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Short Communications

ON THE DETERMINATION OF THE ACTIVATION ENERGY OF SOLID-STATE REACTIONS FROM THE MAXIMUM REACTION RATE OF ISOTHERMAL RUNS

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The method of kinetic analysis of isothermal traces recently proposed by Dharwadkar et al. is criticized. It is concluded that this method would be a proper one in the case of reactions following the mechanism of Prout and Tompkins or Avrami—Erofeev, but it would lead to misinterpretation when diffusion or phase-boundary-controlled reactions are involved.

In a very recent paper [1] Dharwadkar et al. proposed a method of determining the activation energy of thermal decompositions of solids from the maximum reation rate, $(\mathrm{d}\alpha/\mathrm{d}t)_{\max}$, obtained from a series of isothermal runs. They suggested that a plot of $\ln (\mathrm{d}\alpha/\mathrm{d}t)_{\max}$ against the reciprocal of the temperature $(1/T)$ would be a straight line whose slope gives the activation energy, whatever the actual reaction mechanism. It is also stated in [1] that the described procedure is not only simple and time-saving, but yields more reliable values of the activation energy than do conventional procedures.

Dharwadkar et al. [1] consider that the theoretical basis of their method can be found by taking into account that the kinetic data of thermal decomposition reactions fulfil the general equation:

$$\ln \frac{\mathrm{d}\alpha(\mathrm{d}t)}{f(\alpha)} = \frac{-E}{RT} + \ln A \tag{1}$$

where α is the reacted fraction, E is the activation energy, A is the preexponential Arrhenius factor and $f(\alpha)$ is a function depending on the reaction mechanism.

In agreement with Eq. (1), a plot of $\ln (\mathrm{d}\alpha/\mathrm{d}t)$ against $1/T$ for a fixed value of α would give the activation energy. This is also true for $(\mathrm{d}\alpha/\mathrm{d}t_{\max})$, provided that $\alpha_{\max}$ is independent of temperature.

The kinetic analysis of the thermal decomposition of $CdCO_3$ was carried out in [1] and it was reported that the activation energy calculated from the plot of $\ln (\mathrm{d}\alpha/\mathrm{d}t)_{\max}$ *vs.* $1/T$ coincides with the value determined by conventional methods under the consideration that the reaction follows an Avrami—Erofeev mechanism with $n = 3$. On the other hand, it was observed [1] that $\alpha_{\max}$ is constant and equal to 0.42 over the whole temperature range investigated ($660\ \mathrm{K} < T < 745\ \mathrm{K}$). Other authors [2–4] have also reported that α_{max} is temperature-independent for a number of reactions. In the opinion of Young [5], the value of α_{max} has little theoretical significance, although he does not give any comments or examples to justify his assertion.

The aim of the present communication is to look for a connection between the value of α_{max} and the actual reaction mechanism.

It is well known that the rate of a solid-state reaction can be expressed by the general law:

$$\mathrm{d}\alpha/\mathrm{d}t = k \cdot f(\alpha) \tag{2}$$

k being the rate constant expressed by the Arrhenius law:

$$k = A \cdot \exp\,(-E/RT). \tag{3}$$

Therefore, the following relationship applies when the maximum reaction rate occurs:

$$\mathrm{d}^2\alpha/\mathrm{d}t^2 = k \cdot f'(\alpha_{\mathrm{max}}) \cdot (\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{max}} = 0 \tag{4}$$

and, accordingly:

$$f'(\alpha_{\mathrm{max}}) = 0. \tag{5}$$

Equation (5) shows that α_{max} is independent of the rate constant k and, consequently, of the temperature. The values of α_{max} calculated from the $f(\alpha)$ functions more commonly used in the literature to represent the mechanisms of thermal decomposition reactions are included in Table 1. This Table shows that the value of α_{max} would allow discrimination between the actual kinetics of reactions following the Prout and Tompkins or the Avrami–Erofeev mechanism. In fact, the experimental value of α_{max} obtained for the thermal decomposition of $\mathrm{CdCO_3}$ [1] is very close to the one calculated in Table 1 for a reaction following the Avrami–Erofeev mechanism with an exponent $n = 3$.

On the other hand, the expressions for the rates of diffusion and phase-boundary controlled reactions do not fulfil the maximum mathematical conditions. In such cases, ($\mathrm{d}\alpha/\mathrm{d}t$) has its highest value when $\alpha = 0$ and it decrease in proportion as α increases. In other words, $(\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{max}}$ coincides with the initial reaction rate (i.e. the rate at zero time). However, we must bear in mind that the steady-state temperature corresponding to the isothermal conditions selected is not instantaneously attained. Therefore, an apparent value of $(\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{max}}$ would be reached at a reacted fraction α_{max} higher than zero, in spite of the fact that the reaction is following phase-boundary of diffusion kinetics. This means that the process is heat-transfer-controlled in the α range lower than α_{max}. Accordingly, only the values of α higher than α_{max} would be useful for performing the kinetic analysis. In such a case $(\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{max}}$ has no meaning, and a plot of the logarithm of this magnitude against the reciprocal of the temperature would lead to erroneous values of the activation energy.

Table 1

Calculation of α_{max}

Process controlling the reaction rate	$f(\alpha)$	α_{max}
Two-dimensional movement of the phase boundary	$(1-\alpha)^{1/2}$	0.000
Three-dimensional movement of the phase boundary	$(1-\alpha)^{2/3}$	0.000
First-order kinetics	$(1-\alpha)$	0.000
One-dimensional diffusion	$1/2\alpha$	0.000
Two-dimensional diffusion	$-1/\ln(1-\alpha)$	0.000
Three-dimensional diffusion (Jander equation)	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$	0.000
Three-dimensional diffusion (Ginstling—Brounstein equation)	$3/2[(1-\alpha)^{-1/3}-1]$	0.000
Prout and Tompkins mechanism	$\alpha(1-\alpha)$	0.500
Avrami—Erofeev mechanism	$(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$	
	$n = 2$	0.393
	3	0.486
	4	0.527
	5	0.550
	6	0.565

To summarize, we can conclude that the method proposed by Dharwadkar et al. [1] and Young [5] is a proper one for performing the kinetic analysis of reactions following an Avrami Erofeev or a Prout and Tompkins mechanism. However, it must be used with caution if phase-boundary or diffusion-controlled reactions are involved.

References

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