

A new method to explain the model dependence of apparent activation energy derived from a single nonisothermal dynamic curve

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Abstract

A single nonisothermal dynamic curve can be relatively correctly described by several reaction models in model-fitting approach, which yields model-dependent kinetic parameters. The model dependence of the apparent activation energy is explained mathematically by a new method which is developed from the peak property method in this paper. It has been found that the apparent activation energy rises linearly with the increase of the order of n th-order and Avrami–Erofeev reaction models, which can be verified by data from the literature and can explain some phenomena appeared in some articles. Moreover, the apparent activation energies derived from fitting a single nonisothermal dynamic curve to n th-order and Avrami–Erofeev reaction models can be correlated through the activation energy of 1st-order model.

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1. Introduction

Generally, the following rate equation is assumed for the kinetics of solid state reactions

$$d\alpha/dt = A \exp(-E/RT)f(\alpha) \quad (1)$$

where α is the fraction of reactant converted, t the time, E the activation energy, A the frequency factor, and R the gas constant. T is the absolute temperature. The specific form of $f(\alpha)$ represents the hypothetical model of the reaction mechanism. There are various published methods of extrapolate kinetic parameters from a single nonisothermal thermodynamic (TA) curve. The model-fitting approach, in which the kinetic data are fitted to a variety of reaction models based on Eq. (1) or its integral form, is usually performed, for

example, the Achar–Brindley–Sharp–Wendworth [1,2] method and Coats–Redfern method [3]. In the approaches of this kind, the apparent activation energy and frequency factor can then be calculated by fitting various reaction models to the kinetic data and determining the model of best fit on the basis of statistical arguments.

However, a single TA curve may be relatively correctly described by several reaction models founded by Criado and Morales [4] as early as 1977. In many cases [4–11], large differences can be noticed among the kinetic parameters derived from different reaction models. So mis-estimation of the reaction model will result in the distortion of the kinetic parameters. Malek et al. [12,13] gave some expressions about this distortion. Zhou and Grant [14] explained the model dependence of apparent activation energy by dividing the apparent kinetic parameters into the true term and correction term. Galwey [15] pointed out that the values of apparent activation energy decrease linearly with reduction of the exponent for both the power law and

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the Avrami–Erofeev models, and attributed this dependence to the properties of the Coats–Redfern method. However, this explanation seems not to be applied to the n th-order reaction model.

In this paper, we will try to obtain some relationships of the model dependence of apparent activation energy derived from a single nonisothermal dynamic curve by model-fitting approach through a new method. Firstly, the method by using peak properties of a dynamic curve to estimate the kinetic parameters is discussed. Secondly, some expressions about the model dependence of apparent activation energy are obtained and verified by the data from the literature. Lastly, the correlation of apparent activation energies for n th-order and Avrami–Erofeev reaction models is discussed.

2. Peak property method

The method by using peak properties of a dynamic curve to estimate the kinetic parameters was developed based on the assumption that the peak properties of a dynamic curve, such as peak temperature T_m , peak height $(d\alpha/dT)|_m$, and conversion at peak temperature α_m , could represent a unique thermal decomposition [16,17]. One iteration procedure was introduced to obtain accurate kinetic parameters based on this method [18]. For the n th-order reactions, the kinetic model can be classified by the magnitude of α_m and then the kinetic parameters can be determined [19–21].

A conventional nonisothermal dynamic curve, like a DTG or DSC curve, at a heating rate β can be derived from Eq. (1) and expressed mathematically as follows:

$$d\alpha/dT = (A/\beta)\exp(-E/RT)f(\alpha) \quad (2)$$

And its integral form is

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-E/RT} dT = \frac{AE}{\beta R} \frac{e^{-x}}{x^2} h(x) \quad (3)$$

where $x = E/RT$ and the temperature integral $h(x)$ can be expressed by various approximations.

At the peak of a dynamic curve, the condition $d^2\alpha/dT^2 = 0$ is satisfied, which will lead to Eq. (4):

$$A \exp(-E/RT_m) f'(\alpha_m) + \beta E / (RT_m^2) = 0 \quad (4)$$

Combining Eq. (4) with Eq. (3) gives

$$g(\alpha_m) f'(\alpha_m) = -h(x_m) \quad (5)$$

For a definite reaction model, Eq. (5) indicates that the value of the conversion fraction α_m is only related to the value of E/RT_m . Since ordinary reactions have $x = E/RT = 15$ – 70 , correspondingly $h(x) = 0.8879$ – 0.9726 , Eq. (5) can be applied to estimate the limits of α_m for various kinetic models and then classify the kinetic models by the magnitude of α_m [19–21].

For n th-order reaction model (F_n), $f(x) = (1 - \alpha)^n$, Eq. (5) gives

$$1 - \alpha_m = \left[1 - \frac{n-1}{n} h(E/RT_m) \right]^{1/(n-1)} \quad n \neq 1 \quad (6)$$

$$\ln(1 - \alpha_m) = -h(E/RT_m) \quad n = 1 \quad (7)$$

Gao et al. [20] listed the theoretic limits of α_m for n th-order reactions at various n values based on the above two equations. These limits can be used to determine reaction order from the experimental α_m value.

For Avrami–Erofeev reaction model (AE), $f(\alpha) = 1/n(1 - \alpha)[- \ln(1 - \alpha)]^{1-n}$, Eq. (5) gives

$$\ln(1 - \alpha_m) = n - 1 - nh(E/RT_m) \quad (8)$$

3. Model dependence of apparent activation energy

3.1. n th-Order reaction model

For n th-order reaction model, the maximum reaction rate of the dynamic experiments can be expressed as following, by combining Eqs. (2) and (4):

$$d\alpha/dT|_m = [(1 - \alpha_m)/n] (E/RT_m^2) \quad (9)$$

If $n \neq 1$, the above equation can be rearranged as the following by combining with Eq. (6):

$$\begin{aligned} \frac{E}{RT_m^2 (d\alpha/dT)|_m} &= n/(1 - \alpha_m) \\ &= n / \left[1 - \frac{n-1}{n} h(E/RT_m) \right]^{1/(n-1)} \end{aligned} \quad (10)$$

If $n = 1$, Eq. (9) can be rearranged as the following by combining with Eq. (7)

$$\frac{E}{RT_m^2 (d\alpha/dT)|_m} = \exp(h(x_m)) \quad (11)$$

In fact, Eq. (11) can be regarded as one special case of Eq. (10), because we can find that the limit $\lim_{n \rightarrow 1} \{n/[1 - (n-1/n)h(x_m)]^{1/(n-1)}\}$ is just the expression of $\exp(h(x_m))$. So in the following, Eq. (10) represents both the cases and is discussed in detail.

If a single dynamic TA curve is given, the peak temperature and the maximum reaction rate are settled if it has, and the true activation energy is considered to exist. Thus Eq. (10) indicates that the apparent activation energy E only depends on the reaction order n . Fig. 1 shows this dependency for $h(x) = 0.8879$ – 0.9726 and one special approximation of $h(x) = 1$, which is the simplest one and yet often used. It is interesting to notice that a nearly linear relationship is exhibited between the Q ($Q = E/[RT_m^2 (d\alpha/dT)|_m]$) value and the reaction order n . The linear regressions in Fig. 1 have very high correlation coefficient values which nearly equal 1. That is to say, for a given single dynamic curve, if n th-order reaction

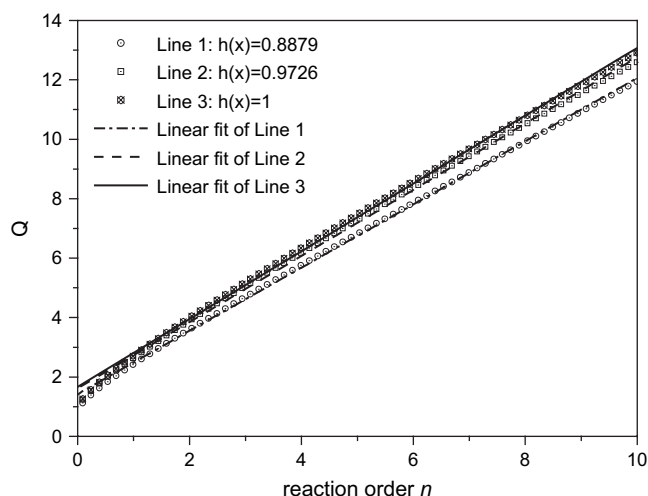


Fig. 1. The dependency of apparent activation energy on the reaction order for n th-order reactions ($0 < n < 10$, $Q = E/[RT_m^2(d\alpha/dT)|_m]$).

model is adopted, the apparent activation energy E can be expressed as a linear function of the reaction order n :

$$E = RT_m^2(d\alpha/dT)|_m(pn + q) \quad (12)$$

where p and q are the regression parameters.

For any common value of $h(x)$ in (0.8879, 0.9726), such a linear relationship will be also expected, and the regression line will lie in the narrow interval between Line1 and Line2 of Fig. 1. What is more, the equation $p + q = \exp(h(x_m))$ is satisfied because Eq. (11) is one special case of Eq. (10) as stated before. In fact, we can check this equation by numerical simulation to support the linear relationship. The linear regression line $y = 0.9963x + 0.0021$ in Fig. 2 indicates that the values of $p + q$ by linear regression of Eq. (12) for $n \in [0.49, 2.99]$ at the interval of 0.005 are nearly equal to the values of $\exp(h(x_m))$, which the $h(x)$ value is sampled from $h(x) \in [0.8879, 0.9726]$ (numerical integrated) at the interval

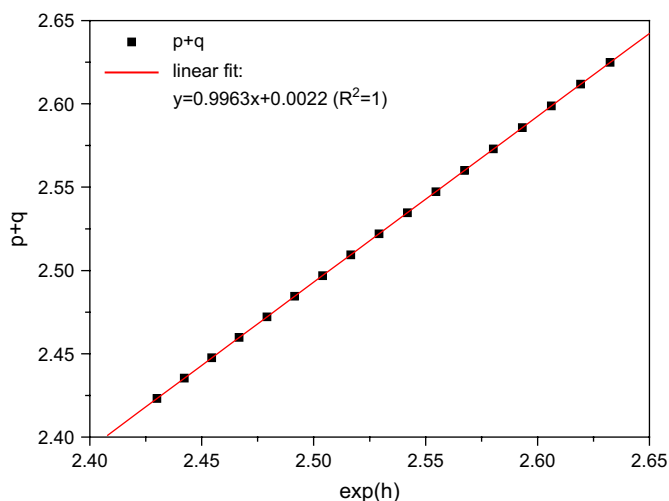


Fig. 2. The relation of $p + q$ (by linear regression of Eq. (13) for $n \in [0.49, 2.99]$ at the interval of 0.005) with $\exp(h)$ ($h(x)$ is sampled from $h(x) \in [0.8879, 0.9726]$ at the interval of 0.005) by numerical simulation.

of 0.005. So p and q of Eq. (12) are not independent, and only one is needed to be determined.

The linear relationship of Eq. (12) reveals the model dependence of apparent activation energy for n th-order reactions, and can explain that some results appeared in the literature. Gao et al. [19] pointed out that the values of apparent activation energy of dynamic thermal degradation of the PMMA sample, which is estimated at several proposed reaction orders from a single heating rate curve, increase linearly with the reaction order (see Fig. 2 in Ref. [19]). This phenomenon is the consequent result of Eq. (12). Recently, Budrugaec and Segal [7] critically analyzed the procedural errors in the kinetic analysis of nonisothermal data and proposed a general algorithm. In Table 2 of his paper, the values of the kinetic parameters obtained for various kinetic models by means of the Coats–Redfern method are presented. We analyzed the values of apparent activation energy for n th-order models at $\beta = 4$ K/min abstracted from this table and have got a well linear relationship, as presented in Fig. 3. Such relationship can also be widely found at other heating rates or in other papers [5,6].

3.2. Avrami–Erofeev reaction model

For Avrami–Erofeev reaction model, the maximum reaction rate of dynamic experiment curves can be expressed as the following, by combining Eqs. (2), (4) and (8):

$$\begin{aligned} \frac{d\alpha}{dT}|_m &= \frac{E}{RT_m^2} \frac{-f(\alpha)}{f'(\alpha)} \\ &= \frac{E}{RT_m^2} \frac{(n-1-nh(x_m)) \exp(n-1-nh(x_m))}{-nh(x_m)} \end{aligned} \quad (13)$$

Denoting $y = -h(x_m)/[(n-1-nh(x_m)) \exp(n-1-nh(x_m))]$, we can obtain

$$E = RT_m^2(d\alpha/dT)|_m ny \quad (14)$$

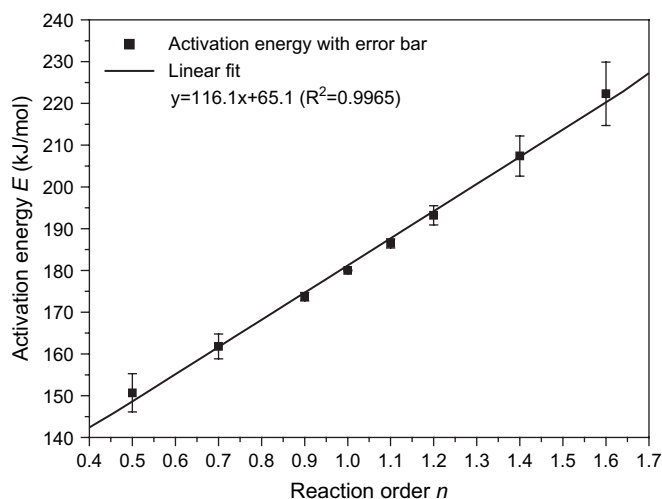


Fig. 3. The linear relationship of apparent activation energy with the reaction order for n th-order model. The data are abstracted from Table 2 of Ref. [7], at $\beta = 4$ K/min as an example.

If the simplest approximation of $h(x) = 1$ is adopted, $y = e = 2.7183$, and thus Eq. (14) becomes

$$E = [RT_m^2(d\alpha/dT)|_m]e]n \quad (15)$$

Obviously, Eq. (15) means apparent activation energy is proportional to the order of Avrami–Erofeev reaction model for a given dynamic curve. Moreover, the variable y can be nearly regarded as a constant for commonly used values of $h(x)$ and n . Fig. 4 indicates that most of the values of y in different conditions lie between 2.45 and 2.65, and increase slightly with $h(x)$ and n . Since the variable y is nearly a constant, the apparent activation energy E will increase linearly with the order n as in Eq. (15).

The data of E and n abstracted from Table 2 of Ref. [7] for Avrami–Erofeev reaction model (here n is the reciprocal of m in this reference) display the linear relationship as Eq. (14) described (see Fig. 5). The fitted line $y = 192.18x - 12.18$ can even be reasonably explained by Eq. (14). The single curve, numerically simulated in Ref. [7] with the kinetic parameters of $E = 180$ kJ/mol, $A = 10^{10}$ /s, $n = 1$ and $\beta = 4$ K/min, presents the peak characteristics of $T_m = 747.0$ K and $(d\alpha/dT)|_m = 0.0152$ /K. So $h(x_m) = 0.937$ and average $y \approx 2.580$ from Fig. 4. Thus Eq. (14) gives the theoretical line $E = 181.9n$, which is very close to the fitted line $y = 192.18x - 12.18$ (see Fig. 5). The difference may due to the slight increase of the variable y with the order n . Because of this slight increase, the fitted line will intercept the axis n at a small positive value (here it is about 0.063), which is found and explained in another way by Galwey [15].

It is noticed that Eqs. (12) and (14) indicate that the apparent activation energy is ONLY closely related with the properties of the curve peak. That is to say, this model dependence of apparent activation energy is independence of the model-fitting methods (for example, differential methods and integral methods). Moreover, the most important data point in model-fitting approach is the peak of the dynamic curve.

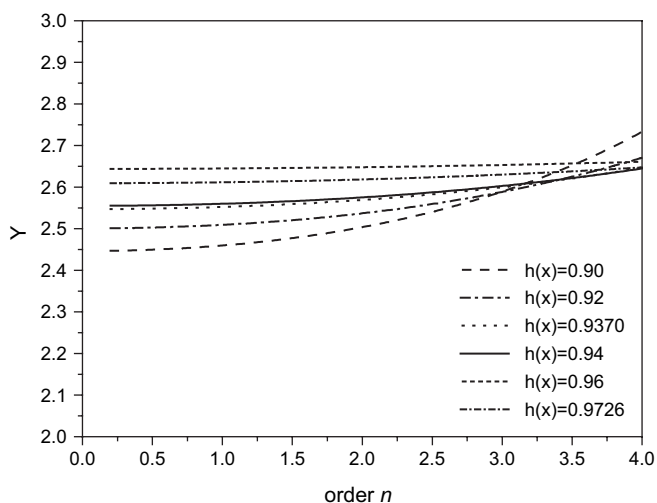


Fig. 4. The values of $y = -h/[(n-1-nh)\exp(n-1-nh)]$ for commonly used values of $h(x)$ and n .

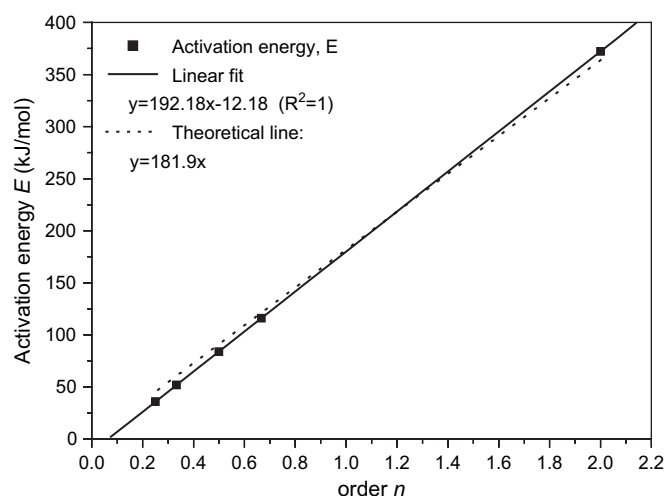


Fig. 5. The linear relationship of E and n abstracted from Table 2 of Ref. [7] for Avrami–Erofeev reaction model.

For the power-law reactions model, $f(\alpha) = 1/n\alpha^{1-n}$, since the dynamic curve shows no peak, the above deducing process cannot be applied. For other reaction models, the above deducing process can also be applied if the reaction models have a general form.

4. Correlation of the two different models

As we know, one single dynamic curve can be fitted to various reaction models by model-fitting approach with very high correlation coefficient values. For example, the curve simulated from the first-order reaction model can be fitted by F_n and AE model with different orders very well [7]. The apparent activation energy fitted by F_n model can be expressed as $E_{F_n} = RT_m^2(d\alpha/dT)|_m(pn_{F_n} + q)$ according to Eq. (12). In the same way, the apparent activation energy fitted by AE model can be expressed as $E_{AE} = RT_m^2(d\alpha/dT)|_m n_{AE}y$ according to Eq. (14). So the apparent activation energies from these two types of reaction models have the correlation:

$$\frac{E_{AE}}{E_{F_n}} = \frac{n_{AE}y}{pn_{F_n} + q} \quad (16)$$

As an approximated estimation, if $h(x) = 1$, $E_{AE} \approx n_{AE}E_{F_1}$, which can be verified by the data from Table 2 of Ref. [7]. In fact, the 1st-order reaction model and AE model with $n_{AE} = 1$ have the same differential and integral forms, so theoretically $E_{AE}|_{n_{AE}=1} = E_{F_1}$. Thus the apparent activation energy of the two reaction models can correlate through E_{F_1} . Eq. (16) indicates that the apparent activation energy of one reaction model can be directly deduced and not necessarily to be gained by model fitting, if that of the other reaction model is pre-determined.

5. Conclusion

A single nonisothermal dynamic curve can be relatively correctly described by several reaction models in model-fitting

approach, which yields model-dependent kinetic parameters. This paper tries to explain the model dependence of apparent activation energy by a new method and finds that apparent activation energy derived from fitting a single nonisothermal curve to n th-order and Avrami–Erofeev reaction models rises linearly with the increase of the order, which is verified by data from the literatures. Since the 1st-order reaction model and AE model with $n_{\text{AE}} = 1$ are identical, the apparent activation energies for n th-order and Avrami–Erofeev reaction models can be correlated. Once the apparent activation energy for 1st-order reaction model is determined, those for n th-order and Avrami–Erofeev reaction models with other orders can be directly computed, which makes the model-fitting process redundant. The model dependence of apparent activation energy gives a clue to explain the kinetic compensation effect, which is under our further investigations.

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