Kinetics

In celebration of the 60th birthday of Dr. Andrew K. Galwey

ACCOMMODATION OF THE ACTUAL SOLID-STATE PROCESS IN THE KINETIC MODEL FUNCTION
I. Significance of the non-integral kinetic exponents

N. Koga and H. Tanaka

Chemistry Laboratory, Faculty of School Education, Hiroshima University, 3-1-33 Shinonome, Minami-ku, Hiroshima 734, Japan

Abstract

The degree of coordination between the kinetic information from the thermoanalytical measurements and the kinetic theory of the solid-state reactions was investigated through the microscopic study of the thermal dehydration of several inorganic salt hydrates. An accommodation function was applied to the conventional kinetic model functions $f(\alpha)$, in an attempt to reduce the disagreement between the actual process and the idealized one assumed in formulating $f(\alpha)$. The significance of the non-integral kinetic exponent in the kinetic model function was discussed with its physico-chemical meanings.

Keywords: kinetics, solid-state reactions

Introduction

Although thermoanalytical (TA) data are of a macroscopic nature averaged over the assemblage of sample, the experimentally resolved shape of the TA curves has widely been used as a possible source for the kinetic understanding of solid-state reactions [1, 2]. The shape of the TA curve is characterized by the kinetic model function $f(\alpha)$ derived on the basis of the physico-geometric assumption of the reaction interface movement [3], because the solid-state reaction is especially characterized by the existence of the specialized zone of locally enhanced reactivity at the reactant/product contact, i.e., reaction inter-
The kinetics are further characterized assuming the Arrhenius-type temperature dependence of the rate constant. The application of the Arrhenius equation, as well as mis-estimation and/or over-simplification of the $f(\alpha)$, are likely to be responsible for different kinetic parameters obtained under different experimental conditions for a given reaction. It is always important to recognize the deviation of the real process from the idealized process assumed in formulating the kinetic equation. The problem concerning the Arrhenius-type temperature dependence of the rate constant is related to the influence of the factors other than the measured temperature, which, in a strict sense, is not controlled in conventional TA techniques. The gradients in the temperature and gaseous pressure generated by the reaction itself seem to be important in evaluating the reliability of the TA curves as a possible source of the kinetic data [4, 5]. Controlled Transformation Rate Thermal Analysis (CRTA) [6] and/or Quasi-isothermal Quasi-isobaric Thermal Analysis (QQTA) [7] seem to be a possible solution. On the other hand, the problem concerning the $f(\alpha)$ is related to the really heterogeneous and complicated reaction behaviour which we are interested in. Scanning electron microscopy (SEM) and optical microscopy have been widely used for such morphological studies. In these techniques, however, the observation of the textural structure of the reactant/product interface is sometimes disturbed by an opaque product layer. Employing the thin-section technique [8, 9], the internal surface including the reactant/product interface can be observed under polarized light. The SEM of the replica makes it possible to observe the more detailed textural structure of the reaction interface as the replicated view [10, 11]. The systematic observation of microscopic views of the reaction morphology plays decisive roles in extending the understanding of the kinetic characteristics of the solid-state reactions and enables us to recognize the deviation of the idealized model assumed for the actual process.

In this paper, the problems of TA kinetics connected with the distortion of the actual process from the idealized model are reviewed. The complexity of the reaction morphology of the solid-state reaction is recognized through the microscopic observation of the thermal dehydration process of several inorganic salts hydrates. The possible way to accommodate the complexity of the actual process in the kinetic equation is briefly discussed by reviewing some differently oriented studies.

The kinetic equation and accommodation function

Assuming the physico-geometry based kinetic model function $f(\alpha)$ and the Arrhenius equation, the TA curves can be analyzed kinetically by the following equation:

\[
\text{J. Thermal Anal., 41, 1994}
\]