Clarification of some kinetic concepts in solid state reactions

J.M. Criado * and A. Ortega

Dpto. de Química Inorgánica e Instituto de Ciencias de Materiales de Sevilla, Centro Mixto C.S.I.C. – Universidad de Sevilla, P.O. Box 1.115, 41080 Seville, Spain

Abstract

It is shown that Chatterjee's method (J. Polym. Sci. Part A, 3 (1965) 4253) cannot be used at all to determine the value of n in solid state thermal decomposition reactions. An attempt is made to clarify some kinetic concepts in the description of solid state reactions.

INTRODUCTION

Many basic problems regarding the mathematical description of solid state reactions are still the subject of controversy. Thus we concluded in an earlier paper [1] that Chatterjee's method [2] of kinetic analysis of solid state reactions cannot be used at all for determining the value of the apparent reaction order n in reactions of the thermal decomposition of solids. However, Fatu and Segal [3] have criticized our previous conclusion and, recently, Koga et al. [4] have analyzed the concept of the fractional conversion α in connection with the validity of Chatterjee's method.

The purpose of the present paper is, firstly, to clarify some aspects concerned with fundamental relationships describing solid state reactions and, secondly, taking into account these relationships, to test the validity of Chatterjee's method by applying it.

Fundamental kinetic relationship

It is well known that the rate of solid state reactions of the type

$$A(s) \rightarrow B(s) + C(g)$$
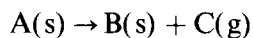
can be expressed in the form

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \tag{1}$$

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* Corresponding author.

or

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = K(T)t \tag{2}$$

where α is the fractional conversion, $f(\alpha)$ and $g(\alpha)$ are functions depending on the reaction mechanism, and K is the rate constant.

The assumption is made that solid state reactions are activated processes and consequently the kinetics are usually described using the Arrhenius equation developed for homogeneous systems. The dependence of the reaction rate on temperature is represented by

$$K(T) = A \exp(-(E/RT)) \tag{3}$$

E being the activation energy and A the pre-exponential factor.

It is apparent that only intensive quantities should be used in the, rate equations (1) and (2). The rate constant $K(T)$ of eqn. (3) is characteristic of the temperature and is independent of any extensive magnitude such as the sample weight W_0.

Assuming a three-dimensional phase-boundary controlled model (R_3 in Table 1) Fatu and Segal [3] and Koga et al. [4] have analyzed the sample mass dependence of $K(T)$. Taking into account a sample particle with spherical symmetry, the value of α is defined as

$$\alpha = \frac{r_0^3 - r^3}{r_0^3} \tag{4}$$

TABLE 1

Symbols and functions of the most commonly used kinetic models

Mechanism	Symbol	$f(\alpha)$
Random nucleation Unimolecular decay law	F_1	$(1 - \alpha)$
Zero-order, Polany–Wigner	R_1	1
Phase-boundary controlled reaction Contracting cylinder	R_2	$(1 - \alpha)^{1/2}$
Phase-boundary controlled reaction Contracting sphere	R_3	$(1 - \alpha)^{1/3}$
Two-dimensional growth of nuclei Avrami–Erofeev equation	A_2	$2[-\ln(1 - \alpha)]^{1/2}(1 - \alpha)$
Three-dimensional growth of nuclei Avrami–Erofeev equation	A_3	$3[-\ln(1 - \alpha)^{2/3}(1 - \alpha)$
One-dimensional diffusion	D_1	$1/2\alpha$
Two-dimensional diffusion	D_2	$1/-\ln(1 - \alpha)$
Three-dimensional diffusion	D_3	$3(1 - \alpha)^{2/3}/2[1 - (1 - \alpha)^{1/3}]$
Three-dimensional diffusion Ginstling–Brounshtein equation	D_4	$3/(2[(1 - \alpha)^{-1/3} - 1])$

where r_0 is the initial radius of the particle at $t = 0$, and r the radius at time t. Taking derivatives of eqn. (4) we have

$$\frac{d\alpha}{dt} = -\frac{3}{r_0^3} r^2 \frac{dr}{dt} \tag{5}$$

If we assume that the radius decreases at constant rate k_r, we can write

$$k_r = -\frac{dr}{dt} \tag{6}$$

Combining eqns. (4)–(6), integrating and rearranging, we get

$$1 - (1 - \alpha)^{1/3} = \frac{k_r}{r_0} t \tag{7}$$

We can replace r_0 with

$$r_0 = \left(\frac{3m_0}{4\pi\rho}\right)^{1/3} \tag{8}$$

where m_0 is the initial mass of the particle and ρ the density. Comparing eqn. (7) with eqn. (2), the rate constant $K(T)$ can be expressed as

$$K(T) = \frac{k_r}{r_0} = \left(\frac{4\pi\rho}{3m_0}\right)^{1/3} k_r \tag{9}$$

In the assumption of Fatu and Segal [3], the sample is composed of a unique particle, hence $W_0 = m_0$. In summary, in eqn. (9) ρ, r_0 and m_0 are intensive quantities so that the rate constant $K(T)$ is correctly expressed and the kinetics can be properly described. This magnitude should be used to evaluate the kinetic parameters of solid state reactions. This fact has been erroneously interpreted in ref. 3.

Remarks about Chatterjee's method

Chatterjee [2] represents the rate of decomposition of a solid state reaction in the form

$$-\frac{dW}{dt} = K_w W^n \tag{10}$$

where W is the active weight of the material remaining at time t, n is the reaction order and K_w is the rate constant.

For the calculation of the reaction order n, two TG curves from two different initial weights of the substance must be recorded, all the other experimental conditions being kept constant. Then W_1, W_2 and the corresponding $(-dW/dt)_1$ and $(-dW/dt)_2$ values can be determined at selected temperatures from each set of curves and n can be evaluated as

$$n = \frac{\log(-dW/dt)_1 - \log(-dW/dt)_2}{\log W_1 - \log W_2} \tag{11}$$

We have demonstrated in ref. 1 that eqn. (11) yields results that have no physical meaning and it has been shown that, provided mass and heat transfer effects have been avoided, the reaction order n obtained from eqn. (11) must be equal to 1 **whatever the reaction mechanism obeyed by the reaction**. This inconsistency is due to the fact that eqn. (10) is not suitable for use in kinetic analysis because the rate constant derived by this equation would depend on the sample weight which is an extensive quantity and only intensive quantities should be used in the rate equation.

For reactions involving solids, the fractional conversion α, defined in the form

$$\alpha = 1 - \frac{W}{W_\infty} \tag{12}$$

where W_∞ is the total weight loss when the reaction is over, is the parameter appropriate for the description of such reactions.

In order to test the validity of eqn. (11) we have constructed two theoretical TG curves at two different sample weights (100 and 200 mg) by assuming, as an example, two different kinetic models, the contracting sphere R_3, $(f(\alpha) = (1-\alpha)^{1/3})$, and the three-dimensional diffusion D_4, $(f(\alpha) = 3/(2[(1-\alpha)^{-1/3} - 1]))$, and the kinetic parameters $E = 167 \text{ kJ mol}^{-1}$ and $A = 2 \times 10^8 \text{ min}^{-1}$, and a heating rate of $6°C \text{ min}^{-1}$. The thermal decomposition of a model compound, $CaCO_3$, has been considered in order to calculate the change in weight as a function of the temperature from different starting weights.

The kinetic analysis of the data in Figs. 1 and 2 was carried out using Chatterjee's method, eqn. (11). The results collected in Table 2 demonstrate
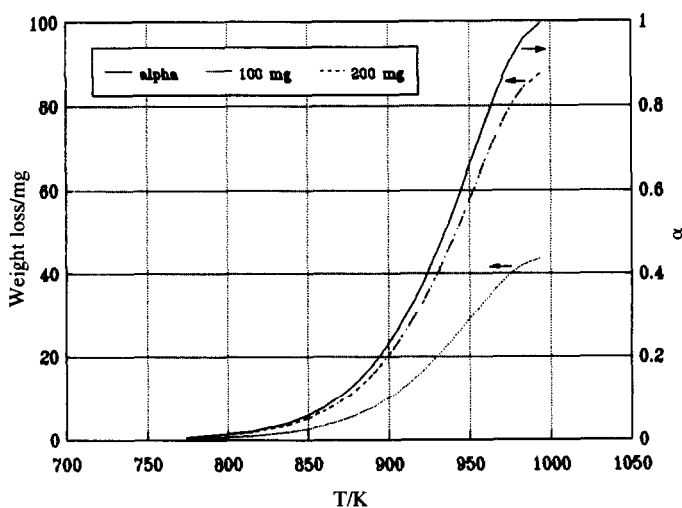

Fig. 1. Theoretical R_3 curves for two starting weights, 100 and 200 mg, and the corresponding $\alpha - T$ trace.
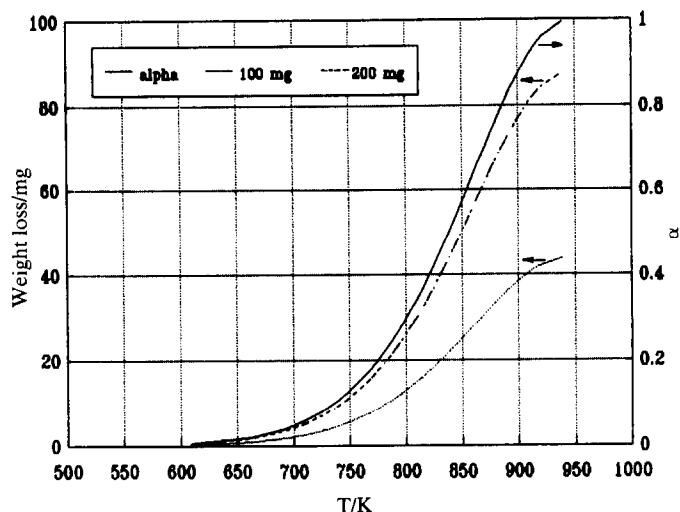
Fig. 2. Theoretical D_3 curves for two starting weights, 100 and 200 mg, and the corresponding $\alpha - T$ trace.

the above statement. Figures 1 and 2 show the corresponding $\alpha - T$ curves. We can see that provided heat and mass transfer effects have been avoided, a unique $\alpha - T$ curve is obtained in both cases. However, if the reaction rate is modified because of mass transfer effects, it is well known [5–7] that an increase in the sample weight gives rise to a movement of the TG curve at higher temperatures, while a broadening of the reaction temperature ranges takes place. These facts mean that values of n different from 1 would be obtained by applying eqn. (11).

We have demonstrated in ref. 1 that the higher the influence of the mass transfer phenomenon, the lower the reaction order obtained from Chatterjee's method. This assertion is in good agreement with the fact that the n values determined by Chatterjee's method for the dehydration of $CaC_2O_4 \cdot H_2O$ [1] and the thermal decomposition of $CaCO_3$, both largely influenced by the mass transport effect [6, 8, 9], are much lower than 1. Similar reasoning could be applied with regard to the influence of the heat transfer effect on the value of the reaction order as determined from eqn. (11).

TABLE 2

Kinetic analysis of the data in Figs. 1 and 2 using Chatterjee's method, eqn. (11)

Mechanism	n value from eqn. (11)
R_3	1
D_3	1

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