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A generalized form of the Kissinger equation

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Abstract

An equation is deduced in this paper and an attempt is made to obtain the peak maxima information theoretically from the differential thermogravimetry curves. The calculations are critically assessed. The Kissinger method, which also deals with the peak maxima, is also discussed. A comparison of the equation due to Kissinger and that of the equation deduced in this paper shows that the Kissinger equation is a special case of this equation. The approximation made in the deduction of the Kissinger equation can be restated as "The extent of reaction at the peak maxima under different heating rates is the same."

INTRODUCTION

There are basically two kinds of methods for evaluating kinetic parameters in thermal analysis [1, 2]. One is the single-heating-rate method and the other is the multi-heating-rate method. In both there are two routines which are most often used, namely the differential method and the integral method.

There is however another method, which is due to Kissinger [3] and is based on the change in the position of the peak maxima with the heating rate being used. Although it was originally deduced for the data obtained from differential thermal analysis (DTA), the method allows the reaction rate and the reaction extent to be obtained from the thermogravimetry (TG). In general, it is difficult to locate the exact peak maxima positions and the reaction process is affected by the reaction environment [4].

In this paper, an equation which is based on premises similar to those used in the Kissinger equation is deduced. This equation is tested and its relation with the Kissinger equation is discussed.

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THEORY

In thermal analysis, the expression that shows the variation of reaction rate with temperature is

$$\mathrm{d}\alpha/\mathrm{d}t = f(\alpha)k(T) \qquad (1)$$

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

$$k(T) = A\exp(-E/RT) \qquad (2)$$

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.

TABLE 1A

The common forms of $f(\alpha)$

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

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

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

The second differential of eqn. (3) is

$$\begin{aligned}\mathrm{d}(\mathrm{d}\alpha/\mathrm{d}t)/\mathrm{d}t = {} & Af(\alpha)(E/RT^2)\beta\exp(-E/RT)\\ & + A\exp(-E/RT)f'(\alpha)(\mathrm{d}\alpha/\mathrm{d}t)\end{aligned} \tag{4}$$

where $f'(\alpha)$ is the derivative form of $f(\alpha)$. A list of $f'(\alpha)$ is shown in Table 1B. β is the linear heating rate and can be expressed as $\mathrm{d}T/\mathrm{d}t$.

At the peak maxima, eqn. (4) should be equal to 0. Then eqn. (4) becomes

$$Af(\alpha)(E/RT^2)\beta\exp(-E/RT) = -A\exp(-E/RT)f'(\alpha)(\mathrm{d}\alpha/\mathrm{d}t) \tag{5}$$

At this peak maximum position, eqn. (5) should hold and all the

TABLE 1B

The common forms of $f'(\alpha)$

Mechanism	$f'(\alpha)$
Acceleratory α–t *curve*	
P1	$3\alpha^{-1/4}$
	$2\alpha^{-1/3}$
	$\alpha^{-1/2}$
	0
	$-(1/3)\alpha^{-3/2}$
E1	1
S-shaped α–t *curve*	
A1.5	$1.5[-\ln(1-\alpha)]^{1/3}\{1/3[-\ln(1-\alpha)\}^{-1}-1\}$
A2	$2[-\ln(1-\alpha)]^{1/2}\{1/2[-\ln(1-\alpha)]^{-1}-1\}$
A3	$3[-\ln(1-\alpha)]^{1/3}\{2/3[-\ln(1-\alpha)]^{-1}-1\}$
A4	$4[-\ln(1-\alpha)]^{3/4}\{3/4[-\ln(1-\alpha)]^{-1}-1\}$
B1	$1-2\alpha$
	$0.5[-\ln(1-\alpha)]^{-1}\{-[-\ln(1-\alpha)]^{-1}-1\}$
	$(1/3)[-\ln(1-\alpha)]^{-2}\{-2[-\ln(1-\alpha)]^{-1}-1\}$
	$(1/4)[-\ln(1-\alpha)]^{-3}\{-3[-\ln(1-\alpha)]^{-1}-1\}$
Deceleratory α–t *curve*	
R2	$-(1-\alpha)^{-1/2}$
R3	$-2(1-\alpha)^{-1/3}$
D1	$-1/(2\alpha^2)$
D2	$-(1-\alpha)^{-1}[\ln(1-\alpha)]^{-2}$
D3	$1.5[1-(1-\alpha)^{1/3}]^{-1}\{-1/3[1-(1-\alpha)^{1/3}]^{-1}-2/3(1-\alpha)^{-1/3}\}$
D4	$-0.5(1-\alpha)^{-2/3}[1-(1-\alpha)^{1/3}]^{-2}$
F1	-1
F2	$-2(1-\alpha)$
F3	$-1.5(1-\alpha)^2$

variables T, $d\alpha/dt$ and α are the values for those parameters at that point. After rearrangement, eqn. (5) can be expressed as

$$f(\alpha_m)E\beta/RT_m^2 = -f'(\alpha_m)(d\alpha/dt)_m \qquad (6)$$

where T_m, $(d\alpha/dt)_m$ and α_m are the values of T, $d\alpha/dt$ and α at this peak maximum. For a specific reaction, the activation energy can be calculated if the reaction mechanism is known and all the peak maximum information can be ascertained from the differential thermogravimetry (DTG) plot. In this paper all the reaction mechanisms in Table 1B are tested from the peak maximum information created by assuming a single particular mechanism. The frequency factor A for each mechanism can then be calculated by using eqn. (1) after the activation energy has been calculated from eqn. (6).

The Kissinger method also deals with the peak maximum position. The equation of the Kissinger method is

$$\ln(\beta/T_m^2) = C - E/RT_m \qquad (7)$$

By changing the heating rate, the peak temperatures can be found and from the linear regression of the $\ln(\beta/T_m^2)$ vs. $1/T_m$ plot the activation energy and other regression parameters can be calculated.

EXPERIMENTAL

The data files for this paper were created by using a computer program which could create the data file for further calculations and the peak information file for this paper at the same time. This involved using a certain initial α value α_0 (0, 0.05, 0.1, 0.15 and 0.2) for the reaction at the initial temperature T_0 (300 K), the activation energy, the frequency factor, the heating rate (5, 10, 20 and 40°C min^{-1}), the interval of sampling Δt (0.01 second per point), and choosing one mechanism for that set of files. Equation (3) with $T = T_0 + \beta t$ (t is the time of heating) and $\alpha = \alpha_0 + (d\alpha/dt)\,\Delta t$ can then be used to obtain the $d\alpha/dt$, T and α values for the calculation. The $d\alpha/dt$ values are compared in each step and the maximum value with the corresponding α and T values stored in the peak file for further calculation.

The programs were run on QUICK BASIC software which provides a fast speed and is easy to edit. The figures were drawn by using QUATTRO software. The units of axes in the figures correspond to units which are the same as those from the available TG equipment.

RESULTS AND DISCUSSION

The reaction mechanisms A2 and R2 were chosen as examples. The kinetic parameters used in the calculation were as follows. The activation energy was taken as 200 kJ mol^{-1}; the frequency factor as 1×10^{10} s^{-1}; the

TABLE 2

Peak maxima information for the A2 mechanism calculated from theoretical data using eqn. (3) [a]

β (°C min^{-1})	Function	Peak temp. T_m (K)	α_m	$(d\alpha/dt)_m$ (10^{-3} s^{-1})
5	A2	835.2	0.6203	2.313
	R2	816.3	0.7338	1.642
10	A2	853.4	0.6201	4.278
	R2	833.7	0.7335	3.040
20	A2	874.0	0.6198	8.321
	R2	853.4	0.7331	5.919
40	A2	894.7	0.6196	15.76
	R2	873.2	0.7328	11.22

[a] Theoretical parameters: $E = 200$ kJ mol^{-1}; $A = 1 \times 10^{10}$ s^{-1}.

heating rates chosen were 5, 10, 20 and 40°C min^{-1}. Table 2 shows peak maxima information for all the heating rates for the A2 and R2 mechanisms. Figures 1 and 2 shows TG and DTG curves for the A2 and R2 mechanisms at a heating rate of 10°C min^{-1} respectively.

Application of new equation

The information in Table 2 was used in eqn. (6) and the activation energies and the frequency factors for all the reaction mechanisms were calculated. The results for the A2 and R2 mechanisms are listed in Tables 3 and 4 respectively. From these data it should be noted that there are

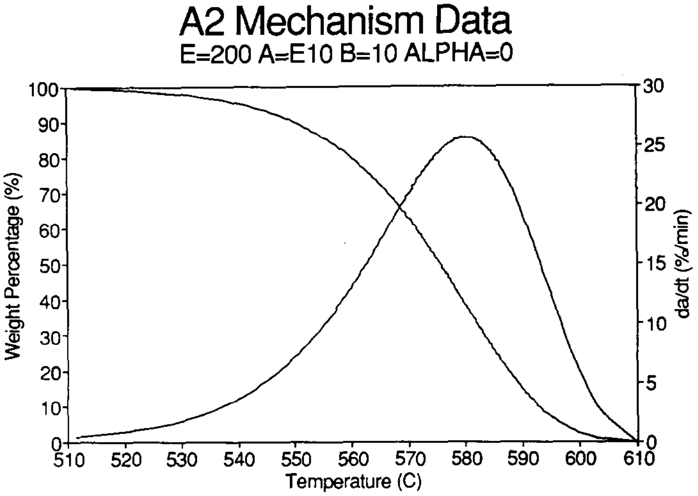

Fig. 1. Theoretical TG and DTG curves for the A2 mechanism at a heating rate of 10°C min^{-1}.

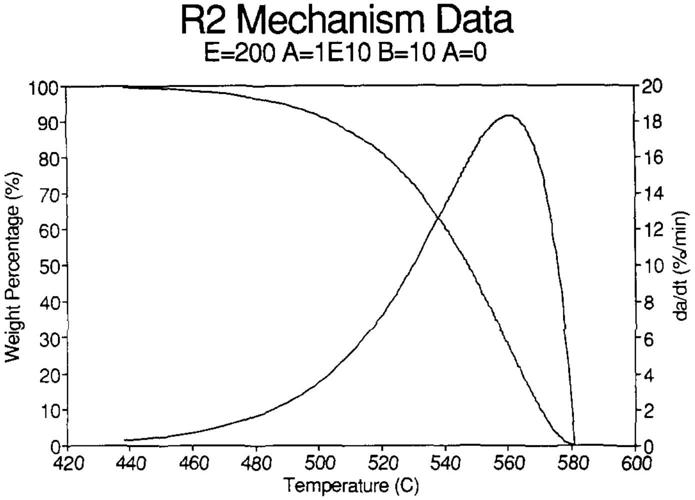

Fig. 2. Theoretical TG and DTG curves for the R2 mechanism at a heating rate of 10°C min^{-1}.

TABLE 3

Results calculated for the A2 mechanism using eqn. (6) and the parameters indicated in Table 2 [a]

	β (°C min^{-1})			
Parameter	5	10	20	40
E (kJ mol^{-1})	204.99	197.79	201.41	199.66
A (10^{10} s^{-1})	2.05	0.732	1.21	0.956

[a] Theoretical parameters: $E = 200$ kJ mol^{-1}; $A = 1 \times 10^{10}$ s^{-1}.

TABLE 4

Results calculated for the R2 mechanism using eqn. (6) and the parameters indicated in Table 2 [a]

	β (°C min^{-1})			
Parameter	5	10	20	40
E (kJ mol^{-1})	205.10	197.73	201.44	199.63
A (10^{10} s^{-1})	2.12	0.721	1.23	0.950

[a] Theoretical parameters: $E = 200$ kJ mol^{-1}; $A = 1 \times 10^{10}$ s^{-1}.

differences between the calculated activation energies and the theoretical value. Although the interval of sampling used in the peak maxima search program (0.01 second per point) is very very small, a smaller sampling interval might improve the analysis. However, the average value of all the calculated activation energies is very close to the theoretical value. This intrinsic problem is the main defect in the application of this method to real cases, for which the data is generally collected in a 3 seconds per point sampling interval. It should be noted that in the calculation of all the information of a curve ($d\alpha/dt$, α and T) any error is amplified in each calculation step. This can be observed by inspection of the theoretical curves in Figs. 1 and 2, where small irregularities can be detected.

The activation energies must then be used here to calculate the frequency factors, so any errors in activation energy are reflected in the calculation of the frequency factor. The presence of the experimental function in the calculation magnifies any error on going from the activation energy to the frequency factor. For example, in Table 3, for the sample with a heating rate of 5°C min^{-1}, the activation energy is 204.99 kJ mol^{-1}, which is slightly larger than the theoretical value (200 kJ mol^{-1}) but the frequency factor A ($2.05 \times 10^{10}\ \mathrm{s}^{-1}$) is twice as large as the theoretical value ($1 \times 10^{10}\ \mathrm{s}^{-1}$).

The use of the new equation can be seen to produce an acceptable value for the activation energy, but some alternative method of identifying the mechanism is needed, and then any small error in the activation energy is magnified in the subsequent calculation of the frequency factor.

Application of the Kissinger method

The Kissinger method may also be programmed utilizing the above data files. The results of the calculation are shown in Table 5. The results show that the calculated activation energies for the A2 and R2 mechanisms are very close to the theoretical values. They are also closer than those calculated by the Ozawa method [5]. This shows the theoretical advantage of the Kissinger method over the Ozawa method.

Although in the Kissinger method the results for A and E are good, the regression factors are not so good. The data comes from a theoretical

TABLE 5

Results from the Kissinger method using eqn. (7) [a]

Mechanism	E (kJ mol^{-1})	R	Standard error
A2	201.55	0.99987	0.0163
R2	201.69	0.99987	0.0164

[a] Theoretical parameters: $E = 200$ kJ mol^{-1}; $A = 1 \times 10^{10}\ \mathrm{s}^{-1}$.

calculation, so the regression factors should be 1 instead of 0.99987 in Table 5. If once again the real case is considered, the difficulty in locating the values of α_m and other parameters associated with the peak maxima will probably make the use of the Ozawa method give better results.

Comparison of the generalized Kissinger equation and the Kissinger equation

In the above discussion it would appear that the Kissinger method has advantages over the use of eqn. (6). The relation between the two equations should be discussed because the Kissinger equation is deduced from an approximation [6].

If eqn. (3) is substituted into eqn. (6), the result is

$$\beta/T_m^2 = -[ARf'(\alpha_m)/E]\exp(-E/RT_m) \tag{8}$$

Taking logarithms gives

$$\ln(\beta/T_m^2) = X - E/RT_m \tag{9}$$

where X is $\ln[-ARf'(\alpha_m)/E]$. This may be compared with the Kissinger equation (eqn. (7)).

It can be seen that the only difference between eqns. (7) and (9) is between the constant C in the eqn. (7) and the corresponding term $X = \ln[-ARf'(\alpha_m)/E]$ in eqn. (9). Because E, A and R are constant for a certain reaction, if there is no change in the value of α_m while the heating rate β is changing, eqn. (9) is actually equivalent to eqn. (7). This means that the Kissinger equation is a "special" case of eqn. (9).

When the peak maxima information in Table 2 is taken into account, the change of the α_m values against the change of the heating rate is very small. Although the reason for this is beyond the scope of the present paper, the Kissinger method must be considered a very good approximation. It should also be noted that in the Kissinger method, it is not necessary to know the reaction mechanism in order to find the activation energy.

CONCLUSIONS

By considering the peak maximum position and related parameters, eqn. (6) can be deduced based on the rate of the reaction, eqn. (1) and the Arrhenius equation (eqn. (2)). The real value of deriving this equation is that it can be developed in such a way that the Kissinger equation can be shown to be a special case of it. This places the Kissinger method on a firmer basis than hitherto.

The result shows that the Kissinger equation is a special case of the new equation; the latter takes the reaction extent at the peak maximum condition as a constant while the heating rate is changing. The advantages of the Kissinger method are that it is not necessary to know the reaction mechanism to calculate the activation energy and one needs only to locate the peak maximum temperature for the calculation. The main disadvantage of the Kissinger method is that it is dependent on the accuracy of the peak position, which may be difficult to find in real reactions.

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