SEPARATION OF DTA PEAKS OF A MULTISTAGE REACTION

N. ITO

Process Research and Development Division, National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305 (Japan)

(Received 29 November 1983)

ABSTRACT

It is important that overlapping DTA peaks of a multistage reaction are mutually separated more clearly in terms of the identification of the reaction and the evaluation of the heat of reaction. Basic equations to predict DTA and TGA curves with respect to two-stage thermal decomposition were derived and numerically solved by using previously given kinetic parameters and heats of decomposition. As a result, it was obvious that the degree of separation of DTA peaks increases with varying heating rate, HR, that is, with an increase of HR in the case of $E_1 > E_2$ and with a decrease of HR in the case of $E_1 < E_2$.

INTRODUCTION

It is known that the thermal decomposition of $CuSO_4 \cdot 5\ H_2O$, $CaC_2O_4 \cdot H_2O$, $PbCO_3$, etc., are multistage reactions. In the corresponding TGA (thermogravimetric analysis) and DTA (differential thermal analysis) curves, two cases can be found: (1) reactions including a multistage reaction take place independently without overlapping with each other; (2) two, three or more reactions overlap one another. In identifying the reaction or evaluating the heat of reaction from the DTA peak areas, the former causes no problem because the weight change on the TGA curve or the DTA peak corresponds to only one reaction. However, the same is not true for the latter, so that the overlapping reactions, namely overlapping DTA peaks, should be separated more clearly.

Many investigations with respect to kinetic analysis [1–5] and measurement of reaction heat [6–8] by use of DTA curves of single reaction have been performed. However, few reports have appeared [9] for a multistage reaction, probably due to its complication. Recently, we discussed the two-stage thermal decomposition of $Mg(IO_3)_2$ from the viewpoint of determining the heats of decomposition; it was found that they can be evaluated by analyzing the experimentally obtained DTA curve [10].

In this communication, basic equations to simulate TGA and DTA curves with respect to two-stage reactions are derived. By use of the peak ratio,

which is the ratio of two overlapping DTA peak areas and is a parameter to represent the degree of separation between two peaks, theoretical considerations can be made in order to obtain more clearly separated DTA peaks.

BASIC EQUATIONS

Two-stage thermal decomposition is taken, being the simplest example of a multistage reaction. For derivation of basic equations the following model describing a two-stage thermal decomposition is considered

Reaction $M_1 \rightarrow M_2 \rightarrow M_3$
Weight $w_1 \quad w_2 \quad w_3$ (kg)
Specific heat $C_{p1} \quad C_{p2} \quad C_{p3}$ (kJ kg^{-1} K^{-1})
Heat of decomposition ΔH_1(kJ kg^{-1}-M$_1$) ΔH_2(kJ kg^{-1}-M$_3$)

By DTA, the temperature difference produced between reference and sample with a rise in temperature is recorded. If no temperature distribution there exists, both in reference material and sample, the heat balance is represented as

(reference)

$$C_{pr}w_r \, d(T_r - T_0)/dt = K_r(T_f - T_r) \tag{1}$$

(sample)

$$d\left\{ \sum_{i=1}^{3} C_{pi}w_i(T_s - T_0) \right\}/dt = K_s(T_f - T_s) - (-\Delta H_1) \, dw_1/dt$$
$$+ (-\Delta H_2) \, dw_3/dt \tag{2}$$

where T_r, T_s, T_f and T_0 (K) are reference, sample, furnace and initial temperatures, respectively, and K_r and K_s (J h^{-1} K^{-1}) are proportional constants with heat transfer in the furnace. The w_i is instant weight of component i, and it was assumed that C_{pr} and C_{pi} are constant in the temperature range in which decomposition is occurring.

Assuming that $K_r = K_s$ and $C_{p1}w_1^0 = C_{pr}w_r$, eqn. (2) − eqn. (1) is written as

$$d\{\delta(T_s - T_0)\}/dt = \left(K_s/C_{p1}w_1^0 \right)(T_r - T_s) - (-\Delta H_1/C_{p1}) \, d\psi_1/dt$$
$$+ \left(-\Delta H_2 w_3^0/C_{p1}w_1^0 \right) d\psi_3/dt + dT_r/dt \tag{3}$$

where $\psi_1 = w_1/w_1^0$, $\psi_2 = w_2/w_2^0$, $\psi_3 = w_3/w_3^0$, $\mu_2 = C_{p2}w_2^0/C_{p1}w_1^0$, $\mu_3 = C_{p3}w_3^0/C_{p1}w_1^0$ and $\delta = \psi_1 + \mu_2\psi_2 + \mu_3\psi_3$. T_r is controlled to rise linearly at a constant rate, HR (K h^{-1}), as

$$T_r = HRt + T_0 \tag{4}$$

Assuming that $\delta = 1$, the variable t (h) is transformed to a dimensionless

temperature θ $(= C_{p1}T/|\Delta H_1|)$ by use of Eqn. (4), so that Eqn. (3) can be rewritten as

$$d(\theta_s - \theta_0)/d\theta_r = \alpha(\theta_r - \theta_s) - d\psi_1/d\theta_r + B_e \, d\psi_3/d\theta_r + 1 \qquad (5)$$

where $\alpha = K_s/C_{p1}w_1^0 HR\beta$, $\beta = C_{p1}/|\Delta H_1|$, $\theta_r = \beta T_r$, $\theta_s = \beta T_s$, $\theta_0 = \beta T_0$ and $B_e = w_3^0 \Delta H_2/w_1^0 \Delta H_1$.

On the other hand, a fractional weight loss ΔW_T obtained from a TGA curve is represented as

$$\Delta W_T = \{ w_1^0 - (w_1 + w_2 + w_3) \}/(w_1^0 - w_3^0) \qquad (6)$$

Considering various forms with regard to the kinetics of the two reactions, the rates of reactions are assumed to be described by the following equations

$$d\psi_1/d\theta_r = -\zeta_1 \, e^{-\epsilon_1/\theta} \psi_1^{n_1} \qquad (7)$$

$$d\psi_2/d\theta_r = +\zeta_1 \, e^{-\epsilon_1/\theta} \psi_1^{n_1} - \zeta_2 \, e^{-\epsilon_2/\theta} \psi_2^{n_2} \qquad (8)$$

$$\psi_3 = 1 - \psi_1 - \psi_2 \qquad (9)$$

and the initial condition is given as

$$\text{at } \theta_r = \theta_s = \theta_0, \psi_1 = 1 \text{ and } \psi_2 = \psi_3 = 0 \qquad (10)$$

where $\epsilon_j = \beta E_j/R$, $\zeta_j = Z_j/\beta HR$ ($j = 1$ or 2), and E_j, Z_j, n_j are activation energy, frequency factor and reaction order for the reaction $M_j \to M_{j+1}$, respectively.

Integrating eqns. (5)–(9) numerically under the initial condition, eqn. (10), a DTA curve from θ_r vs. $\Delta\theta (= \theta_r - \theta_s)$ and a TGA curve from θ_r vs. ΔW_T are simultaneously predicted. In order to examine the effects of the kinetic parameters on the TGA and DTA curves, calculations were carried out by the Runge–Kutta–Gill method using two typical sets of kinetic parameters as

$C_{p1} = 0.418$ kJ kg^{-1} K^{-1}; $K_s = 0.1$ J h^{-1} K^{-1}

$w_1^0 = 50$ mg; $w_2^0 = 18$ mg; $w_3^0 = 10$ mg

$\Delta H_1 = 480$ kJ kg^{-1}-M$_1$; $\Delta H_2 = 1930$ kJ kg^{-1}-M$_3$

(1) In the case of $E_1 > E_2$

$E_1 = 251.2$ kJ mol^{-1}; $Z_1 = 3.6 \times 10^{18}$ h^{-1}; $n_1 = 1.0$

$E_2 = 125.6$ kJ mol^{-1}; $Z_2 = 1.6 \times 10^8$ h^{-1}; $n_2 = 1.0$

(2) In the case of $E_1 < E_2$

$E_1 = 125.6$ kJ mol^{-1}; $Z_1 = 1.6 \times 10^{10}$ h^{-1}; $n_1 = 1.0$

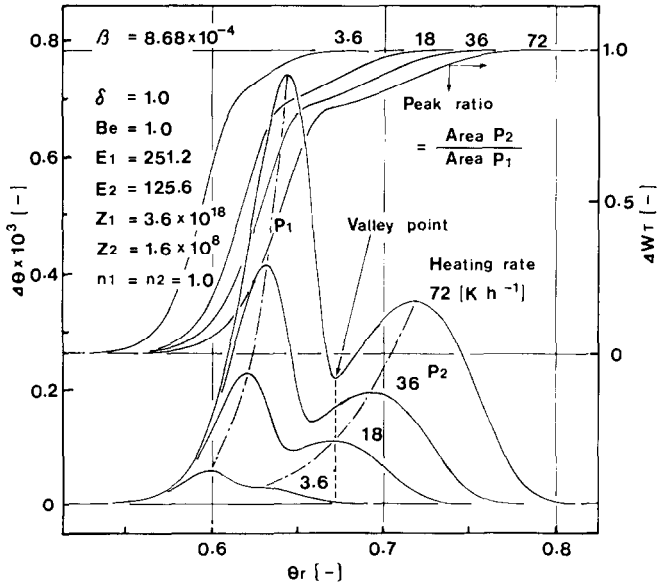$E_2 = 251.2$ kJ mol^{-1}; $Z_2 = 3.6 \times 10^{18}$ h^{-1}; $n_2 = 1.0$

Fig. 1. Theoretical DTA and TG curves in the case of $E_1 > E_2$.

CALCULATION RESULTS AND DISCUSSION

Since it is generally known that in DTA and TGA the initial decomposition temperature shifts to the higher temperature side and the DTA peak
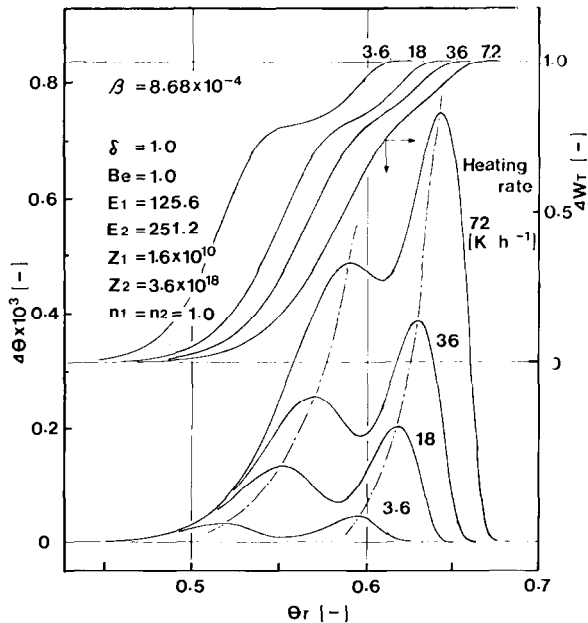

Fig. 2. Theoretical DTA and TG curves in the case of $E_1 < E_2$.

increases with increasing heating rate (HR). HR is considered to be the most important factor affecting the shape of TGA and DTA curves. Therefore, the behavior of TGA and DTA curves with varying HR is shown in Figs. 1 and 2. From these figures, it can be found qualitatively that the degree of separation of two DTA peaks increases with increasing HR in the case of $E_1 > E_2$ while with decreasing HR in the case of $E_1 < E_2$.

In order to represent the degree of separation quantitatively, the peak ratio as shown in Fig. 1 is defined and calculated as

$$\text{peak ratio} = \{\psi_{1v} + B_e(1 - \psi_{3v})\} / \{(1 - \psi_{1v}) + B_e\psi_{3v}\} \tag{11}$$

where ψ_{1v} and ψ_{3v} are fractional abundances of components 1 and 3 at the valley point as seen in Fig. 1, respectively. $B_e (= w_3^0 \Delta H_2 / w_1^0 \Delta H_1)$ is the theoretical peak ratio, that is, the value at the point where the two peaks are completely separated from each other, that is, $\psi_{1v} = 0$ and $\psi_{3v} = 0$.

The relations between peak ratio and HR obtained from the DTA curves in Figs. 1 and 2 are shown in Figs. 3 and 4, respectively. In the case of $E_1 > E_2$ (Fig. 3), the peak ratio approaches the theoretical value, 1, with an increase of HR, namely, the degree of separation between the two peaks increases. However, the peak ratio is nearly 1 with the small value of HR in the case of $E_1 < E_2$ (Fig. 4), and the valley disappears above ~ 120 K h^{-1}: the two peaks become one. The relative position and size of the two DTA peaks is determined mainly by the kinetic parameters and the heats of reactions, it will therefore vary according to the combination of the parameters. However, the discussion described above is considered also to apply to those cases.

The results obtained above give another useful piece of information for evaluating the heat of reaction from each area of the overlapped peaks graphically. Namely, if more accurate values for the heat of reaction is desired, the degree of separation of the DTA peaks can be increased by varying HR.
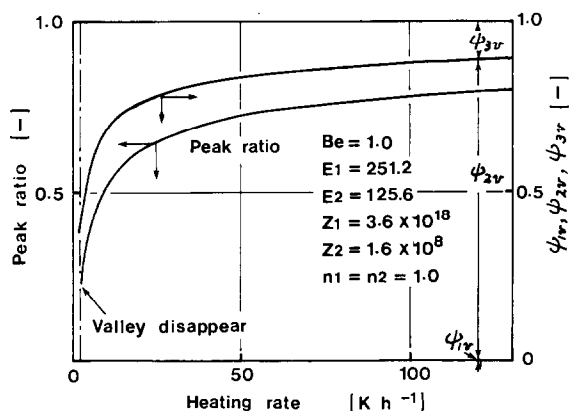

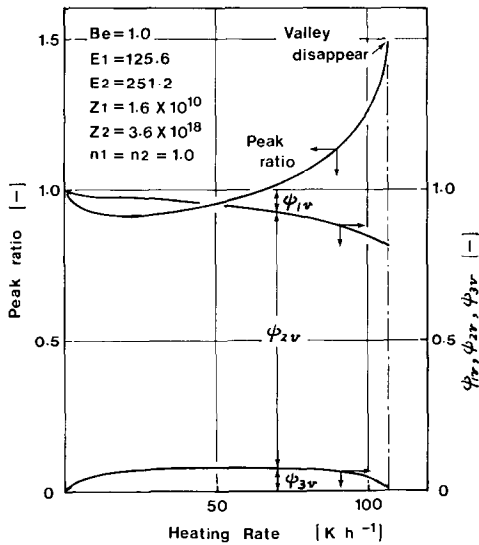Fig. 3. Relation between peak ratio and heating rate, HR, in the case of $E_1 > E_2$.

Fig. 4. Relation between peak ratio and heating rate, HR, in the case of $E_1 < E_2$.

CONCLUSION

The separation of overlapped DTA peaks in a multistage reaction was theoretically discussed in order to identify the reaction or evaluate more accurately the heat of decomposition. DTA and TGA curves were predicted on the basis of basic equations derived to simulate the curves with respect to two-stage thermal decomposition. It was found that the degree of the separation, which is represented quantitatively by the peak ratio in this communication, can be changed by varying the heating rate, HR.

REFERENCES

1 H.E. Kissinger, Anal. Chem., 29 (1957) 1702.
2 H.J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.
3 K. Akita and M. Kase, J. Phys. Chem., 72 (1968) 906.
4 R.L. Reed, L. Weber and S. Gottfried, I.E.C. Fund., 4 (1965) 38.
5 R.T. Yang and M. Steinberg, Anal. Chem., 49 (1977) 998.
6 E. Sturm, J. Phys. Chem., 65 (1961) 1935.
7 R.D. Vold, J. Am. Chem. Soc., 63 (1941) 2915.
8 T. Ozawa, Bull. Chem. Soc. Jpn., 39 (1966) 2071.
9 S. Imai, H. Murotani, H. Morikawa and H. Aoki, Yogyo Kyokai-Shi, 77 (1969) 411.
10 N. Ito, K. Obata, T. Hakuta and H. Yoshitome, Kagaku Kogaku Ronbunshu, 9 (1983) 434.