

ON THE FRACTIONAL CONVERSION α IN THE KINETIC DESCRIPTION OF SOLID-STATE REACTIONS

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For the kinetic description of the solid-state reactions, the dependence of the apparent kinetic parameters on the sample mass and/or particle size is discussed mathematically in relation to some problems on the fractional conversion α . As for the reaction proceeding according to the contracting geometry model, the use of the specific rate constant, independent of the sample mass and particle size, is recommended to obtain the sample mass-independent Arrhenius parameters. It is also pointed out that the distribution of α within the assembly of sample particles disturbs the successful use of α in the kinetic description of the solid-state reactions.

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Introduction

The following kinetic equation is assumed for the solid-state reactions [1, 2].

$$\frac{d\alpha}{dt} = k_{\alpha} f(\alpha) \quad (1)$$

or

$$G(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = k_{\alpha} t \quad (2)$$

where α is the fractional conversion, $f(\alpha)$ is the kinetic model function, derived on the basis of the usual physico-geometrical assumptions on the movement of

reaction interface under an isothermal condition [2, 3], and k_α is a rate constant depending on the $f(\alpha)$ assumed. In the most traditional case of homogeneous-like kinetics the $f(\alpha)$ function has the common form of $(1-\alpha)^n$. Assuming $(1-\alpha)$ to be the function to represent the simplest chemical event, any additional complication due to a more complex reaction mechanism can be understood as a deviation and be treated in a quantitative way by the introduction of a multiplication function [4], such as $(1-\alpha)^{1-n}$, α^m or $\ln(1-\alpha)^p$. This is in accordance with fractal-like kinetics [5], which is able to describe reactions with the geometrical constrain on the basis of the anomalous reaction orders, m , n , or p . It is worth noting, however, that the above kinetic description is adequate, in that the α can satisfactorily be applied to the solid-state reactions, instead of the concentration term used in the real homogeneous kinetics.

On the other hand, some problems on the use of α have been discussed by Criado [6], Fatu & Segal [7] and Blazejowski [8] in connection with the validity of the Chatterjee method [9] of the kinetic analysis for the thermal decomposition of solids, in which the active weight [10] was used for the kinetic description instead of α . Chatterjee represented the kinetic equation in the forms of

$$-\frac{dW}{dt} = k_w W^n \quad (3)$$

and

$$n = \frac{\log(-dW/dt)_1 - \log(-dW/dt)_2}{\log W_1 - \log W_2} \quad (4)$$

where W is the active weight of the reactant remaining at time t , n is the order of reaction in the n th-order law and k_w is a rate constant. The Eq. (4) was used to evaluate the value of n from various thermogravimetric curves recorded for samples with different sample weights at a given temperature.

Criado [6] criticized such a procedure pointing that k_w in Eq. (3) depends on the initial weight of sample, W_0 . In addition, he recommended the use of Eq. (1) by assuming that k_α is independent of W_0 for the n th-order law, $f(\alpha) = (1-\alpha)^n$, being supported by Blazejowski [8]. Assuming the three-dimensional phase boundary controlled, R_3 , law, Fatu & Segal analyzed the sample mass dependence of k_α [7], in which they obtained the opposite results to Criado. From the practical point of view, we agree to the Criado's criticism on Eq. (4), because the heat and mass transfer phenomena would change with W_0 . It is necessary here to understand the relationship between k_α and W_0 mathematically, which influence the other kinetic parameters consequently.

If the volume of original phase of a sample particle with spherical symmetry contracted by moving the reaction interface from the original surface the value of α is defined as

$$\alpha = \frac{r_o^3 - r^3}{r_o^3} \quad (5)$$

where r_o and r are radii of the reactant particle at $t=0$ and $t=t$, respectively. When the movement of reaction interface is regulated by chemical reaction, the value of r is expressed by the following equation:

$$r = r_o - kt \quad (6)$$

where k is a constant. Combining Eq. (6) with Eq. (5), we obtain

$$1 - (1 - \alpha)^{1/3} = \frac{k}{r_o} t \quad (7)$$

which is the R_3 law in an integral form. We can replace r_o with

$$r_o = \left(\frac{3m_o}{4\pi\rho} \right)^{1/3} \quad (8)$$

where m_o is the initial mass of one particle and ρ is the volume density. Comparing Eq. (7) with Eq. (2), the k_α for the R_3 law can be expressed as

$$k_\alpha = \frac{k}{r_o} = \left(\frac{4\pi\rho}{3m_o} \right)^{1/3} k \quad (9)$$

Similarly, if the movement of reaction interface was controlled by diffusion, the parabolic law is applied for the value of r .

$$r = r_o - (2KDt)^{1/2} \quad (10)$$

where K and D are the constant and diffusion coefficient, respectively. Combining Eqs (5) and (10), the equation of Jander, D_3 law [11] can be obtained.

$$[1 - (1 - \alpha)^{1/3}]^2 = \frac{2KD}{r_o^2} t \quad (11)$$

Comparing Eqs (2) and (11), the term of k_α for the D_3 law is given as follows:

$$k_\alpha = \frac{2KD}{r_o^2} = 2 \left(\frac{4\pi\rho}{3m_o} \right)^{2/3} KD \quad (12)$$

As can be seen from Eqs (9) and (12), the k_α depends on the particle size and sample mass for the powder and bulk samples, respectively. The similar relation-

ship can be obtained for other kinetic models of contracting geometry, being consistent with the results of Fatu & Segal [7].

Now we define the terms of $(4\pi\rho/3)^{1/3}k$ and $2(4\pi\rho/3)^{2/3}KD$ in Eqs (9) and (12) as the specific rate constant, k_s , which is independent of both the particle size and mass of one particle. Assuming the temperature dependence of the Arrhenius type on k_s , is given by

$$k_s = A \exp\left(-\frac{E}{RT}\right) \quad (13)$$

where A is the preexponential factor, E the activation energy, R the gas constant and T the temperature. The temperature dependence of k_α can be written as

$$k_\alpha = \frac{A}{m_o^{1/3}} \exp\left(-\frac{E}{RT}\right) \quad (14)$$

and

$$k_\alpha = \frac{A}{m_o^{2/3}} \exp\left(-\frac{E}{RT}\right) \quad (15)$$

for the R_3 and D_3 laws, respectively. Equations (14) and (15) suggest the m_o dependence of the apparent preexponential factor, A_{app} , given by $A/m_o^{1/3}$ and $A/m_o^{2/3}$, respectively. It is also noted that Eqs (14) and (15) are valid only for a unique value of m_o .

As a mathematical consequence of the exponential form of temperature dependence of the k_α [12], variation of E value is also expected, as given abstractly by

$$\ln A + \Delta \ln A = \frac{E + \Delta E}{T + \Delta T} \cdot \frac{1}{R} + \text{Const.} \quad (16)$$

The fact that variation and interdependence of apparent values of $\ln A$ and E arise from the use of α was exemplified by the isothermal decomposition of melted NH_4NO_3 [13]. It was also shown that the unexpected variation of E is avoided by examining the temperature dependence of k_s . The above relationship indicates that the m_o dependence of k_α is a possible cause of the kinetic compensation effect (KCE), being appeared as the effects of particle size and sample mass in the cases of powdered and bulk samples, respectively.

Mathematically, the k_α for the kinetic model of contracting geometry is independent of W_o , when the powdered sample with a unique m_o was examined. In practice, however, the W_o -dependent variation of the k_α was observed [14–17]. This seems to be due to the distribution of α within the sample assembly [18], caused probably by the effects of mass and heat transfer [19–23]. The W_o depen-

dence of the k_{α} also influences the value of A_{app} , in a similar way to Eqs (14) and (15). In this respect, the value of α , which is measured as a certain mean value averaged over all the particles in the assembly, is not appropriate to describe the kinetics based on the models with geometrical constrains, when any systematic and/or unsystematic distribution of α is observed within the assembly of sample particles.

Simple application of the above mentioned equations, proposed originally under the isothermal conditions, to any nonisothermal conditions is generally inaccurate [2]. Appropriate integration under the nonisothermal conditions [24] requires temperature-dependent integration limits of the Arrhenius rate constant [25, 26] leading to introduction of the so-called $p(x)$ function [1, 2, 27]. Only when the approximation of the $p(x)$ is roughly constant, the resultant equations are analogous to isothermally derived ones [2, 3], differing only by a multiplication constant. This implies that the mathematical explanation for the sample mass-dependent values of the kinetic parameters derived nonisothermally is more complicated than that for the isothermally determined parameters. At the same time, it must be remembered that the larger distribution of α could be expected for the source of the nonisothermal kinetic data, i.e., thermoanalytical curves.

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