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Note

THE PROBLEM OF DISCERNING KINETIC MODELS FOR SOLID DECOMPOSITIONS FROM ISOTHERMAL ANALYSES

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It is widely recognized that the mechanism of solid decompositions can be easily determined from the linearity in plots of $F(\alpha)$ vs. t under an isothermal condition, where $F(\alpha)$, α, and t refer to the mechanistic function, the fraction decomposed, and the time, respectively [1–3]. We have reported that the correct $F(\alpha)$ can not be selected uniquely in terms of $F(\alpha)$ vs. t plots for the isothermal dehydration of $CaC_2O_4 \cdot H_2O$, when the exponents n in the mechanistic functions for phase-boundary reactions R_n and m in those for random nucleation and subsequent growth mechanisms A_m were allowed to take any appropriate value in the ranges of $1 \leqslant n \leqslant 3$ and $1 \leqslant m \leqslant 4$ [4].

The assumption of continuous variation in these exponents can be reasonable, since the actual decomposition process seems to be far from the limiting case derived on the basis of the theoretical models and the combination of the limiting cases may occur. Several workers analysed isothermal traces in such a way [5,6]. In addition, any $F(\alpha)$, which is considered to be appropriate in view of the linearity in $F(\alpha)$ vs. t plots, gives rise to nearly identical kinetic parameters in terms of the Arrhenius plot [4,7]. This is another difficulty in determining the correct $F(\alpha)$.

The present study was undertaken to show the difficulty in selecting the correct $F(\alpha)$ in terms of a conventional $F(\alpha)$ vs. t plot under an isothermal condition.

RESULTS AND DISCUSSION

In a previous study, the dehydration of powdered $CaC_2O_4 \cdot H_2O$ proved to follow either the $A_{1.904}$ or $R_{2.018}$ mechanism [4]. In other words, it was not able to select the

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TABLE 1

Various mechanistic functions $F(\alpha)$ in terms of theoretical models

$F(\alpha)$	Symbol	Rate-controlling process
α^2	D_1	One-dimensional diffusion
$\alpha+(1-\alpha)\ln(1-\alpha)$	D_2	Two-dimensional diffusion
$[1-(1-\alpha)^{1/3}]^2$	D_3	Three-dimensional diffusion (Jander function)
$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}$	D_4	Three-dimensional diffusion (Ginstling–Broushtein function)
$\ln[\alpha/(1-\alpha)]$	A_u	Autocatalytic reaction (Prout–Tompkins function)
$1-(1-\alpha)^{1/n}$	R_n	Phase-boundary reaction: $n=1$, 2, and 3 (One-, two-, and three dimensional, respectively)
$[-\ln(1-\alpha)]^{1/m}$	A_m	Random nucleation: $m=1$ Random nucleation and subsequent growth: $m=2$, 3, and 4 (Avrami–Erofeyev functions)

correct $F(\alpha)$ uniquely from the $F(\alpha)$ summarized in Table 1, by means of the conventional isothermal analyses alone.

This can be visualized extensively, using the α–t relation calculated assuming a given $F(\alpha)$ with given values of activation energy E and frequency factor A, with the computer and plotter. Figure 1 shows plots of various $F(\alpha)$ vs. t, when A_1 is assumed to be the correct $F(\alpha)$ with the E and A values of 100 kJ mole^{-1} and 10^{10} s^{-1}, respectively at a temperature of 400 K. It is likely in view of Fig. 1 that it is difficult to differentiate A_m from R_n and A_u.

The difficulty can be illustrated by the following. When one of the functions $F(\alpha)$ such as A_m, R_n, and A_u is given as the appropriate one with the respective values of E and A of 100 kJ mole^{-1} and 10^{10} s^{-1} at a temperature of 400 K, the simultaneously appropriate $F(\alpha)$ was found, as is shown in Table 2.

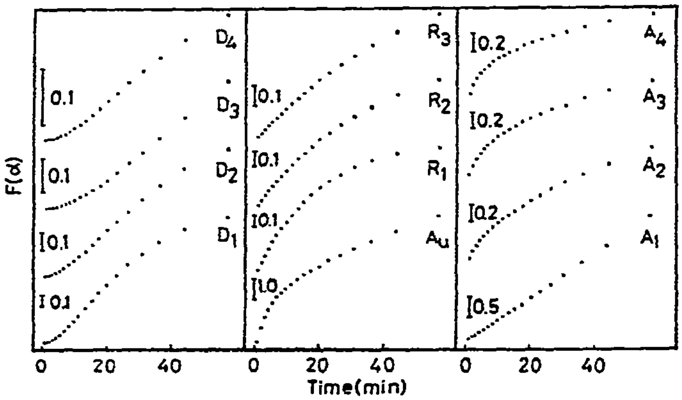


Fig. 1. Plots of various $F(\alpha)$ vs. t assuming an A_1 mechanism with $E=100$ kJ mole^{-1} and $A=10^{10}$ s^{-1} at a temperature of 400 K in the α range 0.05–0.95.

TABLE 2

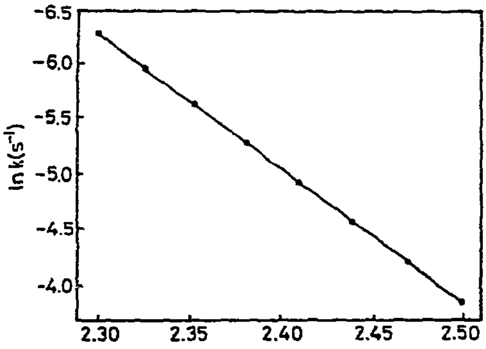
The simultaneously appropriate $F(\alpha)$ corresponding to a given $F(\alpha)$ with the respective values of E and A of 100 kJ mol^{-1} and 10^{10} s^{-1} at a temperature of 400 K in the α range 0.2–0.8

A given $F(\alpha)$	Other appropriate $F(\alpha)$	r
A_2	$R_{1.471}$	0.9998
R_2	$A_{1.587}$	0.9999
A_u	$R_{1.031}$	0.9990
	$A_{3.333}$	0.9999

It is worth showing that almost equal kinetic parameters are obtained in terms of the Arrhenius plot for both the appropriate $F(\alpha)$. Using the calculated α–t relation, when R_2 is given as a correct $F(\alpha)$, with the respective values of E and A of 100 kJ mole^{-1} and 10^{10} s^{-1}, the most appropriate value m for A_m was searched at a temperature range 400–435 K in an α range 0.2–0.8. The m value was found to be 1.587 independently of the temperature examined. The values of E and A were in turn derived as 99.92 kJ mole^{-}1 and $10^{10.32}$ s^{-1}, respectively. Figure 2 shows the Arrhenius plot.

In a similar manner as above, $R_{1.471}$ was found independently of the temperature eamined, when A_2 is assumed as a correct $F(\alpha)$ under the same condition as above. The values of E and A were thus derived as 99.94 kJ mole^{-}1 and $10^{9.83}$ s^{-1}, respectively, from the Arrhenius plot as shown in Fig. 3.

It follows that the discernment among the mechanistic functions $F(\alpha)$ such as A_m, R_n, and A_u is not always possible in view of the $F(\alpha)$ vs. t plot conventionally used in isothermal kinetic analyses, especially if the exponents in A_m and R_n are scanned. This difficulty could not be eliminated, even if plots of α vs. $t/t_{0.5}$ were used, where $t_{0.5}$ is the time for 50% decomposition [8]. In addition, an accurate knowledge of the



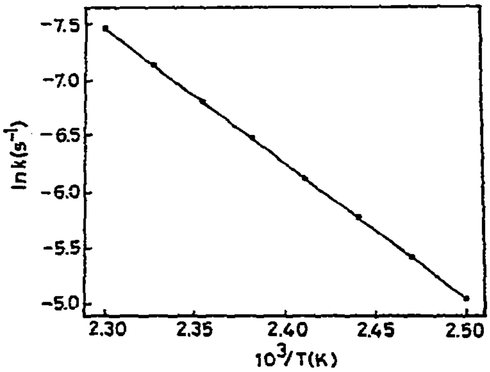


Fig. 2. Arrhenius plot for the $A_{1.587}$ mechanism calculated assuming an R_2 mechanism with $E = 100$ kJ mole^{-1} and $A = 10^{10}$ s^{-1} in the α range 0.2–0.8.

Fig. 3. Arrhenius plot for the $R_{1.471}$ mechanism calculated assuming an A_2 mechanism with $E = 100$ kJ mole^{-1} and $A = 10^{10}$ s^{-1} in the α range 0.2–0.8.

inception time of the decomposition, which is usually difficult to obtain, is necessary in such a plot.

The corresponding dynamic trace [9], recorded at a very low heating rate with a small sample size, may be employed in solving this problem since an agreement of kinetic parameters between the dynamic and isothermal analyses usually results [10]. Alternatively, a structural investigation by means of microscope and/or X-ray diffraction during the decomposition of solids is needed [11].

REFERENCES

1 Y. Masuda and S. Shishido, Thermochim. Acta, 28 (1979) 377.
2 D.A. Young, Decomposition of Solids, Pergamon Press, Oxford, 1966, p. 35.
3 A.K. Galwey and P.W.M. Jacobs, Proc. R. Soc. London, Ser. A, 254 (1960) 455.
4 H. Tanaka, S. Ohshima, S. Ichiba and H. Negita, Thermochim. Acta, 48 (1981) 137.
5 G.D. Anthony and P.D. Garn, J. Am. Ceram. Soc., 57 (1974) 132.
6 H.M. Hauser and J.E. Field, Thermochim. Acta, 27 (1978) 1.
7 D.W. Johnson and P.K. Gallagher, J. Phys. Chem., 75 (1971) 1179.
8 J.H. Sharp, G.W. Brindley and B.N.N. Achar, J. Am. Ceram. Soc., 49 (1966) 379.
9 J. Zsakó, J. Therm. Anal., 5 (1973) 239.
10 G. Flor, A. Marini and V. Berbenni, Z. Naturforsch. Teil A, 34 (1979) 437.
11 J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.