

# The effect of the reaction heat on kinetic analysis by TG under a rising temperature program.

## Part 1

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### Abstract

The reaction heat changes the temperature of the sample, making its temperature different to the rising temperature program imposed upon it. Based on certain assumptions, a relationship between temperature  $T$  and time  $t$  is obtained as a function of the conversion degree  $\alpha$ . A simulation of TG, DTG and  $T-t$  curves under such temperature programs and the ideal rising temperature program has been made, which shows how the reaction heat affects these curves. A kinetic analysis study is also obtained to enable the calculation of the Arrhenius parameters and the determination of reaction mechanisms, by using both the integral and differential methods. The results show that the differential method is much better than the integral method.

### INTRODUCTION

Non-isothermal kinetic analysis has many advantages over classical isothermal kinetic analysis [1]. In practice, most non-isothermal kinetic analysis methods are based on the rising temperature program expressed in the form

$$T = T_0 + \beta t \quad (1)$$

where  $T$  is the temperature of the furnace at time  $t$ ,  $T_0$  is the starting temperature and  $\beta$  is the constant heating rate.

Owing to the mechanistic difficulty of controlling the sample's temperature in presently available TG instrumentation, the rising temperature program is used in the computer work station in a default form controlling the temperature of the furnace. When a reaction has no heat absorbed or heat evolved, the temperature of the furnace is equal to the temperature of the sample. The temperature recorded in the TG curve is supposed to

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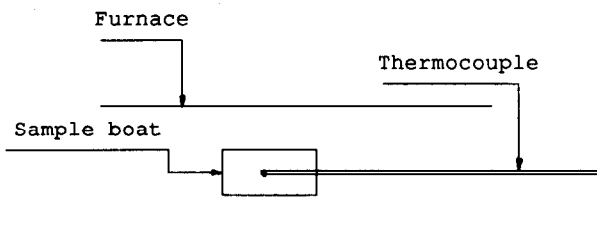


Fig. 1. The typical layout for the location of the thermocouple in a TG unit.

be equal to the temperature of the sample if this temperature is measured by a thermocouple placed adjacent to the sample. Figure 1 is a descriptive diagram showing the location of the thermocouple for a TG instrument with a horizontal furnace system. Thus when no reaction heat is created, the time-temperature curve should be a straight line. Generally speaking, almost every chemical reaction will result in a change of enthalpy, which means that when a reaction occurs in the sample, it would either absorb heat from or evolve heat to the environment. Therefore, the temperature would be a little lower than that of the furnace when the heat is absorbed and a little higher when the heat is evolved. Figure 2 shows an experimental TG curve and temperature-time curve for the dehydration of manganese oxalate dihydrate. The non-linearity of the relationship between temperature and time is obvious. Thus the assumption that during the whole period of reaction the temperature would be rising at a

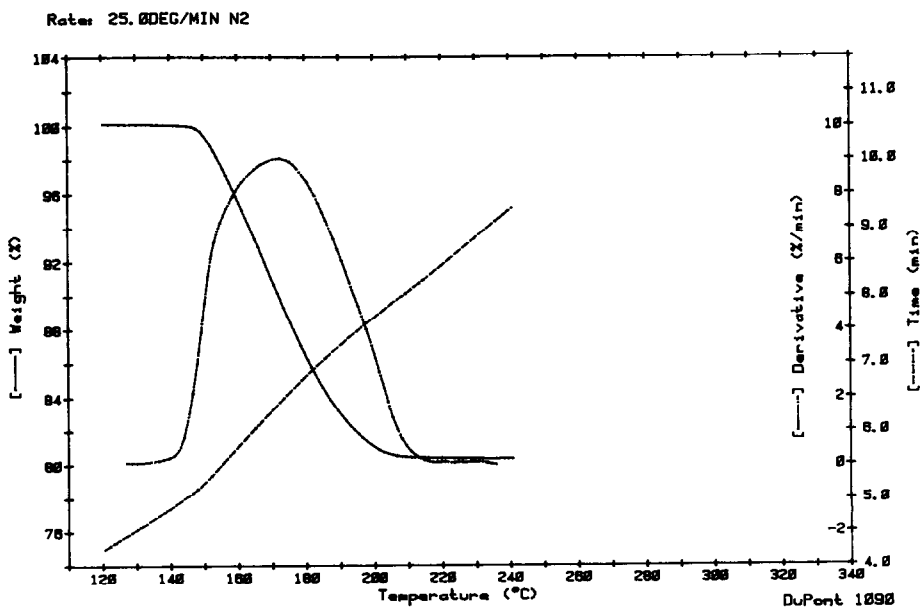


Fig. 2. Typical TG curve for dehydration of manganese oxalate dihydrate.

constant rate is valid only for the ideal situation, not for the actual case. Therefore, it is necessary to simulate the effect of the reaction heat on the temperature–time curve and the TG and DTG curves, and then to judge its effect on the results of the non-isothermal analysis.

## THEORY

Suppose the reaction heat is  $Q$  and the temperature variation caused by  $Q$  is  $\Delta T$ , then the temperature recorded by thermocouple would be

$$T = T_0 + \beta t + \Delta t(t) \quad (2)$$

The reaction heat can be divided into two parts, one related to the sample, the other related to the environment.

The temperature variation  $dT$  of the sample at time  $t$  during  $dt$  time interval would be

$$dT = -\mu [(Q dW/dt)/(C_p W)] dt \quad (3)$$

$$\begin{aligned} \Delta T &= -\mu \int_0^t [(Q dW/dt)/(C_p W)] dt = -\int_W^{W_0} \mu Q dW/(C_p W) \\ &= \mu Q/C_p \ln(W_0/W) \end{aligned} \quad (4)$$

where  $C_p$  is the sample's specific heat,  $W$  is the weight at time  $t$ ,  $\mu$  is a fraction factor representing the amount of the reaction heat that is used to heat or cool the sample.  $Q$  is the reaction heat ( $\text{J g}^{-1}$ ); it is positive for an exothermic reaction and negative for an endothermic reaction.  $W_0$  is the sample weight at time  $t = 0$ .

For a particular reaction,  $Q$ ,  $C_p$  and  $\mu$  should be constant. So let

$$C = \mu Q/C_p \quad (5)$$

$$W_0/W = [W_0/(W_0 - W_t)] / \{ [W_0 - (W_0 - W)] / (W_0 - W_t) \} = a/(a - \alpha) \quad (6)$$

where

$$a = W_0/(W_0 - W_t) \quad (7)$$

$$\alpha = (W_0 - W)/(W_0 - W_t) \quad (8)$$

$\alpha$  is the conversion degree of the sample,  $a$  is a constant related to the initial mass and final residue ( $a > 1$  always).  $C$  is a constant representing the degree of self-heating or self-cooling of the sample.  $W_t$  is the sample weight at the end of the reaction. Then eqn. (2) becomes

$$T = T_0 + \beta t + C \ln[a/(a - \alpha)] \quad (9)$$

So for the actual case of solid decomposition, eqn. (9) and the equations

$$d\alpha/dt = kf(\alpha) \quad (10)$$

and

$$k = A \exp(-E/RT) \quad (11)$$

should be obeyed in considering the effect of the reaction heat;  $k$  is the specific reaction rate constant,  $R$  is the gas constant,  $A$  is the frequency factor and  $E$  is the activation energy.

For the ideal case, ignoring the effect of the reaction heat, eqns. (1), (10) and (11) should be obeyed.

## SIMULATION RESULTS AND DISCUSSION

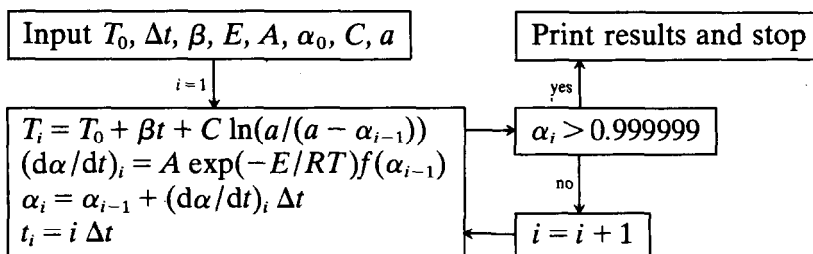
The TG, DTG and  $T-t$  curves can be obtained by solving either eqns. (9), (10) and (11) for the real case, or eqns. (1), (10) and (11) for the ideal case by using a numerical method.

In order to obtain an  $\alpha$  value at each time  $t$ , the approximation

$$\alpha(t + \Delta t) = \alpha(t) + (d\alpha/dt)\Delta t \quad (12)$$

is made, where  $\Delta t$  is a small time interval compared to the time taken for the reaction to go to completion. The smaller  $\Delta t$  is, the better the approximation.

If  $\alpha_0$ ,  $\beta$ ,  $E$ ,  $A$ ,  $\Delta t$ ,  $C$  and  $a$  are given, then the set of data  $t$ ,  $T$ ,  $\alpha$ ,  $d\alpha/dt$  could be calculated for the whole period of the reaction.



The flow chart of the calculation.

For the simulation, the  $f(\alpha)$  chosen is for the A2 mechanism (activation energy  $E = 120 \text{ kJ mol}^{-1}$ ; frequency factor  $A = 1.6 \times 10^{16}$ ). Figure 3(a) shows the changes in the  $T-t$  curves at constant heating rate  $\beta = 10^\circ\text{C min}^{-1}$ , when  $C$  is given different values. Figure 3(b) shows the changes in the TG and DTG curves under the same conditions. Figure 4(a) shows the changes in the  $T-t$  curves at different heating rates when  $C$  is constant; Fig. 4(b) shows the changes of the TG and DTG curves under the same conditions. From Figs. 3 and 4, it can be seen that when  $C$  changes from negative values (corresponding to an endothermic reaction) to positive values (corresponding to an exothermic reaction), the  $T-t$  curves go from a downward slope through a horizontal slope to an upward slope. When the reaction absorbs heat (endothermic), the temperature of

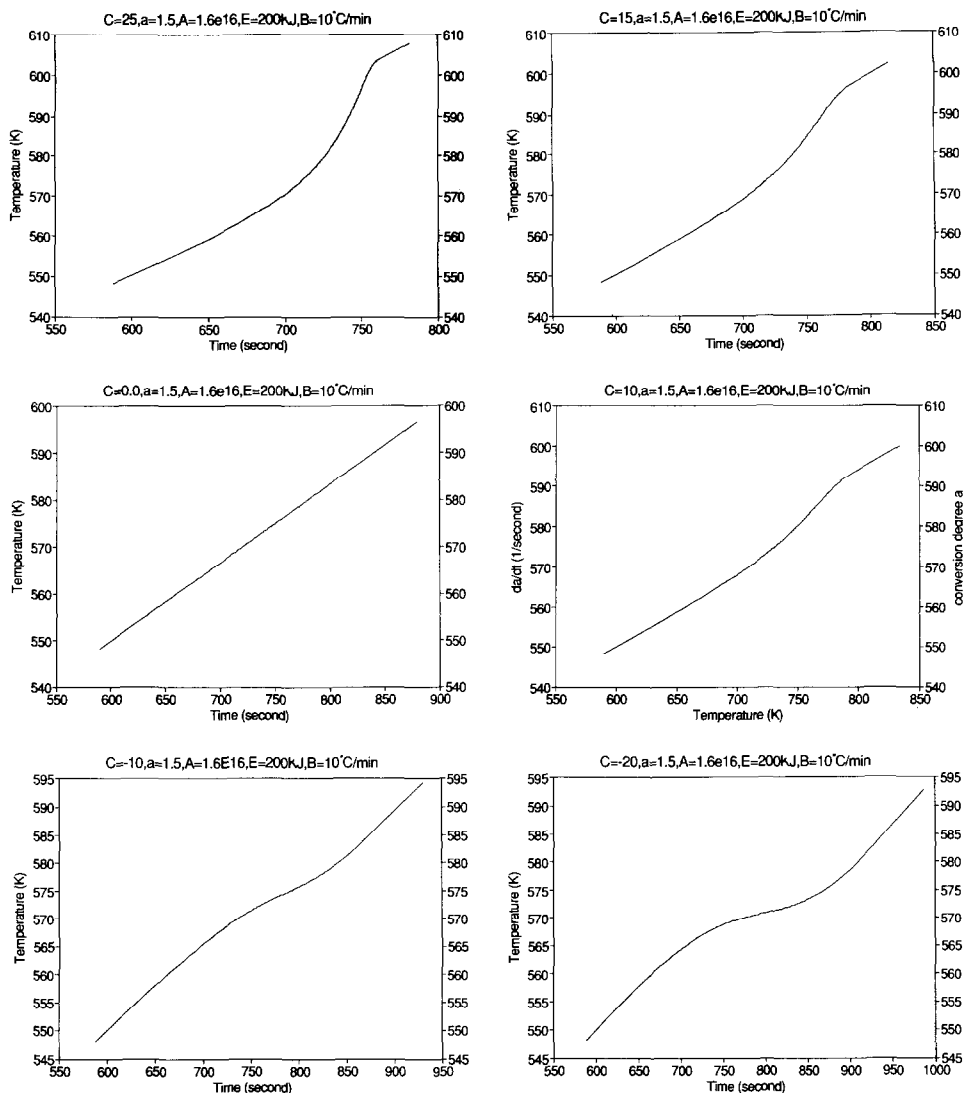


Fig. 3(a). Changes in the  $T-t$  curves at constant heating rate  $\beta = 10^\circ\text{C min}^{-1}$  for various values of  $C$ .

the sample would be lower than that of the furnace and the  $T-t$  curve slopes downward; when the reaction evolves heat, the temperature of the sample would be higher than that of the furnace and the  $T-t$  curve slopes upward; when the reaction has no heat absorbed or evolved the  $T-t$  curve appears a straight line. The peaks of the DTG curves shift from left to right when  $C$  changes, in the same way. When  $C$  is constant, the shapes of the  $T-t$ , TG and DTG curves almost always reflect the same trend at different heating rates.

Tables 1A and 1B shows the changes in the characteristics of the TG

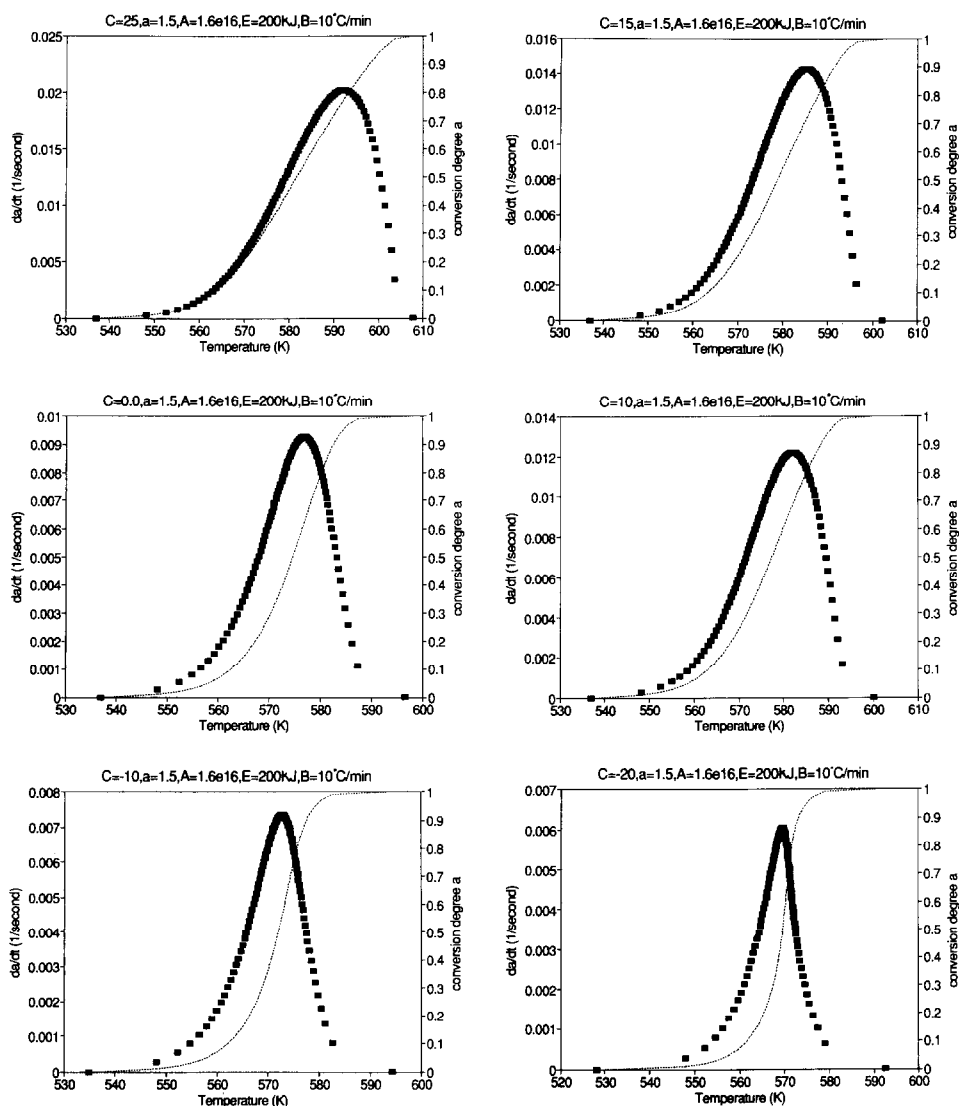


Fig. 3(b). Changes in the TG and DTG curves under the conditions given in Fig. 3(a).

and DTG curves:  $T_i$  is the initial reaction temperature, defined as the temperature at which the  $d\alpha/dt$  is 0.1% of the maximum  $d\alpha/dt$  and  $\alpha$  is almost zero;  $t_i$  is the time required to reach  $T_i$ ;  $(d\alpha/dt)_{\max}$  is the maximum reaction rate;  $\alpha_{\max}$ ,  $T_{\max}$  and  $t_{\max}$  are the conversion degree, temperature and time at which  $(d\alpha/dt)_{\max}$  occurs, respectively;  $T_f$  and  $t_f$  are the temperature and time at which the reaction has finished, defined as the temperature and time when  $\alpha > 0.99999$ . From Tables 1A and 1B, it can be seen that the more negative the value of  $C$  is, the smaller are the values of  $(d\alpha/dt)_{\max}$ ,  $T_{\max}$ ,  $\alpha_{\max}$  and  $T_f$ , but the larger are the values of  $t_{\max}$  and  $t_f$ . The more positive the value of  $C$  is, the larger are the values of

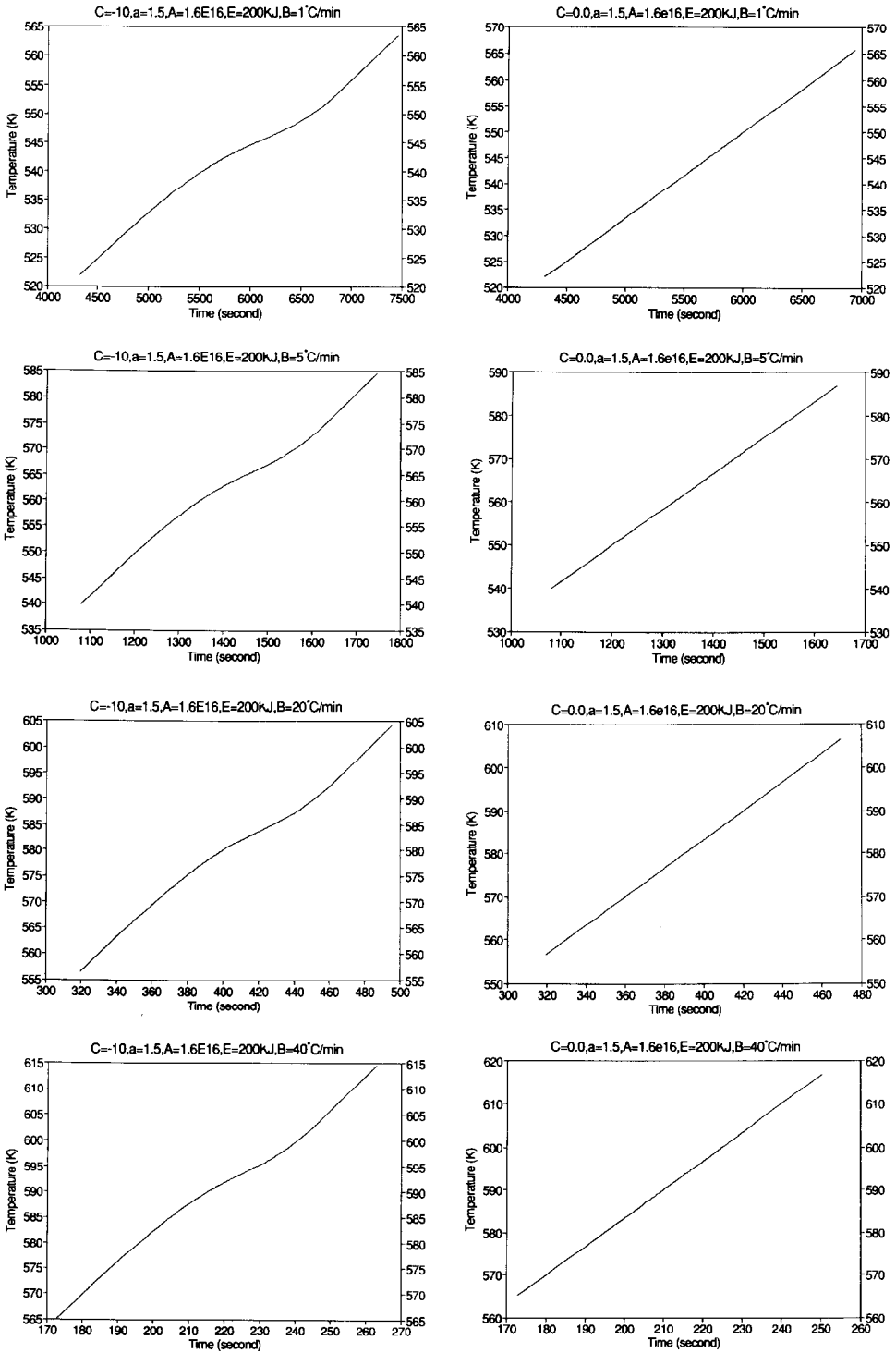


Fig. 4(a). Changes in the  $T-t$  curves at different rates when the  $C$  value is constant.

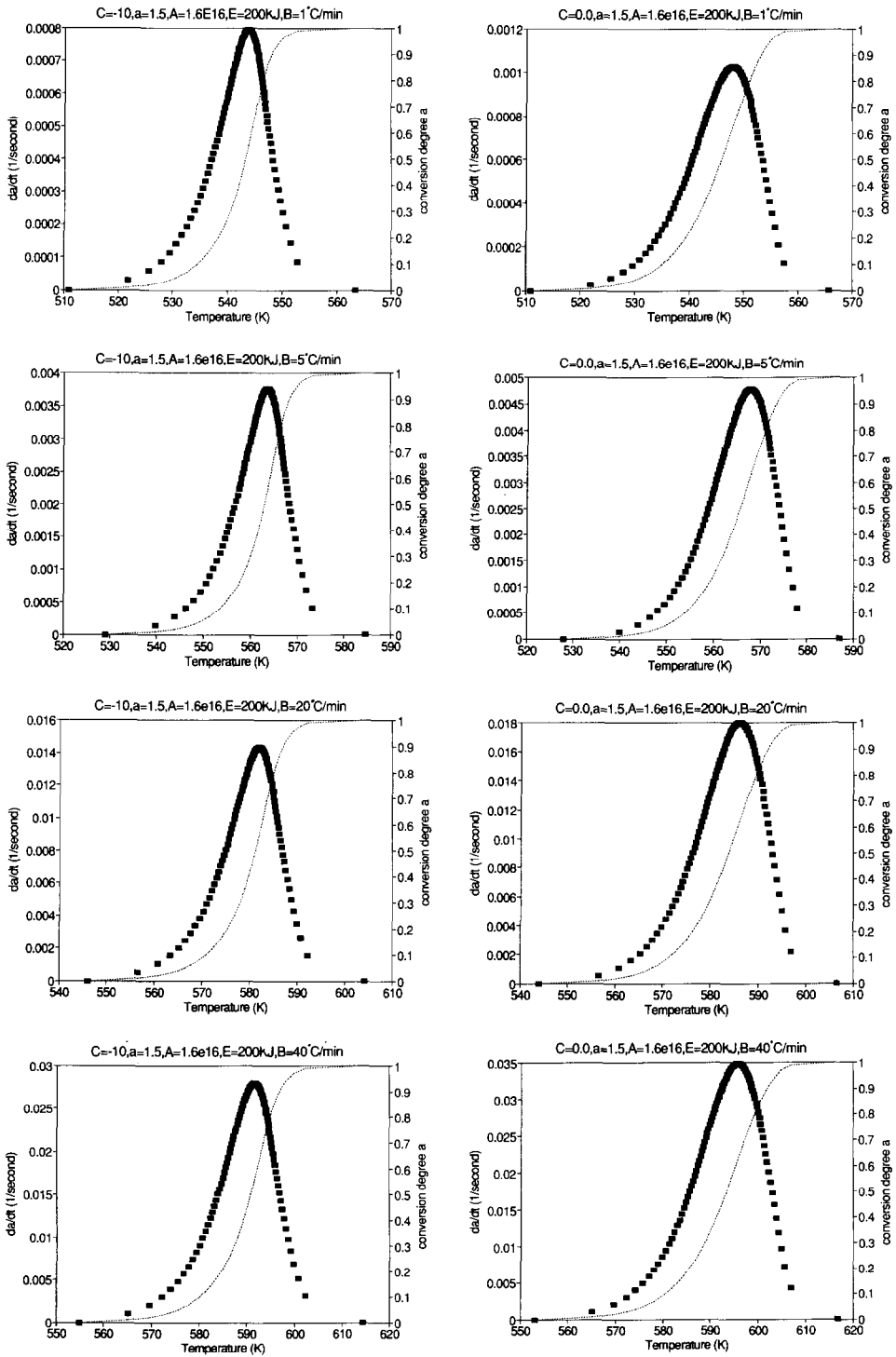


Fig. 4(b). Changes in the TG and DTG curves under the conditions given in Fig. 4(a).



TABLE 1A

Variations in the characteristics of the TG and DTG curves due to the reaction heat

| $\beta$ ( $^{\circ}\text{C min}^{-1}$ ) | $C$ | $T_i^a$<br>(K) | $t_i^c$<br>(s) | $T_f^c$<br>(K) | $t_f^d$<br>(s) | $T_{\max}^e$<br>(K) | $t_{\max}^f$<br>(s) | $\alpha_{\max}^g$ | $(d\alpha/dt)_{\max}^h$<br>( $\text{s}^{-1}$ ) |
|---|-----|----------------|----------------|----------------|----------------|---------------------|---------------------|-------------------|--|
| 1                                       | -10 | 511            | 3600           | 563.4          | 7465           | 543.9               | 5912                | 0.555             | $7.97 \times 10^{-4}$                          |
|   | 0   | 511            | 3600           | 565.8          | 6945           | 547.9               | 5876                | 0.620             | $1.03 \times 10^{-3}$                          |
| 5                                       | -10 | 529            | 839.8          | 584.7          | 1748           | 563.8               | 1422                | 0.560             | $3.77 \times 10^{-3}$                          |
|   | 0   | 529            | 839.7          | 587.0          | 1644           | 568.0               | 1416                | 0.625             | $4.79 \times 10^{-3}$                          |
| 10                                      | -10 | 538            | 529.1          | 594.2          | 931.3          | 572.8               | 764.9               | 0.561             | $7.37 \times 10^{-3}$                          |
|   | 0   | 544            | 529.0          | 596.3          | 879.5          | 577.0               | 762.0               | 0.625             | $9.28 \times 10^{-3}$                          |
| 20                                      | -10 | 544            | 290.7          | 604.1          | 495.4          | 582.1               | 410.3               | 0.560             | $1.44 \times 10^{-2}$                          |
|   | 0   | 544            | 290.6          | 606.5          | 469.6          | 586.2               | 408.5               | 0.620             | $1.80 \times 10^{-2}$                          |
| 40                                      | -10 | 555            | 157.1          | 614.46         | 263.2          | 591.6               | 219.5               | 0.560             | $2.80 \times 10^{-2}$                          |
|   | 0   | 555            | 157.2          | 616.78         | 250.2          | 595.8               | 218.6               | 0.620             | $3.49 \times 10^{-2}$                          |

<sup>a</sup> The initial reaction temperature, defined as the temperature at which  $d\alpha/dt$  is 0.1% of the maximum  $d\alpha/dt$  and  $\alpha$  is almost zero.

<sup>b</sup> The time required to reach  $T_i$ .

<sup>c</sup> The temperature at which the reaction has finished, defined as the temperature when  $\alpha > 0.99999$ .

<sup>d</sup> The time at which the reaction has finished, defined as the time when  $\alpha > 0.99999$ .

<sup>e</sup> The temperature at which  $(d\alpha/dt)_{\max}$  occurs.

<sup>f</sup> The time at which  $(d\alpha/dt)_{\max}$  occurs.

<sup>g</sup> The degree of conversion at which  $(d\alpha/dt)_{\max}$  occurs.

<sup>h</sup> The maximum reaction rate.

$(d\alpha/dt)_{\max}$ ,  $T_{\max}$ ,  $\alpha_{\max}$  and  $T_f$ , but the smaller are values of  $t_{\max}$  and  $t_f$ .  $C$  has no effect on  $T_i$  and  $t_i$  because before any reaction occurs, no reaction heat is absorbed or evolved, so  $T_i$  and  $t_i$  should stay the same, even when the  $C$  value changes dramatically. For the same  $C$  value but at different heating rates, the values of  $\alpha_{\max}$  are almost the same. These characteristics are very important when the reaction mechanisms are being identified by

TABLE 1B

Variations in the characteristics of the TG and DTG curves due to the reaction heat ( $\beta = 10^{\circ}\text{C min}^{-1}$ )

| $C$ | $T_i^a$<br>(K) | $t_i^b$<br>(s) | $T_f^c$<br>(K) | $t_f^d$<br>(s) | $T_{\max}^e$<br>(K) | $t_{\max}^f$<br>(s) | $\alpha_{\max}^g$ | $(d\alpha/dt)_{\max}^h$<br>( $\text{s}^{-1}$ ) |
|-----|----------------|----------------|----------------|----------------|---------------------|---------------------|-------------------|--|
| -20 | 538            | 528.8          | 592.7          | 987.8          | 569.6               | 766.1               | 0.500             | $6.06 \times 10^{-3}$                          |
| -10 | 538            | 529.1          | 594.2          | 931.3          | 572.8               | 764.9               | 0.561             | $7.37 \times 10^{-3}$                          |
|     | 0              | 538            | 529.0          | 596.3          | 879.5               | 577.0               | 0.625             | $9.28 \times 10^{-3}$                          |
| 10  | 538            | 528.9          | 600.1          | 834.3          | 582.2               | 756.3               | 0.690             | $1.22 \times 10^{-2}$                          |
| 15  | 538            | 528.9          | 602.3          | 814.8          | 585.3               | 752.8               | 0.720             | $1.42 \times 10^{-2}$                          |
| 25  | 538            | 528.8          | 607.8          | 782.1          | 592.1               | 744.5               | 0.771             | $2.02 \times 10^{-2}$                          |

<sup>a</sup> The initial reaction temperature, defined as the temperature at which  $d\alpha/dt$  is 0.1% of the maximum  $d\alpha/dt$  and  $\alpha$  is almost zero.

<sup>b</sup> The time required to reach  $T_i$ .

<sup>c</sup> The temperature at which the reaction has finished, defined as the temperature when  $\alpha > 0.99999$ .

<sup>d</sup> The time at which the reaction has finished, defined as the time when  $\alpha > 0.99999$ .

<sup>e</sup> The temperature at which  $(d\alpha/dt)_{\max}$  occurs.

<sup>f</sup> The time at which  $(d\alpha/dt)_{\max}$  occurs.

<sup>g</sup> The degree of conversion at which  $(d\alpha/dt)_{\max}$  occurs.

<sup>h</sup> The maximum reaction rate.

TABLE 2A

Probable mechanism and kinetic parameters calculated by the differential and integral methods ( $C = -10$ )

| $\beta$ ( $^{\circ}\text{C min}^{-1}$ ) | Mechanism <sup>a</sup> | $E^b$ ( $\text{kJ mol}^{-1}$ ) | $A^c$ ( $\text{s}^{-1}$ ) | $R^d$  | $S_{xy}^e$            | $S_b^f$ |
|---|------------------------|--------------------------------|---------------------------|--------|-----------------------|---------|
| <i>Integral method</i>                  |                        |                                |                           |        |                       |         |
| 1                                       | A2                     | 252.2                          | $2.65 \times 10^{21}$     | 0.9954 | $6.23 \times 10^{-2}$ | 2719    |
|   | A1.5                   | 320.2                          | $4.56 \times 10^{30}$     | 0.9957 | $5.33 \times 10^{-2}$ | 1879    |
| 5                                       | A2                     | 248.3                          | $7.46 \times 10^{20}$     | 0.9961 | $5.85 \times 10^{-2}$ | 2515    |
|   | A1.5                   | 333.9                          | $8.46 \times 10^{28}$     | 0.9962 | $7.32 \times 10^{-2}$ | 3149    |
| 10                                      | A2                     | 246.7                          | $4.54 \times 10^{20}$     | 0.9963 | $7.25 \times 10^{-2}$ | 2439    |
|   | A1.5                   | 331.9                          | $3.51 \times 10^{28}$     | 0.9964 | $7.10 \times 10^{-2}$ | 3037    |
| 20                                      | A2                     | 245.2                          | $2.78 \times 10^{20}$     | 0.9966 | $5.55 \times 10^{-2}$ | 2361    |
|   | A1.5                   | 329.9                          | $1.17 \times 10^{28}$     | 0.9967 | $6.87 \times 10^{-2}$ | 2923    |
| 40                                      | A2                     | 243.6                          | $1.70 \times 10^{20}$     | 0.9968 | $5.39 \times 10^{-2}$ | 2282    |
|   | A1.5                   | 327.9                          | $6.15 \times 10^{27}$     | 0.9969 | $6.64 \times 10^{-2}$ | 2807    |
| <i>Differential method</i>              |                        |                                |                           |        |                       |         |
| 1                                       | A2                     | 200.6                          | $1.83 \times 10^{16}$     | 1.000  | 0.3534                | 15444   |
|   | A1.5                   | 287.6                          | $5.35 \times 10^{24}$     | 0.9996 | $6.33 \times 10^{-2}$ | 1441    |
| 5                                       | A2                     | 200.3                          | $1.71 \times 10^{16}$     | 1.000  | 0.3471                | 14948   |
|   | A1.5                   | 286.1                          | $1.97 \times 10^{24}$     | 0.9997 | $6.23 \times 10^{-2}$ | 2685    |
| 10                                      | A2                     | 200.6                          | $1.81 \times 10^{16}$     | 1.000  | 0.3446                | 14757   |
|   | A1.5                   | 285.9                          | $1.43 \times 10^{24}$     | 0.9996 | $6.21 \times 10^{-2}$ | 2657    |
| 20                                      | A2                     | 200.6                          | $1.81 \times 10^{16}$     | 1.000  | 0.3420                | 1456    |
|   | A1.5                   | 285.5                          | $9.69 \times 10^{23}$     | 0.9997 | $6.17 \times 10^{-2}$ | 2626    |
| 40                                      | A2                     | 200.2                          | $1.68 \times 10^{16}$     | 1.000  | 0.3394                | 14368   |
|   | A1.5                   | 284.6                          | $6.13 \times 10^{23}$     | 0.9997 | $6.12 \times 10^{-2}$ | 2591    |

<sup>a</sup> The testing mechanism is A2:  $f(\alpha) = 2(1 - \alpha)[-\ln(1 - \alpha)]^{1/2}$ ;  $E = 200 \text{ kJ mol}^{-1}$ ;  $A = 1.6 \times 10^{-16} \text{ s}^{-1}$ .

<sup>b</sup> Activation energy.

<sup>c</sup> Frequency factor.

<sup>d</sup> The  $R$ -squared or regression factor.

<sup>e</sup> The standard error of  $y$ -estimate.

<sup>f</sup> The standard error of  $x$ -coefficient.

the method suggested by Dollimore et al. [2]. It can be predicted that the reaction mechanism identified by the method mentioned above will change with the change in the  $C$  value.

Generally, the  $C$  value for a certain sample depends on the sample size, sample particle size and the flow rate of the gas. When the sample size is small, the sample particle is fine, and the flow rate is large, then the  $C$  value can be considered close to zero, so the reaction heat effect can be ignored.

Tables 2A and 2B show the probable mechanism and kinetic parameters calculated from the simulated  $T-t$ , TG and DTG curves by using the differential [3] and integral [4] methods, the details of how to determine the mechanism and calculate the kinetic parameters can be found in ref. 5.

From Tables 2A and 2B, it can be seen that the differential method

TABLE 2B

Probable mechanism and kinetic parameters calculated by the differential and integral methods ( $\beta = 10^\circ\text{C min}^{-1}$ )

| C                          | Mechanism <sup>a</sup> | E <sup>b</sup> (kJ mol <sup>-1</sup> ) | A <sup>c</sup> (s <sup>-1</sup> ) | R <sup>d</sup> | S <sub>xy</sub> <sup>e</sup> | S <sub>b</sub> <sup>f</sup> |
|----------------------------|------------------------|--|-----------------------------------|----------------|------------------------------|-----------------------------|
| <i>Integral method</i>     |                        |  |                                   |                |                              |                             |
| -20                        | A2                     | 302.5                                  | $9.35 \times 10^{25}$             | 0.9814         | 0.1171                       | 6182                        |
|                            | R2                     | 531.8                                  | $3.20 \times 10^{32}$             | 0.9857         | 0.1791                       | 9448                        |
| -10                        | A2                     | 246.7                                  | $4.54 \times 10^{20}$             | 0.9961         | $5.69 \times 10^{-2}$        | 2438                        |
|                            | A4                     | 118.8                                  | $5.12 \times 10^8$                | 0.9962         | $2.49 \times 10^{-2}$        | 1066                        |
| 0                          | A2                     | 200.6                                  | $1.78 \times 10^{16}$             | 1.000          | $1.98 \times 10^{-3}$        | 283                         |
|                            | A4                     | 90.1                                   | $4.12 \times 10^7$                | 1.000          | $1.01 \times 10^{-3}$        | 120                         |
| 10                         | A2                     | 162.8                                  | $4.50 \times 10^{12}$             | 0.9977         | $5.17 \times 10^{-2}$        | 1458                        |
|                            | A1.5                   | 220.1                                  | $8.59 \times 10^{17}$             | 0.9978         | $5.67 \times 10^{-2}$        | 1629                        |
| 15                         | A2                     | 147.5                                  | $1.54 \times 10^{11}$             | 0.9950         | $6.59 \times 10^{-2}$        | 1727                        |
|                            | A4                     | 69.2                                   | 7165                              | 0.9946         | $2.78 \times 10^{-2}$        | 729                         |
| 25                         | A2                     | 122.3                                  | $5.89 \times 10^8$                | 0.9893         | $9.13 \times 10^{-2}$        | 2019.8                      |
|                            | A4                     | 56.5                                   | 398.8                             | 0.9874         | $4.16 \times 10^{-2}$        | 920.8                       |
| <i>Differential method</i> |                        |  |                                   |                |                              |                             |
| -20                        | A2                     | 200.6                                  | $1.81 \times 10^{16}$             | 1.000          | 0.4411                       | 23534                       |
|                            | A1.5                   | 304.5                                  | $7.81 \times 10^{25}$             | 0.9979         | $7.81 \times 10^{-2}$        | 4112                        |
| -10                        | A2                     | 200.6                                  | $1.81 \times 10^{16}$             | 1.000          | 0.3446                       | 14757                       |
|                            | A1.5                   | 285.9                                  | $1.43 \times 10^{24}$             | 0.9996         | $6.23 \times 10^{-2}$        | 2857                        |
| 0                          | A2                     | 199.9                                  | $1.58 \times 10^{16}$             | 1.000          | $2.99 \times 10^{-2}$        | 1043                        |
|                            | A4                     | 95.4                                   | $2.70 \times 10^6$                | 1.000          | $7.68 \times 10^{-5}$        | 2.68                        |
| 10                         | A2                     | 200.8                                  | $1.88 \times 10^{16}$             | 1.000          | 0.2401                       | 6901                        |
|                            | A1.5                   | 258.2                                  | $3.64 \times 10^{21}$             | 0.9999         | $5.11 \times 10^{-2}$        | 1470                        |
| 15                         | A2                     | 200.9                                  | $1.92 \times 10^{16}$             | 1.000          | 0.2301                       | 6044                        |
|                            | A3                     | 148.6                                  | $2.63 \times 10^{11}$             | 0.9994         | $2.63 \times 10^{-2}$        | 670                         |
| 25                         | A2                     | 201.1                                  | $2.02 \times 10^{16}$             | 1.000          | 0.2231                       | 493                         |
|                            | A3                     | 157.2                                  | $1.67 \times 10^{12}$             | 0.9991         | $3.66 \times 10^{-2}$        | 810                         |

<sup>a</sup> The testing mechanism is A2:  $f(\alpha) = 2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$ ;  $E = 200 \text{ kJ mol}^{-1}$ ;  $A = 1.6 \times 10^{16}$ .<sup>b</sup> The activation energy.<sup>c</sup> The frequency factor.<sup>d</sup> The  $R$ -squared or regression factor.<sup>e</sup> The standard error of  $y$ -estimate.<sup>f</sup> The standard error of  $x$ -coefficient.

always gives better results than the integral method. It seems that the reaction heat has almost no effect on the results given by the differential method, but has a significant effect on those given by the integral method. An explanation may be as follows.

The differential method used here is based on the equation

$$\ln[(d\alpha/dt)/f(\alpha)] = \ln A - E/(RT) \quad (13)$$

It is derived directly from the basic equation

$$d\alpha/dt = A \exp[-E/(RT)]f(\alpha) \quad (14)$$

Equation (14) should always be valid, whatever the  $T-t$  curve; so is eqn.

(13). However, if you use the differential equation in the form

$$\ln[\beta(d\alpha/dT)/f(\alpha)] = \ln A - E/RT \quad (15)$$

then a dependence upon the linearity of the  $T-t$  plot arises. Therefore, the authors strongly suggest using eqn. (13) rather than eqn. (15) in the differential method.

In the integral method, the approximation

$$\ln[G(\alpha)/T^{1.921503}] = \ln(AE/\beta R) + 3.7720501 - 1.921503 \ln E - E/RT \quad (16)$$

was made for the integral equation, where

$$G(\alpha) = \exp(-E/RT) dt \quad (17)$$

and  $T$  obeys eqn. (1). However, owing to the effect of the reaction heat,  $T$  does not obey eqn. (1) but obeys eqn. (9), so this approximation would not be valid at all. Therefore, the results of kinetic analyses by this method are different from true values.

The activation energy  $E$  and frequency factor  $A$  given by the integral method increase with decreasing  $C$  value. For the same  $C$  value,  $E$  and  $A$  are almost the same at different heating rates. However, changing the  $C$  value does not change the probable mechanism.

## CONCLUSIONS

(1) The reaction heat has a significant effect on the  $T-t$ , TG and DTG curves. When the reaction is endothermic, the  $T-t$  curve slopes downward  $(d\alpha/dt)_{\max}$ ,  $\alpha_{\max}$ ,  $T_{\max}$  and  $T_f$  become smaller, but  $t_{\max}$  and  $t_f$  become larger. When the reaction is exothermic, the  $T-t$  curve slopes upward  $(d\alpha/dt)_{\max}$ ,  $\alpha_{\max}$ ,  $T_{\max}$  and  $T_f$  become larger, but  $t_{\max}$  and  $t_f$  becomes smaller; it has no effect on  $T_f$  or  $t_f$ .

(2) The relationship between time and the sample's temperature under the rising temperature program when considering the effect of the reaction heat is given by an equation of the form

$$T = T_0 + \beta t + C \ln[a/(a - \alpha)]$$

(3) The Arrhenius parameters given by the differential method are very close to the true value; those given by the integral method show a regular change with changes in the  $C$  value. However, the probable mechanisms given by these two methods do not change. It can be concluded that the differential method has an advantage over the integral method when a reaction is endothermic or exothermic.

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