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Derivation of a general formula and a general area method for latent heat via differential thermal analysis

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Abstract

In this paper, a generalized expression for latent heat has been derived by considering temperature gradients within the sample, and the usual situation in which the specific heat of the sample changes during the transition and specific heats in both low- and high-temperature states are functions of the temperature. For a reversible transition, when the specific heat of a sample is a slowly changing function of the temperature, the errors caused by the temperature gradient within the sample can theoretically be minimized by averaging the latent heats obtained from both the heating and cooling process. It is also pointed out that the latent heat is proportional to the area enclosed by peak curve and the imaginary equivalent non-latent heat baseline. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Differential thermal analysis; Equivalent non-latent heat baseline; Latent heat; Temperature-dependent specific heat; Temperature gradient

1. Introduction

Differential thermal analysis (DTA) is a powerful tool [1–4] which has a wide range of applications, such as the determination of purity, crystallinity, solid reactions, thermal decomposition, phase transitions and the determination of phase diagrams.

Although DTA is very useful, there are shortcomings in the basic Gray–Speil theory [5,6] which cannot satisfactorily explain the physical meaning of each eigen point of the DTA curve. The Gray–Speil theory is very simple in that it assumes that the specific heat of a sample is uniform during the phase transition, with no regard to the fact that the specific heat is a function of temperature. We have generalized the Gray–Speil theory and have derived a general latent heat formula [7] which can be used to cope with phase changes for which the specific heat is a temperature-dependent quantity. The present paper considers temperature gradients within the sample and improves the earlier work [7] to give a stricter and more general result.

2. Derivation of latent heat formula

Assume that a phase change occurs during a test and the heat conductivity of the holder is so high that the

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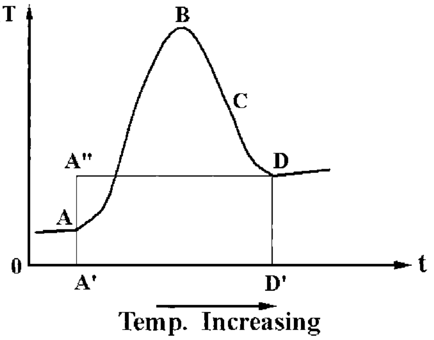

Fig. 1. A typical DTA heating (endothermic) phase change curve $\Delta T = T_r - T_s$, is the reference temperature, and T_s the sample temperature.

temperature gradient within the holder can be neglected. The specific heats of a sample are c_L and c_H, respectively, in the low- and high-temperature states, and they are functions of temperature. In Fig. 1, there is a typical DTA transition curve. Fig. 2 shows the relationship between energy and temperature of a sample particle with a unit mass.

Firstly, we consider a heating phase change process. As shown in Fig. 1, at point A the phase change occurs. When the sample holder temperature reaches T_A ($T_A = T_{tr}$, T_{tr} is the transition temperature of the sample), only the small section of the sample that contacts the holder wall reaches the transition temperature T_{tr}. The temperature of other parts of the sample is still lower than the temperature T_A because of the temperature gradient. For specific experimental conditions, assuming the temperature of a sample particle i to be T_{Li} and the temperature difference between the holder wall and the particle to be ΔT_{Li}, we have the relation $T_{Li} = T_{tr} - \Delta T_{Li}$. In this definition, ΔT_{Li} is always bigger than zero.

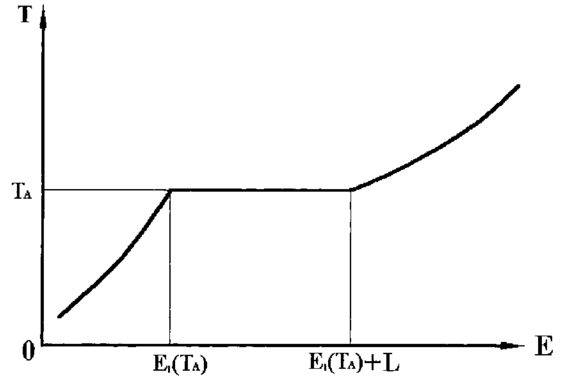

Fig. 2. The diagram between energy and temperature of a sample.

At point D, the whole sample has finished the phase change. The outer surface of the sample reaches temperature T_D, and the distribution of the temperature gradients within the sample has just stabilized, causing the curve to return to the point D, the position of the baseline of the DTA curve. Assume the temperature of a sample particle i to be T_{Hi}, the temperature difference between the holder and the sample to be ΔT_{Hi}, and there is a relation $T_{Hi} = T_D - \Delta T_{Hi}$. Again, ΔT_{Hi} is always positive.

Fig. 2 is a typical diagram showing the relationship between the sample energy and temperature. Using E_{Li} and E_{Hi}, respectively, to represent the energy of a sample particle i with a unit mass corresponding to the point A and point D in the DTA curve, we have:

$$E_{Li} = E_1(T_{Li}); \tag{1}$$

$$E_{Hi} = E_1(T_A) + L + E_2(T_{Hi}); \tag{2}$$

where L is the latent heat of the sample per unit mass, E_1 the energy of the sample with a unit mass in a low-temperature state, and E_2 the energy increment (the energy zero point is set at the phase-transition point) of the sample with a unit mass.

From $T_{Li} = T_A - \Delta T_{Li}$, $T_{Hi} = T_D - \Delta T_{Hi}$, we have:

$$\begin{aligned} E_{Hi} - E_{Li} = \Delta E_i = E_1(T_A) + L + E_2(T_{Hi}) \\ - E_1(T_{Li}) \end{aligned} \tag{3}$$

$$\begin{aligned} L &= \Delta E_i - E_1(T_A) - E_2(T_{Hi}) + E_1(T_{Li}) \\ &= \Delta E_i - E_1(T_A) - E_2(T_D - \Delta T_{Hi}) \\ &\quad + E_1(T_A - \Delta T_{Li}) = \Delta E_i - E_2(T_D) \\ &\quad + [E_2'(T_D)\Delta T_{Hi} - E_1'(T_A)\Delta T_{Li}] \\ &\quad - \frac{1}{2!}[E_2''(T_D)(\Delta T_{Hi})^2 - E_1''(T_A)(\Delta T_{Li})^2] \\ &\quad + \cdots + \frac{(-1)^{n-1}}{n!}[E_2^{(n)}(T_D)(\Delta T_{Hi})^n \\ &\quad - E_1^{(n)}(T_A)(\Delta T_{Li})^n] + \cdots \end{aligned} \tag{4}$$

Assume the whole latent heat in the heating phase change process is $\mathscr{L}_{\text{heating}}$, we have:

$$\begin{aligned}\mathscr{L}_{\text{heating}} &= \sum_i m_i L = \sum_i m_i \Delta E_i - \sum_i m_i E_2(T_\text{D}) \\ &\quad + \sum_i m_i[E_2'(T_\text{D})\Delta T_{\text{H}i} - E_1'(T_\text{A})\Delta T_{\text{L}i}] \\ &\quad - \frac{1}{2!}\sum_i m_i[E_2''(T_\text{D})(\Delta T_{\text{H}i})^2 \\ &\quad - E_1''(T_\text{A})(\Delta T_{\text{L}i})^2] + \cdots \\ &\quad + \frac{(-1)^{n-1}}{n!}\sum_i m_i[E_2^{(n)}(T_\text{D})(\Delta T_{\text{H}i})^n \\ &\quad - E_1^{(n)}(T_\text{A})(\Delta T_{\text{L}i})^n] + \cdots \qquad (5)\end{aligned}$$

That is:

$$\mathscr{L}_{\text{heating}} = \sum_i m_i \Delta E_i - M E_2(T_\text{D}) + \delta \qquad (6)$$

where

$$\begin{aligned}\delta &\equiv \sum_i m_i[c_\text{H}(T_\text{D})\Delta T_{\text{H}i} - c_\text{L}(T_\text{A})\Delta T_{\text{L}i}] \\ &\quad - \frac{1}{2!}\sum_i m_i\left[\frac{\mathrm{d}c_\text{H}(T_\text{D})}{\mathrm{d}T}(\Delta T_{\text{H}i})^2\right. \\ &\quad \left.- \frac{\mathrm{d}c_\text{L}(T_\text{A})}{\mathrm{d}T}(\Delta T_{\text{L}i})^2\right] + \cdots \frac{(-1)^{n-1}}{n!} \\ &\quad \times \sum_i m_i\left[\frac{\mathrm{d}^{n-1}c_\text{H}(T_\text{D})}{\mathrm{d}T^{n-1}}(\Delta T_{\text{H}i})^n\right. \\ &\quad \left.- \frac{\mathrm{d}^{n-1}c_\text{L}(T_\text{A})}{\mathrm{d}T^{n-1}}(\Delta T_{\text{L}i})^n\right] + \cdots \qquad (7)\end{aligned}$$

where $\sum_i$ signifies that the sum is taken over all sample particles and the following definition are valid: $E_1'(T_\text{A}) = c_\text{L}(T_\text{A})$, $E_2'(T_\text{D}) = c_\text{H}(T_\text{D})$, $E_1''(T_\text{A}) = (\mathrm{d}c_\text{L}(T_\text{A}))/\mathrm{d}T$, $E_2''(T_\text{D}) = (\mathrm{d}c_\text{H}(T_\text{D}))/\mathrm{d}T, \ldots$.

In the Eq. (6), the term $\sum_i m_i \Delta E_i$ is the heat energy absorbed in the process interval from A to D, and this energy includes both the latent heat and the heat used to increase the temperature of sample after the phase transition from T_A to T_D. This total energy is proportional to the area enclosed by peak curve and the base line ΔT=0 from temperature T_A to T_D, which is the area A′ABCDD′ as shown in Fig. 1 and can be represented by $\text{AREA}_{\text{peak\_h}}$. The term $ME_2(T_\text{D})$ is the energy absorbed to increase the sample temperature after the phase transition from T_A to T_D. This energy is proportional to the area enclosed by the horizontal line A″D and the base line ΔT=0 from temperature T_A to T_D, the area A′AA″DD′ shown in Fig. 1, and can be represented by $\text{AREA}_{\text{base\_h}}$. The term δ represents the influence of the temperature gradient within the sample and the change of specific heat with change of temperature.

The physical meaning of Eq. (6) is very clear: The latent heat of the sample equals the total energy absorbed in the transition from T_A to T_D minus the energy absorbed to increase the sample temperature after the phase transition from T_A to T_D, plus the correction term δ.

Eq. (6) can be rewritten:

$$\mathscr{L}_{\text{heating}} = K(\text{AREA}_{\text{peak-h}} - \text{AREA}_{\text{base-h}}) + \delta \qquad (6\text{A})$$

where K is a parameter which relates an area of DTA with energy [1] and K is a function of heating rate and Newton's constant of the sample holder.

Eqs. (6) and (6A) are general. They are valid irrespective of the relationship between the specific heat and the temperature of the sample.

We next consider the cooling phase-transition process.

As illustrated in Fig. 3, corresponding to point A and point D, we use E_1 and E_2 to represent the energy of sample particle with a unit mass, respectively, in the low- and high-temperature states (The same as in the heating process, where subscripts L=low-temperature state, and H=high-temperature state).

As shown in Fig. 3, at point A a phase change occurs. When sample holder temperature reaches T_A (T_A=T_tr, T_tr is the transition temperature of the sample), only the small section of the sample in contact

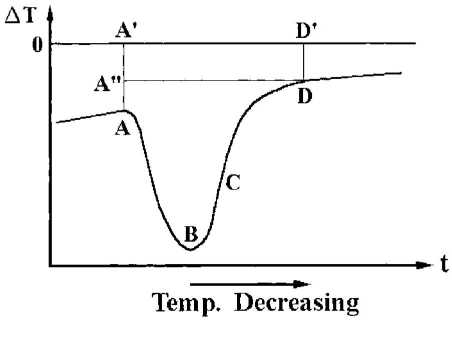

Fig. 3. A typical DTA cooling (exothermic) phase change curve.

with the holder reaches the transition temperature T_{tr}. The temperature of other parts of the sample is still higher than T_{A} because of the temperature gradient. For specific experimental conditions, assuming the temperature of a sample particle i to be $T_{\mathrm{H}i}$ and the temperature difference between the particle and holder wall to be $\Delta T_{\mathrm{H}i}$, we have the relationship $T_{\mathrm{H}i}=T_{\mathrm{A}}+\Delta T_{\mathrm{H}i}$. In this definition, $\Delta T_{\mathrm{H}i}$ is always positive.

At point D, the whole sample has finished the phase change. The outer surface of the sample reaches temperature T_{D}, and the distribution of the temperature gradients within the sample has just stabilized, causing the curve to return to the point D, the position of the baseline of the DTA curve. If the temperature of a sample particle i is $T_{\mathrm{L}i}$ and the temperature difference between the sample and the holder is $\Delta T_{\mathrm{H}i}$, then $T_{\mathrm{L}i}=T_{\mathrm{D}}+\Delta T_{\mathrm{L}i}$. Again, the $\Delta T_{\mathrm{H}i}$ is always positive. We also have Eqs. (1) and (2) and by a process similar to that used earlier to derive $\mathscr{L}_{\text{heating}}$, we obtain:

$$\mathscr{L}_{\text{cooling}} = \sum_i m_i \Delta E_i - M[E_1(T_{\mathrm{A}}) - E_1(T_{\mathrm{D}})] - \delta' \tag{8}$$

where

$$\begin{aligned}\delta' \equiv {} & \sum_i m_i[c_{\mathrm{H}}(T_{\mathrm{A}})\Delta T_{\mathrm{H}i} - c_{\mathrm{L}}(T_{\mathrm{D}})\Delta T_{\mathrm{L}i}] \\ & + \frac{1}{2!}\sum_i m_i \left[\frac{\mathrm{d}c_{\mathrm{H}}(T_{\mathrm{A}})}{\mathrm{d}T}(\Delta T_{\mathrm{H}i})^2 \right. \\ & \left. - \frac{\mathrm{d}c_{\mathrm{L}}(T_{\mathrm{D}})}{\mathrm{d}T}(\Delta T_{\mathrm{L}i})^2\right] + \cdots + \frac{1}{n!}\sum_i m_i \\ & \times \left[\frac{\mathrm{d}^{n-1}c_{\mathrm{H}}(T_{\mathrm{A}})}{\mathrm{d}T^{n-1}}(\Delta T_{\mathrm{H}i})^n \right. \\ & \left. - \frac{\mathrm{d}^{n-1}c_{\mathrm{L}}(T_{\mathrm{D}})}{\mathrm{d}T^{n-1}}(\Delta T_{\mathrm{L}i})^n\right] + \cdots \end{aligned} \tag{9}$$

Eq. (8) also can be rewritten as:

$$\mathscr{L}_{\text{cooling}} = K'(\mathrm{AREA}_{\text{peak-c}} - \mathrm{AREA}_{\text{base-c}}) - \delta' \tag{8A}$$

where parameter K' is a function of both cooling rate and Newton's constant of the sample holder, and the $\mathrm{AREA}_{\text{peak\_c}}$ is the area A$'$AA$''$BCDD$'$ and the $\mathrm{AREA}_{\text{base\_c}}$ is the area A$'$A$''$DD$'$ as shown in Fig. 3.

The physical meaning of Eq. (8) or Eq. (8A) is also very clear. The latent heat of the sample represents that the total energy, $\sum_i m_i \Delta E_i$ or K' $\mathrm{AREA}_{\text{peak\_c}}$, released in the interval from A to D minus the energy, $M[E_1(T_{\mathrm{A}})-E_1(T_{\mathrm{D}})]$ or K' $\mathrm{AREA}_{\text{peak\_c}}$, released on lowering the sample temperature from T_{A} to T_{D}, and minus a correction term, δ', which is caused by the temperature gradient within the sample and the change of the specific heat.

Here, we must indicate that the T_{A} in Eq. (7) is the sample transition temperature, so it is the same as the T_{A} in Eq. (9) if there are no any superheating and supercooling phenomena. However, the T_{D} in Eq. (7) (the temperature corresponding to point D of Fig. 1, which is bigger than T_{A}) differs from that in Eq. (9), which is lower than T_{A}.

Eqs. (8) and (8A) are also general. No matter what relationship exists between the specific heat and the temperature, Eqs. (8) and (8A) are valid.

3. Discussion

From Eqs. (6) and (8), we know that $\mathrm{AREA}_{\text{peak\_h}}$, $\mathrm{AREA}_{\text{base\_h}}$, $\mathrm{AREA}_{\text{peak\_c}}$ and $\mathrm{AREA}_{\text{base\_c}}$ can be drawn easily from the DTA curve, but it is very difficult to estimate the value of δ and δ'. In a real experiment, δ and δ' are usually neglected and this causes systematic errors. If δ is small enough to be negligible compared with $\mathscr{L}$, we can use only one heating or cooling DTA curve to obtain the exact value of the latent heat.

From the definitions of δ and δ', it can be concluded that the smaller $\sum_i m_i$ and ΔT_i, the smaller will be δ and δ'. Therefore within the sensitivity of the apparatus, δ and δ' can be minimized by decreasing the sample mass, lowering the heating and cooling rate and improving the heat conducting condition of the sample.

For many organic compounds such as organic polymer materials, their phase transitions are often accompanied with some metastable state transitions and they often demonstrate some unordinary phenomena such as superheating or supercooling. Because of the effects of the metastable states, the latent heat obtained is usually not the really pure latent heat. How to obtain the really pure latent heat in these situations is a great subject, and we will try to study it in the future.

If the heating rate equals the cooling rate, K in Eq. (6A) has the same value as K' in Eq. (8A). For a very special situation in which the phase transition is reversible and there are no superheating and supercooling phenomena and the heating rate equals the cooling rate, by adding Eqs. (6) and (8) and averaging, the latent heat follows as:

$$\begin{aligned}\mathscr{L} &= \tfrac{1}{2}[\mathscr{L}_{\text{heating}} + \mathscr{L}_{\text{cooling}}] \qquad (10)\\ &= \frac{K}{2}[(\text{AREA}_{\text{peak-h}} - \text{AREA}_{\text{base-h}})\\ &\quad + (\text{AREA}_{\text{peak-c}} - \text{AREA}_{\text{base-c}})]\\ &\quad + \tfrac{1}{2}(\delta - \delta')\end{aligned}$$

No matter what relationship exists between the specific heat and the temperature, for a reversible phase transition, the Eq. (10) is valid if the heating rate equals the cooling rate.

On account of the influence of the temperature gradient within the sample and the change of specific heat with temperature, δ and δ' are not equal to zero and they do not generally have the same value. When the specific heat of the sample is only a slowly varying function of the temperature, the high rank terms of ΔT in both Eqs. (7) and (9) are so small that they can be omitted, the absolute value and the sign of δ and δ' are mainly determined by those of the first term of Eqs. (7) and (9), $\sum_i m_i[c_H(T_D)\Delta T_{Hi} - c_L(T_A)\Delta T_{Li}]$ and $\sum_i m_i[c_H(T_A)\Delta T_{Hi} - c_L(T_D)\Delta T_{Li}$. For a particular heating or cooling rate, the higher the specific heat of the sample, the greater the heat energy absorbed or released per unit time by the sample from the surroundings, and the bigger the temperature gradient within the sample according to the well-known heat transfer principle. If $c_H > c_L$, then $\Delta T_H > \Delta T_L$, so $c_H\Delta T_H - c_L\Delta T_L > 0$ must be true. On the other hand, if $c_H < c_L$, we must have $c_H\Delta T_H - c_L\Delta T_L < 0$. δ therefore has the same sign as $c_H - c_L$. If $c_H = c_L =$constant, δ and δ' are equal to zero and the conventional Gray–Speil treatment only represents a special condition of our theory when $c_H = c_L =$constant.

Besides an abrupt change in c_p during the transition, if the specific heat of the sample is a slow changing function of the temperature at the measured temperature interval, we know that the value of δ and δ' are mainly determined by the value of $\sum_i m_i[c_H(T_D)\Delta T_{Hi} - c_L(T_A)\Delta T_{Li}]$ and $\sum_i m_i[c_H(T_A)\ \Delta T_{Hi} - c_L(T_D)\ \Delta T_{Li}]$, therefore δ is approximately equal to δ'. Many real reversible transition situations satisfy this condition. And if we use Eq. (10) to calculate latent heat of a reversible transition, the absolute error can be reduced to $(\delta - \delta')/2$. Because the δ and δ' have the same sign, we have $|\delta - \delta'|/2 \leq |\delta|$ and $|\delta'|$. By using Eq. (10), we can at least reduce half of the errors caused in the situation by only using Eq. (6) or Eq. (8). The latent heat formula can be rewritten as:

$$\begin{aligned}\mathscr{L} &\approx \frac{K}{2}[(\text{AREA}_{\text{peak-h}} - \text{AREA}_{\text{base-h}})\\ &\quad + (\text{AREA}_{\text{peak-c}} - \text{AREA}_{\text{base-c}})] \qquad (10\text{A})\end{aligned}$$

and δ and δ' can be estimated from following equation:

$$\begin{aligned}\delta \approx \delta' &\approx \frac{K}{2}[(\text{AREA}_{\text{peak-h}} - \text{AREA}_{\text{base-h}})\\ &\quad - (\text{AREA}_{\text{peak-c}} - \text{AREA}_{\text{base-c}})] \qquad (10\text{B})\end{aligned}$$

4. General area method for latent heat in DTA

Under a certain experimental condition, it is very difficult to calculate the value of the correction item δ directly for a specific sample. In the following we will introduce an area method to deal with the correction item δ.

Now, we consider a second-order phase transition. During this transition, the latent heat is zero, but the specific heat has a change. For simplicity, we assume $c_H > c_L$, where c_H or c_L is the function of temperature. As shown in Fig. 4 the phase-transition curve in the heating process is the curve AD. From this trace it is easy to find that the phase transition takes place at the point A and when all the samples have fulfilled the transition and have reached a stable state the curve reaches the point D. From Eq. (6A):

$$\begin{aligned}\mathscr{L}_{\text{heating}} &= K[\text{AREA}(\text{ADD}'\text{A}'\text{A})\\ &\quad - \text{AREA}(\text{A}''\text{DD}'\text{A}'\text{AA}'')] + \delta\\ &\quad - K[\text{AREA}(\text{A}''\text{DAA}'')] + \delta \qquad (11)\end{aligned}$$

From $\mathscr{L}_{\text{heating}} = 0$, we can obtain $\delta = K[\text{AREA}(\text{A}''\text{DAA}'')]$ in which the δ is associated with the area in the DTA.

Now, let us consider a transition in which the value of the latent heat is non-zero and the relation $c_H > c_L$ is still valid. The phase-transition curve is shown in Fig. 5. The curve AD is determined as follows: dividing the real phase-transition process into two different processes. One process represents phase transition and the other represents the temperature variation of all

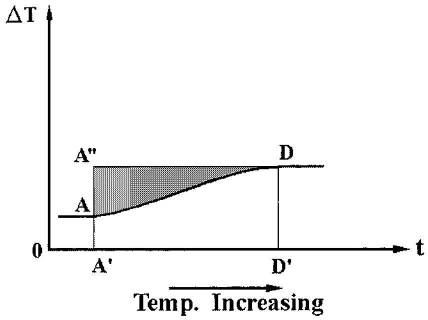

Fig. 4. A typical second class transition of DTA in the heating process.

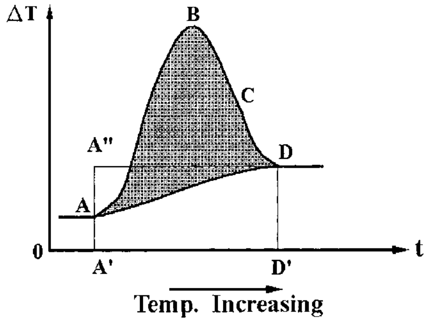

Fig. 5. A typical (exothermic) transition curve of DTA in the heating process.

sample particles. Linking the heat that is provided to enhance the temperature of the sample per unit time with the equivalent temperature difference between the environment and the outer surface of the sample, we have a relation: $K\Delta T_{\mathrm{eff}}=\mathrm{d}Q_{\mathrm{s}}/\mathrm{d}t$. From this relation we can draw the curve AD, which is called equivalent non-latent heat baseline. According to Eq. (6A):

$$\mathscr{L}_{\mathrm{heating}} = K[\mathrm{AREA}(\mathrm{ABCDD'A'A}) - \mathrm{AREA}(\mathrm{A''DD'AA''})] + \delta \qquad (12)$$

Using the relation δ=AREA(A″DAA″), we finally get:

$$\begin{aligned}\mathscr{L}_{\mathrm{heating}} &= K[\mathrm{AREA}(\mathrm{ABCDD'A'A}) \\ &\quad -\mathrm{AREA}(\mathrm{A''DD'AA''}) \\ &\quad +\mathrm{AREA}(\mathrm{A''DAA''})] \\ &= K[\mathrm{AREA}(\mathrm{ABCDA})] \\ &= K(\text{area enclosed by peak and its} \\ &\quad \text{equivalent non-latent heat baseline})\end{aligned} \qquad (13)$$

The AREA(ABCDA) is the gray area of Fig. 5.

If we can draw the equivalent non-latent heat baseline from the pretransition baseline and post-transition baseline, it becomes very easy for us to calculate the latent heat from the area enclosed by peak and the equivalent non-latent heat baseline.

In a real process, under a certain experimental condition, if the latent heat is zero, the temperature span between the beginning and the end of the transition peak is $(T_{\mathrm{D}}-T_{\mathrm{A}})_{L=0}$. Under the same condition, if the latent heat is not zero, the temperature span between the beginning and the end of the transition peak $(T_{\mathrm{D}}-T_{\mathrm{A}})_{L\neq 0}$ is generally not equal to $(T_{\mathrm{D}}-T_{\mathrm{A}})_{L=0}$. The reason is that the thermal conductivity of the sample is virtually finite. During the transition only some parts of the heat which is transferring within the sample is provided to enhance the temperature of the sample. No matter what kind of the transition (exothermic or endothermic) takes place, the temperature span $(T_{\mathrm{D}}-T_{\mathrm{A}})_{L\neq 0}$ must differ from that of $(T_{\mathrm{D}}-T_{\mathrm{A}})_{L=0}$. Under a normal condition, the thermal conductivity of the sample can be represented as η. When we deal with the true phase-transition process in which the latent heat is not zero, the equivalent non-latent heat baseline can be regarded as a non-latent heat-transition curve of the sample with the equivalent thermal conductivity η'. As discussed above, in the general situations the η is not equal to η'. If the equivalent thermal conductivity η' can be calculated, by using the above method, the equivalent non-latent heat baseline can be determined correctly, and the latent heat can also be obtained exactly. Actually, it is impossible for us to obtain the equivalent thermal conductivity η' of a real example, so it is almost impossible to obtain the exact value of latent heat with this area method. In some special conditions, such as the sample with high thermal conductivity or other approximate situations, the equivalent non-latent heat baseline can be replaced by the true non-latent heat-transition curve.

Wunderlich [1] has advanced an approximate method to deal with latent heat value in DTA in the situation that the heat capacity is a function of temperature, in which the main idea is much like that of the equivalent non-latent heat baseline here.

In the cooling phase-transition process, the latent heat formula can also be represented by Eq. (13) which is similar to the heating phase-transition process. The method of determining the equivalent non-latent heat baseline is the same as that in the heating transition process.

The above discussion of area method reveals that the temperature gradients within the sample can not omitted simply. In the general situations, to obtain the exact value of latent heat of sample, the effects of temperature gradients must be considered.

5. Conclusion

In this paper, a more rigorous general expression for latent heat is derived by considering temperature gradients within the sample and the physically realistic situation in which the specific heat of the sample changes during the transition and is also a function of the temperature in both the low- and high-temperature states.

Because of the temperature gradient within the sample, if the specific heat of sample has an abrupt change at the transition, using only the heating or cooling DTA curve to calculate latent heat of the sample will result in some errors. Irrespective of the relationship between specific heat and temperature the error can be minimized, within the sensitivity of the apparatus, by decreasing the amount of the sample, lowering the heating and cooling rate and improving the heat conducting condition of the sample. If the specific heat of the sample is a slowly changing function of temperature, the error caused by temperature gradients within the sample can also be minimized for a reversible transition, by using the area method in DTA and averaging the latent heats obtained from both the heating and cooling processes.In the general situation, the errors caused by the real temperature gradients within the sample can not be neglected. In the DTA area method, this correction item δ equals the area enclosed by extrapolated post-transition baseline and the equivalent non-latent heat baseline between initial point of transition and the first point of the stable postbaseline, and the latent heat is proportional to the area enclosed by peak curve and the equivalent non-latent heat baseline.

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