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The importance of the pre-history of a sample on its thermal behavior.
Part 2

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Abstract

In this paper, we discuss the application of single-heating-rate methods on only one set of rising-temperature thermogravimetric data to evaluate the kinetics of reactions with pre-history. The results show that the correct reaction mechanism can always be obtained by manually changing the initial value of the original data (without changing the final value of the original data for the reaction). For a reaction with a reaction function (differential form) not of the form $(1-\alpha)^n$, the real pre-history conditions of the sample, the real activation energy and the real frequency factor can be obtained. For a reaction with a reaction function of the form $(1-\alpha)^n$, only the real activation energy can be obtained, owing to the impossibility of obtaining the real pre-history conditions.

INTRODUCTION

In Part 1 [1], the influence of pre-history on the shape of thermogravimetric (TG) and derivative thermogravimetric (DTG) curves was discussed. Single-heating-rate methods and multi-heating-rate methods for the evaluation of the kinetic parameters were used and the results were discussed. The conclusions showed that the use of multi-heating-rate methods gave the correct activation energies of the samples with pre-history. The problem was that it was impossible to obtain the correct reaction mechanism for the samples with pre-history from the multi-heating-rate methods only: a combination of the single-heating-rate methods and the multi-heating rate methods was required to achieve this.

In this paper, the single-heating-rate differential (SHRD) method is

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investigated in order to obtain the kinetic parameters and the reaction mechanism for those samples with pre-history. Owing to the approximation present in the single-heating-rate integral (SHRI) method [1], the calculation results will always show some deviation from the correct value. The application of the SHRI method has not therefore been discussed in this paper.

THEORY

In thermal analysis, the expression for the reaction rate as a function of the temperature is

$$d\alpha/dt = f(\alpha)k(T) \qquad (1)$$

where α is the extent of the reaction and $f(\alpha)$ is the function of α which represents the reaction mechanism; Table 1 shows a list of the most commonly used equations. $k(T)$ is the rate constant at temperature T and

TABLE 1

The common forms of $f(\alpha)$ and $G(\alpha)$

Mechanism		$G(\alpha)$	$f(\alpha)$
Acceleratory α–t *curve*			
P1	Power law	$\alpha^{1/4}$	$4\alpha^{3/4}$
		$\alpha^{1/3}$	$3\alpha^{2/3}$
		$\alpha^{1/2}$	$2\alpha^{1/2}$
		α	1
		$\alpha^{3/2}$	$2/3\alpha^{-1/2}$
E1	Exponential law	$\ln \alpha$	α
S-Shaped α–t *curve*			
A1.5	Avrami–Erofeev	$[-\ln(1-\alpha)]^{2/3}$	$1.5(1-\alpha)[-\ln(1-\alpha)]^{1/3}$
A2	Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
A3	Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
A4	Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$
B1	Prout–Tompkins	$\ln[\alpha/(1-\alpha)]$	$\alpha(1-\alpha)$
		$[-\ln(1-\alpha)]^2$	$0.5(1-\alpha)[-\ln(1-\alpha)]^{-1}$
		$[-\ln(1-\alpha)]^3$	$1/3(1-\alpha)[-\ln(1-\alpha)]^{-2}$
		$[-\ln(1-\alpha)]^4$	$1/4(1-\alpha)[-\ln(1-\alpha)]^{-3}$
Deceleratory α–t *curve*			
R2	Contracting surface	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
R3	Contracting volume	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$
D1	1-D Diffusion	α^2	$1/2\alpha$
D2	2-D Diffusion	$(1-\alpha)\ln(1-\alpha)+\alpha$	$-[\ln(1-\alpha)]^{-1}$
D3	3-D Diffusion	$[1-(1-\alpha)^{1/3}]^2$	$1.5[1-(1-\alpha)^{1/3}]^{-1}(1-\alpha)^{2/3}$
D4	Ginstling–Brouns	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	$1.5[1-(1-\alpha)^{1/3}]^{-1}$
F1	First order	$-\ln(1-\alpha)$	$1-\alpha$
F2	Second order	$1/(1-\alpha)$	$(1-\alpha)^2$
F3	Third order	$[1/(1-\alpha)]^2$	$0.5(1-\alpha)^3$

it generally takes the Arrhenius equation form

$$k(T) = A \exp(-E/RT) \tag{2}$$

where A is the pre-exponential factor or frequency factor, E is the activation energy, R is the gas constant and T is the absolute temperature.

If eqn. (2) is combined with eqn. (1) and rearranged, then

$$(\mathrm{d}\alpha/\mathrm{d}t)/f(\alpha) = A \exp(-E/RT) \tag{3}$$

The logarithmic form of eqn. (3) is then taken, to give

$$\ln[(\mathrm{d}\alpha/\mathrm{d}t)/f(\alpha)] = \ln A - E/RT$$

By feeding the experimental data from a single heating-rate curve, a plot of $\ln[(\mathrm{d}\alpha/\mathrm{d}t)/f(\alpha)]$ vs. $1/T$ is obtained by testing all the functions $f(\alpha)$ in Table 1. The linear regression may then be calculated and the activation energy E and the frequency factor A can be calculated from the slope and intercept of the regression line. This method is called the SHRD method.

EXPERIMENTAL

The data files for this paper were created by using a computer program. The pre-history is designated (as in Part 1 [1]) by supposing that it is due to a loss in mass before the decomposition commences. It may then be represented by α_0, which is equal to 0.2. The computer program then needs the initial temperature T_0 (300 K), the activation energy, the frequency factor, the heating rate, the interval of sampling Δt, (0.01 second per point) and one mechanism, for that data file. Equation (3) with $T = T_0 + \beta t$ (t is the time of heating) and $\alpha = \alpha_0 + (\mathrm{d}\alpha/\mathrm{d}t)\,\Delta t$ were used to obtain the $\mathrm{d}\alpha/\mathrm{d}t$, T and the α values for the calculation. In order to be consistent with the data transferred from the Du Pont thermal analyzer 1090 unit, $\mathrm{d}\alpha/\mathrm{d}t$ was calculated in units of % min^{-1} by multiplying the theoretical $\mathrm{d}\alpha/\mathrm{d}t$ by $100 \times 60 \times (1-\alpha)$. The α data was also transferred to the weight percentage.

The flowchart of the program for the SHRD method has been published [2]. The calculation for the reaction then proceeds by iteratively increasing the initial value of the curve from 80 to 150% without changing the temperature, the weight percentage and $\mathrm{d}\alpha/\mathrm{d}t$ (% min^{-1}) values of the original data. Then the kinetic parameters are calculated in the same way as that used in the calculation of the original data. One reason for this step is that the weight percentage and $\mathrm{d}\alpha/\mathrm{d}t$ data transmitted from the Du Point TA 1090 unit are in units of percentage and % min^{-1} respectively. The real α and $\mathrm{d}\alpha/\mathrm{d}t$ need to be calculated by using the initial and final points of the reaction curve. The change in the initial value will modify the reaction range of the samples caused by pre-history and the changing initial value here is the assumed initial value of the sample without pre-history.

The programs were run on QUICKBASIC software, which provided fast calculation and ease of controlling the program. All the reaction curves were generated using the QUATTRO software from the data files created from the program discussed above.

RESULTS AND DISCUSSION

The theoretical kinetic parameters used in the present calculation are: activation energy, 200 kJ mol^{-1}; frequency factor, 1×10^{10} s^{-1}. The heating rate is 10°C min^{-1}; the mechanisms tested in this paper are R2, F2, A2, D3 and the third reaction function o the Prout–Tompkins B13, for which $f(\alpha) = (1/3)(1-\alpha)[-\ln(1-\alpha)]^{-2}$. The initial weight loss α_0 equals 0.2, or the maximum weight percentage is 80% when the final weight equals 0.

As stated in Part 1 [1], the shapes of the TG and DTG reaction curves do not change. Figures 1 and 2 show the patterns of the TG and DTG curves for the A2 and R2 mechanisms respectively, both with and without pre-history, at a heating rate of 10°C min^{-1}.

Following the idea used in the Experimental section, the initial value of the curve required for the calculation is changed manually, starting from the value of the "recorded" maximum value of the curve (80%). The values used are 90%, 95%, 100%, 105%, 110% and 150%. Here, 100% is the value at which the reaction is supposed to start if there is no pre-history associated with the samples.

The results of the calculation are listed in the Tables 2–6 for the R2, F2, A2, D3 and B13 mechanisms respectively. Owing to the differences in the results, they are discussed separately according to the reaction function form: $f(\alpha)$ for the R2 and F2 mechanisms are of the form $(1-\alpha)^n$, and

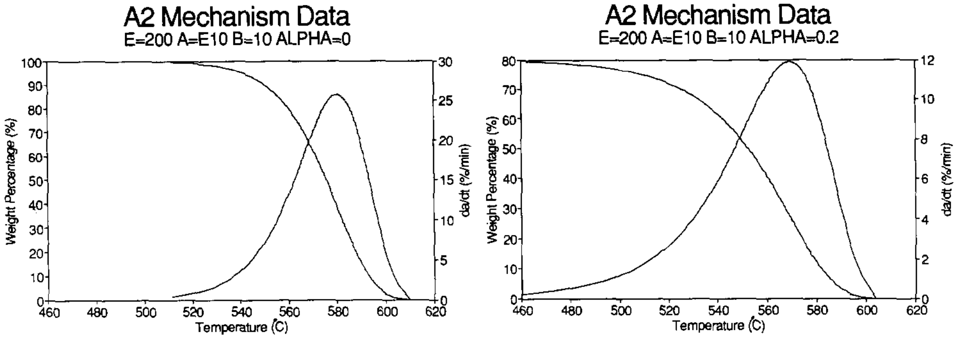

Fig. 1. The theoretical TG and DTG curves for the A2 mechanism at a heating rate of 10°C min^{-1} without any pre-history, and with a prior weight loss of 20%.

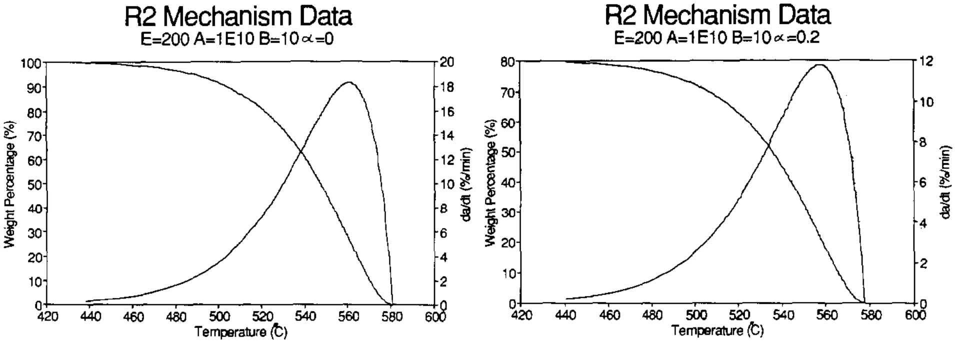

Fig. 2. The theoretical TG and DTG curves for the R2 mechanism at a heating rate of 10°C $\min^{-1}$ without any pre-history, and with a prior weight loss of 20%.

TABLE 2

Calculation results for the R2 mechanism [a]

Maximum (%)	E (kJ mol^{-1})	A (10^{10} s^{-1})	R [b]	S_{yx} [c] ($\times 10^{-5}$)
80	200.009	0.896	1	5.542
90	200.009	0.844	1	5.542
95	200.008	0.822	1	6.615
100	200.008	0.801	1	4.720
105	200.008	0.782	1	4.794
110	200.009	0.764	1	4.623
150	200.007	0.654	1	4.254

[a] Theoretical values: $E = 200$ kJ mol^{-1}; $A = 1 \times 10^{10}$ s^{-1}. [b] The regression factor. [c] The standard deviation.

TABLE 3

Calculation results for the F2 mechanism [a]

Maximum (%)	E (kJ mol^{-1})	A ($\times 10^{10}$ s^{-1})	R [b]	S_{yx} [c] ($\times 10^{-6}$)
80	200.003	0.640	1	7.908
90	200.003	0.720	1	7.908
95	200.003	0.760	1	8.121
100	200.003	0.800	1	7.270
105	200.003	0.840	1	7.545
110	200.004	0.880	1	7.076
150	200.003	1.20	1	7.075

[a] Theoretical values: $E = 200$ kJ mol^{-1}; $A = 1 \times 10^{10}$ s^{-1}. [b] The regression factor. [c] The standard deviation.

TABLE 4

Calculation results for the A2 mechanism [a]

Maximum (%)	E (kJ mol^{-1})	A ($\times 10^{10}$ s^{-1})	R [b]	S_{yx} [c] ($\times 10^{-2}$)
90	145.758	0.00038	0.9938	7.258
90	185.102	0.100	0.9999	0.9308
95	193.491	0.323	0.99999	0.3326
100	200.011	0.801	1	0.0048
105	204.804	1.56	0.99999	0.3765
110	209.560	3.01	0.99999	0.3450
150	225.246	25.4	0.9997	25.37

[a] Theoretical values: $E = 200$ kJ mol^{-1}; $A = 1 \times 10^{10}$ s^{-1}. [b] The regression factor. [c] The standard deviation.

TABLE 5

Calculation results for the D3 mechanism [a]

Maximum (%)	E (kJ mol^{-1})	A ($\times 10^{10}$ s^{-1})	R [b]	S_{yx} [c] ($\times 10^{-2}$)
80	264.748	1.27×10^4	0.9944	20.04
90	218.285	12.1	0.9998	2.861
95	207.764	2.53	0.99998	1.043
100	200.004	0.801	1	0.0018
105	193.907	0.325	0.99999	0.665
110	188.730	0.151	0.99997	1.061
150	167.576	0.00660	0.9997	2.875

[a] Theoretical values: $E = 200$ kJ mol^{-1}; $A = 1 \times 10^{10}$ s^{-1}. [b] The regression factor. [c] The standard deviation.

TABLE 6

Calculation results for the B13 mechanism [a]

Maximum (%)	E (kJ mol^{-1})	A ($\times 10^{10}$ s^{-1})	R [b]	S_{yx} [c] ($\times 10^{-2}$)
80	277.920	2.13×10^4	0.9867	50.93
90	222.649	14.5	0.9994	8.869
95	209.809	2.78	0.9999	3.408
100	200.001	0.800	1	0.0004
105	192.178	0.300	0.99995	2.215
110	185.970	0.138	0.9998	3.755
150	157.463	0.00427	0.9990	7.932

[a] Theoretical values: $E = 200$ kJ mol^{-1}; $A = 1 \times 10^{10}$ s^{-1}. [b] The regression factor. [c] The standard deviation.

they are discussed in the same group; the others, namely A2, D3 and B13, are discussed in another sub-section.

Results for the R2 and F2 mechanisms

From the results in Tables 2 and 3, it can be seen that the activation energies are almost the same as the theoretical value and the regression factors are perfect ($R = 1$). This means that the correct activation energy can be obtained and the correct reaction mechanism can be known. However, the frequency factor A changes slightly, but the standard deviation values S_{yx} are very small which means the error is very small. The reason for this is almost the same as that discussed in Part 1 [1].

Whether or not there is a pre-history, the real reaction extent α' of the sample can be expressed as

$$\alpha' = (\alpha - \alpha_0)/(1 - \alpha_0)$$

where α is the reaction extent of the sample without pre-history when $\alpha_0 = 0$. Taking the form of the reaction function $f(\alpha)$ into account, gives

$$f(\alpha) = (1 - \alpha)^n$$

and α' needs to be substituted into $f(\alpha)$ because the new curve is taken as the calculation data. This gives

$$f(\alpha') = (1 - \alpha')^n = (1 - \alpha)^n/(1 - \alpha_0)^n = f(\alpha)/(1 - \alpha_0)^n \tag{4}$$

Further,

$$\mathrm{d}\alpha'/\mathrm{d}t = (\mathrm{d}\alpha/\mathrm{d}t)/(1 - \alpha_0) \tag{5}$$

When eqns. (4) and (5) are substituted into eqn. (3), there is a factor of $(1 - \alpha_0)^{1-n}$ introduced in the frequency factor term. This means the frequency factor for the new data will deviate from the theortical value by a factor of $(1 - \alpha_0)^{1-n}$.

In this paper, the frequency factor terms are calculated by taking the range of the manually chosen initial final values (0% in this paper) as the full scale and 80% as the reaction starting point. For example, when the manually chosen initial value is taken as 90%, α_0 for the starting point equals $(90 - 80)/90$, which is 0.1111. Owing to the difference in the n values in the power of $(1 - \alpha_0)$, the calculated frequency factors are increased for the F2 mechanism but decreased for the A2 mechanism, as can be seen in Tables 3 and 4.

From the above discussion, the correct mechanism can be found and the activation energy can be calculated, but the evaluation of the frequency factor is still a problem. The same is true for the SHRI method, owing to the difficulty in finding the actual pre-weight loss or the initial point of the pre-history.

Results for the A2, D3 and B13 mechanisms

In Tables 4, 5 and 6, the results for the A2, D3 and B13 mechanisms are shown. From the results it can be seen that there is an optimum condition when considering the regression factors and the standard deviation values. At the optimum condition, the theoretical activation energy values are obtained and the maximum value of the optimum condition is the real starting value of the reaction without pre-history. Therefore, by changing the initial values of the reaction, the actual values of the pre-history of the samples can be determined and the real activation energy can be obtained.

The reason for the above conclusion is based on eqn. (3) and the conversion of the extent of reaction. While the initial value of the reaction is changed, the $d\alpha'/dt$ and $f(\alpha')$ values are also changed. But only when the real starting value of the pre-history is reached does the $f(\alpha')$ value reach the real value which is used in the data creating process. At the same time, $d\alpha'/dt$ is changed to $(d\alpha/dt)/(1-\alpha_0)$, which is dependent on the α_0 value. Then at the point of the real pre-history condition, the activation energy can be calculated because it is independent of the α_0 value.

After the real pre-history condition is found and the true value of the activation energy determined, another aspect that needs to be discussed is the calculation of the frequency factor. As discussed in the above paragraph, at the real pre-history condition, there is still a difference between the calculated frequency factor and the real frequency factor (in this case the theoretical value used to create the data). This difference arises because the value of the frequency factor is influenced by the value of $d\alpha'/dt$. In Tables 4, 5 and 6, the frequency factors have the same values at the real pre-history condition. They can be converted to the real frequency factor by multiplying the theoretical value 1×10^{10} by a factor of $1-\alpha_0$ ($\alpha_0 = 0.2$ in this paper) (see eqn. (5)).

Proposed kinetic evaluation process for samples with pre-history

From the above discussion, a proposed process for obtaining the reaction mechanism, for evaluating the activation energy and the frequency factor values for a sample with pre-history, the following can be proposed.

First, starting from the original data which is for the sample with pre-history, increasing the initial value of the data which is caused by weight loss or decreasing the initial value for weight gain, run the computer program to obtain the activation energies and the frequency factor values for each condition until the optimum condition is reached, which means a regression factor near to 1 and the lowest standard deviation value.

In this step, the problem is to find the correct reaction mechanism. Some mechanisms may show very good regression factors and standard deviation values from the beginning. However, they can be distinguished from the correct mechanism by the changes in the regression factor and the standard deviation values. For the correct mechanism, the regression factor and the standard deviation value are very sensitive to the initial value, whereas those of false mechanisms are not. Therefore, the correct reaction mechanism can be obtained and the real pre-history condition known.

Second, the form of the reaction mechanism must be taken into account. If there is no change in the activation energies and regression factor values (with a value of 1) but changes in the frequency factors, that mechanism for which the reaction function is of the form $(1-\alpha)^n$ is the correct mechanism, and its is impossible to obtain the frequency factor and the real pre-history condition by using single-heating-rate methods. The activation energy shown in such a calculation is acceptable.

For those reactions whose reaction functions are not of the forms $(1-\alpha)^n$, the real frequency factor can be calculated by multiplying that obtained at the pre-history condition by a factor of $1-\alpha_0$. Here the α_0 value can be calculated by taking the real pre-history condition as the full scale and the starting point value of the original data as the initial point.

CONCLUSIONS

The single-heating-rate methods can be used to evaluate the kinetics of a reaction with pre-history. The correct reaction mechanism and the activation energy can be obtained by changing the initial value of the original data to obtain the kinetic parameters. On changing the initial values, the correct reaction mechanism is the one which gives the best regression factor and standard deviation at only a certain initial value.

After the correct reaction mechanism is found, the form of the reaction function (differential form) should be considered. For a reaction function of the form $(1-\alpha)^n$, the activation energy can be obtained but not the frequency factor value, because of the impossibility of obtaining the real pre-history condition. For other reaction mechanisms, both the activation energy and the frequency factor can be obtained by taking the calculated activation energy at the real pre-history condition as the real activation energy and multiplying the calculated frequency factor by a factor of $1-\alpha_0$ to obtain the real frequency factor.

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