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The correlation between the value of α at the maximum reaction rate and the reaction mechanisms. A theoretical study

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Abstract

In this paper, a relationship between the value of α at the maximum reaction rate (α_{max}) and the reaction mechanism has been deduced mathematically from the fundamental rate equations for the solid state reaction. This relation can be expressed as $f'(\alpha_{max}) G(\alpha_{max}) = -1 + 2RT_{max}/E$. The effect of activation energy on α_{max} has also been discussed. When $E/RT_{max} > 20$, the values of α_{max} fall in a narrow range dependent on the reaction mechanism. This work gives a theoretical verification to the kinetic analysis procedure proposed by Dollimore and co-workers.

INTRODUCTION

Non-isothermal kinetic analysis is widely used in studying solid state reactions. Dollimore and co-workers [1–3] have pointed out the significance of the onset, maximum and final temperatures in the kinetic analysis of TG curves. Different reaction mechanisms have their own characteristic geometric shapes which can be represented by these three temperatures, as well as by the range of α at the maximum reaction rate, here termed α_{max}. In their studies, several selected E and A values were used to calculate the α_{max}. The results show that α_{max} depends only on the reaction mechanism, not on the frequency factor A or the activation energy E. They assumed that each mechanism therefore has a specific constant value of α_{max}. The procedure is simply to narrow down the number of probable kinetic models using this information. In this paper, some theoretical work is presented which verifies this assumption.

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DERIVATIONS AND RESULTS

For non-isothermal kinetic analysis, the progress of a solid state reaction can be expressed as a differential equation

$$d\alpha/dt = (A/\beta)\exp(-E/RT)f(\alpha) \tag{1}$$

or its integral form

$$G(\alpha) = \int 1/f(\alpha)\,d\alpha = (A/\beta)\int \exp(-E/RT)\,dT \tag{2}$$

where $f(\alpha)$ and $G(\alpha)$ represent the reaction mechanism, E is the activation energy, A the frequency factor, T the temperature in kelvin, β the constant heating rate, and α the degree of conversion.

If we set $E/RT = x$, then eqn. (2) becomes

$$\begin{aligned} G(\alpha) &= (A/\beta)\int \exp(-E/RT)\,dT = (AE/\beta R)\int [\exp(-x)/x^2]\,dx \\ &= (AE/R\beta)p(x) \end{aligned} \tag{3}$$

where $p(x)$ does not have an analytical solution. A series approximation for $p(x)$, called the asymptotic expansion [4], was used. Its expression is

$$\begin{aligned} p(x) = [\exp(-x)/x^2]\{1 - (2!/x) + (3!/x^2) - \cdots \\ + (-1)^n[(n+1)!/x^n] + \cdots\} \end{aligned} \tag{4}$$

Taking only the first two terms of each series

$$p(x) = (x-2)\exp(-x)/x^3 \tag{5}$$

Inserting eqn. (5) into eqn. (3)

$$G(\alpha) = (AE/\beta R)(x-2)\exp(-x)/x^3 \tag{6}$$

Differentiating eqn. (1) with T gives

$$\begin{aligned} d^2\alpha/dT^2 &= (A/\beta)\exp(-E/RT)f'(\alpha)(d\alpha/dT) \\ &\quad + (E/RT^2)(A/\beta)\exp(-E/RT)f(\alpha) \end{aligned} \tag{7}$$

Inserting eqn. (1) into eqn. (7)

$$\begin{aligned} d^2\alpha/dT^2 &= (A/\beta)\exp(-E/RT)f'(\alpha)(d\alpha/dT) + (E/RT^2)(d\alpha/dT) \\ &= [(A/\beta)\exp(-E/RT)f'(\alpha) + (E/RT^2)](d\alpha/dT) \end{aligned} \tag{8}$$

When the maximum reaction rate has been reached

$$d^2\alpha/dT^2 = 0 \tag{9}$$

That is

$$[(A/\beta)\exp(-E/RT)f'(\alpha) + (E/RT^2)](d\alpha/dT) = 0 \tag{10}$$

Solving eqn. (10) will give either

$$(A/\beta)\exp(-E/RT)f'(\alpha)+(E/RT^2)=0 \tag{11}$$

or

$$(\mathrm{d}\alpha/\mathrm{d}T)=0 \tag{12}$$

Equation (12) gives the minimum reaction rate, so it is not included in the study.

Inserting $x = E/RT$ into eqn. (11), and rearranging

$$f'(\alpha)=-1/[(AE/\beta R)\exp(-x)/x^2] \tag{13}$$

Equation (6) multiplied by eqn. (13) results in

$$G(\alpha_{\mathrm{max}})f'(\alpha_{\mathrm{max}})=-(x-2)/x=-1+2RT_{\mathrm{max}}/E \tag{14}$$

Table 1 lists the common forms of $f(\alpha)$, $G(\alpha)$ and α_{max} derived from eqn. (14). It is difficult to find an explicit expression of α_{max} for D2, D4 and B1; therefore, an iteration method was used to solve these three equations. Table 2 gives the α_{max} values calculated for each mechanism with different values of E/RT_{max}. The results show that when $E/RT_{\mathrm{max}} > 20$, the values of α_{max} for different E/RT_{max} values fall into a very narrow specific range for

TABLE 1

The common forms of $G(\alpha)$ and $f(\alpha)$, with the α_{max} values derived from eqn. (14)

Mechanism	$G(\alpha)$	$f(\alpha)$	α_{max}
P1	$\alpha^{1/4}$	$4\alpha^{3/4}$	1
A1.5	$(-\ln(1-\alpha))^{2/3}$	$1.5(1-\alpha)(-\ln(1-\alpha))^{1/3}$	$1-\exp(-1+4RT_{\mathrm{max}}/3E)$
A2	$(-\ln(1-\alpha))^{1/2}$	$2(1-\alpha)(-\ln(1-\alpha))^{1/2}$	$1-\exp(-1+RT_{\mathrm{max}}/E)$
A3	$(-\ln(1-\alpha))^{1/3}$	$3(1-\alpha)(-\ln(1-\alpha))^{2/3}$	$1-\exp(-1+2RT_{\mathrm{max}}/3E)$
A4	$(-\ln(1-\alpha))^{1/4}$	$4(1-\alpha)(-\ln(1-\alpha))^{3/4}$	$1-\exp(-1+RT_{\mathrm{max}}/2E)$
B1	$\ln(\alpha/(1-\alpha))$	$\alpha(1-\alpha)$	$\ln(\alpha/(1-\alpha))(1-2\alpha) = -1+2RT_{\mathrm{max}}/E$
R2	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$	$1-(2-2RT_{\mathrm{max}}/E)^{-2}$
R3	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$	$1-(3/2-RT_{\mathrm{max}}/E)^{-3}$
D1	α^2	$1/2\alpha$	1
D2	$(1-\alpha)\ln(1-\alpha) + \alpha$	$(-\ln(1-\alpha))^{-1}$	$-[(1-\alpha)\ln(1-\alpha)+\alpha]/ [(-\ln(1-\alpha))^2(1-\alpha)] = -1+2RT_{\mathrm{max}}/E$
D3	$(1-(1-\alpha)^{1/3})^2$	$1.5(1-(1-\alpha)^{1/3})^{-1}(1-\alpha)^{2/3}$	$1-(3/2-RT_{\mathrm{max}}/E)^{-3}$
D4	$1-2\alpha/3-(1-\alpha)^{2/3}$	$1.5((1-\alpha)^{-1/3}-1)^{-1}$	$-0.5(1-2\alpha/3-(1-\alpha)^{2/3})/ [(1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^2] = -1+2RT_{\mathrm{max}}/E$
F1	$-\ln(1-\alpha)$	$(1-\alpha)$	$1-\exp(-1+2RT_{\mathrm{max}}/E)$
F2	$1/(1-\alpha)-1$	$(1-\alpha)^2$	$0.5-RT_{\mathrm{max}}/E$
F3	$1/(1-\alpha)^2-1$	$0.5(1-\alpha)^3$	$1-(1/3+4RT_{\mathrm{max}}/3E)^{1/2}$

TABLE 2

The values of α_{max} for each mechanism according to different values of E/RT_{max}

Mechanism	α_{max} for E/RT_{max} values of						
	20	40	60	80	100	120	∞
P1	1.000	1.000	1.000	1.000	1.000	1.000	1.000
A.15	0.6067	0.6197	0.6239	0.6259	0.6272	0.6280	0.6321
A2	0.6133	0.6228	0.6259	0.6276	0.6284	0.6290	0.6321
A3	0.6197	0.6259	0.6280	0.6284	0.6292	0.6298	0.6321
A4	0.6228	0.6276	0.6290	0.6296	0.6301	0.6305	0.6321
B1	0.1901	0.1831	0.1805	0.1795	0.1784	0.1773	0.1763
	0.8099	0.8169	0.8195	0.8205	0.8216	0.8227	0.8237
R2	0.7230	0.7370	0.7415	0.7436	0.7449	0.7458	0.7500
R2	0.6720	0.6884	0.6936	0.6962	0.6976	0.6987	0.7037
D1	1.000	1.000	1.000	1.000	1.000	1.000	1.000
D2	0.7875	0.8131	0.8204	0.8237	0.8256	0.8275	0.8335
D3	0.6356	0.6720	0.6830	0.6884	0.6915	0.6936	0.7037
D4	0.7205	0.7511	0.7596	0.7634	0.7658	0.7676	0.7755
F1	0.5934	0.6133	0.6197	0.6228	0.6247	0.6259	0.6321
F2	0.4500	0.4750	0.4833	0.4875	0.4900	0.4917	0.5000
F3	0.3675	0.3945	0.4037	0.4084	0.4112	0.4131	0.4226

each mechanisms. We tested the values of E/RT_{max} used by Dollimore and co-workers [1–3] and found that they were all larger than 20. The results in Table 2 cover those given by Dollimore et al. [1–3], except for the B1 mechanism. For the B1 mechanism, two α_{max} values were obtained which both differ from the values reported in refs. 1–3.

Rechecking $G(\alpha)$ for the B1 mechanism, it is found that $G(\alpha) = \ln(\alpha/(1-\alpha))$ for B1 is an incorrect interpretation. The integral of $f(\alpha) = \alpha(1-\alpha)$ for B1 should give $G(\alpha) = \lim[\ln(\alpha/(1-\alpha)) - \ln(\alpha_0/(1-\alpha_0))]$ instead of $G(\alpha) = \ln(\alpha/(1-\alpha))$. If we take the correct form of $G(\alpha)$, a reasonable α_{max} should be obtained. However, as α_0 tends to an infinitely small value, $G(\alpha)$ will tend to an infinite value, and when $\alpha_0 = 0$, $G(\alpha)$ is equal to infinity, which gives rise to difficulty in using $G(\alpha)$ to calculate α_{max}. Due to the fact that the *a* reaction occurs only when some nuclei exist in the solid, these nuclei may be defects in the solid, i.e., some small volume of product was already present in the solid when it was prepared. Thus, α_0 can never be zero; it should always be a very small value.

Table 3 gives the calculated α_{max} values with different values of α_0 and E/RT_{max}. From Table 3, it can be seen that α_{max} also falls within a very narrow range between 0.5523 and 0.5000 when α_0 ranges from 1.0E − 4 to zero. The range of α_{max} mainly depends on the values of α_0 and the results now cover the data given by Dollimore and co-workers [1–3].

TABLE 3

The values of α_{max} for the B1 mechanism according to different values of α_0 and E/RT_{max}

α_0	α_{max} for E/RT_{max} values of						
	20	40	60	80	100	120	∞
1.0E − 4	0.5469	0.5495	0.5505	0.5510	0.5512	0.5519	0.5523
1.0E − 6	0.5326	0.5344	0.5350	0.5353	0.5355	0.5356	0.5424
1.0E − 20	0.5098	0.5103	0.5105	0.5106	0.5107	0.5107	0.5108
0.00	0.5000	0.5000	0.5000	0.5000	0.5000	0.5000	0.5000

Table 4 shows a comparision of the α_{max} ranges for each mechanism obtained in this study with those given by Dollimore and co-workers, it is clear that all the α_{max} ranges obtained by Dollimore et al. fall in the α_{max} range given in the present study. The α_{max} range for each mechanism given in this study has considered all possible values of activation energy E, frequency factor A and heating rate β, if $E/RT_{max} > 20$, while the α_{max} range for each mechanism given by Dollimore et al. was obtained by taking several selected values of E, A and heating rate β; therefore, the α_{max} range for each mechanism given in this study is more general, and should replace those suggested by Dollimore and co-workers.

TABLE 4

The comparison of the α_{max} ranges obtained in this study with those given in refs. 1–3

Mechanism	α_{max} range	
	This study	Refs. 1–3
P1	1.00	1.00
A1.5	0.6067–0.6321	N/A
A2	0.6133–0.6321	0.62–0.63
A3	0.6197–0.6321	0.63
A4	0.6228–0.6321	0.63–0.65
B1	0.5528–0.5000	0.54–0.55
R2	0.7230–0.7500	0.73–0.74
R3	0.6720–0.7037	0.69
D1	1.00	1.00
D2	0.7875–0.8335	0.81–0.82
D3	0.6356–0.7037	0.67–0.68
D4	0.7205–0.7755	0.75–0.76
F1	0.5934–0.6321	0.62
F2	0.4500–0.5000	0.48
F3	0.3675–0.4226	0.40

TABLE 5

The acceptable range of activation energy values for different values of T_{max}

T_{max}/K	E/kJ mol^{-1}	T_{max}/K	E/kJ mol^{-1}
373.15	>62.05	973.15	>161.82
473.15	>78.68	1073.15	>178.32
573.15	>95.30	1173.15	>194.93
673.15	>111.91	1273.15	>211.70
773.15	>128.56	1373.15	>228.33
873.15	>145.69		

The different heating rates will affect the values of α_{max}, because lowering the heating rate will make T_{max} lower, and therefore E/RT_{max} becomes larger. As a result, α_{max} will tend to be close to the value at $E/RT_{max} = \infty$. It can be predicted that a higher heating rate will lower α_{max}, and that a lower heating rate will increase α_{max}, following the same reasoning. It seems that the frequency factor A does not have any influence on α_{max}. However, A may influence the value of T_{max}, thus changing E/RT_{max}, and affecting α_{max} (this study is in progress).

It would be very helpful to give the acceptable range of activation energy values rather than that of E/RT_{max}, if one were to apply the proposed α_{max} range to the determination of the reaction mechanism. Table 5 lists the acceptable ranges of activation energy values at different T_{max} values and Fig. 1 shows the plot of the acceptable values of E versus the values of T_{max}.

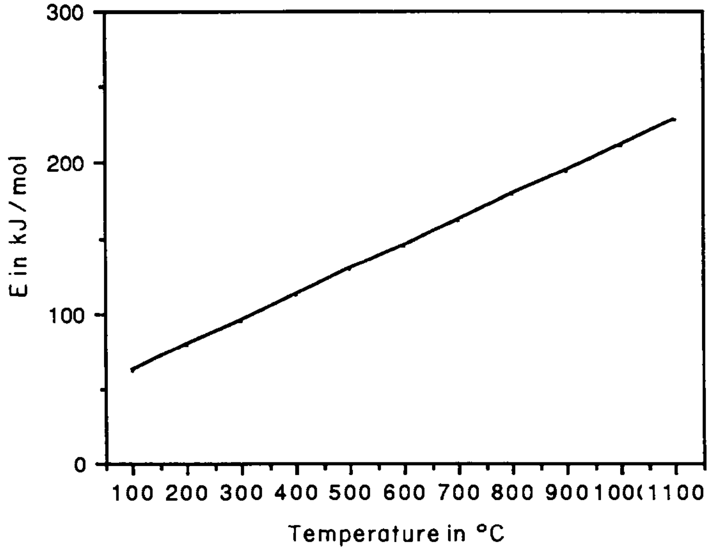

Fig. 1. The acceptable range of activation energy E values versus T_{max}.

TABLE 6

Applicability of the typical E and T_{max} values for the decompositions of some selected solid substances to the proposed method of Dollimore et al. [3]

Substance	Decomposition products	T_{max}/°C	E/kJ mol^{-1}	Ref.	Applicable
$CaC_2O_4 \cdot H_2O$	$CaC_2O_4 + H_2O$	237	143.3	3	Yes
$CuSO_4 \cdot 5H_2O$	$CuSO_4 \cdot 3H_2O + 2H_2O$	47–63	104	5	Yes
$CuSO_4 \cdot 3H_2O$	$CuSO_4 \cdot H_2O + 2H_2O$	70–86	134	5	Yes
$CaHPO_4 \cdot 2H_2O$	$CaHPO_4 + 2H_2O$	136–203	190	6	Yes
$BaCl_2 \cdot 2H_2O$	$BaCl_2 + 2H_2O$	40–61	146	7	Yes
PbC_2O_4	$PbO + CO_2 + CO$ (in air)	370–400	151	8	Yes
ZnC_2O_4	$ZnO + CO_2 + CO$ (in air)	438	252.9	3	Yes
$CaCO_3$	$CaO + CO_2$	814	205.7	3	Yes

The area above the linear plot represents the acceptable activation energy region, and the area below the linear plot represents the unacceptable activation energy region. If one wishes to use the proposed α_{max} to determine the reaction mechanism, it must first be confirmed that the E value deduced from the kinetic analysis falls in the acceptable region.

Table 6 lists typical values of E and T_{max} for several selected solid substances. It can be concluded that the method proposed by Dollimore et al. [3] is applicable to all the materials listed in Table 6. It is also valid for most solid substances undergoing decomposition.

CONCLUSIONS

A relationship between the maximum reaction rate α_{max} and the reaction mechanism has been deduced mathematically from the fundamental rate equations for a solid state reaction. This relation can be expressed as $f'(\alpha_{max})G(\alpha_{max}) = -1 + 2RT_{max}/E$.

The effect of the activation energy on α_{max} has also been discussed. When $E/RT_{max} > 20$, α_{max} does not depend on the frequency factor A or activation energy E, but depends only on the reaction mechanism.

The kinetic procedure proposed by Dollimore and co-workers [1–3] is applicable to most solid systems undergoing decomposition.

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