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APPLICABILITY OF FRIEDMAN PLOT

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By expanding the initial equation, it is shown that the Friedman method for estimating the activation energy of chemical reactions by using both the conversion and the rate in the thermoanalytical data has wide applicability to crystal growth from pre-existing nuclei, diffusion and other processes in which a single unit process is involved.

In 1964 Friedman published a paper describing a method for the kinetic analysis of thermogravimetric data [1]: logarithms of the rate of weight loss at different heating rates are plotted against the reciprocal absolute temperature at a given weight loss to obtain the activation energy, and the mechanism is elucidated from the intercept of the plots. The method was applied to data on the thermal decomposition of glass fiber-reinforced phenol resin by thermogravimetry (TG). The decomposition was found to be a fifth-order reaction, and the activation energy and the pre-exponential factor were estimated. Tanabe and Otsuka later applied the method to the decomposition of magnesite, observed by differential scanning calorimetry (DSC), and they obtained satisfactory results [2]. However, the method has not been applied widely, presumably because it needs both the conversion and the rate of conversion.

It has recently become readily possible to calculate the conversion from the measured rate of conversion and vice versa with a microcomputer. In particular, the conversion can be precisely calculated from the rate. Moreover, the Friedman plot has wide applicability other than thermal decompositions by TG and DSC, and it has advantages over other methods. The applicability and the advantages are described in this short communication.

As in the TG of random scission in the main chain of a polymeric sample and mechanical thermal analysis, the measured quantity in thermal analysis is not necessarily equal or proportional to the amount of the reacting species or the reacting chemical structure, so that the conversion, C, measured in thermal analysis is a function of the amount of the reacting species or the reacting structure, x, as follows:

$$C = f(x) \tag{1}$$

The reaction proceeds in accordance with the usual kinetic formula:

$$\frac{dx}{dt} = A \exp\left(-\frac{\Delta E}{RT}\right) g(x) \tag{2}$$

where t, A, ΔE, R and T are the time, the pre-exponential factor, the activation energy, the gas constant and the temperature, respectively.

Introducing the reduced time, θ [3, 4], we get

$$\frac{dx}{d\theta} = Ag(x) \tag{3}$$

and

$$\frac{d\theta}{dt} = \exp\left(-\frac{\Delta E}{RT}\right) \tag{4}$$

Therefore,

$$\frac{dC}{dt} = \frac{dC}{dx}\frac{dx}{d\theta}\frac{d\theta}{dt} \tag{5}$$

It is clear from Eq. (5) that dC/dx and $dx/d\theta$ are both constant at a given conversion and that dC/dt is proportional to $\exp(-\Delta E/RT)$. When we plot the logarithm of the rate, dC/dt, against the reciprocal absolute temperature at a given conversion, we get a linear plot, and the activation energy can be obtained from the slope. When the conversion is equal to x, we get $Ag(x)$ from the intercept and we can elucidate the mechanism. This method of kinetic analysis is also applicable to various data other than TG and DSC data on chemical reactions, if the processes proceed in accordance with Eqs (1) and (2). The thermal shrinkage of elongated polymer films [5] and mechanical property change by torsional braid analysis [6, 7] are such cases.

Since Eqs (3), (4) and (5) hold for any temperature change, including isothermal cases, this method can be applied to any data obtained isothermally and in any temperature change. In thermal analysis, the temperature of the sample usually deviates from the programmed temperature due to the endothermic or exothermic process under investigations. This deviation may cause some error in a kinetic analysis based on the integration of Eq. (2) on the assumption of a linear increase of the temperature. However, in the Friedman plot such an assumption is not included, so that its applicability is not limited. Although other kinetic methods, such as that of Freeman and Carrol [8], are not based on integration, most of them are based on kinetic equations other than Eq. (2), so that their applicability is limited and they tend to lead to false results, as has already been discussed elsewhere [9].

The Friedman plot can also be applied to crystal growth from pre-existing nuclei, for which the following equations hold [10]:

$$-\ln(1-C) = Z\theta^m \tag{7}$$

where C, Z and m are the crystallized fraction, a constant and an integer equal to the dimension of the crystal growth, respectively.

$$\frac{\mathrm{d}C}{\mathrm{d}\theta} = mZ_0(1-C)\theta^{m-1} \tag{8}$$

where Z_0 is a constant, and the reduced time, θ, Z and Z_0 are given below:

$$\theta = \int h(T)\,\mathrm{d}t \tag{9}$$

$$Z = gNv_0^m \tag{10}$$

and

$$Z_0 = gNv_0^{m-1} \tag{11}$$

where g and N are, respectively, a constant dependent on the geometrical dimension of the crystal growth and the density of the nuclei, and the linear rate of crystal growth, $v(T)$, is equal to $v_0h(T)$. From Eq. (8:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{\mathrm{d}C}{\mathrm{d}\theta}h(T) \tag{12}$$

Since θ and $\mathrm{d}C/\mathrm{d}\theta$ are constant at a given conversion, $\mathrm{d}C/\mathrm{d}t$ is proportional to $v(T)$ and reflects its temperature-dependence. Similarly to the chemical reactions mentioned above, we can observe the temperature-dependence of the linear growth rate of the crystal and we can perform a kinetic analysis as described previously [10].

This method can also be applied to isothermal and non-isothermal diffusion data, because the fundamental non-isothermal equation of diffusion is as follows [11]:

$$D_0\nabla^2\xi = \frac{\partial\xi}{\partial\theta} \tag{13}$$

where ∇^2 and ξ are, respectively, a Laplacian operator and the concentration of the diffusing species. The reduced time in Eq. (13) is an integral similar to Eq. (9), and the diffusion constant, D, is as follows:

$$D = D_0h(T) \tag{14}$$

By introducing the initial and boundary equations, we can solve the above Eq. (13) similarly to the usual fundamental isothermal equation of diffusion. For example, an equation for diffusion and chemical reaction in spherical body (the

Serin--Ellickson equation) was recently simplified for kinetic analysis by an approximation [12]. The obtained equation of $dC/d\theta$ is a function dependent only on the reduced time, and dC/dt is obtained as follows:

$$\frac{dC}{dt} = \frac{D}{a^2}\frac{dC}{d\theta} \tag{15}$$

where a is the length for the diffusion; for example, it is the radius for spherical and cylindrical specimens and the thickness for a plate. Since $dC/d\theta$ is constant at a given conversion, dC/dt is proportional to the diffusion constant, and the kinetic analysis can be performed as reported before [11].

As is seen above, the Friedman plot for obtaining the temperature-dependence of the rate constant (or the activation energy) is not restricted within the linear heating and cooling, though it needs both the conversion and the rate of conversion. Since it is applicable to the general kinetic equations, its applicability is not so limited as other methods based on the limited equations [9]. Moreover, the plot can be applied not only to chemical reactions, but also to the various processes in which a single unit process is involved. Thus, it has advantages over the other methods, and it should be widely applied to obtain the temperature-dependence of the rate constant from various thermoanalytical data, while further kinetic analysis can be performed by deriving relations between two quantities among C, $dC/d\theta$ and θ from the estimated temperature-dependence of the rate constant (or the activation energy) and the experimental data on C, dC/dt and the temperature as a function of the time [3, 4, 10, 11, 13]. Among the above relations, the relation between C and $dC/d\theta$ (or a quantity proportional to $dC/d\theta$) is easily obtained, because

$$\frac{dC}{d\theta} = \frac{dC}{dt} exp\left(\frac{\Delta E}{RT}\right) \tag{16}$$

or

$$\frac{dC}{d\theta} = \frac{1}{h(T)}\frac{dC}{dt} \tag{17}$$

and the mechanism of the observed process can be elucidated from the relation.

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Zusammenfassung – - Durch Erweiterung der ursprünglichen Gleichung wird gezeigt, daß die Friedman-Methode zur Bestimmung der Aktivierungsenergie chemischer Reaktionen unter Verwendung sowohl der Konversion als auch der Geschwindigkeit in thermoanalytischen Daten breite Anwendungsmöglichkeiten auf dem Gebiet des Wachstums von Kristallen aus Keimen, der Diffusion und anderer aus nur einem Grundprozeß bestehenden Vorgänge bietet.

Резюме — Расширением первоначального уравнения, показано, что метод Фридмэна для установления энергии активации химических реакций с использованием параметров превращения и скорости в термоаналитических данных широко применимо к процессу роста кристаллов на основе существующих центров кристаллизации, к процессу диффузии и другим процессам, в которых имеет место единственный процесс.