NON-ISOTHERMAL KINETICS OF DIFFUSION
AND ITS APPLICATION TO THERMAL ANALYSIS

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Non-isothermal kinetics of diffusion are derived, extending the fundamental equation of diffusion to non-isothermal conditions, and the equation is solved for a few typical cases. From these theoretical considerations, two methods of analyzing thermoanalytical data of diffusion are proposed. One of the methods is applied to EGA curves of the volatilization of toluene from epoxy resin cured with ethylenediamine. The diffusion constants obtained as a function of temperature for two plate-specimens of different thicknesses at various heating rates are in good agreement with each other. The temperature dependence of the diffusion constant observed for a powdered sample is also in good agreement with those observed for the two plate-specimens.

To date, the majority of kinetic researches have been made isothermally. However, the kinetics need to be extended to non-isothermal conditions, since there are many practical processes which proceed non-isothermally, and moreover thermal analyses are widely applied to kinetic investigations. While the isothermal investigation of kinetics is easy and desirable and the analysis of the thermoanalytical data is somewhat complicated, the isothermal method cannot be utilized when the thermal response time of the observed system is large compared with the rate of the process.

Although many methods have been proposed to analyse thermoanalytical data kinetically, most of them are based on the simple homogeneous chemical reaction and hence their applicability is limited. The author earlier [1, 2] set forth methods of kinetic analysis of thermoanalytical data in which kinetic equations of homogeneous chemical reactions of the general type are extended to the non-isothermal case. Flynn [3] recently pointed out the necessity of non-isothermal kinetics and discussed non-isothermal kinetics of homogeneous chemical reactions. The non-isothermal kinetics of homogeneous chemical reactions have been reported for fairly complicated polymer reactions [1, 2] and the nucleation-and-growth process [4], and have been applied to the thermal decomposition of polymers [1, 5–7], the volatilization of hydrogen chloride combined with amino groups in epoxy resins [8], and the crystallization of polymers [4, 9, 10]. However, many other types of process remain for which the kinetics have not yet extended to the non-isothermal case, and this needs to be done. In the present paper the equations of...
diffusion are extended to non-isothermal conditions and applied to analyse thermoanalytical data of vaporization of toluene from an epoxy resin cured with ethylenediamine.

Theory of non-isothermal kinetics of diffusion

When there is no formation and no consumption of the diffusing substance, the fundamental equation of diffusion is as follows:

\[ Dp^2\xi = \frac{\partial \xi}{\partial t} \] (1)

where \( D \), \( \xi \), \( t \) and \( p^2 \) are the diffusion constant, the concentration of the diffusing substance, the time and a Laplacian, respectively. Generally, the diffusion constant is a function of temperature, \( T \), i.e.:

\[ D = D_0 h(T) \] (2)

where \( D_0 \) is a constant. When Eq. (1) is extended to non-isothermal conditions, we obtain:

\[ D_0p^2\xi = \frac{\partial \xi}{\partial \theta} \] (3)

where:

\[ \theta = \int_0^t h(T) \, dt \] (4)

In the previous papers [1, 2], \( \theta \) is called the reduced time, and is applied to the rate constant of chemical reactions of the Arrhenius type. It is now generalized for the rate constant to have any temperature-dependence. When the temperature-dependence of the diffusion constant is of the Arrhenius type:

\[ \theta = \int_0^t \exp \left( -\frac{\Delta E}{RT} \right) \, dt \] (5)

where \( \Delta E \) and \( R \) are the activation energy and the gas constant, respectively, and for the case when the substance is heated at a constant rate, \( \alpha \), from low temperature where little reaction occurs:

\[ \theta = \frac{\Delta E}{\alpha R} p \left( \frac{\Delta E}{RT} \right) \] (6)

where \( p \) is the \( p \)-function proposed by Doyle [11], its value having been published by Akahira [12] and Doyle [11].

Now, Eq. (3) is the fundamental equation for non-isothermal diffusion, and the reduced time is used instead of the actual time. We can easily find the solution.