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Estimation of activation energy by isoconversion methods

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Abstract

There are three isoconversion methods in which relations at a given conversion and at the maximum rate of conversion are used for estimating activation energy. It is shown that they can be derived from a common fundamental equation which includes the reduced time. The wide applicability of these methods is a result of the general form of this fundamental equation. The logical interrelation among these methods is described, and comparison is made of their applicability and accuracy. Further usefulness of the reduced time is discussed.

INTRODUCTION

Early in 1966, Flynn and Wall published a paper [1] in which they proposed a method for estimating activation energy by linear heating thermal analysis. In their method, an approximately linear relation between the logarithm of the heating rate and the reciprocal of the absolute temperature at a given conversion is used; the activation energy is proportional to the slope. Independently, the present author proposed the same isoconversion method in a paper published at the end of 1965 [2].

Another isoconversion relation was utilized by Friedman in 1964 [3]. In his method, a proportionality between the rate of conversion and the rate constant at a given conversion is applied to obtain the temperature dependence of the rate constant. Friedman derived this method for an *n*th order reaction. However, the wide applicability of this method was proved later [4].

An approximately linear relation was used to derive the third method for estimating activation energy [5]. At a given conversion, the logarithm of the heating rate divided by the square of the absolute temperature is related approximately linearly to the reciprocal of the absolute temperature, and

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

the slope is proportional to the activation energy. In 1956, Kissinger first found that this relation holds at the maximum rate of conversion, rigorously for first-order reactions and approximately for other *n*th order reactions [6], but Akahira, one of the pioneers in the application of thermal analysis to kinetics [7], and Sunose found later in 1969 [5] that this relation is valid at a given conversion.

The first and third methods were also shown to be applicable at the maximum rate of conversion [8]. The wide applicability of the first and third methods at the maximum rate of conversion is based on the fact that the conversion at the maximum rate of conversion is constant and independent of the heating rate in the case of linear heating, if the rate constant follows the Arrhenius law. Therefore, for the same reason, an expanded Friedman method can also be applied at the maximum rate of conversion; this was first demonstrated by Chen and Winer [9] for first-order reactions and its wide applicability was shown later by Ozawa and Kato [10]. Thus the methods applied to the maximum rate of conversion can be considered to be variations of the isoconversion methods.

As shown above, we have three types of isoconversion methods, i.e. the Flynn–Wall–Ozawa method [1,2,8], the expanded Friedman method [3,4] and the Kissinger–Akahira–Sunose method [5,6,8].

These three methods can be derived from a common fundamental equation, and therefore they have common features, i.e. wide applicability and, hence, high reliability. In addition to the isoconversion methods, numerous methods for estimating activation energy have so far been proposed (see for example ref. 11). However, their applicability is limited, and they tend to yield false results, so that their reliability is low. The common features of the isoconversion methods are explained in this paper from their derivation. The logical interrelation is also discussed and comparison is made of their accuracy.

DERIVATION

To demonstrate the interrelation, the derivation is briefly shown below. The fundamental equation, from which the isoconversion methods are derived, is

$$C = F(\theta) \tag{1}$$

where C, θ and $F(\theta)$ are respectively the conversion, the reduced time and an eigen-valued function of the reduced time. The reduced time is given by

$$\theta = \int \exp\left(-\frac{\Delta E}{RT}\right) \mathrm{d}t \tag{2}$$

where ΔE, R, T and t are the activation energy, the gas constant, the absolute temperature and the time respectively. Therefore, the Arrhenius law is assumed to be valid, with the rate constant k being given by

$$k = A \exp\left(-\frac{\Delta E}{RT}\right) \tag{3}$$

Equation (1) holds for diffusion [12] and chemical reactions consisting of a single elementary process. For a growth process from pre-existing nuclei, such as crystallization from pre-existing nuclei, this is also the case [13]. This derivation can also be applied to thermal shrinkage of polymeric films [10,14] and thermally stimulated current [15] provided that the process proceeds by a single elementary process and that the temperature dependence of the rate constant is consistent with eqn. (3).

At a given conversion, where $F(\theta)$ is a constant

$$\theta = \text{constant} \tag{4}$$

θ is given below for linear heating at a constant rate ϕ from a low temperature where the rate of conversion is negligible

$$\theta = \frac{\Delta E}{\phi R} p\left(\frac{\Delta E}{RT}\right) \tag{5}$$

where p is the p function proposed by Doyle [16].

Two approximations are applied to derive the isoconversion methods, i.e.

$$\log p(y) = -2.315 - 0.4567y \quad \text{for } 60 \geqslant y \geqslant 20 \tag{6}$$

and

$$p(y) = \frac{\exp(-y)}{y^2} \text{for } 50 \geqslant y \geqslant 20 \tag{7}$$

The latter is more approximate than the former [16]. The applicable range should also be noted. By combining eqns. (4) and (6), we obtain the Flynn–Wall–Ozawa method, i.e.

$$\log \phi + 0.4567\frac{\Delta E}{RT} = \text{constant} \tag{8}$$

Similarly, by combining eqns. (4) and (7), the Kissinger–Akahira–Sunose method can be derived:

$$\frac{\ln \phi}{T^2} + \frac{\Delta E}{RT} = \text{constant} \tag{9}$$

For crystallization with random nucleation, some modification is necessary to eqns. (8) and (9). This was first pointed out by Matusita and Sakka [17] and modified equations were derived rigorously later [13].

To derive the expanded Friedman method, the derivative equation of eqn. (1) is used

$$\frac{\mathrm{d}C}{\mathrm{d}\theta}=F'(\theta) \tag{10}$$

At a given conversion, where the left-hand side of the above equation is constant

$$\frac{\mathrm{d}C}{\mathrm{d}\theta}=\frac{\mathrm{d}C}{\mathrm{d}t}\frac{\mathrm{d}t}{\mathrm{d}\theta}=\frac{\mathrm{d}C}{\mathrm{d}t}\exp\left(\frac{\Delta E}{RT}\right)=\text{constant} \tag{11}$$

because of eqn. (3). Therefore, $\mathrm{d}C/\mathrm{d}t$ is proportional to $\exp(-\Delta E/RT)$, and hence, to the rate constant.

At the maximum rate of conversion

$$\frac{\mathrm{d}^2C}{\mathrm{d}t^2}=0 \tag{12}$$

By double differentiation of eqn. (1) and using eqn. (7), we obtain

$$\frac{\mathrm{d}^2C}{\mathrm{d}t^2}=\theta\frac{\mathrm{d}^2C}{\mathrm{d}\theta^2}+\frac{\mathrm{d}C}{\mathrm{d}\theta}=0 \tag{13}$$

Because only θ is involved and the heating rate is not contained in the above equation, θ and C are constant at the maximum rate of conversion, so that the isoconversion methods can all be applied to this point.

A wider applicability of the expanded Friedman method should be pointed out here. For a general temperature dependence of the rate constant, i.e.

$$k \propto h(T) \tag{14}$$

where $h(T)$ expresses the general dependency, we use the generalized reduced time

$$\theta=\int h(T)\,\mathrm{d}t \tag{15}$$

and

$$\frac{\mathrm{d}\theta}{\mathrm{d}t}=h(T) \tag{16}$$

so that

$$\frac{\mathrm{d}C}{\mathrm{d}\theta}=\frac{\mathrm{d}C}{\mathrm{d}t}\frac{1}{h(T)}=\text{constant} \tag{17}$$

Thus $\mathrm{d}C/\mathrm{d}t$ is proportional to the temperature dependence [4].

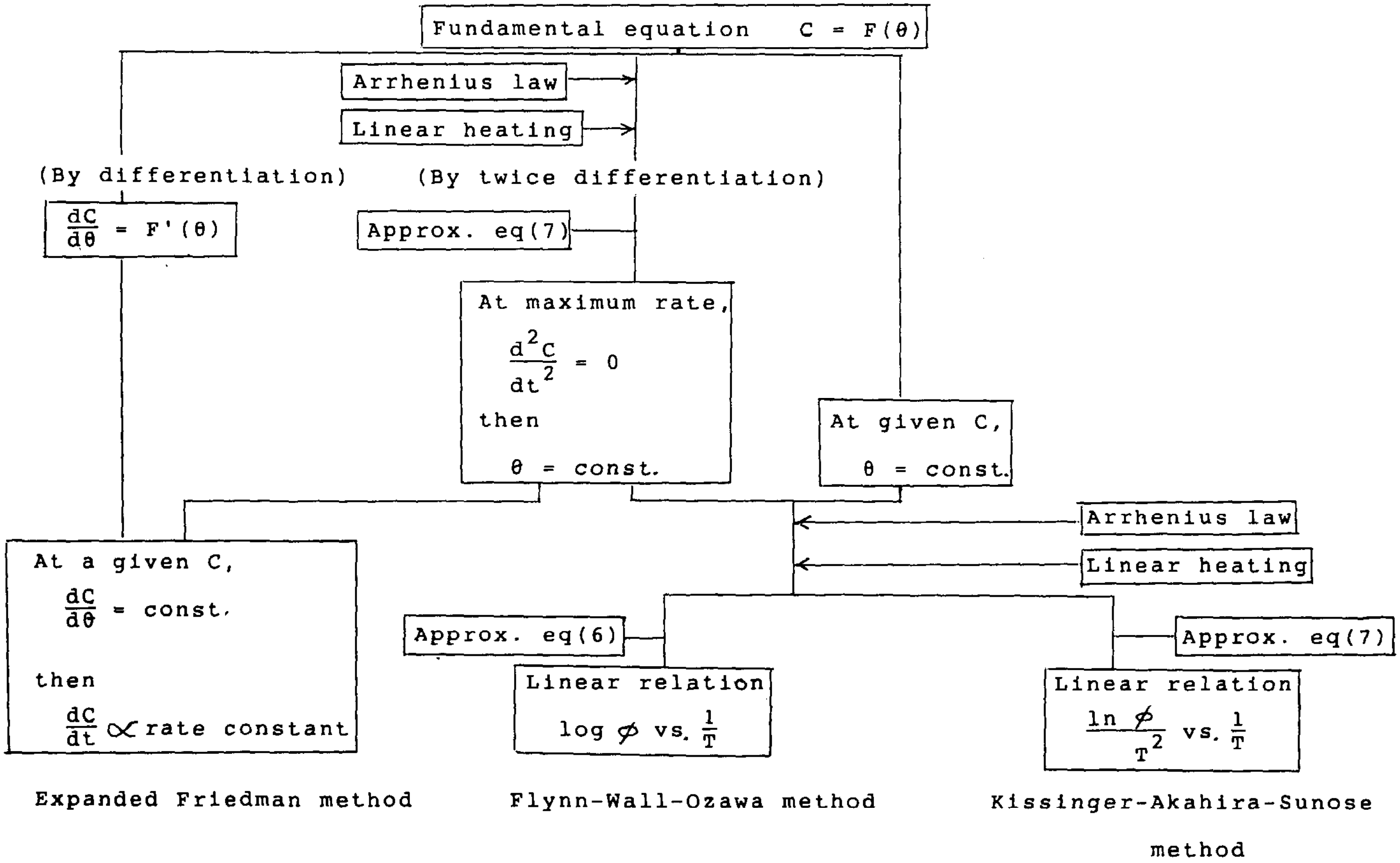

Fig. 1. Logical sequence and interrelation of isoconversion methods. Sequence is shown from top to bottom, and the arrows indicate prerequisites or assumptions.

INTERRELATION

The logic and prerequisites in the above derivation are shown in Fig. 1. In the derivation of the expanded Friedman method, the only prerequisite is eqn. (1), and the applicability is, therefore, the largest, so that its reliability is the highest, although the conversion and the rate of conversion are both needed. In the other two methods, two prerequisites (or assumptions) are included, i.e. the Arrhenius law and the linear heating at a constant rate. Furthermore, approximations for the p function are also used. Because the approximation in the Flynn–Wall–Ozawa method is more accurate than that in the Kissinger method and the coefficient in eqn. (8) can be modified by using a preliminarily determined value of y [1,11], the former is more accurate than the latter. It should also be pointed out that the quantities used to estimate the activation energy are simpler in the Flynn–Wall–Ozawa method than those in the other method. For these two reasons, the Flynn–Wall–Ozawa method is more accurate and straightforward than the Kissinger method.

THE USEFULNESS OF THE REDUCED TIME

As shown in Fig. 1, the concept of the reduced time is very useful to derive the widely applicable methods and also to interrelate them with each other. Without this concept, the wide applicability of the Kissinger [6] and Friedman [3] methods could not be exploited.

In addition, this concept can be used in further kinetic analysis. By using the estimated activation energy, we can calculate the reduced time as a function of the conversion. Because the following equation holds for isothermal processes, the relation between θ and C is equal to that for an isothermal process:

$$\theta = t \exp\left(-\frac{\Delta E}{RT}\right) \qquad (18)$$

Therefore, kinetic analysis methods for isothermal processes are also applicable to the relation between the reduced time and the conversion. This is also the case for the relation between the reduced time and the rate of conversion.

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