

Differential Thermal Analysis under the Decreasing Mass Condition

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A theoretical treatment of the DTA for the heterogeneous reaction accompanied by the decrease in the mass is presented. The basic equations for mass and heat balance are solved simultaneously by means of the numerical integration, and both the behavior of the DTA curve and the effects of various parameters on the numerical values of the integrations are investigated, and compared with the conventional results of the reaction with no changes in the mass. As a result, the shape of the curve does not vary essentially and the peak height falls only slightly. Although the area under the peak represents the sum of the total heat of reaction and the additional change in the sensible heat of the reactant during the reaction, the magnitude of the latter term is usually small enough to neglect.

1. Introduction

Differential thermal analysis (DTA) is widely used for the quantitative determination of the heat of reaction calculating the area under the curve. This method is effective only for a transition of a crystalline lattice, whose mass is held constant during the reaction, and there is an abundance of literatures on the subject¹⁻³⁾. In recent years, DTA has been applied to the heterogeneous reactions which evolve gases, such as the thermal dehydration of clays⁴⁻⁶⁾, the decomposition of coal^{7, 8)} and the pyrolysis of polymers⁹⁻¹⁵⁾. DTA applied to these reactions have been restricted to the qualitative or semi-quantitative characterization, since the reactions are accompanied by the decrease in mass and the base lines are drifted in the DTA curves. In such cases, a sample cell with a lid has been used or the reactant has been diluted with an inert substance enough to neglect the change in mass, however the DTA still has poor accuracy for the quantitative analysis.

In the present paper, the DTA curve for the substance accompanied by the decrease in mass is analysed by solving a couple of the fundamental equations for the reaction rate and the heat balance simultaneously. Also the effects of several parameters of reaction kinetics and of heat transfer upon the relationship between the area under the peak and the heat of reaction are demonstrated. These results are compared with those under the constant mass condition, and the diluent effect of the inert substance is discussed theoretically.

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2. Fundamental equations of DTA under the decreasing mass condition

When a sample material is placed in a cell and the reaction is initiated by supplying heat from the furnace to the cell, the reaction starts with the evolution of a gas as shown below.



A typical DTA curve and a heating curve are illustrated in Fig. 1. As the reaction proceeds, the base line of the DTA curve begins to drift from the reference temperature, T_r to the furnace temperature, T_f . Therefore, in the following analysis, the furnace temperature is to be substituted for the reference temperature, and the difference between the furnace temperature and the sample temperature, $(T_f - T)$ is to be termed "differential temperature"*.

Prior to the analysis, the following assumptions are to be applied.

- (i) The reaction takes place only in the liquid (or solid) phase, and the evolving gas, undergoing no auxiliary changes and not affecting the residual sample, is exhausted rapidly out of the system.
- (ii) The reaction is of n -th order as to the unreacted fraction of the sample, and the rate constant has an Arrhenius type dependency on temperature.
- (iii) During the reaction, the properties of the sample, such as, the heat capacity, the heat of reaction and the kinetic parameters (activation energy, order of reaction and frequency factor) are held constant.
- (iv) During the reaction, the heat transfer coefficient and the area of heat transfer are held constant, i.e., the sample cell is considered to be a shallow cylinder.
- (v) The reactive substance is well stirred, as done in the literature of Borchardt and Daniels¹⁶⁾, and with such a system the temperatures of the reference and the sample are almost uniform. This permits the system to be described by a first-order differential model.

Reed, et al¹⁷⁾, described the way to effect the kinetic parameters from the DTA curves by solving the equations for the reaction rate and the heat balance when the temperature distributions in the cells are negligible. In the present work, the additional assumption (i) being taken into account, the equations of interest are

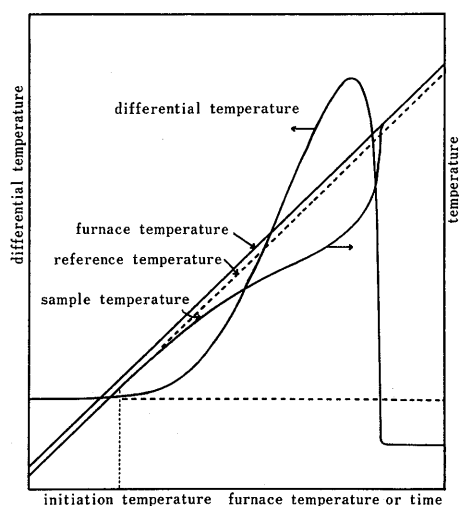


Fig. 1 Endothermic DTA curve under the decreasing mass condition

* In such a situation it is implied that the referential substance is not always necessary, but in practice it would be unfavorable to some extent in view of the common mode rejection (CMR) that the differential thermocouple is installed between the sample cell and the furnace wall.

$$\begin{cases} c_p w \frac{dT}{dt} = hA(T_f - T) - (-\Delta H) \frac{dw}{dt} & (1) \\ -\frac{d(w/w_o)}{dt} = Z \exp(-E/RT) \left(\frac{w}{w_o}\right)^n & (2) \\ T_f = Kt & (3) \end{cases}$$

As a tentative assignment, the furnace temperature is assumed to be elevated from 0°K. Thus, the initial conditions are

$$t = 0 : T = 0, w = w_o \quad (4)$$

It is convenient to introduce the following thermal parameters

$$\alpha = c_p w_o / hA, \quad \beta = c_p / |\Delta H| \quad (5)$$

and to transform the fundamental equations into the dimensionless equations, as Reed et al. did in their work¹⁷⁾.

$$\begin{cases} \psi \frac{d\theta}{d\tau} = (\theta_f - \theta) - S \frac{d\psi}{d\tau} & (6) \\ -\frac{d\psi}{d\tau} = \zeta e^{-\varepsilon/\theta} \cdot \psi^n & (7) \end{cases}$$

$$\theta_f = \theta'_f \tau \quad (8)$$

The initial conditions are

$$\tau = 0 : \theta = 0, \psi = 1 \quad (9)$$

where,

$$\begin{cases} \theta = \beta T, \quad \psi = w/w_o, \quad \tau = t/\alpha \\ \varepsilon = \beta(E/R), \quad \zeta = \alpha \cdot Z, \quad \theta'_f = \alpha \cdot \beta K \end{cases}$$

(Henceforth, the variables will be referred to in terms of the basic quantity from which they are derived. For example, ε will be called the activation energy, θ'_f the heating rate and so on.)

S is +1 or -1, depending upon whether the reaction is exothermic or endothermic. Replacing time, τ by the furnace temperature, θ_f as the independent variable

$$\begin{cases} \psi \frac{d\theta}{d\theta_f} = \frac{\theta_f - \theta}{\theta'_f} - S \frac{d\psi}{d\theta_f} & (10) \\ -\theta'_f \frac{d\psi}{d\theta_f} = \zeta e^{-\varepsilon/\theta} \cdot \psi^n & (11) \end{cases}$$

the initial conditions

$$\theta_f = \theta = 0, \psi = 1 \quad (12)$$

The nonsteady heating curve of the sample material prior to the initiation of reaction is evolved by integrating Eq. (10) to the exclusion of the reaction term

$$\theta = \theta_f - \theta'_f (1 - e^{-\theta_f/\theta'_f}) \quad (13)$$

In case of $\theta \gg \theta'_f$, θ is approximated to $(\theta_f - \theta'_f)$ and then it is found that the differential temperature between the furnace and the reactive sample material coincides with the dimensionless heating rate. Thus, in performing the calculations, the initial condition is taken at a temperature measured just prior to an observable departure of the DTA curve from the base line, θ_o .

$$\theta_f = \theta_o + \theta'_f, \quad \theta = \theta_o, \quad \psi = 1 \quad (14)$$

Integrating Eq. (10) from the initiation of reaction to infinity gives

$$\int_{\theta_0}^{\infty} \psi d\theta = \int_{\theta_0+\theta'_f}^{\infty} \frac{\theta_f - \theta}{\theta'_f} d\theta_f - S \int_1^0 d\psi \quad (15)$$

The second term in the right hand side of the above equation corresponds to the dimensionless total heat of reaction and is evaluated to be +1 or -1, depending upon whether the reaction is exothermic or endothermic. The first term in the right hand side represents the total heat transferred and corresponds to the area under the peak. Whereas, the left hand side term represents the change in sensible heat caused by the decrease in mass during the reaction. This term can be integrated using the simultaneous measurements of both DTA and TGA (thermal gravimetric analysis), and then this integrated value is subtracted from the peak area to effect the total heat of reaction.

3. Fundamental equations for the diluent effect

If the sample is diluted with a substance of the same specific heat, and the fraction of the diluent is termed ϕ , then the equation of heat balance becomes

$$\{(1-\phi)\psi + \phi\} \frac{d\theta}{d\theta_f} = \frac{\theta_f - \theta}{\theta'_f} - (1-\phi)S \frac{d\psi}{d\theta_f} \quad (16)$$

Taking the same amount of the diluent to the referential cell and its temperature being represented by θ_r , the heat balance for the referential substance becomes

$$\phi \frac{d\theta_r}{d\theta_f} = \frac{\theta_f - \theta_r}{\theta'_f} \quad (17)$$

Subtracting Eq. (17) from Eq. (16) gives

$$(1-\phi)\psi \frac{d\theta}{d\theta_f} - \phi \frac{d(\theta_r - \theta)}{d\theta_f} = \frac{\theta_r - \theta}{\theta'_f} - (1-\phi)S \frac{d\psi}{d\theta_f} \quad (18)$$

Integrating

$$\int_{\theta_0}^{\infty} \psi d\theta + \phi \theta'_f = \frac{1}{1-\phi} \int_{\theta_0+\theta'_f}^{\infty} \frac{\theta_r - \theta}{\theta'_f} d\theta_f - S \int_1^0 d\psi \quad (19)$$

The first term in the right hand side of the above equation corresponds to the peak area of the DTA curve and represents the heat transferred per unit amount of the reactant. The second term is the dimensionless heat of reaction.

4. Fundamental equations under the constant mass condition

The same calculations are performed for the reactive sample under a constant mass condition in order to compare with those under a decreasing mass condition. The equation of heat balance becomes

$$\frac{d\theta}{d\theta_f} = \frac{\theta_f - \theta}{\theta'_f} - S \frac{d\psi}{d\theta_f} \quad (20)$$

in place of Eq. (10). As for the referential substance, the equation of heat balance becomes

$$\frac{d\theta_r}{d\theta_f} = \frac{\theta_f - \theta_r}{\theta'_f} \quad (21)$$

In this case the area under the peak is evaluated by

$$\int_{\theta_0+\theta'_f}^{\infty} \frac{\theta_r - \theta}{\theta'_f} d\theta_f$$

and is found to be equal to the dimensionless heat of reaction, $(-S)$ (see Appendix).

5. Numerical calculations of the fundamental equations

The set of Eqs. (10) to (12), Eq. (18), and the set of Eqs. (20), (21) can be solved by analytical methods, providing the nonlinearity in θ is removed; otherwise, one must resort to numerical techniques. In this paper these numerical methods are adopted and among these, the authors performed the successive calculations with use of Adams-Moulton method, one of the predictor-corrector methods, which has relatively small calculation time. Since the fundamental equation (20) has an decreasing term ψ in the denominator, the solution of the equation is inclined to become unstable and come to diverge as the reaction proceeds. In order to prevent from diverging, the increment of the successive steps of the calculation must be reduced several times. Eqs. (15) and (19) are integrated numerically using the trapezoidal rule at each step of the successive calculation.

The accuracy of the numerical solutions is examined by comparing with that of the integrated values. The standard deviation of the solution is $\pm 0.3 \times 10^{-2}$ against to the total heat of reaction, i.e., 1.

All the calculations are performed for the case of an endothermic reaction ($S = -1$). The initiation temperature of the reaction, θ_0 is determined as the point where the value of the reaction rate becomes appreciable, e.g., $-d\psi/d\theta_f = 0.2 \times 10^{-2}$.

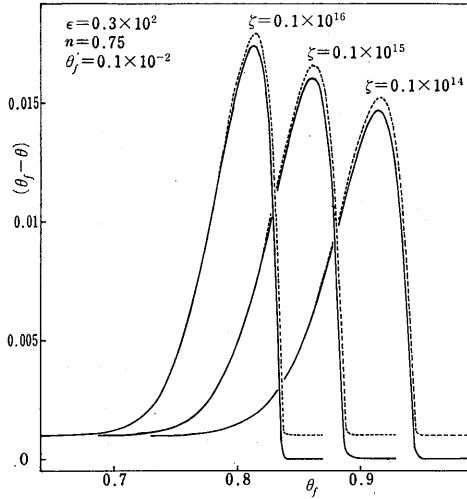
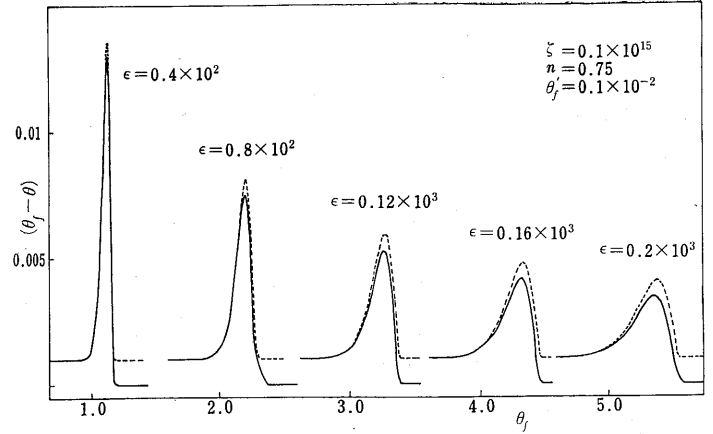
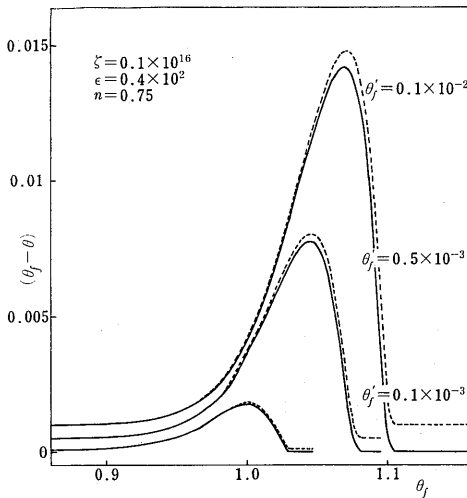
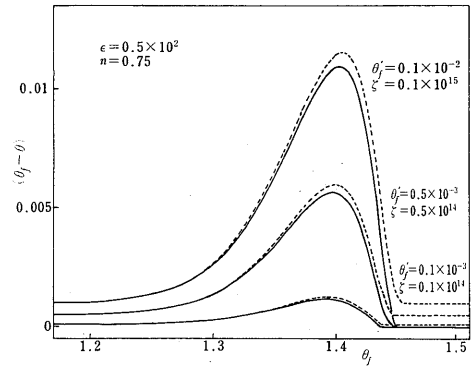
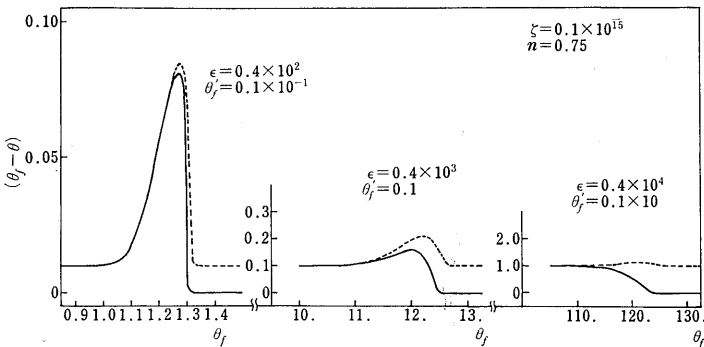
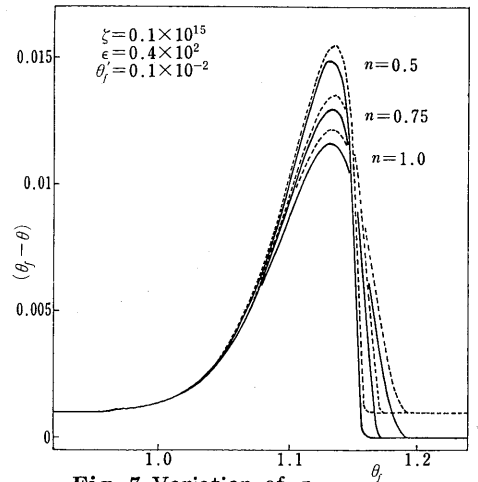
A Facom 270-30 digital computer at the Computer Center of the Chubu Institute of Technology was used for the calculations.

6. Characteristics of DTA curves

The responses and sensitivity of the curve to systematic changes in the various dimensionless input parameters were investigated. Several sets of problems were solved in which all of the input parameters for a given set were held constant except one. Results are shown in Figs. 2 to 7. In the figures the solid line represents the DTA under the decreasing mass condition, while the dotted curve under the constant mass condition. The numerical values chosen for the kinetic parameters are representative of the pyrolysis of polystyrene, as shown in the literature¹⁸⁾, and the heat of polymerization of polystyrene was chosen for the numerical value of the heat of reaction. On the basis of these values, the parameters were changed within the following ranges.

$$\begin{aligned}\varepsilon &: 0.3 \times 10^2 \sim 0.4 \times 10^4 \\ \zeta &: 0.1 \times 10^{14} \sim 0.1 \times 10^{16} \\ n &: 0.5 \times 10^0 \sim 0.1 \times 10^1 \\ \theta_f' &: 0.1 \times 10^{-8} \sim 0.1 \times 10^1\end{aligned}$$

The effect of varying the frequency factor, ζ , by two orders of magnitude can be seen in Fig. 2. As ζ is increased, the curve is shifted to the left, and the peak of the curve rises. Variation of ε has an effect upon the DTA curve as shown in Fig. 3. Again, both the location and shape of the curve are affected, but the dependence is

Fig. 2 Variation of ζ Fig. 3 Variation of ε Fig. 4 Variation of θ'_f Fig. 5 Variation of α Fig. 6 Variation of β Fig. 7 Variation of n

inverse to that observed for ζ . It is found in these figures that both solid and dotted curves have almost the same location of the peak. Therefore, the dependence of the location of the peak upon those parameters, ε , ζ is considered approximately identical to the results of Reed, et al¹⁷. Thus, it can be seen that an increase in ε affects the peak location to approximately the same extent as a decrease in $\ln \zeta$.

Variation in dimensionless heating rate has a relatively small effect on the location of the DTA curve (Fig. 4). As θ_f' is increased, the curve is increased, the curve is shifted slightly to the right, and at the same time the peak height increases.

A variation in the thermal properties of the system (α , β) affects all three of the previously mentioned input parameters. Since both ζ and θ_f' vary linearly with α , it is expected that as α is increased, both θ_f' and ζ rise and that the peak height rises, whereas both effects on the location of the peak are cancelled with each other. Therefore, the location of the peak is held constant with the variation in α . This corresponds to the situation of varying the heat input rate under the constant heating rate. This behavior is observed in Fig. 5 where α is varied by one order of magnitude.

The effect of varying β , by two order of magnitude, on the DTA curve is demonstrated in Fig. 6. Since both ε and θ_f' vary linearly with β , it can be seen that the location of the curve is shifted to the right and the peak height rises, as β increases. In Fig. 6 the scales of both abscissa and ordinate are increased by each one order of magnitude, depending upon the increasing β . Thus, it is observed that the shape of the DTA curve is flattened and the sensitivity of the DTA falls as β increases. In case of $\varepsilon = 0.4 \times 10^4$, there found no peak in the curve under the decreasing mass condition, and only the drifted base line is observed. This corresponds to the large amount of the sensible heat change compared with the heat of reaction. In case of the dotted curve, the peak is appreciable but its height is very small compared with θ_f' . Since the sensitivity and the resolving power of the DTA apparatus are extremely low in such a case, it is suggested that the DTA should have little value.

The effect of varying n on the shape of the DTA curve is shown in Fig. 7. Although the location of the peak remains nearly unchanged, the peak height increases significantly with decreasing n . The curve begins to be flattened out as n increases, but as the reverse is the case, the curve begins to have a sharp peak.

7. Comparison with the results under the constant mass condition

All the above results are compared with those under the constant mass condition (as shown by dotted curve in all figures). In every case, the differences between the both results are very small, and especially in the region of the small value of β (Fig. 6), both curves coincide fairly well with each other. The effect of the various parameters upon the differences between the peak heights under the both conditions is tabulated in Table 1. The peak height under the decreasing mass condition is always lower than that under the constant mass condition. The variation of the three kinetic parameters has a slight effect on the peak height difference, but from the effect of n on the difference, it is recognized that the difference increases slightly with in-

creasing sharpness of the peak. Whereas, the heating rate, θ'_f has a significant effect,

Table 1. Comparison between peak heights

effect of ζ ($\varepsilon=0.4 \times 10^2$ $n=0.75$ $\theta'_f=0.5 \times 10^{-2}$)	
	peak height
$\zeta=0.1 \times 10^{14}$	0.313×10^{-3}
0.1×10^{15}	0.309×10^{-3}
0.1×10^{16}	0.305×10^{-3}
effect of ε ($\zeta=0.1 \times 10^{14}$ $n=0.75$ $\theta'_f=0.1 \times 10^{-2}$)	
	peak height
$\varepsilon=0.3 \times 10^2$	0.560×10^{-3}
0.4×10^2	0.600×10^{-3}
0.5×10^2	0.616×10^{-3}
effect of n ($\zeta=0.1 \times 10^{16}$ $\varepsilon=0.3 \times 10^2$ $\theta'_f=0.5 \times 10^{-2}$)	
	peak height
$n=0.5$	0.310×10^{-3}
0.75	0.289×10^{-3}
1.0	0.273×10^{-3}
effect of θ'_f ($\zeta=0.1 \times 10^{14}$ $\varepsilon=0.3 \times 10^2$ $n=0.75$)	
	peak height
$\theta'_f=0.1 \times 10^{-2}$	0.650×10^{-4}
0.5×10^{-2}	0.313×10^{-3}
0.1×10^{-1}	0.600×10^{-3}

and the difference increases markedly with increasing θ'_f . However, the numerical value of the temperature difference is relatively small and does not exceed the heating rate, θ'_f . It is expected from the effect of n in that table that the maximum difference should take place at the most sharp peak condition, i.e., at which the reaction has an impulse function of the reaction rate. In this case, the fundamental equations become simple and can be solved easily with such an analytical method as the Laplace transformation. Under the constant mass condition, the equation of heat balance coincides with Eq. (20) excluding the fact that the reaction term is imposed at the initiation in an impulsive manner. The solution becomes

$$\theta = \theta_f - (\theta'_f + 1)e^{-(\theta_f - \theta_0 - \theta'_f)/\theta'_f} \quad (22)$$

Thus, the value of the DTA peak is equal to $(\theta'_f + 1)$, whereas under the decreasing mass condition, the peak value is found to be unity. Therefore, the maximum difference of the peak value between the both conditions is equal to the heating rate, θ'_f .

8. Calculation of the heat of reaction by integration

The area under the DTA curve under the constant mass condition always coincides with $(-S)$, whereas it has the value bigger than $(-S)$ under the decreasing mass condition since the additive term representing the change in sensible heat is included. The numerical values of the dimensionless peak area are represented in the first

Table 2. Integrated values and peak areaeffect of ζ ($\varepsilon=0.4 \times 10^2$ $n=0.75$ $\theta'_f=0.5 \times 10^{-3}$)

	total area	$\int_{\theta_0}^{\infty} \psi d\theta$	$-\int_1^0 (\theta - \theta_0) d\psi$
$\zeta=0.1 \times 10^{14}$	1.215	0.2162	0.2167
0.1×10^{15}	1.195	0.1958	0.1960
0.1×10^{16}	1.177	0.1779	0.1781

effect of ε ($\zeta=0.1 \times 10^{15}$ $n=0.75$ $\theta'_f=0.5 \times 10^{-3}$)

	total area	$\int_{\theta_0}^{\infty} \psi d\theta$	$-\int_1^0 (\theta - \theta_0) d\psi$
$\varepsilon=0.3 \times 10^2$	1.152	0.1523	0.1526
0.4×10^2	1.195	0.1958	0.1960
0.5×10^2	1.236	0.2373	0.2378

effect of n ($\zeta=0.1 \times 10^{16}$ $\varepsilon=0.4 \times 10^2$ $\theta'_f=0.5 \times 10^{-3}$)

	total area	$\int_{\theta_0}^{\infty} \psi d\theta$	$-\int_1^0 (\theta - \theta_0) d\psi$
$n=0.5$	1.175	0.1746	0.1744
0.75	1.177	0.1779	0.1781
1.0	1.181	0.1814	0.1817

effect of θ'_f ($\zeta=0.1 \times 10^{15}$ $\varepsilon=0.5 \times 10^2$ $n=1.0$)

	total area	$\int_{\theta_0}^{\infty} \psi d\theta$	$-\int_1^0 (\theta - \theta_0) d\psi$
$\theta'_f=0.1 \times 10^{-3}$	1.224	0.2250	0.2274
0.5×10^{-3}	1.241	0.2421	0.2424
0.1×10^{-2}	1.248	0.2487	0.2491

column of Table 2, and the integrated value of the left hand side of Eq. (14), i.e., the change in sensible heat of the sample material, is tabulated in the second column. This term can be modified with the integration by parts

$$\int_{\theta_0}^{\infty} \psi d\theta = -\int_1^0 (\theta - \theta_0) d\psi \quad (23)$$

The numerical value of this integration is also listed in the last column. It is observed in that table that the difference between the peak area and the change in sensible heat coincides with the dimensionless heat of reaction (1) within the error of the numerical calculation. The effect of the varying kinetic parameters on the term of the sensible heat is demonstrated in the table. This term decreases slightly with increasing ζ and with decreasing both ε and n . These phenomena correspond to the change in sharpness of the DTA peak as shown in the previous figures. Although the sensible heat term increases with the increasing heating rate, θ'_f , this term is much less than unity when β is sufficiently small. Thus, under the decreasing mass condition it is also possible to estimate the heat of reaction directly from the area under the DTA curve. When it is possible to measure the DTA and the TGA simultaneously, the integration of the sensible heat term can be done (the left hand side of Eq. (14) or the right hand side of Eq. (23)), and gives more accurate estimation of the heat of reaction.

9. The diluent effect

There are many literatures about the diluent effect upon the DTA curve^{8, 19, 20)}, and in these work the effects of the varying thermal conductivity and heat capacity of the diluent upon the area of the curve are investigated. Some theoretical analysis has been done under an assumption that the heat capacity of the sample remains constant during the reaction by introducing the diluent^{1, 21)}. In this section, the validity of the dilution applied to the sample whose mass decreases in the reaction is discussed.

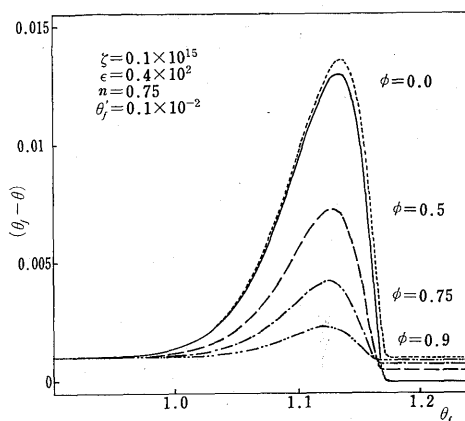


Fig. 8 Diluent effect

Fig. 8 shows the diluent effect on DTA curves, where the sample is diluted with the diluent with the same specific heat capacity and the fractions of the diluent, ϕ are 0.0, 0.5, 0.75 and 0.9. Numerical values of the area and the sensible heat term per unit mass of the sample material are tabulated in Table 3. The sensible heat term is somewhat larger than that of non-diluting case ($\phi=0.0$), and increases slightly with increasing ϕ . As mentioned in the previous section, both of the integrated terms also increase with the increasing heating rate.

Thus, the dilution method which is often used

Table 3. Diluent effects on peak area

$\theta'_f=0.1 \times 10^{-2}$	$\phi=0.0$	$\phi=0.5$	$\phi=0.75$	$\phi=0.9$
total area	1.178	1.179	1.179	1.180
$\int_{\theta_0}^{\infty} \psi d\theta + \phi \theta'_f$	0.1844	0.1844	0.1845	0.1845
$(\zeta=0.1 \times 10^{15} \quad \epsilon=0.4 \times 10^2 \quad n=0.75)$				
$\theta'_f=0.1 \times 10^{-2}$	$\phi=0.0$	$\phi=0.5$	$\phi=0.75$	$\phi=0.9$
total area	1.200	1.203	1.204	1.204
$\int_{\theta_0}^{\infty} \psi d\theta + \phi \theta'_f$	0.2009	0.2019	0.2025	0.2028
$(\zeta=0.1 \times 10^{15} \quad \epsilon=0.4 \times 10^2 \quad n=0.75)$				

to prevent the drift of the base line is found to be unprofitable for the quantitative determination of the heat of reaction. Moreover, in practice, the sensitivity and the accuracy of the DTA fall considerably when the diluent is added.

10. Concluding remarks

The DTA curve for the gas-liquid (or solid) phase reaction accompanied by the decrease in mass is analysed theoretically by solving simultaneously a set of the equations for the reaction rate and for the heat balance, and then the effects of several parameters of the kinetics and the heat transfer on the behavior of the DTA curve are demonstrated. By integrating the equations, the relationship between the peak area and the total heat of reaction is discussed quantitatively. These results are

compared with those obtained under the constant mass condition, and also the validity of the dilution is examined theoretically. Thus, the following results are obtained.

- (i) The DTA curve under the decreasing mass condition has nearly the same behavior as that under the constant mass condition.
- (ii) The differences between the peak heights under the both conditions do not exceed the dimensionless heating rate.
- (iii) Under the decreasing mass condition, it is feasible to estimate the heat of reaction directly from the area of the DTA curve.
- (iv) The change in the sensible heat is evaluated directly from the simultaneous measurements of both TGA and DTA, and the total heat of reaction can be calculated accurately.
- (v) The dilution with an inert substances has no profitable effect on the quantitative characterization of the DTA curve.

Notation

A :	area of heat transfer
c_p :	specific heat
E :	activation energy
ΔH :	heat of reaction
h :	heat transfer coefficient
K :	heating rate
n :	order of reaction
R :	gas constant
S :	parameter indicating exo- or endothermic reaction
T :	absolute temperature
t :	time
w :	weight of reactant
Z :	frequency factor
α :	$c_p w_0 / hA$
β :	$c_p / \Delta H $
ε :	dimensionless activation energy
ζ :	dimensionless frequency factor
θ :	dimensionless temperature
θ'_f :	dimensionless heating rate
τ :	dimensionless time
ϕ :	fraction of diluent
ψ :	fraction of unreacted reactant

—Subscripts—

f :	furnace
o :	initiation of reaction
r :	referential condition

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Appendix

Vold¹⁾ used the final point of the reaction as the limit of the integration in their work on the heat of transition of stearic acid, and did not adopt the total area under the peak, as shown in Fig. 9.

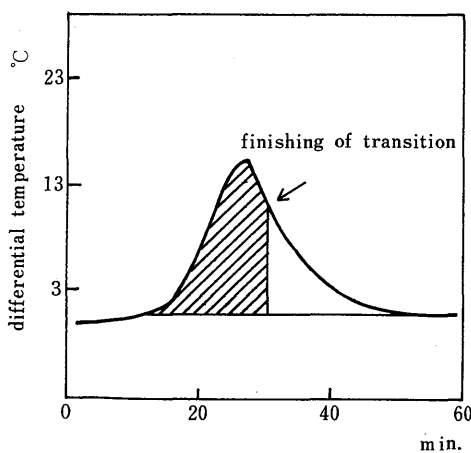


Fig. 9 DTA curve for transition¹⁾

The equations of heat balance for the transition are Eqs. (20) and (21), and subtraction of Eq. (21) from (20) gives

$$-\frac{d(\theta_r - \theta)}{d\theta'_f} = \frac{\theta_r - \theta}{\theta'_f} - S \frac{d\psi}{d\theta'_f}$$

Integrating from the initiation to infinity gives

$$\int_{\theta_0 + \theta'_f}^{\infty} \frac{\theta_r - \theta}{\theta'_f} d\theta'_f = 1$$

It is found clearly that the total heat of reaction coincides with the peak area. But if the upper limit of integration is considered to be the finishing point of the transition, θ is not always equal to θ_r at that point. Therefore, the integration of the left hand side of Eq. (24) does not fall to

zero. Consequently, it is contradictory to evaluate the heat of transition from the peak area hatched in the figure.