Determination of Arrhenius Parameters from a Single Rate Curve

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A simple fitting method was proposed to determine Arrhenius parameters from a single rate curve without demanding for integral curve at the same time. This is the merit of the fitting method since the commonly used differential methods still require integral curve besides the original rate curve.

Thermal analyses such as thermogravimetry (TG) and evolved gas analysis (EGA) are all performed in temperature-programmed processes. Several schemes have been proposed to estimate Arrhenius parameters from a temperature-programmed process.[1-12] Integral methods are convenient and therefore well used to estimate activation energy from a TG curve.[1-7] For evolved gas analysis, differential methods can be applied.[8-12] However, the current differential methods require integral curve besides the original rate curve at the same time. In this paper, we will report a fitting method for first-order reaction in order to determine Arrhenius parameters from a rate curve only, without requirement to integrate the original rate curve again.

In general, temperature is expressed as equation (1) in temperature-programmed process. Instead of equation (1), temperature is expressed in another form as equation (2) in our method.[13] In which, η is determined when initial temperature and final temperature are given. And ξ has an exclusive value corresponding to a specific heating rate β.

$$T = T_0 + \beta t \qquad (1)$$

$$\frac{1}{T} = \frac{1}{T_0} - \eta \ln(1 + \xi t) \qquad (2)$$

As is well known, the integrating of Arrhenius equation was difficult when equation (1) was used and approximate expressions had to be adopted. In contrast, when equation (2) is used Arrhenius equation turns into equation (3), where

$$k_0 = A e^{-\frac{E}{RT_0}}, \quad \gamma = \frac{\eta E}{R}.$$

It is obvious that equation (3) is easy to be integrated for time. Therefore, based on equation (2) integral form of rate expression of a first-order reaction (eq (4)) is written by equation (5).

$$k = A e^{-\frac{E}{RT}} = k_0 (1 + \xi t)^\gamma \qquad (3)$$

$$-\frac{dm}{dt} = km \qquad (4)$$

$$-\ln\left(\frac{m}{m_0}\right) = \frac{k_0[(1 + \xi t)^{1+\gamma} - 1]}{\xi(1 + \gamma)} \qquad (5)$$

In equation (5) m_0 is the initial mass of a reactant. Signal value (or peak strength) Q of an evolved gas detected in an on-line detector can be expressed in equation (6), where f is response factor of the evolved gas in the detector.

$$Q = f \cdot \left(-\frac{dm}{dt}\right) = f \cdot k_0 (1 + \xi t)^\gamma m_0 \exp\left\{-\frac{k_0[(1 + \xi t)^{1+\gamma} - 1]}{\xi(1 + \gamma)}\right\} \qquad (6)$$

The ratio of Q_p at the maximum reaction rate to Q_i at any other point in rate curve can be further expressed in equation (7).

$$\frac{Q_p}{Q_i} = \left(\frac{1 + \xi t_p}{1 + \xi t_i}\right)^\gamma \cdot \exp\left\{\frac{-k_0}{\xi(1 + \gamma)}\left[(1 + \xi t_p)^{1+\gamma} - (1 + \xi t_i)^{1+\gamma}\right]\right\} \qquad (7)$$

At the maximum reaction rate equation (8) holds true. Furthermore, we defined an identical equation as equation (9).

$$\xi\gamma = k_0 (1 + \xi t_p)^{1+\gamma} \qquad (8)$$

$$\left(\frac{1 + \xi t_p}{1 + \xi t_i}\right)^{1+\gamma} \equiv q \qquad (9)$$

By taking equation (8) and equation (9) into equation (7) and making several rearrangements, equation (10) was derived, where

$$\alpha = \frac{\ln q}{\ln q - 1 + 1/q}.$$

$$Q_p^\alpha (1 + \xi t_p) = q Q_i^\alpha (1 + \xi t_i) \qquad (10)$$

So, for a rate curve recorded at a given heating rate, one can suppose an appropriate value for the identical equation (9) at first, then use equation (10) to determine time t_i and peak strength Q_i in the rate curve according to the q value, and at last take the obtained t_i value into equation (9) to calculate γ value, i.e., activation energy. Pre-exponential factor can be further calculated by equation (8).

As an illustration, thermal decomposition of a polyamide 6 (fine powders, less than 15 μg. The original pellets were supplied by Ube Industrial Co., Japan.), which was proven to be a first-order reaction,[14] was carried out in a pyrolyzer (2020D, Frontier Lab., Japan) set at 10 K/min from 373 K to 773 K in helium gas flow of 60 mL/min. The evolved gas was analyzed by an on-line gas chromatograph (HP 6890 series, USA) with a short empty capillary column. Since polyamide 6 decomposed almost 100% into its monomer,[15] the peak strength recorded was proportional to (–dm/dt) of the sample. The measured rate curve is shown in Figure 1. Peak time t_p was observed at 32.47 minute. When the maximum peak strength Q_p was normalized as unity, $Q_p^\alpha (1 + \xi t_p)$ was a constant (= 3.675) independent of q value. If one set q value for eq (9) equal to 3 (accordingly α = 2.544), $qQ^\alpha(1 + \xi t)$ value can be calculated at several different times along the rate curve. When $qQ^\alpha(1 + \xi t)$ is equivalent to
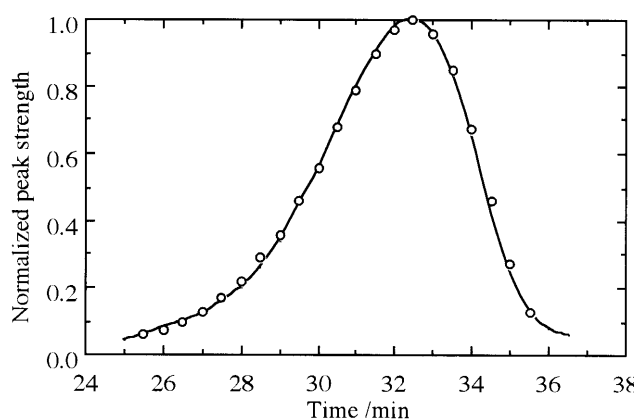
Figure 1. Comparison of calculated peak strength (open circle) based on equation (6) with measured peak strength (solid line) for thermal decomposition of a polyamide 6 at heating rate of 10 K/min from 373 K to 773 K.

Table 1. The calculated result for determining time t_i when q=3

t /min	$Q_{obs.}$	$1+\xi t$	$qQ_{obs.}^{\alpha}(1+\xi t)$
30.00	0.550	3.4717	2.276
30.25	0.610	3.4923	2.979
30.50	0.680	3.5129	3.951
30.75	0.750	3.5330	5.098

α=2.544 when q=3. $Q_p^{\alpha}(1+\xi t_p)$=3.675

$Q_p^{\alpha} (1 + \xi t_p)$, the corresponding time t is the desired t_i in equation (10). The result calculated at q = 3 is indicated in Table 1 as an example. It is found that t_i = 30.42 minute in this case. Then, taking the t_i value into equation (9) gives γ = 22.35. Similar calculations were made at other q values. As the average γ = 22.86 for the chosen q values, the average activation energy corresponds to 199.7 kJ/mol. With taking the average

activation energy into equation (8), pre-exponential factor was calculated to be A = $9.42 \times 10^{12} s^{-1}$. For comparison, TG measurements for the polyamide 6 were carried out in nitrogen gas flow of 40 mL/min at several different heating rates. Based on the TG data, E and A values were calculated by Ozawa method.[5] Similar values of 201.2 kJ/mol and $1.48 \times 10^{12} s^{-1}$ were obtained.

To further verify the E and A values obtained in equation (9) and equation (8), peak strength was calculated using the E and A values. The calculated peak strength was presented in Figure 1. It can be seen that the calculated peak strength is well agreed with the measured peak strength. Therefore, it can be concluded that the fitting method is right and applicable.

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