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ERRORS IN THE DETERMINATION OF ACTIVATION ENERGIES OF SOLID-STATE REACTIONS BY THE PILOYAN METHOD, AS A FUNCTION OF THE REACTION MECHANISM

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The errors in the activation energies of solid-state reactions determined with the Piloyan method are more larger than those previously assumed in the literature. On the other hand, the errors in the kinetic parameters are strongly dependent on the kinetic law obeyed by the reaction. A theoretical explanation of this behaviour is given.

The Piloyan method was developed from the general equation describing the reaction rate under non-isothermal conditions:

$$\frac{d\alpha}{dt} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{1}$$

where α is the reacted fraction at time t; A is the pre-exponential Arrhenius factor; E is the activation energy; and $f(\alpha)$ is a function depending on the reaction kinetics. On taking logarithms and rearranging, Eq. (1) becomes

$$\ln\frac{d\alpha}{dt} = \ln A + \ln f(\alpha) - \frac{E}{RT} \tag{2}$$

Piloyan et al. [1] consider than when the value of α lies between 0.05 and 0.5 at the usual heating rates, a change in temperature has a greater effect on $d\alpha/dt$ than on the change in α. According to these authors, therefore the term $\ln f(\alpha)$ can be neglected and Eq. (2) can be written in the form

$$\ln\frac{d\alpha}{dt} = -\frac{E_p}{RT} + \text{constant} \tag{3}$$

where the subscript p refers to the approximate value of E estimated from Eq. (1).

Piloyan et al. [1] state that the error in the E_p values obtained from the plots of $\ln d\alpha/dt$ against the reciprocal of the temperature is estimated at between 15 and 20% with respect to the actual activation energy E. However, it is noteworthy that it is often assumed in the literature [2, 3] that the above method yields accurate values of the activation energy.

The aim of the present paper is to determine the errors involved in the activation energies calculated with Piloyan's method for the different kinetic models proposed in the literature for the kinetic analysis of solid-state reactions.

Experimental

Magnesite from Navarra (Spain) was used. This carbonate exhibits the following chemical composition: SiO_2 ..... 1.76%, Fe_2O_3 ..... 1.12%, Al_2O_3 ..... 0.32%, CaO ..... 0.98%, MgO ..... 45.35%, loss of ignition ..... 50.50%.

The experiments were performed at a vacuum of 0.133 Pa (10^{-3} Torr), using a Cahn electrobalance, model RG. The DTG and TG curves were recorded with a Yew 3066 three-pen recorder. A Stanton Redcroft temperature controller held the temperature constant to within ±1° in the hot zone of the vertical furnace.

The temperature was measured with a chromel–alumel thermocouple placed just outside the electrobalance tube, as near as possible to the sample. A heating rate of 12 deg $\min^{-1}$ was used.

Results and discussion

In order to calculate the error in the activation energy calculated from Eq. (3), mathematical analysis of this equation is necessary.

If the DTA or DTG curve is recorded at a linear heating rate β, the integration of Eq. (1) leads to

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{AE}{\beta R} p(x) \tag{4}$$

where $x = E/RT$ and $g(\alpha)$ is a function depending on the actual kinetic law.

Taking logarithms, Eq. (4) becomes

$$\ln g(\alpha) = \ln \frac{AE}{\beta R} + \ln p(x) \tag{5}$$

It is well known [4, 5] that the function $p(x)$ cannot be expressed in a closed form, although there exist several approximations with a high degree of accuracy. One of the most popular and simple of these approximations is that of Doyle [6]:

$$\log p(x) = -2.315 - 0.4567x \tag{6}$$

It has been shown previously [7] that the accuracy of Eq. (6) is better than 10% for E/RT higher than 10.

By substituting Eq. (6) into Eq. (5):

$$\ln g(\alpha) = \ln \frac{AE}{\beta R} - 5.33 - 1.05 \frac{E}{RT} \tag{7}$$

From Eqs (2) and (7):

$$\ln \frac{d\alpha}{dt} = \ln [f(\alpha) g(\alpha)^{\frac{1}{1.05}}] + \text{constant} \tag{8}$$

If the following relationship can be established:

$$\ln [f(\alpha) g(\alpha)^{\frac{1}{1.05}}] = a \ln g(\alpha) + b \tag{9}$$

(a and B being constant, then from Eqs (7), (8) and (9):

$$\ln \frac{d\alpha}{dt} = - 1.05 a \frac{E}{RT} + \text{constant} \tag{10}$$

From a comparison of Eqs (3) and (10) it can be seen that if Eq. (9) applies then the slope of the straight line obtained from the plot of ln ($d\alpha/dt$) against $1/T$ must give an apparent activation energy $E_p = 1.05aE$. The percentage error in the activation energy calculated from Eq. (3) can therefore be expressed as

$$\epsilon = \frac{E_p - E}{E} 100 = (1.05a - 1)100 \tag{11}$$

In order to see if the above assumptions hold, we have collected in Table 1 the mathematical expressions of the functions $f(\alpha) g(\alpha)^{1/1.05}$ and $g(\alpha)$, corresponding to the most common kinetic laws of solid-state reactions, and have used Eq. (9) to obtain the corresponding values of a, given in Table 1 together with their linear correlation coefficients and their corresponding values of ϵ.

The results in Table 1 show that Eq. (9) holds in the range $0.05 \leqslant \alpha \leqslant 0.5$, whatever the reaction mechanism used in the literature for kinetic analysis of the solid-state reaction with the Piloyan method. Moreover, the values of ϵ in Table 1 reveal that the errors involved in the activation energies determined by this method are much larger than those assumed in [1].

In order to check the above conclusions, we have concstructed the theoretical thermogravimetric curves in Figs 1, 2 and 3 for all the kinetic laws in Table 1, by assuming the following kinetic parameters: $E = 133$ kJ/mol, $A = 10^{12}$ min^{-1} and heating rate $\beta = 5$ deg min^{-1}. The Arrhenius equation has been integrated by means of the 4th degree rational approximation proposed by Senum and Yang [8]:

Table 1 The mathematical expressions of the functions $f(\alpha)g(\alpha)^{1/1.05}$ and $g(\alpha)$ corresponding to the most common kinetic laws, the corresponding values of a calculated from Eq. (9), and the percentage error in the activation energy given by Eq. (11)

Symbol	$f(\alpha)g(\alpha)^{1/1.05}$	$g(\alpha)$	a	r	ϵ, %
R1	$\alpha^{1/1.05}$	α	$\frac{1}{1.05}$	1.0000	– 0.25
R2	$(1-\alpha)^{1/2}(2(1-\alpha)^{1/2}))^{1/1.05}$	$2(1-(1-\alpha)^{1/2})$	0.80	0.9984	– 16.00
R3	$(1-\alpha)^{2/3}(3(1-(1-\alpha)^{1/3})^{1/1.05}$	$3(1-(1-\alpha)^{1/3})$	0.76	0.9975	– 20.20
F1	$(1-\alpha)(-\ln(1-\alpha)^{1/1.05}$	$-\ln(1-\alpha)$	0.68	0.9933	– 28.60
A2	$2(-\ln(1-\alpha))^{0.976}(1-\alpha)$	$(-\ln(1-\alpha))^{1/2}$	1.45	0.9937	+ 52.25
A3	$3(1-\alpha)(-\ln(1-\alpha))^{0.984}$	$(-\ln(1-\alpha)^{1/3}$	2.25	0.9960	+ 136.25
D1	$\frac{1}{2}\alpha^{0.905}$	α^2	0.45	1.0000	– 52.75
D2	$-\frac{((1-\alpha)\ln(1-\alpha)+\alpha)^{1/1.05}}{\ln(1-\alpha)}$	$(1-\alpha)\ln(1-\alpha)+\alpha$	0.40	0.9995	– 58.00
D3	$\frac{3(1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^{0.905}}{2}$	$(1-(1-\alpha)^{1/3})^2$	0.35	0.9977	– 63.25
D4	$\frac{3((\frac{1-2\alpha}{3})-(1-\alpha)^{2/3})^{1/1.05}}{2((1-\alpha)^{-1/3}-1)}$	$(\frac{1-2\alpha}{3}-(1-\alpha))^{2/3}$	0.39	0.9975	– 59.50

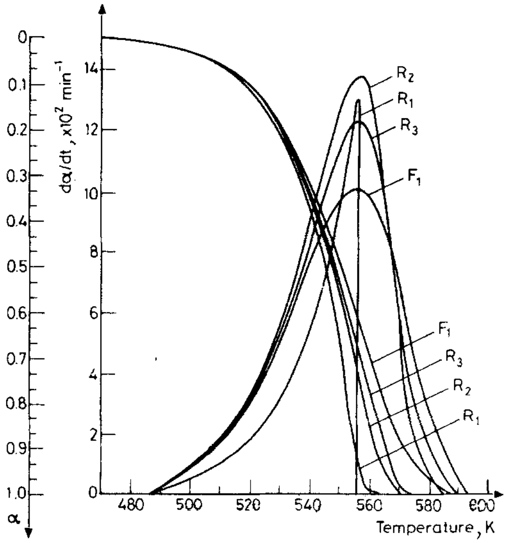

Fig. 1 Theoretical thermogravimetric curves obtained at a heating rate of 5 deg/min by assuming F1, R1, R2 and R3 mechanisms, respectively, and the following kinetic parameters: $E = 32$ Kcal/mol and $A = 10^{12}$ min^{-1}

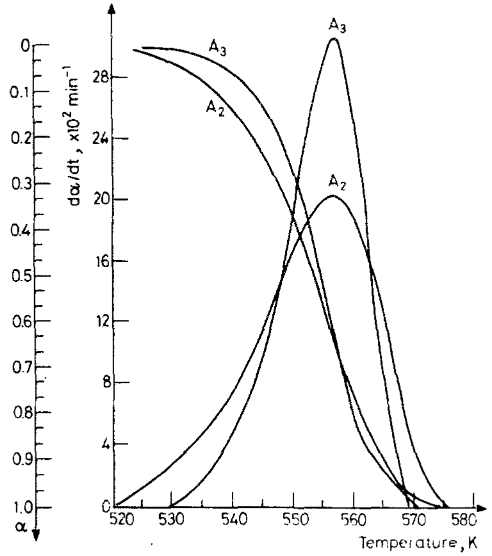

Fig. 2 Theoretical thermogravimetric curves obtained at a heating rate of 5 deg/min by assuming A2 and A3 mechanisms, respectively, and the following kinetic parameters: $E = 32$ Kcal/mol and $A = 10^{12}$ min^{-1}

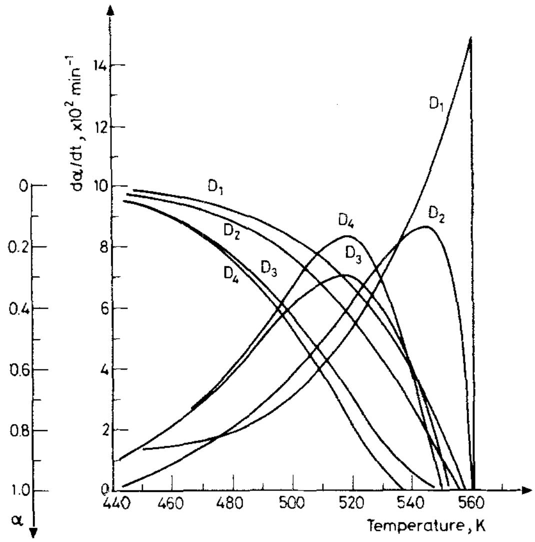

Fig. 3 Theoretical thermogravimetric curves obtained at a heating rate of 5 deg/min by assuming D1, D2, D3 and D4 mechanisms, respectively, and the following kinetic parameters: $E = 32$ Kcal/mol and $A = 10^{12}$ min^{-1}

Table 2 The activation energies calculated from analysis of the kinetic data in Figs 1, 2 and 3, by means of Eqs (3) and (7), and the percentage error E in the activation energy E_p, obtained with the Piloyan method

Type	Symbol	E_p, kJ mol^{-1}	r	E, kJ mol^{-1}	r	ϵ, %
Polanyi—Wigner equation. Zero-order	R1	133.8	1.0000	135.4	1.0000	−0.01
Random nucleation. Unimolecular decay law	F1	92.0	0.9951	135.2	1.0000	−31.18
Phase boundary-controlled reaction (Contracting area)	R2	111.6	0.9987	135.0	1.0000	−16.56
Phase boundary controlled reaction (Contracting volume)	R3	104.5	0.9980	135.0	1.0000	−21.84
Two dimensional growth of nuclei. Avrami equation	A2	209.0	0.9964	135.4	1.0000	56.28
Three dimensional growth of nuclei. Avrami equation	A3	324.0	0.9975	135.1	1.0000	142.18
One dimensional diffusion. Parabolic law	D1	62.7	0.9999	135.6	1.0000	−53.09
Two dimensional diffusion	D2	54.4	0.9995	135.1	1.0000	−59.32
Three diemnsional diffusion. Jander equation	D3	50.4	0.9980	135.3	1.0000	−62.31
Three dimensional diffusion. Ginstlig—Brounshtein equation	D4	54.5	0.9992	134.3	1.0000	−59.28

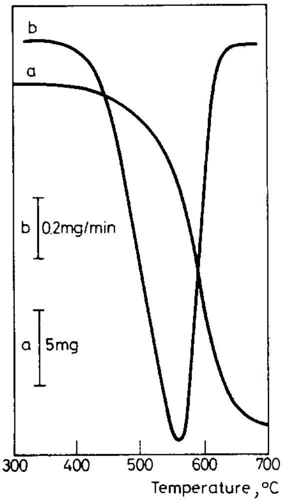

Fig. 4 TG and DTG curves of the thermal decomposition of $MgCO_3$ at a heating rate of 12 deg/min

$$\int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{E}{R}\,\frac{\exp(-x)}{x}\,\frac{x^3+18x^2+88x+96}{x^4+20x^3+120x^2+240x+120} \qquad \left(x=\frac{E}{RT}\right) \tag{12}$$

which involves an error lower than $10^{-3}\%$.

The activation energies calculated from analysis of the kinetic data of Figs 1, 2 and 3 by means of Eqs (3) and (7), are given in Table 2. These results show the excellent agreement between the values of E determined from Eq. (7) and those previously assumed for calculating the corresponding TG curves. On the other hand, good agreement is also obtained between the values of the errors ϵ in the activation energies E_p obtained with the Piloyan method and those calculated in Table 1.

In order to obtain additional experimental evidence, the TG and DTG curves of the thermal decomposition of $MgCO_3$ in Fig. 4 were simultaneously recorded under a vacuum of 0.133 Pa (10^{-3} Torr) and a heating rate of 12 deg min^{-1}.

It was concluded earlier [9] that under these experimental conditions the above reaction follows a "contracting sphere" phase boundary model (i.e. $g(\alpha) = 3(1-(1-\alpha)^{1/3})$). The activation energy E obtained from kinetic analysis of the TG data in Fig. 4 by means of Eq. (7), after assuming the above kinetic model, is included in Table 3, together with the value of E_p obtained from analysis of the DTG curve in Fig. 4 by means of the Piloyan method with Eq. (3). It can be seen that the value of ϵ is in good agreement with that calculated in Table 1, which confirms our above statements.

It can be concluded that the Piloyan method leads to very large errors in the determination of the activation energy of solid-state reactions. Therefore, it cannot be used at all for the kinetic analysis of these reactions.

Table 3 Activation energies of thermal decomposition of $MgCO_3$ calculated by means of Eqs (3) and (7), and the percentage error ϵ in the activation energy E_p obtained with the Piloyan method

Mechanism	E_p, kJ mol^{-1}	r	E, kJ mol^{-1}	r	ϵ, %
Phase boundary-controlled reaction. (Contracting volume) (R3)	88.2	0.9991	123.7	0.9986	−28.71

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Zusammenfassung — Die Fehler der nach der Piloyan-Methode bestimmten Aktivierungsenergien von Festkörperreaktionen sind größer als bisher in der Literatur angenommen und stark abhängig von der Reaktionsordnung. Eine theoretische Erklärung dieses Verhaltens wird gegeben.

Резюме — Отмечается, что ошибки определения энергий активации твердотельных реакций по методу Пилояна значительно большие по сравнению с тем, что ранее предполагалось в литературе. С другой стороны, показано, что ошибки определения кинетических параметров в значительной степени зависимы от закона кинетики, описывающего реакцию. Приведено теоретическое объяснение такого поведения.