

The influence of temperature shifts on the kinetic evaluation of non-isothermal thermogravimetric data

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Abstract

Temperature shifts which are due to the experimental setup are taken into account in the present study in the evaluation of kinetic procedures. When the temperature shifts considered have a linear relationship with heating rate, it is found that the coefficients in such relationships will decide the changing trend of the calculated activation energy and frequency factor values. This can explain some published results.

However, in the above case the evaluation of the kinetic mechanism is rendered extremely difficult. In such cases there is a high possibility that a kinetic analysis will result in the prediction of an incorrect reaction mechanism. While the problem can be solved by minimizing the coefficients mechanically, performing experiments in a very narrow heating rate range is strongly recommended.

INTRODUCTION

The kinetic interpretation of solid state decomposition reactions can be achieved by using isothermal and/or non-isothermal methods [1–5]. The isothermal methods are considered to be the classical methods although such kinetic evaluation procedures are very time-consuming. The non-isothermal methods are however much easier to apply. In solid state kinetic analysis, it is often the preferred choice. The design of modern thermobalances often precludes an accurate and precise isothermal experiment because it always takes time to raise the sample under study to the desired isothermal temperature. As a consequence there are many kinetic studies reported which use non-isothermal methods [6–12]. One of the existing problems is the inconsistency of kinetic results from different studies on the same material. General explanations offered are the differences in the experimental conditions and the kinetic evaluation procedure. Nevertheless, the main reason for this inconsistency comes from the inaccurate measurement of temperature in most thermal methods while other signals can be

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collected accurately [13–15]. This inaccurate temperature measurement can be due to the accuracy of thermocouple, the position of thermocouple in the furnace, the shape of the sample pan and sample size, etc.

From published kinetic reports using the non-isothermal methods [11, 12, 16–19], it is apparent that in some cases [11, 12, 16, 17] the calculated activation energy E decreased when the programmed heating rate β increased, but in other cases [18, 19] the opposite was found. This demonstrates a deviation from the general assumption in the use of multi-heating-rate kinetic evaluations that the activation energy is unchanged while the heating rate is changing. An attempt to explain this phenomenon theoretically is made in this article. Furthermore, the proposed kinetic evaluation procedure [20] is supported with more results.

There are studies about the position of thermocouple in conventional TG equipment [13–15], but one interesting factor that must be considered is the temperature difference ΔT between the programmed temperature and the recorded temperature, changing as the programmed heating rate changes. Figure 1 shows the recorded temperature against time at linear heating rates of 10 and 50°C min⁻¹ from a TA SDT 2960 thermal analyzer. The dashed line is the programmed temperature or theoretical furnace temperature. It can be seen that the temperature difference increases as the heating rate increases. Based on the literature [13–15], the temperature difference between that of the furnace and the thermocouple can be expressed as

$$\Delta T_1 = T_f - T_t = a_1 + b_1 \beta \quad (1)$$

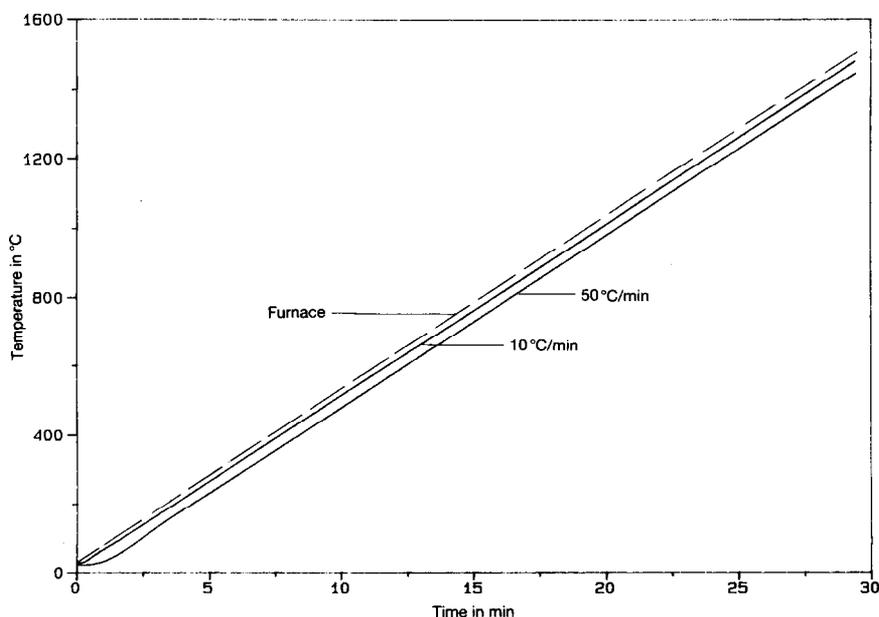


Fig. 1. Recorded temperature against time at heating rates of 10 and 50°C min⁻¹.

where a_1 and b_1 are constants related to the work station, T_f is the furnace temperature and T_t is the temperature recorded by the thermocouple. If the temperature difference between that of the thermocouple and the sample follows the same relationship, then

$$\Delta T_2 = T_t - T_s = a_2 + b_2\beta \quad (2)$$

where T_s is the sample temperature; a_2 and b_2 are constants. The combination of eqns. (1) and (2) will give the relationship of the temperature difference between that of the furnace and the sample in the form of

$$\Delta T = \Delta T_1 - \Delta T_2 = T_f - T_s = a + b\beta \quad (3)$$

where a and b are constant. Both a and b can be positive or negative and are decided by the work station being used.

Other theories and related equations for non-isothermal kinetic evaluation can be found in refs. 11, 12 and 20.

EXPERIMENTAL SECTION

Computer programs applied to kinetic evaluation and symbols used in this article are the same as those published [11, 12, 20]. The data files were created as before [11, 12, 20] and the temperature shift was introduced into those files by inputting the appropriate temperature difference according to eqn. (3). T_s is the temperature to be used in the calculation and T_f is the programming temperature. a and b values used were 5 and 0.5, 10 and 0.5, 5 and 0.1, -5 and -0.5 , 40 and 0.5. The reaction mechanisms applied were A2 and R2 (see refs. 11, 12 and 20 for meaning) with heating rates of 5, 10, 20 and $40^\circ\text{C min}^{-1}$. The theoretical activation energy values are $200.00 \text{ kJ mol}^{-1}$. The frequency factor values are $1 \times 10^{10} \text{ s}^{-1}$.

The calculation of kinetic parameters was performed by using programs named as, the single-heating-rate differential method (SHRD) [11, 12, 20], the single-heating-rate integral method (SHRI) [21], the Friedman method (MHRD) [22] and the Ozawa method (MHRI) [23]. The single-heating-rate methods (SHRD and SHRI) need only one set of experimental data while the multi-heating-rate methods (MHRD and MHRI) need at least two sets of experimental data.

RESULTS AND DISCUSSION

The calculation results from the SHRD, SHRI, MHRD and MHRI methods for correct reaction mechanisms are listed in Tables 1a, 1b, 2a, 2b, and 3. In the following discussion the influence of a temperature shift of the kind noted above is shown to influence various kinetic features, notably (1) the mechanism determination from the proposed kinetic evaluation procedure [20], and (2), the changes in the calculated activation energy and

TABLE 1a
Calculation results from the single-heating-rate methods of A2 mechanism

$\beta / ^\circ\text{C min}^{-1}$	Parameter ^a	$\Delta T = 0$			$\Delta T = 5 + 0.5\beta$			$\Delta T = 5 + 0.1\beta$			$\Delta T = 10 + 0.5\beta$		
		SHRD	SHRI	SHRD	SHRI	SHRD	SHRI	SHRD	SHRI	SHRD	SHRI	SHRD	SHRI
5	$E/\text{kJ mol}^{-1}$	200.02	199.93	196.38	196.17	197.34	197.17	193.97	193.69				
	$A/\text{s}^{-1} \times 10^9$	10.0	9.74	7.67	7.32	8.24	7.90	6.41	6.05				
	R	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000			
10	$E/\text{kJ mol}^{-1}$	200.03	199.93	195.29	195.03	197.18	196.98	192.94	192.60				
	$A/\text{s}^{-1} \times 10^9$	10.0	9.94	7.14	6.90	8.18	7.98	6.01	5.75				
	R	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000			
20	$E/\text{kJ mol}^{-1}$	200.06	199.93	193.13	192.77	196.81	196.57	190.85	190.41				
	$A/\text{s}^{-1} \times 10^9$	10.1	9.84	6.18	5.83	8.02	7.71	5.25	4.90				
	R	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000			
40	$E/\text{kJ mol}^{-1}$	200.11	199.93	188.89	188.33	196.03	195.71	186.68	186.05				
	$A/\text{s}^{-1} \times 10^9$	10.2	9.87	4.66	4.29	7.67	7.31	3.99	3.63				
	R	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000			

^a Theoretical values are $E = 200.00 \text{ kJ mol}^{-1}$ and $A = 100 \times 10^{10} \text{ s}^{-1}$; R is the regression factor.

TABLE 1b
Calculation results from the single-heating-rate methods of A2 mechanism

$\beta/^\circ\text{C min}^{-1}$	Parameter ^a	$\Delta T = 0$			$\Delta T = -5 - 0.5\beta$			$\Delta T = 40 - 0.5\beta$			$\Delta T = -40 + 0.5\beta$		
		SHRD	SHRI	SHRD	SHRI	SHRD	SHRI	SHRD	SHRI	SHRD	SHRI	SHRD	SHRI
5	$E/\text{kJ mol}^{-1}$	200.02	199.93	203.69	203.72	182.15	181.50	218.71	219.25				
	$A/\text{s}^{-1} \times 10^9$	10.0	9.74	13.1	13.1	2.63	2.34	38.2	40.6				
	R	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000				
10	$E/\text{kJ mol}^{-1}$	200.03	199.93	204.83	204.89	183.69	183.05	217.04	217.54				
	$A/\text{s}^{-1} \times 10^9$	10.0	9.94	14.1	14.3	3.04	2.77	34.5	35.6				
	R	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000				
20	$E/\text{kJ mol}^{-1}$	200.06	199.93	207.11	207.21	186.32	185.74	214.28	214.63				
	$A/\text{s}^{-1} \times 10^9$	10.1	9.84	16.4	16.6	3.79	3.46	26.8	28.0				
	R	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000				
40	$E/\text{kJ mol}^{-1}$	200.11	199.93	211.87	211.87	191.11	190.62	209.32	209.46				
	$A/\text{s}^{-1} \times 10^9$	10.2	9.87	22.1	22.7	5.44	5.07	18.9	19.2				
	R	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000				

^a Theoretical values are $E = 200.00 \text{ kJ mol}^{-1}$ and $A = 100 \times 10^{10} \text{ s}^{-1}$; R is the regression factor.

TABLE 2a
Calculation results from the single-heating-rate methods for R2 mechanism

$B/^\circ\text{C min}^{-1}$	Parameter ^a			$\Delta T = 5 + 0.5\beta$			$\Delta T = 5 + 0.1\beta$			$\Delta T = 10 + 0.5\beta$			
	$E/\text{kJ mol}^{-1}$	$A/\text{s}^{-1} \times 10^9$	R	SHRD	SHRI	SHRD	SHRI	SHRD	SHRI	SHRD	SHRI	SHRD	SHRI
5	200.00	199.94	1.000	196.19	196.01	196.19	196.01	196.19	196.01	196.19	196.01	196.19	196.01
	10.0	9.75	1.000	7.45	7.13	7.45	7.13	7.45	7.13	7.45	7.13	7.45	7.13
	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10	200.01	199.94	1.000	195.03	194.80	195.03	194.80	195.03	194.80	195.03	194.80	195.03	194.80
	10.0	9.96	1.000	6.87	6.67	6.87	6.67	6.87	6.67	6.87	6.67	6.87	6.67
	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
20	200.02	199.93	1.000	192.73	192.42	192.73	192.42	192.73	192.42	192.73	192.42	192.73	192.42
	10.0	9.85	1.000	5.84	5.54	5.84	5.54	5.84	5.54	5.84	5.54	5.84	5.54
	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
40	200.03	199.93	1.000	188.22	187.74	188.22	187.74	188.22	187.74	188.22	187.74	188.22	187.74
	10.0	9.88	1.000	4.24	3.94	4.24	3.94	4.24	3.94	4.24	3.94	4.24	3.94
	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

^aTheoretical values are $E = 200.00 \text{ kJ mol}^{-1}$ and $A = 1.00 \times 10^{10} \text{ s}^{-1}$; R is the regression factor.

TABLE 2b
Calculation results from the single-heating-rate methods for R2 mechanism

$B/^{\circ}\text{C min}^{-1}$	Parameter ^a	$\Delta T = 0$			$\Delta T = -5 - 0.5\beta$			$\Delta T = 40 - 0.5\beta$			$\Delta T = 40 + 0.5\beta$		
		SHRD	SHRI	SHRD	SHRI	SHRD	SHRI	SHRD	SHRI	SHRD	SHRI		
5	$E/\text{kJ mol}^{-1}$	200.00	199.94	203.86	203.92	181.29	180.66	219.64	220.20				
	$A/\text{s}^{-1} \times 10^9$	10.0	9.75	13.4	13.3	2.29	2.04	43.6	46.6				
	R	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000				
10	$E/\text{kJ mol}^{-1}$	200.01	199.94	205.05	205.14	182.85	182.25	217.93	218.44				
	$A/\text{s}^{-1} \times 10^9$	10.0	9.96	14.6	14.9	2.68	2.44	37.5	40.6				
	R	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000				
20	$E/\text{kJ mol}^{-1}$	200.02	199.93	207.43	207.60	185.58	185.04	214.98	215.40				
	$A/\text{s}^{-1} \times 10^9$	10.0	9.85	17.2	17.5	3.40	3.11	29.6	31.2				
	R	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000				
40	$E/\text{kJ mol}^{-1}$	200.3	199.93	212.19	212.50	190.56	190.15	209.73	209.95				
	$A/\text{s}^{-1} \times 10^9$	10.0	9.88	23.8	24.8	5.04	4.73	20.2	20.6				
	R	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000				

^a Theoretical values are $E = 200.00 \text{ kJ mol}^{-1}$ and $A = 1.00 \times 10^{10} \text{ s}^{-1}$; R is the regression factor.

TABLE 3

Average activation energy values ^a from the multi-heating-rate methods

$\Delta T =$	A2		R2	
	MHRD	MHRI	MHRD	MHRI
0	200.01(±0.06)	204.21(±0.31)	200.01(±0.01)	203.79(±0.91)
5 + 0.5 β	269.92(±7.89)	275.70(±8.25)	277.83(±7.59)	283.21(±12.47)
5 + 0.1 β	208.91(±0.85)	213.31(±0.23)	209.78(±1.02)	213.77(±0.76)
10 + 0.5 β	266.72(±7.28)	272.43(±7.45)	274.40(±13.24)	279.71(±15.39)
-5 - 0.5 β	159.83(±1.52)	163.16(±3.45)	157.24(±4.89)	160.18(±3.56)
40 - 0.5 β	143.79(±2.80)	146.78(±3.30)	140.87(±4.03)	143.51(±4.57)
-40 + 0.5 β	299.61(±8.97)	306.02(±5.62)	309.66(±19.59)	315.65(±20.55)

^a Theoretical activation energy values for A2 and R2 mechanisms are 200.00 kJ mol⁻¹; the values in parentheses are the standard deviation ranges.

frequency factor values. Finally solutions for the influence of such temperature shifts on kinetic evaluation procedure are proposed.

Mechanism determination

From Tables 1a, 1b, 2a and 2b, it can be seen that under a certain condition, SHRD and SHRI methods provide very good agreement of the activation energy and frequency factor values. This shows that both methods can be used to obtain kinetic information from a single heating rate experiment. However, when results from multi-heating-rate methods given in Table 3 are taken into account, it can be seen that there is a significant difference in the activation energy values when they are compared with those from the single-heating-rate methods for certain conditions. For instance, when $\Delta T = 5 + 0.5\beta$, the calculated activation energy values for the A2 mechanism from SHRD and SHRI methods at 5°C min⁻¹ are 196.38 and 196.17 kJ mol⁻¹ respectively which are different from those calculated from the MHRD and MHRI methods of 227.58 and 238.21 kJ mol⁻¹ respectively. The kinetic evaluation procedure that has been advocated previously includes the use of kinetic parameters derived from the single-heating-rate and the multi-heating-rate methods. Therefore in the above situation the determined reaction mechanism will not be A2 and the final kinetic results will be wrong. This means that if the temperature shift already discussed is present then the results from the single-heating-rate technique and the multi-heating-rate methods will produce results which are at variance with the A2 mechanism of the model system.

When the b value (see Tables 1a, 1b, 2a and 2b) is positive, the calculated activation energy values from the multi-heating-rate methods are larger than those from the single-heating-rate methods for the theoretical mechanism.

From the activation energy values at $b = 0.1$ and $b = 0.5$ when $a = 5$, it can be seen that the larger the b value, the bigger the difference in the activation energy values. Also, when $b = 0.5$ and a increases from 5 to 10, a bigger difference in the activation energy values is found.

When $b < 0$, the opposite trend to that for $b > 0$ is found. When b equals 0 however, there will not be any difference in the activation energy values from the single-heating-rate methods and the multi-heating-rate methods [20].

The application of the proposed kinetic evaluation procedure in these conditions will give totally inaccurate results [20]. The main error is in the determination of the reaction mechanism. For example, when $\Delta T = 5 + 0.5\beta$, the indicated reaction mechanism determined from the proposed procedure will be A1.5 for data from the A2 mechanism and F1 for data from the R2 mechanism. This means that the accuracy of kinetic determination is largely dependent upon the accuracy of temperature measurement. Under the conditions being considered, the instrumental setup will largely affect the final results.

Changes in the calculated activation energy and the frequency factor values

When the relation between the activation energy value and the heating rate used is taken into account, the calculated results from the SHRD method listed in Tables 1a, 1b, 2a and 2b are shown in Figs. 2 and 3. From the figures it can be seen that when $b > 0$, the calculated activation energy value decreases as the heating rate increases. When $b < 0$, the opposite is found. The changes are much more related to the b value. The larger the b

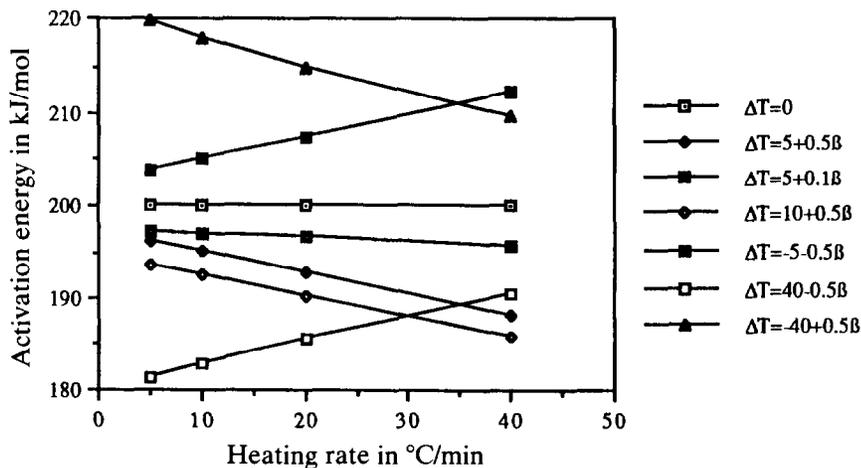


Fig. 2. The calculated activation energy value against the heating rate at different temperature shift conditions for A2 mechanism.

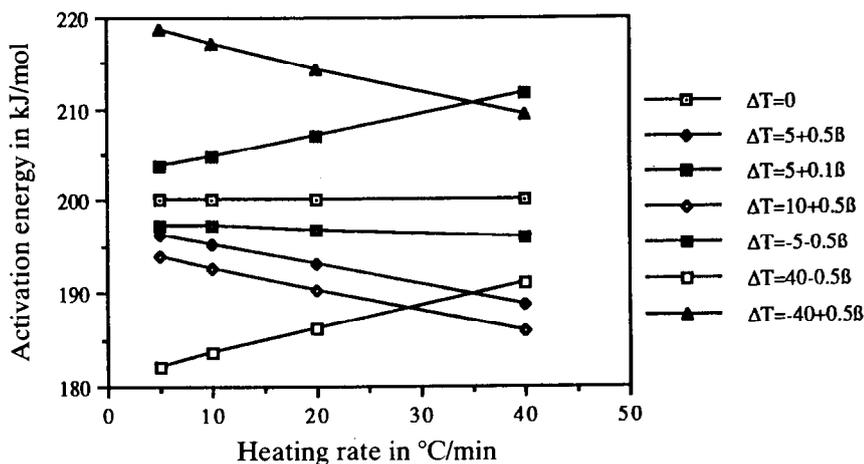


Fig. 3. The calculated activation energy value against the heating rate at different temperature shift conditions for R2 mechanism.

value, the larger the changes in activation energy values. These two cases are in accordance with those found in literature [11, 12, 16–19]. Results from refs. 11, 12, 16 and 17 have shown that the calculated activation energy decreased when heating rate increased which in this article is likely to happen when b has a positive value. Results from refs. 18 and 19 might have a negative b value.

If a temperature shift occurs as noted above then the correct reaction mechanism may not be determined. However, it is also found that when there is temperature shift in the experimental system, the calculated activation energy value will show the same trend as above whichever reaction mechanism is chosen.

Solutions for temperature shift effect in the kinetic evaluation procedure

From the above discussions, it can be seen that the b value will decide the trend of changes in the calculated activation energy and frequency factor values while the a value will decide the overall shift of the calculated values [20]. The combination of them will probably change the reaction mechanism determined and the calculated activation energy and frequency factor values. It is then very easy to find the first solution for this problem: if a and b values can be made to be very small, such problems found in kinetic evaluation procedures due to temperature shift will not exist. This is an engineering problem rather than a kinetic evaluation problem.

Another solution for this problem is as proposed before [20], namely to perform experiments at a narrow range of heating rates. In Figs. 2 and 3 it can be seen that the calculated activation energy values at heating rates of 5 and 10°C min⁻¹ have closer values for the single-heating-rate methods.

TABLE 4

Average activation energy values ^a from the multi-heating-rate methods of data at heating rates of 5 and 10°C min⁻¹

$\Delta T =$	A2		R2	
	MHRD	MHRI	MHRD	MHRI
0	200.00(±0.03)	209.34(±0.25)	200.00(±0.01)	209.21(±0.84)
5 + 0.5 β	227.58(±3.42)	238.21(±4.02)	230.25(±3.59)	240.84(±5.28)
5 + 0.1 β	202.92(±0.58)	212.40(±0.20)	203.26(±0.86)	212.61(±0.67)
10 + 0.5 β	224.84(±3.21)	235.34(±3.15)	227.37(±4.24)	237.83(±6.25)
-5 - 0.5 β	179.21(±0.89)	187.59(±1.72)	177.71(±2.46)	185.89(±1.76)
40 - 0.5 β	160.66(±1.03)	168.17(±1.46)	158.64(±2.12)	165.94(±2.16)
-40 + 0.5 β	252.97(±4.21)	264.78(±2.82)	256.96(±7.68)	268.78(±9.25)

^a Theoretical activation energy values for A2 and R2 mechanisms are 200.00 kJ mol⁻¹; the values in parentheses are the standard deviation ranges.

When the multi-heating-rate methods are taken into account, the results coming from the data at heating rates of 5 and 10°C min⁻¹ are listed in Table 4. It can be seen that the calculated activation energy values are much closer to those from the single-heating-rate methods. At the same time, the standard deviation ranges (Table 4) become smaller than those by using large heating rate range (Table 3). This process can minimize the possibility of obtaining incorrect reaction mechanisms and finally the wrong activation energy and frequency factor values. When combined with the above solution, the best results will be obtained.

CONCLUSIONS

When there are temperature shifts due to the experimental setup, the kinetic evaluation may be in error. If the temperature shift between the programmed and sample temperature is not related to the heating rate, then kinetic evaluation is possible. If, however, the temperature shift is heating rate related, then the kinetic evaluation needs experiments performed at a narrow heating rate range.

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