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SOME CONSIDERATIONS REGARDING THE DETERMINATION OF THE ACTIVATION ENERGY OF SOLID-STATE REACTIONS FROM A SERIES OF ISOTHERMAL DATA

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It has been demonstrated that the kinetic data on solid-state reactions show a good fitting to the expression $g(\alpha) = kt$, regardless of the nature of the $g(\alpha)$ function previously assumed for performance of the calculations. Moreover, the activation energy value obtained from the Arrhenius law is quite independent of the kinetic function assumed.

It has been proved in previous papers [1, 2] that the actual mechanism of solid-state reactions cannot be discriminated by means of the kinetic analysis of a single TG curve. Moreover, it has been pointed out that any theoretical TG curve calculated by assuming a particular kinetic law satisfies quite well all the other kinetic equations developed in the literature for the description of solid-state reactions.

In general, it seems to be accepted that the isothermal methods allow to discernment of the real kinetic model obeyed by the reaction better than the non-isothermal ones. It is well known that the "Ln Ln method" developed by Hancock and Sharp [3] and the "reduced time" master curves described by Sharp et al. [4] have been proposed in the literature for discriminating the actual kinetics of solid-state reactions from isothermal traces. On the other hand, the reaction mechanism has very often been decided from the $g(\alpha)$ function that gives the best fit to the general kinetic equation

$$g(\alpha) = k(t - t_0) \tag{1}$$

where k is the rate constant, t is time, t_0 is an empirical constant whose value increases upon increase of the time required to reach the steady-state temperature after introduction of the sample into the furnace; and $g(\alpha)$ is a function depending on the reaction mechanism. The $g(\alpha)$ functions more commonly used in the literature for the description of solid-state reactions are listed in Table 1.

It is noteworthy that some authors [5] have reported that a series of isothermal traces show a good fit to Eq. (1) for the more than one of the functions in Table 1. We therefore considered it of interest to carry out systematic research in order to determine if Eq. (1) allows discrimination of the real kinetic law obeyed by solid-state reactions.

Results and discussion

In order to determine if the isothermal data on a reaction following a particular mechanism fit the kinetic law corresponding to other reaction mechanisms, we have constructed from Eq. (1) the series of isothermal curves in Figs 1 and 2 by assuming a first-order kinetic law (f_1) and a Ginstling–Brounshtein diffusion mechanism (D_2), respectively. The following kinetic parameters have been assumed: $t_0 = 0$, $E = 30$ (F_1), 40 (D_2) kcal/mol and $A = 10^7$ min^{-1}. The constant k at different temperatures has been calculated from the Arrhenius equation:

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{2}$$

A being the Arrhenius pre-exponential factor, E the activation energy, R the gas constant and T the absolute temperature.

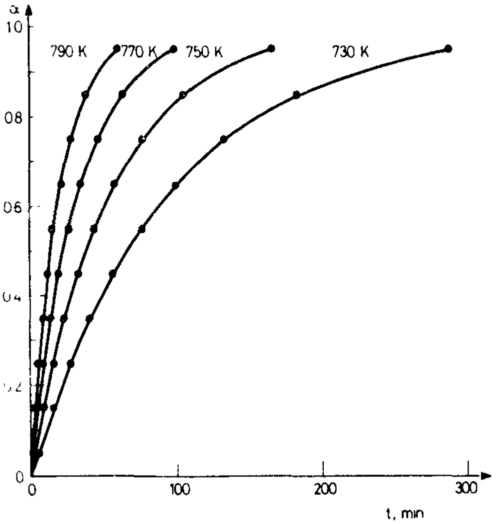

Fig. 1 Theoretical isothermal curves constructed for a first-order kinetic law by assuming the following kinetic parameters: $E = 30$ kcal/mol and $A = 10^7$ min^{-1}

The values of the rate constants obtained from kinetic analysis of the data in Figs 1 and 2 for the $g(\alpha)$ functions in Table 1 are included in Tables 2 and 3, together with the corresponding linear correlation coefficients. On the other hand, Tables 4 and 5 show the results obtained for both the activation energies and the correlation coefficients calculated by plotting the rate constants in Tables 2 and 3 according to the Arrhenius equation.

The results in Tables 2 and 3 suggest that the data in Figs 1 and 2 show a reasonably good fit to all the kinetic laws in Table 1. Moreover, the data in Tables 4 and 5

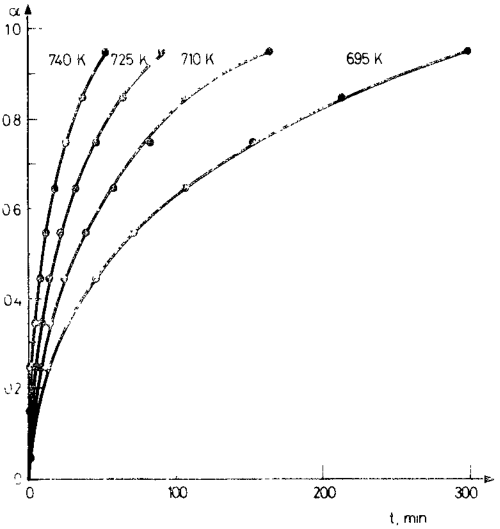

Fig. 2 Theoretical isothermal curves constructed for a D_2 kinetic law by assuming the following parameters: $E = 40$ kcal/mol and $A = 10^7$ min^{-1}

seem to indicate clearly that the proper value of the activation energy is obtained independently of the kinetic equation taken for the calculations.

The above conclusion would be explained if the $g(\alpha)$ functions in Table 1 were linearly correlated with one another over a broad range of values of the reacted fraction, α. In such a case the following relationship would hold:

$$g(\alpha) = ag_1(\alpha) + b \tag{3}$$

where $g(\alpha)$ represents any of the functions in Table 1, $g_1(\alpha)$ is one of these functions arbitrarily taken as a reference, and a and b are constants.

If the kinetic equation actually followed by the reaction satisfies Eq. (3), the experimental data would necessarily fit the kinetic equations of both the $g_1(\alpha)$ function and all the other functions satisfying expression [3]. Therefore, if we consider that, according to Eq. (1)

$$g_1(\alpha) = k_1(t - t_{01}) \tag{4}$$

from Eqs (2) and (4) we obtain

$$g(\alpha) = ak_1(t - t_{01}) + b = ak_1\left[t - \left(t_{01} + \frac{b}{a}\right)\right] \tag{5}$$

If we introduce the constant $t'_{01} = t_{01} + (b/a)$, Eq. (5) becomes

$$g(\alpha) = ak_1(t - t'_{01}) \tag{6}$$

Table 1 Algebraic expressions of integral functions for the most commonly mechanisms operating in solid state decompositions

Mechanism	$g(\alpha)$
Zero-order	α
R_2	$2(1-(1-\alpha)^{1/2})$
R_3	$3(1-(1-\alpha)^{1/3})$
F_1	$-\mathrm{Ln}(1-\alpha)$
A_2	$(-\mathrm{Ln}(1-\alpha))^{1/2}$
A_3	$(-\mathrm{Ln}(1-\alpha))^{1/3}$
D_1	α^2
D_2	$(1-\alpha)\,\mathrm{Ln}(1-\alpha)+\alpha$
D_3	$(1-(1-\alpha)^{1/3})^2$
D_4	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

Table 2 Rate constant and regression coefficient values obtained from the analysis of data in Fig. 1 for the most commonly used mechanisms ($0.15 = \alpha = 0.85$)

Mechanism	730 K		750 K		770 K		790 K	
	k	*r*	*k*	*r*	*k*	*r*	*k*	*r*
Zero-order	0.00419	0.9706	0.00728	0.9705	0.01227	0.9705	0.02016	0.9706
R_2	0.00646	0.9920	0.01122	0.9920	0.01890	0.9920	0.03105	0.9920
R_3	0.00754	0.9964	0.01309	0.9963	0.02206	0.9963	0.03624	0.9964
F_1	0.01044	0.9999	0.01812	0.9999	0.03054	0.9999	0.05016	0.9999
A_2	0.00573	0.9867	0.00995	0.9866	0.01677	0.9866	0.02754	0.9867
A_3	0.00401	0.9754	0.00697	0.9754	0.01174	0.9754	0.01929	0.9755
D_1	0.00439	0.9968	0.00762	0.9968	0.01285	0.9983	0.02111	0.9968
D_2	0.00344	0.9983	0.00597	0.9983	0.01106	0.9983	0.01653	0.0082
D_3	0.00131	0.9883	0.00228	0.9889	0.00385	0.9889	0.00632	0.9888
D_4	0.00091	0.9964	0.00158	0.9965	0.00267	0.9964	0.00439	0.9964

From a comparison of Eqs (1) and (6) we can conclude that the slope of $g(\alpha)$ as a function of time is equal to $k = k_1 a$. This means that the ratio between the rate constants determined from two different functions of $g(\alpha)$ is equal to the ratio of the corresponding values of constant a in Eq. (3). Moreover, taking into account that both k_1 and k must fit the Arrhenius law, we can write

$$k = Ae^{-E/RT} = aA_1 e^{-E_1/RT} \tag{7}$$

where the subscript 1 refers to the kinetic parameters determined from the function taken as reference. Therefore, we can conclude from Eq. (7) that $E = E_1$ and $A = aA_1$; in other words, all the functions fitting the experimental data and Eq. (3)

Table 3 Rate constant and regression coefficient values obtained from the analysis of data in Fig. 2 for the most commonly used mechanisms (0.15 = α = 0.85)

Mechanism	695 K		710 K		725 K		740 K	
	k	r	k	r	k	r	k	r
Zero-order	0.00317	0.9597	0.00586	0.9598	0.01053	0.9596	0.01851	0.9596
R_2	0.00492	0.9859	0.00907	0.9860	0.01631	0.9858	0.02866	0.9859
R_3	0.00575	0.9918	0.01061	0.9919	0.01906	0.9917	0.03350	0.9918
F_1	0.00798	0.9983	0.01472	0.9983	0.02646	0.9982	0.04651	0.9983
A_2	0.00453	0.9778	0.00802	0.9779	0.01442	0.9777	0.02535	0.9778
A_3	0.00304	0.9637	0.00560	0.9639	0.01007	0.9636	0.01770	0.9637
D_1	0.00336	0.9956	0.00620	0.9956	0.01114	0.9955	0.01958	0.9955
D_2	0.00264	0.9999	0.00487	0.9999	0.00875	0.9999	0.01538	0.9999
D_3	0.00101	0.9933	0.00186	0.9932	0.00335	0.9933	0.00590	0.9933
D_4	0.00070	0.9991	0.00129	0.9991	0.00233	0.9991	0.00409	0.9992

Table 4 Activation energy and regression coefficient values obtained from the Arrhenius plot of data in Table 2

Mechanism	E, kcal/mol	A, min^{-1}	r
Zero-order	30	$4 \cdot 10^6$	1.0000
R_2	30	$6 \cdot 10^6$	1.0000
R_3	30	$7 \cdot 10^6$	1.0000
F_1	30	$9 \cdot 10^6$	1.0000
A_2	30	$5 \cdot 10^6$	1.0000
A_3	30	$4 \cdot 10^6$	1.0000
D_1	30	$4 \cdot 10^6$	1.0000
D_2	30	$3 \cdot 10^6$	1.0000
D_3	30	$1 \cdot 10^6$	1.0000
D_4	30	$9 \cdot 10^5$	1.0000

lead to the same value of the activation energy, while their Arrhenius pre-exponential factors are proportional to the corresponding values of constant a.

In order to confirm the applicability of the above assumptions, we have taken the $g(\alpha)$ function R_3 in Table 1 as reference i.e. $g_1(\alpha) = 3[1 - (1 - \alpha)^{1/3}]$ and have used Eq. (3) to obtain the values of a and b shown in Tables 6 and 7, together with their linear correlation coefficients.

The results in Table 6 reveal that all the $g(\alpha)$ functions in Table 1 seem to satisfy Eq. (3) in the range $0.05 \leqslant \alpha \leqslant 0.95$. Table 7 shows that the fitting is still better in the range $0.15 \leqslant \alpha \leqslant 0.80$ frequently used for the kinetic analysis of solid-state reactions.

To summarize, we can conclude that the activation energy of a solid-state reaction obtained from a series of isothermal curves is the same regardless of the kinetic law

Table 5 Activation energy and regression coefficient values obtained from the Arrhenius plot of data in Table 3

Mechanism	*E*, kcal/mol	*A*, min	*r*
Zero-order	40	$1 \cdot 10^{10}$	1.0000
R_2	40	$2 \cdot 10^{10}$	1.0000
R_3	40	$2 \cdot 10^{10}$	1.0000
F_1	40	$3 \cdot 10^{10}$	1.0000
A_2	40	$2 \cdot 10^{10}$	1.0000
A_3	40	$1 \cdot 10^{10}$	1.0000
D_1	40	$1 \cdot 10^{10}$	1.0000
D_2	40	$1 \cdot 10^{10}$	1.0000
D_3	40	$4 \cdot 10^{9}$	1.0000
D_4	40	$2 \cdot 10^{9}$	1.0000

Table 6 Regression coefficient and *a* & *b* values calculated by correlating the functions $g(\alpha)$ and $g_1(\alpha)$ according to Eq. (3), in the interval $0.05 = \alpha = 0.95$

Mechanism	*a*	*b*	*r*
Zero-order	1.9482	− 0.2474	0.9733
R_2	1.2011	− 0.0586	0.9901
F_1	0.6541	0.1210	0.9901
A_2	1.2766	− 0.3800	0.9901
A_3	1.7825	− 0.8610	0.9941
D_1	1.8346	0.1300	0.9959
D_2	2.1752	0.2081	0.9913
D_3	4.6235	0.3160	0.9593
D_4	7.7220	0.2440	0.9839

Table 7 Regression coefficient and *a* & *b* values calculated by correlating the functions $g(\alpha)$ and $g_1(\alpha)$ according to Eq. (3), in the interval $0.15 = \alpha = 0.80$

Mechanism	*a*	*b*	*r*
Zero-order	1.6534	− 0.1610	0.9917
R_2	1.1395	− 0.0368	0.9994
F_1	0.7592	0.0696	0.9977
A_2	1.2734	− 0.4100	0.9965
A_3	1.7567	− 0.8900	0.9909
D_1	1.6925	0.1730	0.9978
D_2	2.2660	0.2220	0.9912
D_3	6.2893	0.2752	0.9759
D_4	8.6977	0.2410	0.9869

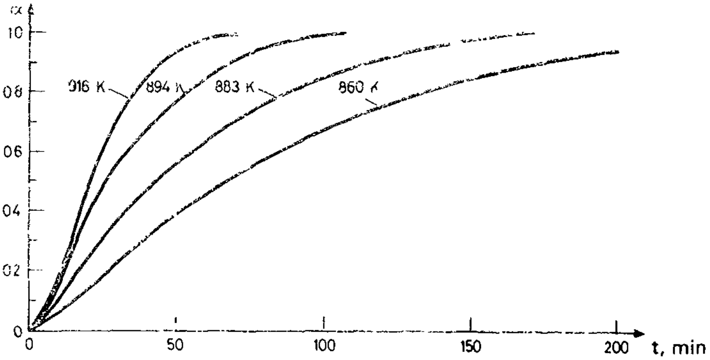

Fig. 3 Isothermal traces for the thermal decomposition of $CaCO_3$ in vacuum

previously assumed for the calculations. This is roughly true even if $t_0 = 0$ for, as shown in Table 6 and 7, the values of *b* are very small.

In order to check the above conclusion by experimental means we have obtained the series of isothermal curves in Fig. 3 for the thermal decomposition of $CaCO_3$. The values of the rate constants calculated from these isothermal curves by assuming each of the kinetic laws in Table 1 are given in Table 8, together with the corresponding linear correlation coefficients. The value of the activation energy calculated by applying the Arrhenius law to the rate constants in Table 8 is shown in Table 9. We can see that the results in Tables 8 and 9 agree quite well with our previous forecast.

Table 8 Rate constant and regression coefficient values obtained from the isothermal traces in Fig. 3 by using the most commonly used kinetic law

Mechanism	860 K		883 K		894 K		916 K	
	k	*r*	*k*	*r*	*k*	*r*	*k*	*r*
Zero-order	0.00375	0.9787	0.00747	0.9908	0.01097	0.9849	0.01818	0.9864
R_2	0.00745	0.9984	0.01198	0.9987	0.01957	0.9982	0.03410	0.9989
R_3	0.00953	0.9997	0.01410	0.9997	0.02405	0.9997	0.04251	0.9998
F_1	0.01602	0.9922	0.01968	0.9989	0.03705	0.9944	0.06716	0.9961
A_2	0.00668	0.9992	0.01016	0.9981	0.01706	0.9992	0.02960	0.9995
A_3	0.00423	0.9980	0.00689	0.9955	0.01118	0.9971	0.01905	0.9982
D_1	0.00519	0.9948	0.00874	0.9996	0.01392	0.9982	0.02203	0.9992
D_2	0.00487	0.9994	0.00689	0.9985	0.01210	0.9977	0.02203	0.9992
D_3	0.00243	0.9840	0.00269	0.9905	0.00534	0.9818	0.01000	0.9882
D_4	0.00141	0.9971	0.00182	0.9966	0.00337	0.9942	0.00621	0.9971

Table 9 Activation energy and regression coefficient values obtained from the Arrhenius plot of data in Table 8

Mechanism	E, kcal/mol	A, min	r
Zero-order	44	$8 \cdot 10^8$	0.9980
R_2	43	$7 \cdot 10^8$	0.9906
R_3	43	$7 \cdot 10^8$	0.9830
F_1	42	$5 \cdot 10^8$	0.9544
A_2	43	$4 \cdot 10^8$	0.9860
A_3	43	$3 \cdot 10^8$	0.9920
D_1	44	$8 \cdot 10^8$	0.9940
D_2	43	$4 \cdot 10^8$	0.9800
D_3	42	$7 \cdot 10^7$	0.9300
D_4	43	$9 \cdot 10^7$	0.9700

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Zusammenfassung — Es wird gezeigt, daß die kinetischen Daten von Festkörperreaktionen gut dem Ausdruck $g(\alpha) = kt$ entsprechen, ungeachtet der Natur der zur Ausführung der Berechnungen angenommen Funktion $g(\alpha)$. Darüber hinaus ist der nach dem Arrhenius'schen Gesetz erhaltene Wert für die Aktivierungsenergie ganz unabhängig von der angenommenen kinetischen Funktion.

Резюме — Показано, что данные кинетики твердотельных реакций хорошо описываются выражением $g(\alpha) = kt$, независимо от характера функции $g(\alpha)$, ранее учитываемой при проведении вычислений. Кроме того, значение энергии активации, полученной из уравнения Аррениуса, польностью независимо от принимаемой кинетической функции.