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A NEW APPROACH TO KINETIC STUDY OF NUCLEATION AND GROWTH PROCESS BY THERMAL ANALYSIS

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ABSTRACT

A new approach for kinetic analysis of nucleation-and-growth process is proposed; Arrhenius type of temperature dependence of the rates of both elementary processes is assumed and the reciprocal absolute temperature is decreased at a constant rate. For the process, a fundamental non-isothermal kinetic equation is obtained, and to estimate the dimension of the growth and the overall activation energy, a method is derived from the fundamental equation.

INTRODUCTION

Methods for kinetic analysis of thermoanalytical data of a process consisting of a single elementary process were established and have been applied to various processes, for example, random scission in main chain of polymers,1) phase boundary controlling process,2) crystallization from pre-existing nuclei3) and diffusion.4) However, only a limited method was proposed to a process in which nucleation and its successive growth are involved, and we can obtain only limited information by the method.5)

On the other hand, thermal analysis has been carried out generally at a constant rate of heating or cooling, and the above methods have been applied to thus obtained data, while a desorption spectrum, i.e., a volatilization curve of sorbed species, has been obtained in a way that the reciprocal absolute temperature decreases at a constant rate.6) In this case, reduced time,1,7) θ is a following simple function of the temperature, if the Arrhenius type of temperature dependence of the rate constant holds.

$$\theta = \frac{R}{bE}\exp\left(-\frac{E}{RT}\right) \qquad (1)$$

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In the above equation, E, R and T are the activation energy, the gas constant and the absolute temperature, and the temperature changes as the following function of time, t.

$$\frac{1}{T} = \frac{1}{T_o} - bt \tag{2}$$

where T_o is the initial temperature and b is a constant.

Therefore, a simple fundamental kinetic equation is expected for the case, and we can expect also simple relations of the kinetic parameters with observed data for the kinetic analysis. In this report, the fundamental equation is described and simple methods for kinetic analysis are proposed.

THEORETICAL CONSIDERATION

The kinetic equation of the nucleation-and-growth process under general non-isothermal conditions was reported elsewhere.7) However, it is complicated, so that the equation is derived below for the case of linear decrease of the reciprocal absolute temperature.

To derive the kinetic equation, an analogy devised by Evans5, 8) is very useful. Raindrops on a pond and waves caused by them are compared to the process, in which the nucleation and the growth front correspond to the raindrops and the waves, respectively. However, there is a fundamentally different point between the two cases, and the difference should be taken into account. Multiple waves can pass over a particular point on the pond, while only one growth front can pass over a particular point in the sample. Therefore, the area of the pond where any waves have not yet passed over and the unconverted portion of the sample may be corresponded with each other. To calculate them, Poisson's distribution is applied by using the expected number of waves which passed over the particular point.

The raindrops, which fell from the beginning to the time u at a distance r from particular point, can send waves to the point until the time t, provided that the distance r equals to the distance which the wave can traverse in the time interval from u to t. Thus, the expected number of waves which passed over the point until t is given as follows·

$$E = \int_0^{r(t)} 2\pi r \int_0^{u} N \, dt \, dr \qquad (3)$$

where E and N are the expected number and the rate at which raindrops fall or the rate of nucleation.

Now, in the process of nucleation and growth,

$$N = N_o \exp(- E_n/RT) \qquad (4)$$

$$r = \int_u^t v_o \exp(-E_g/RT) \, dt \qquad (5)$$

where E_n and E_g are the activation energies of nucleation and growth, respectively, and N_o and v_o are constants. By introducing eqs (4) and (5) into eq (3) under the condition of eq (2), we have

$$E = \frac{Z}{b^3} \exp(- \frac{E_n + 2E_g}{RT}) \qquad (6)$$

where Z is a constant as follows;

$$Z = \frac{2\pi N_o v_o{}^2 R^3}{E_n(E_n+E_g)(E_n+2E_g)} \qquad (7)$$

The fundamental kinetic equation can be derived by applying Poisson's distribution;

$$- \ln(1 - C) = \frac{Z}{b^3} \exp(- \frac{E_n+2E_g}{RT}) \qquad (8)$$

where C is the conversion, and by differentiating, we have

$$\frac{dC}{dt} = \frac{Z(E_n+2E_g)}{b^2R} \exp(- \frac{E_n+2E_g}{RT}) (1 - C) \qquad (9)$$

For general case of growth dimension, we can derive the following equations similarly.

$$- \ln(1 - C) = \frac{Z_m}{b^{m+1}} \exp(- \frac{E_n+mE_g}{RT}) \qquad (10)$$

and

$$\frac{dC}{dt} = \frac{Z_m(E_n+mE_g)}{b^m R} \exp(- \frac{E_n+mE_g}{RT}) (1 - C) \qquad (11)$$

where m is equal to the dimension of the growth and Z_m is constant but different from Z for m = 1 or 3.

For the case that the growth proceeds from pre-existing nuclei, N in eq (3) is a constant and we obtain the following simple equations for the two-dimensional growth;

$$-\ln(1-C) = \frac{Z'}{b^2}\exp\left(-\frac{2E_g}{RT}\right) \tag{12}$$

and

$$\frac{dC}{dt} = \frac{2Z'E_g}{bR}\exp\left(-\frac{2E_g}{RT}\right)(1-C) \tag{13}$$

where Z' equals to $\pi N v_o^2 R^2/E_g^2$.

Similarly, for the one-dimensional and three-dimensional growth

$$-\ln(1-C) = \frac{Z'_m}{b^m}\exp\left(-\frac{mE_g}{RT}\right) \tag{14}$$

and

$$\frac{dC}{dt} = \frac{mZ'_mE_g}{b^{m-1}R}\exp\left(-\frac{mE_g}{RT}\right)(1-C) \tag{15}$$

METHODS FOR KINETIC ANALYSIS

As seen in eqs (8), (10), (12) and (14), similar relations between -ln(1-C), t and b hold for all types of processes discussed in this paper. Thus, two ways of the analysis are devised and both need thermoanalytical curves obtained by changing b.

At a given temperature -ln(1-C) is inversely proportional to b^{m+1} or b^m. Thus, we get a straight line by plotting log(-ln(1-C)) against log b, and m or m+1 can be estimated. As far as the plots at different temperatures give the same slope, one of the kinetic models described in this paper are valid for the case. To confirm this result, observation by other means, such as microscopy, is desirable.

At a given conversion, $\exp(-E_o/RT)/b^{m+1}$ or $\exp(-mE_g/RT)/b^m$ is constant, where E_o means the overall activation energy equal to E_n+mE_g, because -ln(1-C) is constant. Thus, when we plot log b versus 1/T at a given conversion, we get a straight line, the slope of which is $-E_o/R(m+1)$ or $-E_g/R$. If the kinetic models described in this paper are valid in a certain conversion range from the beginning, the above plots at different conversions give straight lines parallel to each other, and the slopes are also equal to each other. The parallel lines and the equality of the for kinetic analysis can be applied to the case and the real kinetic parameters can be obtained.

By differentiating eqs (9), (11), (13) and (15), we can obtain a relation at the maximum rate of the process. Namely,

$$\frac{d^2C}{dt^2} = 0 \tag{16}$$

Then,

$$-\ln(1 - C) = 1 \tag{17}$$

Therefore, at the maximum rate, the conversion becomes a constant value, which is independent on b and equals to 1 - 1/e. Thus, the same plot of log(-ln(1-C)) versus 1/T can also be applied to the maximum rate, as in the other methods.[3,4, 9)

DISCUSSION

First of all, we should examine whether the temperature can be raised as described in this paper with the ususal apparatuses. When the sample is heated up to 1100 K from 300 K within one hour, the final and maximum rate of heating is 60 K/min. This rate can be achieved with the usual apparatuses, and for this type of temperature program, computer control is easily applied.

However, another problem should be pointed out. That is baseline shift in DSC curves. As the heating rate is gradually increased in a quadratic function of temperature, the baseline also gradually increased, so that the integration for estimating the conversion should be made by taking the baseline shift into account. For using the temperature at the maximum rate of the process, it is desirable to redraw the curve by subtracting the baseline shift around the peak of the DSC curve.

It should be noted that eqs (12) and (14) can be converted to the following equation, where Z_{mo} is a constant.

$$-\ln(1 - C) = Z_{mo}\theta^m \tag{18}$$

In this equation θ is the same with eq (1) and E is replaced by E_g. Thus, it is shown that eqs (12) and (14) are the specific forms of the fundamental kinetic equation of the growth from pre-existing nuclei for general temperature changes reported previously.3)

It is also interesting to note that the power of b in the fundamental kinetic equations, i.e., eqs (1), (8), (10), (12) and (14), is the same as that of the constant rate for linear temperature changes for all types of processes discussed here.1, 3, 4, 5) Thus, the power of b or the linear constant rate is equal to the number of involved elementary processes, if we assign number of one, two and three to the one-dimensional, the two-dimensional and the three-dimensional growth mechanisms, respectively.

Finally, the author would like to point out importance of theoretical considerations, such as reported here. Relations between observed data and kinetic parameters can be derived from kinetic models by mathematical derivation, and it is the very beginning of the analysis of thermoanalytical data. Without these derived relations, we cannot do anything for kinetic analysis. Therefore, this paper is one of attempts to expand the application thermal analysis.

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