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NON-ISOTHERMAL KINETICS AND GENERALIZED TIME

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ABSTRACT

The fundamental equations for non-isothermal kinetics of various processes are reviewed. They are the same in their mathematical form as the isothermal kinetic equation, and time is replaced by generalized time. The independent variables contained in the equations are only generalized times, which determine the conversion of the process. The usefulness of this concept of generalized times is discussed, and they are found to be useful for the systematic description of non-isothermal processes as well as for prediction and control. The essential prerequisites to sound kinetic analysis of thermoanalytical data are briefly discussed.

INTRODUCTION

In 1925, Akahira and his co-worker [1] published papers on the kinetic analysis of thermogravimetric data, and they made an attempt to evaluate the thermal endurance of electrical insulating materials with a Honda thermobalance. It appears to be the first attempt to obtain kinetic information by thermoanalytical methods. However, kinetic analysis was not developed further from this pioneering work, presumably due to the lack of need.

It was since the 1960s that kinetic analysis was widely applied to thermoanalytical data, especially since publication of the paper by Freeman and Carroll [2]. This is because thermoanalytical tools became popular in this period and thermal analysis became easily applicable to various fields of science and technology, since apparatuses with automatic control and recording became commercially available in this period.

Since then, numerous methods have been proposed for the kinetic analysis of thermoanalytical data. However, most of them are based on limited kinetic models, and hence their applicability is limited. In spite of this limitation, they have often been applied to processes which are not within their limits, and they often led to false results. One example of these cases is shown in Fig. 1, where the method proposed by Anderson and Freeman [3] was applied by the present author to thermogravimetric data of polycaprolactam in vacuum. By this method, it is deduced from the results that the kinetic parameters are dependent on the heating rate.

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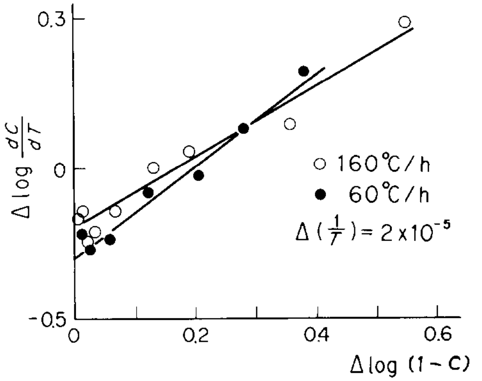

Fig. 1. Anderson–Freeman plot of thermogravimetric data of polycaprolactam in vacuum. The heating rates are indicated in the figure.

In contrast with this, the method proposed by the present author led to a mechanism of random scission in the main chain of the polymer; the elucidated mechanism is consistent with previous isothermal observations and the estimated kinetic parameters are constant and independent of heating rate [4]. This was the very beginning when the present author became deeply conscious of the methods of kinetic analysis of thermoanalytical data and their models, on which the methods are derived. Since then, the present author has developed the non-isothermal kinetics of various processes and proposed methods derived from non-isothermal kinetics. By using theoretically calculated thermoanalytical data, he also demonstrated the falsity of results derived by misapplication of methods to processes beyond their range of applicability [5]. Many methods have been proposed for kinetic analysis; however, the mechanism of random scission in the main chain of a polymer, for instance, is still beyond the range of most of the methods proposed till now.

To elucidate the real kinetic mechanism and to obtain the real kinetic parameters, the method should be applicable as widely as possible to various processes, and a certain procedure should be included in the method to check the validity of the method in the particular application. Furthermore, it is desirable to develop non-isothermal kinetics for various kinetic models, because thermoanalytical data can be clearly analyzed by non-isothermal kinetics.

Non-isothermal kinetics are also very useful beside thermal analysis, because many natural processes proceed non-isothermally, for instance, in industrial processes, as well as in practical processes, though kinetic investigation has been made isothermally and it has scarcely been applied to non-isothermal processes except in thermal analysis.

In this paper, non-isothermal kinetics are reviewed with a focus on a very useful concept, generalized time. These non-isothermal kinetic theories can be applied to normal chemical reactions, diffusion, nucleation-and-growth processes, and generalized time is very effective for systematically describing the kinetic aspects of these non-isothermal processes as well as isothermal processes. Non-isothermal processes can also be predicted by applying this concept of generalized time.

GENERALIZED TIME

Usually, the fundamental isothermal kinetic equation for the unit process is in a form such as that written below:

$$\frac{d\xi}{dt} = k\mathrm{f}(\xi) \tag{1}$$

where ξ, t, k and $\mathrm{f}(\xi)$ are, respectively, the fraction of formed species, the time, the rate constant and a function of ξ. Because the rate constant is usually dependent on temperature, the above equation can be transformed for non-isothermal processes by introducing the generalized time, θ [4,6]:

$$\theta = \int \mathrm{g}(T)dt \tag{2}$$

where the rate constant as a function of temperature is

$$k = k_0\mathrm{g}(T) \tag{3}$$

and k_0 is a constant independent of temperature. Thus

$$\frac{d\xi}{d\theta} = k_0\mathrm{f}(\xi) \tag{4}$$

The above equation is the fundamental kinetic equation which can be applied to both isothermal and non-isothermal processes, and the fundamental variables contained in the equation are only the fraction of the formed species (or the reacting species) and the generalized time. Thus, the generalized time is the fundamental variable, and the fraction of the formed species is dependent only on this single independent variable, while the fraction of the formed species is dependent on the actual time and the temperature in the conventional isothermal equation.

Generalized time has the dimension of time. It can be calculated if we know the temperature dependence of the rate constant, i.e., $\mathrm{g}(T)$ in eqn. (3), or the activation energy in the case of an Arrhenius type of temperature dependence.

The concept of generalized time can also be introduced to diffusion as follows [7]:

$$\frac{d\xi}{d\theta} = D_0\nabla^2\xi \tag{5}$$

where ξ is the concentration of a diffusing species. This equation is the fundamental equation for diffusion, and it is applicable to both isothermal diffusion and non-isothermal diffusion. Under initial and boundary conditions, we can solve this equation quite similarly to the usual isothermal equation for diffusion [7]. From this equation, the method for kinetic analysis of thermoanalytical data of diffusion was also derived [7]. This equation gives us a theoretical base in considering non-isothermal kinetics of diffusion-controlling processes, such as some solid decompositions.

USEFULNESS OF GENERALIZED TIME

The fundamental non-isothermal kinetic equations (4 and 5) are very simple equations, in which time in the isothermal equation is only replaced by generalized time. Because generalized time is a single measure of the conversion of the process, the conversion of the process proceeding under various types of temperature change becomes a single function of generalized time.

Typical examples illustrating the above principle are thermal deterioration of electrical insulating materials, in which temperature changes irregularly [8]. One example is shown in Fig. 2. Because the weight of an enamelled wire is a definite function of the fraction of formed species, ξ, it becomes dependent only on generalized time. Therefore, a single master curve is obtained, when we plot weight against generalized time, though the temperature was kept constant or changed linearly between two temperature limits, as indicated in the figure. A similar relation was also published previously for the thermal decomposition of urea as a latent heat thermal energy storage material [9].

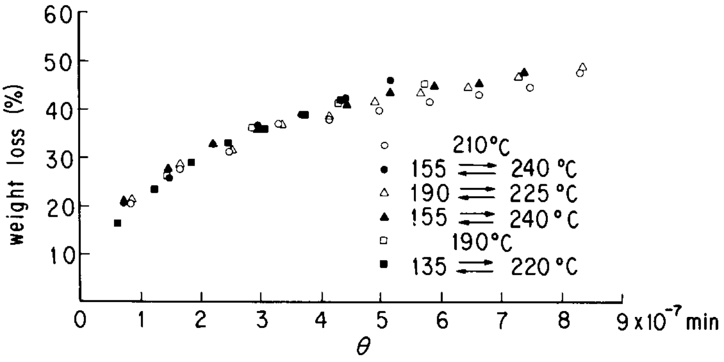

Fig. 2. Weight loss of polyvinyl formal enamelled wire versus generalized time. The deterioration temperature is indicated in the figure, and the temperature was kept isothermally or linearly changed between indicated temperature limits.

Other examples are relations between $\mathrm{d}C/\mathrm{d}\theta$ and C or θ [6], which are volatilization of hydrochloric acid from epoxide resin [10] and thermal decomposition of poly(methyl methacrylate) in vacuum [11]. Because the conversion, C, is a definite function of generalized time, a plot of $\mathrm{d}C/\mathrm{d}\theta$ versus C or θ is also a master curve systematically describing the kinetic aspect of the processes.

The above examples clearly illustrate the applicability of generalized time, and its effectiveness in the systematic description of non-isothermal kinetics is also clearly demonstrated. Generalized time is only a measure of the conversion of processes, and it is a measure combining the effects of actual time and temperature on the processes. The present author has called generalized time by the name of "reduced time" [4], because the actual time is reduced to a generalized time by taking account of the *accelerating* effect of temperature.

STOCHASTIC APPROACH

By introducing generalized time, the non-isothermal kinetic equation for crystal growth from pre-existing nuclei is also easily derived [12]. The distance of crystal growth, r, is given, similarly to eqn. (4), as follows:

$$\frac{\mathrm{d}r}{\mathrm{d}t} = v \text{ or } \frac{\mathrm{d}r}{\mathrm{d}\theta} = v_0 \tag{6}$$

where the linear growth rate, v, is a function of temperature, as given below:

$$v = v_0 g_g(T) \tag{7}$$

The distance is, therefore, the integration of eqn. (6), and

$$r = v_0\theta \tag{8}$$

In a simple example of three-dimensional growth, the crystalline fraction, C, is given below:

$$-\ln(1 - C) = \tfrac{4}{3}\pi N r^3 \tag{9}$$

and

$$-\ln(1 - C) = \tfrac{4}{3}\pi N v_0^3 \theta^3 \tag{10}$$

where N is the number of existing nuclei in the unit volume. Because the expectancy of the crystal growth front passing over a particular point at the time and/or temperature, θ, is equal to the number of nuclei in a sphere, whose diameter and center are, respectively, $r = v_0\theta$ and the particular point, we can get the above equation by applying Poisson's distribution of the stochastic theory.

In the case of the growth mechanism with concurrent random nucleation [13], the fundamental non-isothermal kinetic equation is somewhat complicated, because the density of the nuclei, N, becomes a certain function of the generalized time for nucleation, which is different from the generalized time for crystal growth given above.

Namely,

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \nu \text{ or } \frac{\mathrm{d}N}{\mathrm{d}\theta_\mathrm{n}} = \nu_0 \tag{11}$$

$$N = \nu_0 \theta_\mathrm{n}(\tau) \tag{12}$$

where ν, the rate of nucleation as a function of temperature, is

$$\nu = \nu_0 \mathrm{g}_\mathrm{n}(T) \tag{13}$$

and θ_n is the generalized time for the nucleation given below:

$$\theta_\mathrm{n}(\tau) = \int_0^\tau \mathrm{g}_\mathrm{n}(T)\mathrm{d}t \tag{14}$$

The generalized time for growth at time, t, is given below:

$$\theta_\mathrm{g} = \int_\tau^t \mathrm{g}_\mathrm{g}(T)\mathrm{d}t \tag{15}$$

and

$$v = v_0 \mathrm{g}_\mathrm{g}(T) \tag{16}$$

Thus, we obtain the following fundamental equation of three dimensional growth:

$$\begin{aligned} -\ln(1-C) &= 4\pi\nu_0 v_0^3 \int_0^t \theta_\mathrm{n}(\tau)\theta_\mathrm{g}(\tau)^2 \mathrm{d}\theta_\mathrm{g}(\tau) \text{ or} \\ -\ln(1-C) &= \tfrac{4}{3}\pi\nu_0 v_0^3 \int_0^t \theta_\mathrm{n}(\tau)\mathrm{d}\theta_\mathrm{g}(\tau)^3 \end{aligned} \tag{17}$$

The fundamental and non-isothermal kinetic equations for one- and two-dimensional crystal growth from pre-existing nuclei can be derived easily and similarly to eqn. (10) [12]. In the case of concurrent nucleation and one- or two-dimensional crystal growth, the equations can also be derived similarly to eqn. (17); however, the equations applicable to kinetic analysis can only be obtained for case of linear heating or cooling [13], and the integration in eqn. (17) can be made when we know the temperature dependence of nucleation and growth.

These equations can be applied, for instance, to the crystallization of amorphous materials. In most cases, a Kissinger plot [14] has been applied to processes without any rigorous considerations, but the method tends to lead to false results, as was correctly pointed out by Matusita and Sakka [15]. Because some solid reactions proceed by the mechanism of nucleation and growth, application of these equations to processes should also be considered.

These equations are an expansion of the Johnson–Mehl–Avrami–Erofeev equation for isothermal crystallization. It is very interesting to note that eqn. (10) is quite similar in its mathematical form to the above isothermal equations, in which time is replaced by generalized time. Two different generalized times are contained in eqn. (17), because two different unit processes, i.e., nucleation and growth, are involved in the process. It seems that multiple generalized times are, in general, contained in non-isothermal kinetic equations, when multiple unit processes are involved in the overall process, and the number of generalized times seems equal to the number of unit processes involved.

Even in these processes, the independent variables contained in the kinetic equation are only generalized times, and they are measures of the conversion of the overall processes. It is also important to point out that in non-isothermal cases the rate of each unit process can be controlled by controlling the temperature change, because the accelerating effects in multiple generalized times are different from each other, while time is a common variable in isothermal processes.

It is also to be noted that the stochastic approach applied in the derivation of the above kinetic fundamental equations is very useful and elegant. For instance, this approach can be applied for derivation of the non-isothermal kinetic equation of usual chemical reactions. One simple example is the equation for the first order reaction, and the same equation as eqn. (4) can be derived by the stochastic approach. Because the expected number of hypothetical reactions of a particular molecule is proportional to the generalized time, we obtain the following non-isothermal equation by applying Poisson's distribution.

$$-\ln(1-C) = A\theta \tag{18}$$

where A is the proportionality constant, which is equal to the frequency factor. Therefore, the stochastic approach will probably be applied to the derivation of the fundamental non-isothermal kinetic equations of various processes.

HEATING OR COOLING MODE AND GENERALIZED TIME

When the temperature dependence of the rate constant is known, we can calculate the generalized time. For the following three cases of temperature change, the generalized time was already calculated for an Arrhenius type temperature dependence [4].

(1) $T = T_0 + \beta t$ (19)

(2) $1/T = 1/T_0 + \beta t$ (20)

and

(3) $T = T_0 + \exp(\beta t)$ (21)

where T_0 and β are the initial temperature and a constant, respectively.

Usually, linear heating or cooling, i.e., eqn. (19), has been adopted in thermal analysis. However, generalized time becomes a complicated function of temperature, such as given by Doyle [16]. In a thermal desorption spectrum, heating by eqn. (20) has often been used, and generalized time is also not so simple as in isothermal cases, in which generalized time is proportional to the actual time.

Therefore, it is desirable to investigate some other types of temperature change, as was pointed out by Kambe [17]. The desirable one is the temperature change for which a simple relation of conversion with other measured quantities can be obtained. If generalized time becomes proportional to temperature, the observed relation between conversion and temperature also becomes very simple similar to the isothermal relation between conversion and time. Hence, the temperature should be changed as follows:

$$\Theta \propto (T - T_0) \tag{22}$$

For an Arrhenius type temperature dependence, eqn. (22) holds, when the temperature changes as follows:

$$t = \int_{T_0}^{T} \beta \exp\left(\frac{\Delta E}{RT}\right) \mathrm{d}T \tag{23}$$

because for the temperature change, such as eqn. (23)

$$\int_{T_0}^{T} \exp\left(-\frac{\Delta E}{RT}\right) \mathrm{d}t = \beta(T - T_0) \tag{24}$$

where β is the proportionality constant. Usually the rate of the process is negligible at the initial temperature, and eqn. (23) can be approximated as follows:

$$t = \beta \int_{0}^{T} \exp\left(\frac{\Delta E}{RT}\right) \mathrm{d}T \tag{25}$$

When we adopt this type of temperature change, the kinetic analysis becomes very simple, because the usual method for kinetic analysis of isothermal data can be applied by replacing time with temperature. However, to adopt correctly the above mode of heating or cooling, it is essential to know the activation energy.

KINETIC METHODS FOR THERMOANALYTICAL DATA

To avoid obtaining false kinetic results, we must be conscious of two points, i.e., the coverage of the method used in the analysis and a check of its applicability.

The coverage of the applied method should be as large as possible. From this viewpoint, the following two points are the prerequisites.

(1) In thermal analysis, the measured quantities are not always proportional to the fraction of the formed species. The measured quantities must be in a definite function of the fraction, and the quantities should not be dependent on the measuring conditions, such as temperature, frequency of stress in mechanical thermal analysis and frequency of voltage in thermoelectrometry.

(2) The starting equation, from which the method is derived, should not be based on a particular mechanism, such as an n-order reaction, so that it must not be a particular formula but a general and abstract formula, such as eqn. (1).

Thus, differential methods [18], such as that proposed by Freeman and Carroll [2], are not appropriate methods, but integral methods, such as those by the present author and Flynn and Wall [19], are in accordance with the above prerequisites. The method proposed by Friedman [20] is also good from the above prerequisites, because the method is derived directly from the prerequisites.

One of the problems of the integral method is a complicated mathematical equation derived by integration of the right-hand side of eqn. (2), i.e., the p-function proposed by Doyle [16]. In order to avoid this complicated mathematical equation in the methods, the present author recommended the method proposed by Friedman [20], because the temperature dependence of the rate constant is directly observed at a given conversion in this method, but it needs both the data of the conversion and the rate of conversion [21]. However, the recent advancement of computer technology made this procedure acceptable.

CONCLUDING REMARKS

The concept of generalized time, in which the accelerating effect of temperature is taken into account, is useful and effective in systematic description of the various non-isothermal processes, as is clearly shown in this paper, because generalized time is the only independent variable in the fundamental non-isothermal kinetic equations. It is also very interesting that multiple generalized times are contained in the overall kinetic equations of processes where multiple unit processes are involved. This concept of generalized time can be used in the prediction and control of practical industrial processes, as well as natural processes.

Usually, kinetic relations have been derived by integration of the rate equations. However, it is also shown that the stochastic approach is also very effective in the derivation. This approach will probably be applied to derive the overall non-isothermal kinetic relations.

Two essential prerequisites are presented for the methods to obtain the real kinetic mechanism and parameters by analysis of thermoanalytical data.

These two points should be taken into account in the derivation of methods as well as in the analysis of thermoanalytical data. The independence of the mechanism and parameters obtained on heating rate and/or conversion is an assurance for the soundness of the results, and the experimental master curves using generalized time can also be used for this purpose.

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