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The effect of the reaction heat on kinetic analysis by TG under a rising temperature program.
Part 2

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Abstract

In Part 1 (Thermochim. Acta, 215 (1993) 83–95), the effect of reaction heat changes upon the rising temperature program was accounted for by using a relationship between a sample's temperature T and time t as a function of the degree of conversion α. The simulation and the kinetic analysis was made for the extreme situation of the temperature recorded by thermocouple being exactly the same as that of the sample. In the present study, another extreme case is considered, that the temperature recorded by the thermocouple is exactly the same as that of the furnace. On this assumption, a simulation of TG, DTG and T–t curves under both such a temperature program and the ideal rising temperature program was made, showing how the reaction heat affects these curves. As before, a kinetic analysis can be achieved for the calculation of the Arrhenius parameters, and the determination of the reaction mechanisms performed, by using integral or differential methods. The data obtained show that the kinetic parameters and the reaction mechanism are all changed to some extent by the effect of the reaction heat.

INTRODUCTION

The non-isothermal kinetic analysis has been reviewed in some detail by Šesták et al. [1]. The expression generally adopted is

$$T = T + \beta t \tag{1}$$

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

As already mentioned in Part 1 [2], in TG instrumentation the rising temperature program is used in the computer work station in a default form which controls the furnace temperature. In one extreme case it might be shown that when no heat is absorbed or evolved, eqn. (1) is obeyed.

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However, for endothermic or exothermic reactions the sample's temperature would be different from the rising temperature program operated in such cases on the furnace. In Part 1 it was shown that a relation between the sample's temperature T and the time t could be written as

$$T = T_0 + \beta t + C \ln[a/(a - \alpha)] \tag{2}$$

where

$$C = \mu Q / C_p \tag{3}$$

$$a = W_0/(W_0 - W_f) \tag{4}$$

$$\alpha = (W_0 - W)/(W_0 - W_f) \tag{5}$$

and C_p is the sample's specific heat, W is the weight at time t, μ 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 (J g^{-1}), W_0 is the sample's weight at time $t = 0$, W_f is the sample weight at the end of the reaction, α is the conversion degree of the sample, a is a constant related to the initial mass and final residue ($a > 1$ always) and C is a constant representing the degree of self-heating or self-cooling of the sample. In Part 1, it was also shown that if the temperature recorded by the thermocouple is that of the sample, then kinetic evaluations might be affected.

In this paper we consider another extreme condition, that the temperature recorded by the thermocouple is exactly the same as that of the furnace. This condition implies that the location of the thermocouple is far from the sample, and therefore gives a true record of the furnace temperature, but may be in error if this temperature is also designated as the sample's temperature.

SIMULATION RESULTS AND DISCUSSIONS

Generally speaking, the decomposition of the solid state obeys the equations

$$d\alpha/dt = kf(\alpha) \tag{6}$$

$$k = A \exp(-E/RT) \tag{7}$$

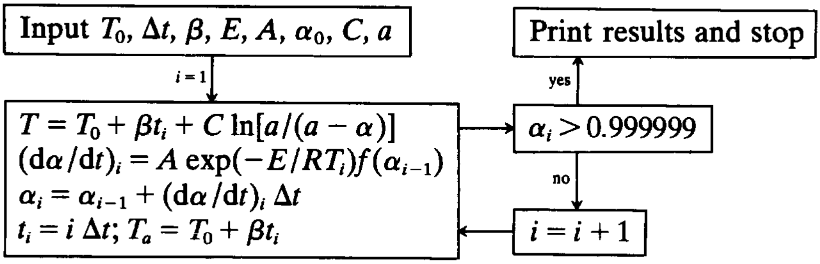
In a particular case, for a given set of Arrhenius parameters and a stated mechanism, the TG, DTG and T–t curves can be obtained by using a numerical method: (a) solving the case in which the endothermic or exothermic character of the reaction affects the sample's temperature, by using eqns. (1), (2), (6) and (7); (b) solving the ideal case in which sample temperature is not affected by the endothermic or exothermic character of the reaction, by using eqns. (1), (6) and (7).

As in Part 1, calculation of the α value at each selected time t was made by using the approximation

$$\alpha(t + \Delta t) = \alpha(t) + (\mathrm{d}\alpha/\mathrm{d}t)\,\Delta t \qquad (8)$$

where Δt is a small time interval compared to the time taken for the reaction to go to completion. The smaller Δt, the better the approximation.

If α_0, β, A, Δt, C and a are given, then the set of data t_i, T_a, T_i, α_i $(\mathrm{d}\alpha/\mathrm{d}t)_i$ could be calculated for the whole period of reaction. T_a is the temperature recorded by the thermocouple at time t_i, T_i is the temperature of the sample at time t_i.



The flow chart for the calculation.

This flow chart can be seen to be only slightly different to that given in Part 1.

In the simulation, the $f(\alpha)$ chosen is for the A2 mechanism (activation energy $E = 200\,\mathrm{kJ\,mol^{-1}}$; frequency factor $A = 1.6 \times 10^{16}$). Figure 1(a) shows the changes in the T–t curves at constant heating rate $\beta = 10°\mathrm{C\,min^{-1}}$, when C is given different values; Fig. 1(b) shows the changes of the TG and DTG curves under the same conditions. Figure 2(a) shows the change in the T–t curves at different heating rates when C is constant; Fig. 2(b) shows the changes in the TG and DTG curves under the same conditions. From Figs. 1 and 2, 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 appear linear, but the time taken for completing the reaction becomes shorter. Therefore, the temperature recorded by thermocouple would be higher than in the ideal case when C is negative and lower than the ideal case when C is positive at the same conversion degree α. The peaks of the DTG curves shift from right to left, and become wider when C changes in the same way. The TG curve becomes narrow when C changes from negative to positive. When C is constant, the shapes of the T–t, TG and DTG curves reflect the same trend in changes at the different heating rates.

Tables 1A and 1B show the changes of the characteristics of the TG

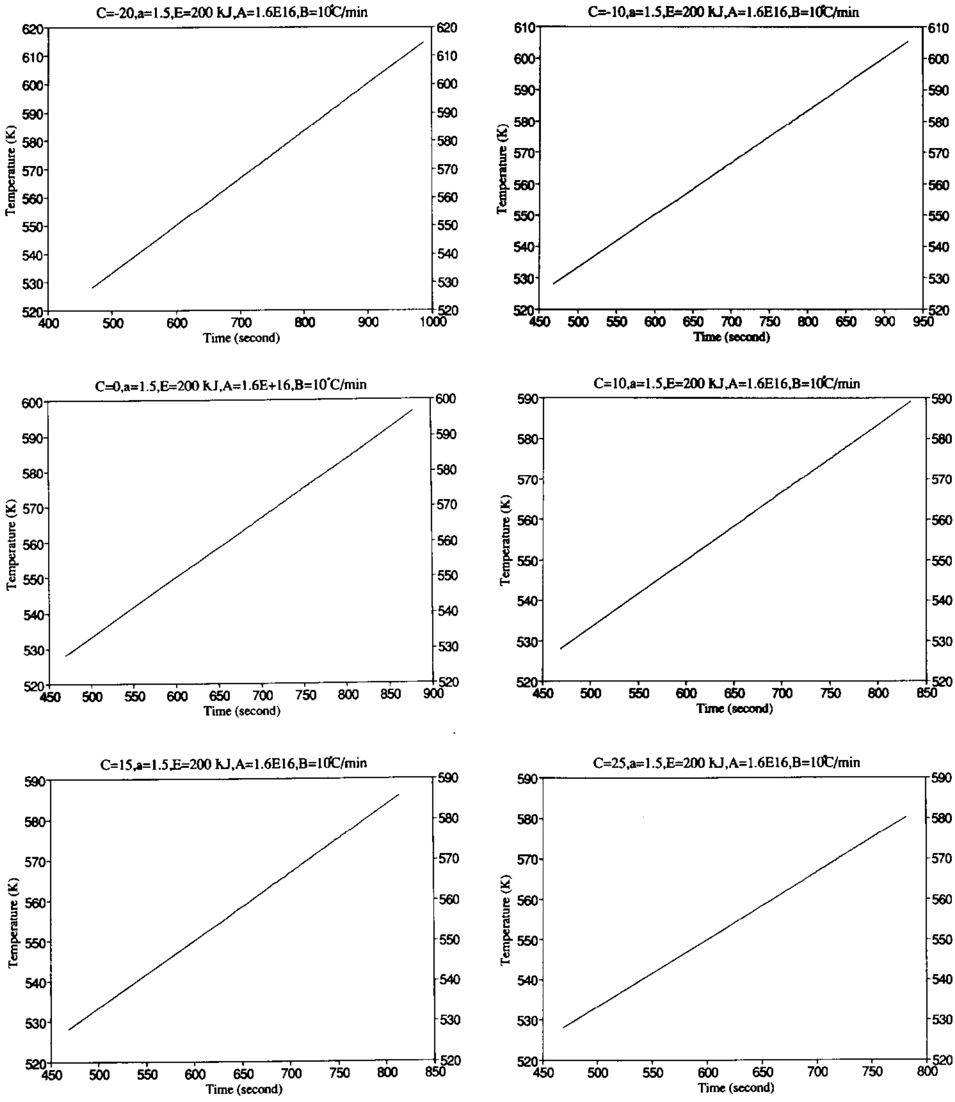


Fig. 1(a). Changes in the T–t curves at constant heating rate of $\beta = 10°\text{C min}^{-1}$ for various values of C.

and DTG curves: T_i is the initial reaction temperature, defined as the temperature at which $d\alpha/dt$ is 0.1% of the maximum $d\alpha/dt$ and α is almost zero; t_i is the time required to reach T_i; $(d\alpha/dt)_{max}$ is the maximum reaction rate; α_{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 the time at which the reaction has finished, defined as the temperature and the time when $\alpha = 0.999999$. From Tables 1A and 1B, it can be seen that the more negative the value of C is, the smaller are the values of $(d\alpha/dt)_{max}$ and α_{max}, but the larger are the values of T_f, t_f, T_{max}

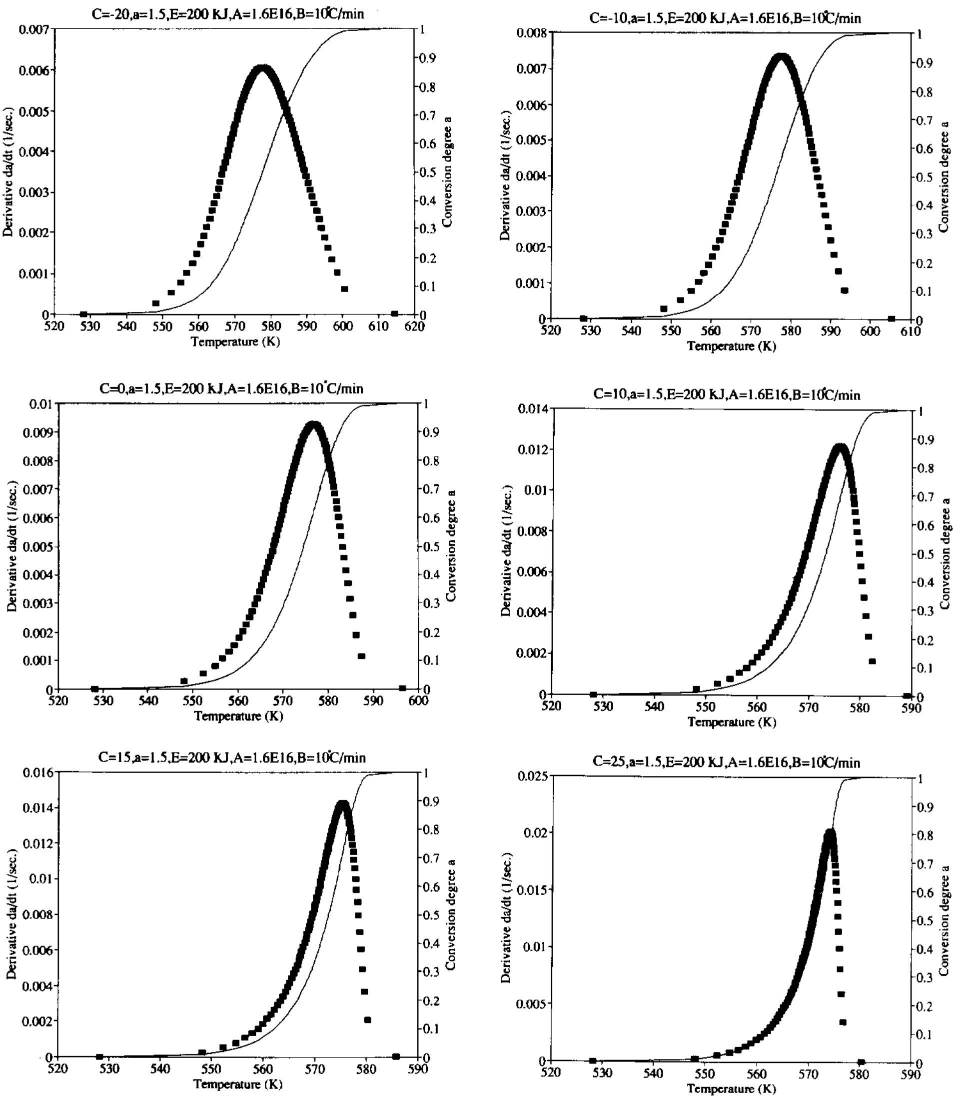


Fig. 1(b). Changes in the TG and DTG curves under the conditions given in Fig. 1(a).

and t_{max}. The more positive the value of C is, the larger are the values of $(d\alpha/dt)_{max}$ and α_{max}, but the smaller are the values of T_{max}, t_{max}, T_f and t_f. However, the values of T_{max} only change a little compared with the other parameters. C has no effect on T_i and t_i because before reaction occurs no reaction heat is absorbed or evolved so T_i and t_i should stay the same even though C changes dramatically. For the same C value but at different heating rates, the values of α_{max} are almost the same.

All that is mentioned above means that the TG, DTG and T–t curves all change their shapes because of the effect of the reaction heat. This would make it difficult to apply the method suggested by Dollimore et al.

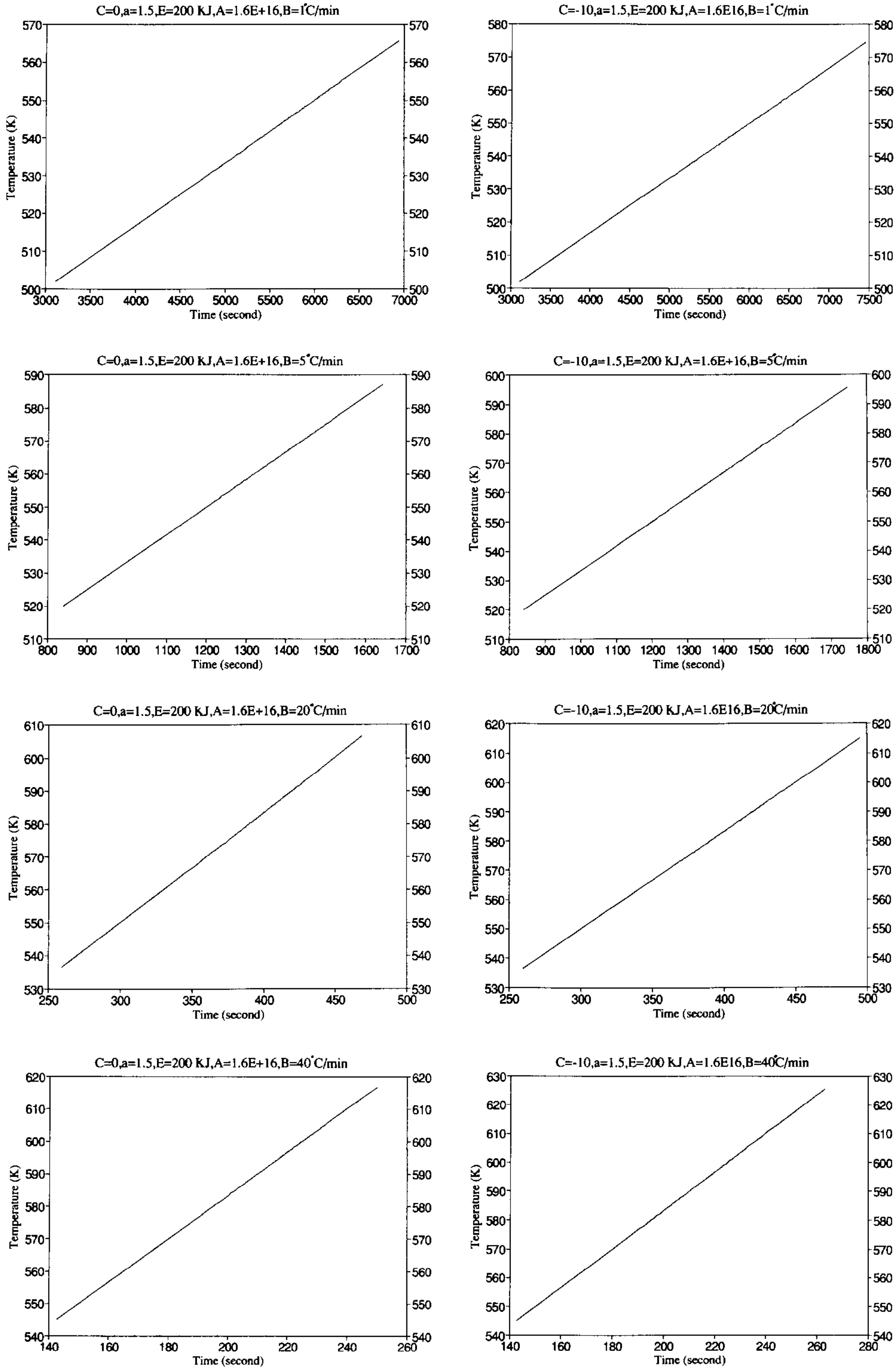


Fig. 2(a). Changes in the T–t curves at different rates when the C value is constant.

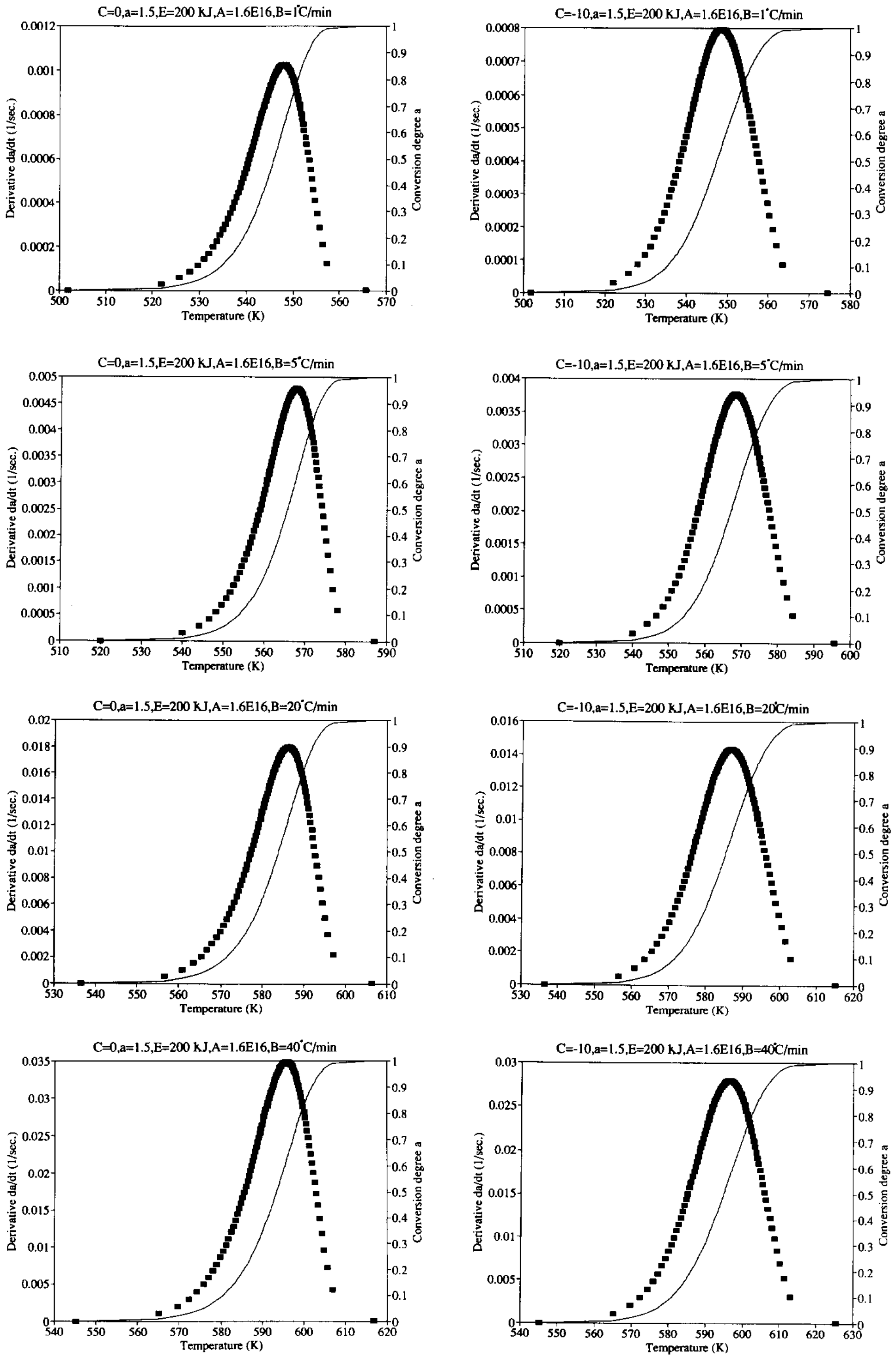


Fig. 2(b). Changes in the TG and DTG curves under the conditions given in Fig. 2(a).

TABLE 1A

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

β (°C min^{-1})	C	T_i[a] (K)	t_i[b] (s)	T_f[c] (K)	t_f[d] (s)	T_{max}[e] (K)	t_{max}[f] (s)	α_{max}[g]	$(d\alpha/dt)_{max}$[h] (s^{-1})
1	−10	511	3600	574.4	7465	548.5	5912	0.555	7.97×10^{-4}
	0	511	3600	565.8	6945	547.9	5876	0.620	1.03×10^{-3}
5	−10	529	839.8	595.6	1748	568.5	1422	0.560	3.77×10^{-3}
	0	529	839.7	587.0	1644	568.0	1416	0.625	4.79×10^{-3}
10	−10	538	529.1	605.3	931.3	577.5	764.9	0.561	7.37×10^{-3}
	0	544	529.0	596.3	879.5	577.0	762.0	0.625	9.28×10^{-3}
20	−10	544	290.7	615.1	495.4	586.8	410.3	0.560	1.44×10^{-2}
	0	544	290.6	606.5	469.6	586.2	408.5	0.620	1.80×10^{-2}
40	−10	555	157.1	625.4	263.2	596.3	219.5	0.560	2.80×10^{-2}
	0	555	157.2	616.8	250.2	595.8	218.6	0.620	3.49×10^{-2}

[a] The initial reaction temperature, defined as the temperature at which the $d\alpha/dt$ is 0.1% of the maximum $d\alpha/dt$ and α is almost zero.
[b] The time required to reach T_i.
[c] The temperature at which the reaction has finished, defined as the temperature when $\alpha > 0.99999$.
[d] The time at which the reaction has finished, defined as the time when $\alpha > 0.99999$.
[e] The temperature at which $(d\alpha/dt)_{max}$ occurs.
[f] The time at which $(d\alpha/dt)_{max}$ occurs.
[g] The degree of conversion at which $(d\alpha/dt)_{max}$ occurs.
[h] The maximum reaction rate.

[3] for determining the reaction mechanism and calculating the Arrhenius parameters. A more detailed study of this aspect is now in progress.

Tables 2A and 2B show the probable mechanism and Arrhenius parameters calculated from the simulated T–t, TG and DTG curves by using the differential [4] and integral [5] methods; the details of how to

TABLE 1B

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

C	T_i[a] (K)	t_i[b] (s)	T_f[c] (K)	t_f[d] (s)	T_{max}[e] (K)	t_{max}[f] (s)	α_{max}[g]	$(d\alpha/dt)_{max}$[h] (s^{-1})
−20	538	528.8	614.6	987.8	577.7	766.1	0.500	6.06×10^{-3}
−10	538	529.1	605.2	931.3	577.5	764.9	0.561	7.37×10^{-3}
0	538	529.0	596.3	879.5	577.0	762.0	0.625	9.28×10^{-3}
10	538	528.9	589.1	834.3	576.1	756.3	0.690	1.22×10^{-2}
15	538	528.9	585.8	814.8	575.5	752.8	0.720	1.42×10^{-2}
25	538	528.8	580.4	782.1	574.1	744.5	0.771	2.02×10^{-2}

[a] The initial reaction temperature, defined as the temperature at which the $d\alpha/dt$ is 0.1% of the maximum $d\alpha/dt$ and α is almost zero.
[b] The time required to reach T_i.
[c] The temperature at which the reaction has finished, defined as the temperature when $\alpha > 0.99999$.
[d] The time at which the reaction has finished, defined as the time when $\alpha > 0.99999$.
[e] The temperature at which $(d\alpha/dt)_{max}$ occurs.
[f] The time at which $(d\alpha/dt)_{max}$ occurs.
[g] The degree of conversion at which $(d\alpha/dt)_{max}$ occurs.
[h] The maximum reaction rate.

TABLE 2A

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

β (°C min^{-1})	Mechanism [a]	E [b] (kJ mol^{-1})	A [c] (s^{-1})	R [d]	S_{xy} [e]	S_b [f]
Integral method						
1	A2	167.7	9.58×10^{12}	0.9966	5.98×10^{-2}	1765
	A1.5	226.5	4.85×10^{18}	0.9967	6.85×10^{-2}	2019
	A3	108.9	1.67×10^{7}	0.9964	3.57×10^{-2}	1054
5	A2	169.7	1.92×10^{13}	0.9970	5.71×10^{-2}	1706
	A1.5	229.4	7.37×10^{18}	0.9971	6.43×10^{-2}	1921
	A3	110.2	4.47×10^{7}	0.9968	3.36×10^{-2}	1004
10	A2	170.7	2.61×10^{13}	0.9972	5.59×10^{-2}	1680
	A1.5	230.6	8.81×10^{8}	0.9973	6.25×10^{-2}	1877
	A3	110.7	6.83×10^{7}	0.9970	3.26×10^{-2}	981
20	A2	171.5	3.46×10^{13}	0.9974	5.48×10^{-2}	1654
	A1.5	231.8	1.03×10^{7}	0.9974	6.07×10^{-2}	1834
	A3	111.3	1.03×10^{8}	0.9972	3.18×10^{-2}	959
40	A2	172.4	4.51×10^{13}	0.9975	5.38×10^{-2}	1631
	A1.5	232.9	1.17×10^{19}	0.9976	5.91×10^{-2}	1796
	A3	111.8	1.54×10^{8}	0.9973	3.09×10^{-2}	939
Differential method						
1	A2	133.9	5.41×10^{9}	0.9879	0.2403	7096
	D3	744.6	1.71×10^{40}	0.9993	0.1236	3650
5	A2	137.5	2.03×10^{10}	0.9895	0.2426	7257
	D3	756.1	5.97×10^{40}	0.9994	0.1170	3199
10	A2	139.5	3.73×10^{10}	0.9902	0.2434	7320
	D3	761.1	5.79×10^{41}	0.9995	0.1145	3445
20	A2	141.2	6.45×10^{10}	0.9909	0.2442	7386
	D3	766.5	7.69×10^{41}	0.9995	0.1125	3402
40	A2	142.6	1.05×10^{11}	0.9913	0.2452	7455
	D3	771.1	5.13×10^{42}	0.9995	0.1109	3368

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

determine the mechanism and calculate the Arrhenium parameters can be found in ref. 6.

From Tables 2A and 2B, it can be seen that neither the differential nor the integral methods give good results. The reaction mechanism shifted from A2 to D3 by using the differential method, and although the reaction mechanism still stays in the group of sigmoid curves, the activation energy E and frequency factor A are lowered when $C = -10$ at different heating rates. The reaction mechanism is shifted from D3 to R2 then to D1, and the activation energy E and frequency factor A are increased for the A2 mechanism by using the differential method; the reaction mechanism shifts

TABLE 2B

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

C	Mechanism[a]	E[b]	A[c]	R[d]	S_{xy}[e]	S_b[f]
Integral method						
−20	A2	144.3	7.99×10^{10}	0.9896	0.0913	2357
	A1.5	195.4	4.15×10^{15}	0.9899	0.1139	2941
−10	A2	170.7	4.54×10^{20}	0.9961	5.69×10^{-2}	2438
	A1.5	230.6	8.82×10^{18}	0.9973	6.25×10^{-2}	1877
0	A2	200.6	1.78×10^{16}	1	1.98×10^{-3}	283
	A4	90.1	4.12×10^{7}	1	1.01×10^{-3}	120
10	A2	230.4	1.25×10^{9}	0.9969	5.18×10^{-2}	2075
	R2	406.1	4.19×10^{32}	0.9994	4.35×10^{-2}	1739
	R3	425.7	3.99×10^{32}	0.9998	2.92×10^{-2}	1168
15	A2	245.7	3.47×10^{20}	0.9932	7.16×10^{-2}	3056
	R2	434.1	3.92×10^{32}	0.9996	4.16×10^{-2}	1778
25	A2	275.1	2.20×10^{23}	0.9820	0.1126	5419
	R2	488.7	3.48×10^{32}	0.9960	0.1004	4831
	D1	874.4	9.69×10^{49}	0.9995	0.0774	3728
Differential method						
−20	A2	93.95	2.11×10^{6}	0.9588	0.2210	5713
	D3	627.9	1.70×10^{38}	0.9959	0.2528	6535
−10	A2	139.5	3.73×10^{10}	0.9902	0.2434	7321
	D3	761.1	1.43×10^{42}	0.9995	0.1145	3445
0	A2	199.9	1.58×10^{16}	1	2.99×10^{-2}	1043
	A4	95.4	2.70×10^{6}	1	7.68×10^{-5}	2.68
10	A2	277.3	1.88×10^{24}	0.9908	0.3245	13004
	R3	421.6	1.40×10^{36}	0.9964	9.96×10^{-2}	3992
15	A2	320.8	2.93×10^{27}	0.9804	0.3509	15005
	R3	476.8	1.71×10^{38}	0.9968	9.74×10^{-2}	4162
25	A2	416.3	2.38×10^{36}	0.9509	0.4183	20151
	R2	543.4	1.70×10^{41}	0.9909	0.1661	7997

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

[b] Activation energy.

[c] Frequency factor.

[d] The R-squared or regression factor.

[e] The standard error of y-estimate.

[f] The standard error of x-coefficient.

from A1.5 to R3, R2, then D1, when C changes from negative to positive at the constant heating rate.

CONCLUSIONS

When we assume that the temperature recorded by the thermocouple is the temperature of the furnace of the TG instrumentation, the following conclusions can be drawn.

(1) The reaction heat has a significant effect on the T–t, TG and DTG

curves. The T–t, TG and DTG curves become narrow for an exothermic reaction; the T–t, TG and DTG curves become broad for an endothermic reaction. The T–t curve is linear in all cases. The values of $(\mathrm{d}\alpha/\mathrm{d}t)_{\max}$ and $\alpha_{\max}$ become larger, but $T_{\max}$, $t_{\max}$, T_f and t_f become smaller for an exothermic reaction; the reverse is true for an endothermic reaction.

(2) The calculated Arrhenius parameters and the reaction mechanisms identified by both the differential and integral methods are all different from the ideal case. The mechanism shifts to other mechanisms; the Arrhenius parameters are lowered for an endothermic reaction and increased for an exothermic reaction when the mechanism is fixed.

(3) To avoid this case, the experimental conditions should always be set up so that the location of the thermocouple is as near the sample boat as possible; the sample size should be very small; the flow rate of the dynamic atmosphere should be as high as possible.

(4) It is necessary to develop new approaches for overcoming the difficulty caused by the effect of the reaction heat.

REFERENCES

1 J. Šesták, V. Satava and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 333.
2 X. Gao, D. Chen and D. Dollimore, Thermochim. Acta, 215 (1993) 83.
3 D. Dollimore, T.A. Evans, Y.F. Lee, G.P. Pee and F.W. Wilburn, Thermochim. Acta, 196 (1992) 255.
4 D. Dollimore, G.R. Heal and B.W. Krupay, Thermochim. Acta, 24 (1978) 201.
5 P.M. Madhusudanan, K. Krishnan and K.N. Ninan, Thermochim. Acta, 97 (1986) 189.
6 X. Gao and D. Dollimore, Thermochim. Acta, 215 (1993) 47.