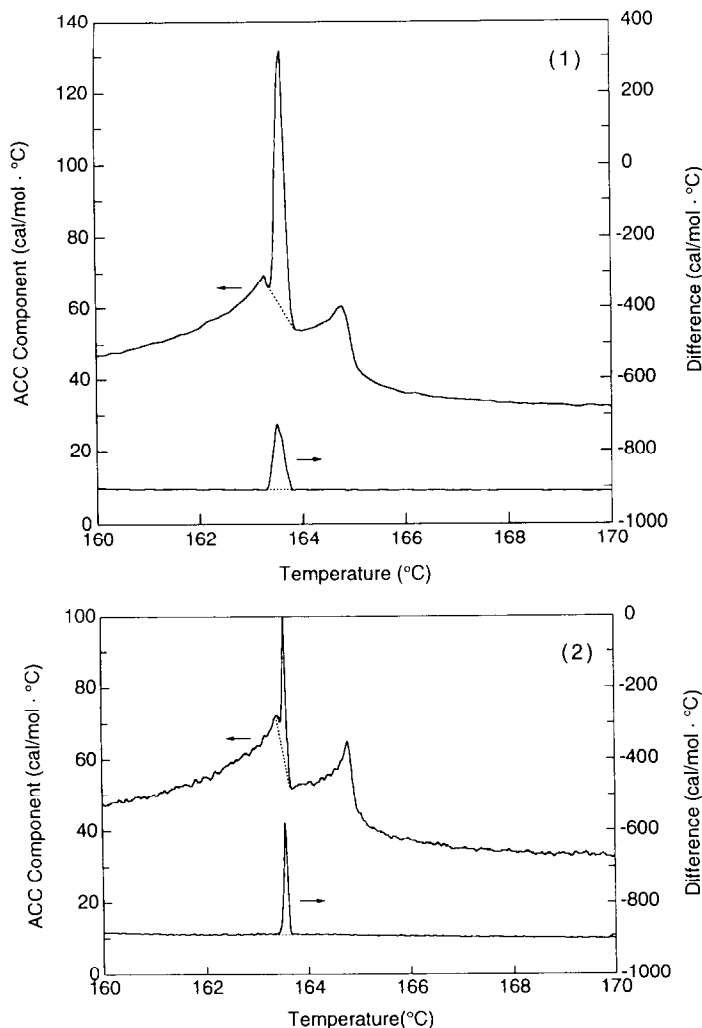


Fig. 5. (1) The ACC component (top) and the difference (bottom) between DSC and ACC components in the experiment 1, (2) experiment 2, (3) experiment 3, (4) experiment 4 and (5) experiment 5. In every plot of the curves of the ACC component, we can see an anomalous small peak at the onset temperature of the first order transition region. The dotted curves in the ACC component which indicate the mean linear heat capacity in the first order transition region were estimated by linearly connecting the ACC components between the onset temperature and the final temperature of the first order phase transition. The latent heat for these experiments is summarized in Table 1.

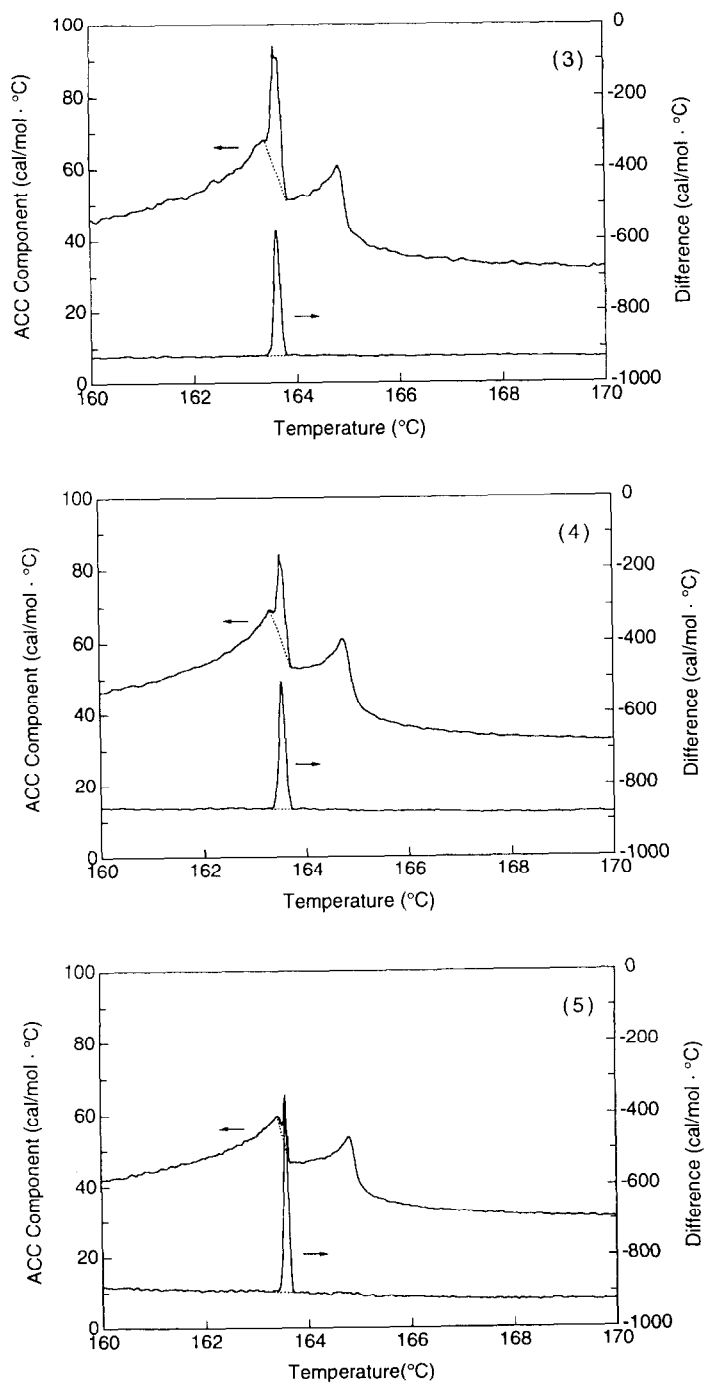


Fig. 5(3)–(5).

is worthwhile noticing a small anomaly at the onset heat capacity and furthermore, the ACC component agrees with the mean heat capacity in the beginning in the first order transition region. The latter behavior might be related to the fact that in the beginning the strength of the non-linearity is rather weak and therefore, its contribution is unremarkable.

We estimated the latent heat from the part in the DSC component beyond the dotted line. A typical result is shown in Fig. 2. The latent heat in Table 1 is nearly independent of the experiments. This gives the latent heat evaluated accurately at the first order phase transition. Therefore, by use of dynamic DSC, we propose a method to estimate latent heat at a first order phase transition.

The above estimation is important in precise thermodynamic analyses. When we consider Clapeyron's equation [7], latent heat derived by the above procedure should be used. On considering the relation between enthalpy difference (latent heat) and entropy difference at a first order transition temperature

$$T_0 = L/(S_2 - S_1) \quad (12)$$

obtained from Eqs. (3a) and (3b), it is also important to use the precise value of latent heat.

Finally, we do not know the reason why latent heat in Table 1 varies somewhat. It might be due to the fact that the movement of the phase boundary depends on imperfections, etc.

5. Conclusion

To the author's knowledge, few experimental trials in differential AC calorimetry have been conducted so far [5,6]. In them, \tilde{K} of Eqs. (7) and (8) has been ignored. However, it should be stressed that, in the simultaneous measurement of DSC and ACC, it is not necessary to ignore \tilde{K} in Eqs. (7) and (8). We can easily obtain the absolute value of the linear heat capacity of a sample under the presence of \tilde{K} . As pointed out in Section 3, the ACC component gives linear heat capacity. At a second order phase transition, we can obtain linear heat capacity with critical behavior. The experiments performed at a second order phase transition of NaNO_2 proved that linear heat capacity could be obtained from dynamic DSC. On the other hand, we need to pay special attention in the experiments at a first order phase transition. We have proposed a method to estimate the precise latent heat at a first order phase transition. The method was applied to the estimation of latent heat at a first order phase transition of NaNO_2 . In fact, the latent heat in NaNO_2 was consistently obtained under various experimental conditions. For the further study of the behavior of phase boundary, we have to analyze the non-linear response at a certain temperature in a first order transition region.

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