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Empirical kinetic models in thermal analysis

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Abstract

The applicability of the empirical kinetic model in thermal analysis is discussed. It is shown that for a reliable kinetic analysis of a single experimental curve the value of the true activation energy should be known a priori.

INTRODUCTION

The kinetic analysis of thermal analysis (TA) data has received a great deal of attention in the last two decades. One of the most typical problems of empirical kinetics is usually associated with the formulation of the so-called kinetic model, i.e. the $f(\alpha)$ function in the kinetic equation

$$d\alpha/dt = A\ e^{-x} f(\alpha) \tag{1}$$

where A is the pre-exponential factor, x is the reduced activation energy ($x = E/RT$) and α is the degree of conversion.

There are several kinetic models derived from the geometry of the reaction interface [1]. The mathematical formulae of the most frequently cited models are summarized in Table 1. These kinetic model functions derived on the basis of physical–geometrical assumptions of regularly shaped bodies can hardly describe real heterogeneous systems where we have to consider, for example, irregular shapes of reacting bodies, polydispersity, shielding and overlapping effects of phases involved in the process etc.

From this point of view it would be useful to find an empirical $f(\alpha)$ function containing the smallest possible number of constants, so that it is

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

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TABLE 1

The kinetic models

Model	Symbol	$f(\alpha)$
Johnson-Mehl-Avrami	A_n	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$
Two-dimensional reaction	R_2	$(1-\alpha)^{1/2}$
Three-dimensional reaction	R_3	$(1-\alpha)^{1/3}$
Two-dimensional diffusion	D_2	$1/[-\ln(1-\alpha)]$
Jander equation	D_3	$3/2(1-\alpha)^{2/3}/[1-(1-\alpha)^{2/3}]$
Ginstling-Brounshtein	D_4	$3/2[(1-\alpha)^{-1/3}-1]$

flexible enough to describe real TA data as closely as possible [1]. Later this concept led to the idea that such an empirical kinetic model would provide a general expression for all the kinetic equations shown in Table 1.

Unfortunately, these two aspects are very often confused. We therefore believe it is useful to discuss these problems which influence the applicability of empirical kinetic models in thermal analysis.

THE EMPIRICAL KINETIC MODELS

Twenty years ago, Šesták and Berggren [2] proposed an empirical kinetic model of the form

$$f(\alpha)=\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^r \tag{2}$$

It was believed [1,2] that this kinetic equation, containing three exponential terms, could describe any TA curve. Further mathematical analysis [3] of eqn. (2) has shown that no more than two kinetic exponents are necessary. Therefore after eliminating the third exponential term in eqn. (2) the final form obtained is

$$f(\alpha)=\alpha^m(1-\alpha)^n \tag{3}$$

Equation (3) is known as the Šesták–Berggren (SB) kinetic model. Exponents m and n have the significance of kinetic parameters of the process. If the exponent m is set equal to zero, the remaining exponent n is then called the reaction order (RO). This approach is often used for a general description of all heterogeneous processes, although it has only limited applicability [4].

Both the SB and RO models can also be understood in terms of the accommodation function introduced by Šesták [5]. In this case the heterogeneous kinetics are assumed to be a distorted case of the simpler homogeneous kinetics. The accommodation function then expresses a deviation of the more complex reaction mechanism from the ideal case.

Recently we have shown [6] that the SB model cannot be considered as a general expression of the kinetic models (Table 1) for the true (or fixed value) activation energy E. Nevertheless, this is not so evident for any arbitrarily chosen value of the activation energy which is called here the apparent activation energy E_{app}. Therefore we will discuss this problem in the following sections.

The reaction order model

Criado et al. [7] have shown that any TA curve can be described by the RO model instead of the true one for a certain value of the apparent activation energy. Recently it was found [8] that the ratio of the apparent and true activation energy (E_{app}/E) can be expressed for the apparent RO model by the following equation:

$$\frac{E_{app}}{E} = -\left(\frac{f(\alpha_p)}{f'(\alpha_p)}\right)\frac{n_{app}}{1-\alpha_p} \tag{4}$$

where α_p is the degree of conversion at the maximum of the TA peak and n_{app} is an apparent kinetic exponent of the RO model. The value of n_{app} is characteristic for the true kinetic model but α_p depends also on x_p (reduced activation energy at the maximum of the TA peak). Therefore the value of E_{app}/E slightly increases with increasing x_p for diffusion models (i.e. D_2, D_3 and D_4). On the other hand, the E_{app}/E ratio decreases with increasing x_p for the A_n model, according to the equation [9]

$$\frac{E_{app}}{E} = \frac{n-1}{x_p\pi(x_p)} + 1 \tag{5}$$

where n is the true kinetic exponent of the A_n model and $\pi(x)$ is the approximation of the temperature integral in the form [10]

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{6}$$

It is noteworthy that the empirical relationship $E_{app}/E = 1.05n - 0.05$ found by Criado et al. [7] corresponds to the general equation (5) for $x_p = 38.3$. The limiting values of the n_{app} and E_{app}/E parameters are summarized in Table 2 for the kinetic models discussed.

TABLE 2

The values of apparent parameters ($x_p \to \infty$) for the RO model

True model	n_{app}	E_{app}/E
A_n	1	n
D_2	0.269	0.483
D_3	0.666	0.5
D_4	0.420	0.495

The Šesták–Berggren model

The ratio of the apparent and true activation energy can be expressed for the SB model in the following form [8]:

$$\frac{E_{\text{app}}}{E} = -\left(\frac{f(\alpha_{\text{p}})}{f'(\alpha_{\text{p}})}\right)\left(\frac{n_{\text{app}}}{1-\alpha_{\text{p}}} - \frac{m_{\text{app}}}{\alpha_{\text{p}}}\right) \tag{7}$$

By rewriting eqn. (1) for an apparent activation energy we obtain

$$y_{\text{app}}(\alpha) = (\mathrm{d}\alpha/\mathrm{d}t)\exp(E_{\text{app}}/RT) \tag{8}$$

The $y_{\text{app}}(\alpha)$ function defined by eqn. (8) is proportional to the $f(\alpha)$ function that represents the apparent kinetic model of the process. Therefore by plotting the $y_{\text{app}}(\alpha)$ dependence the apparent kinetic model can be determined.

The $y_{\text{app}}(\alpha)$ function has a maximum at α_{M} for the SB model. It is evident that if the kinetic exponent m is equal to zero (i.e. for the RO model) then $\alpha_{\text{M}} = 0$. However, E_{app} should not be negative and it follows from eqn. (7) that α_{M} has to be lower than α_{p}. Therefore, the maximum is confined to the interval $0 < \alpha_{\text{M}} < \alpha_{\text{p}}$ and it can be used to determine the apparent kinetic exponent ratio [9]:

$$\frac{m_{\text{app}}}{n_{\text{app}}} = \frac{\alpha_{\text{M}}}{1-\alpha_{\text{M}}} \tag{9}$$

It should be stressed that any change in the value of the apparent activation energy leads to a different value of the $m_{\text{app}}/n_{\text{app}}$ ratio. Therefore the two apparent kinetic exponents are mutually interdependent. A characteristic n_{app} vs. m_{app} dependence can be found for each true kinetic model. These plots (full lines) calculated using eqns. (7) and (9) are shown in Fig. 1. The broken lines correspond to the different values of the maxima of the $y_{\text{app}}(\alpha)$ function. An important feature of the n_{app} vs. m_{app} plot is that it is characteristic feature for the true kinetic model. Nevertheless, it can be seen that these plots are identical for the D_3 and R_3 models. There is also one common curve corresponding to the A_n model, regardless of the value of the true kinetic exponent n. Similar behaviour was observed also for other types of reference plot [11,12].

Many studies are concerned with the kinetic analysis of a single TA curve. However, the methods are somewhat problematic because of the apparent kinetic models. For example, the popular Freeman and Carroll method [13] was derived for the RO model. Therefore this method always gives apparent parameters n_{app} and E_{app} corresponding to the RO model regardless of the true kinetic model. Similarly, it must be borne in mind that the non-linear or multiple linear regression methods can lead to incorrect results because any TA curve can be interpreted within the scope

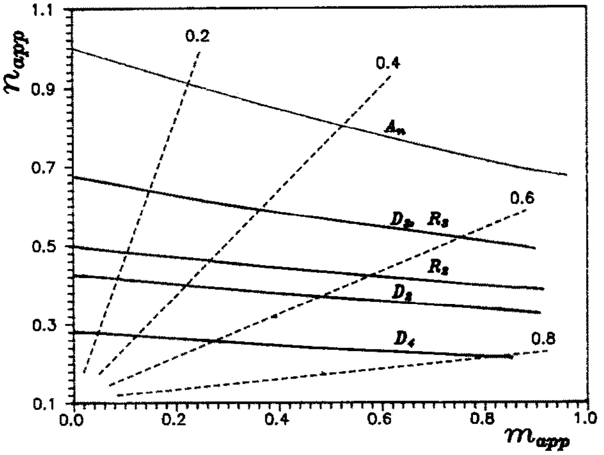

Fig. 1. Characteristic plots of apparent kinetic exponents of the apparent SB model corresponding to several true kinetic models (full lines). The α_M values are shown by broken lines.

of several apparent kinetic models (RO or SB), depending on the value of the apparent activation energy.

If the true activation energy is known, however, the SB kinetic model can be found very useful for real heterogeneous systems [4,14,15] where other kinetic models cannot be successfully used for a quantitative description of the experimental data.

CONCLUSION

It was shown that any TA curve corresponding to the kinetic models discussed can be well described by empirical RO or SB models for a certain value of the apparent activation energy. This behaviour is inherent to the kinetic equation as expressed by eqn. (1). Therefore it seems to be practically impossible to perform correctly the kinetic analysis of a single TA curve unless the true value of the activation energy is known a priori.

Nevertheless, the flexibility of the empirical kinetic models allows the description of very complicated heterogeneous processes where simple kinetic models can hardly be applied. It should be stressed, however, that in this case the true value of activation energy has to be previously determined.

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