



Surface nucleation and anisotropic growth models for solid-state reactions



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ABSTRACT

Nucleation-growth models for the kinetic analysis of gas–solid reactions in which nucleation proceeds at the surface of the particles are reported. The growth of the nuclei is assumed to be anisotropic, i.e. with a very fast surface rate compared to the bulk one. The nucleation and growth processes are assumed to occur with, respectively, an areic frequency γ (nb. nuclei $\text{m}^{-2} \text{s}^{-1}$) and an areic reactivity ϕ ($\text{mol m}^{-2} \text{s}^{-1}$), both depending only on the thermodynamic variables (such as temperature, partial pressures ...) established during the reaction. Depending on the shape of the particles, the direction of growth and the localization of the rate-determining step, eighteen analytical expressions of kinetic rate are obtained. The importance of particle size is also put in evidence.

1. Introduction

Among the numerous studies devoted to the kinetic analysis of solid-gas reactions during the last decades, it appears that the solid characteristics (in case of powders) are most often neglected at the expense of the mathematical methods developed for understanding the mechanism of reaction. Generally the kinetic analysis of the experimental data leads to a so-called “triplet” which consists of the kinetic model in the form of a $f(\alpha)$ function, and of the values of the apparent activation energy noted E_a and of the pre-exponential term noted A , the rate of reaction being expressed by $da/dt = A \exp(-E_a/RT) f(\alpha)$. Tables of $f(\alpha)$ equations have been published many times [1,2]. These expressions are generally grouped according to the shape of the isothermal α -time curves as acceleratory, sigmoid and deceleratory. Among the rate equations which produce sigmoid $\alpha(t)$ curves, there are two groups of laws depending on whether the nucleation proceeds.

For a random bulk nucleation, one can obtain the well-known Avrami law [3–5] if the nucleus generation is a single-step process, or the Erofeev law [6] for a multi-steps nucleation based on Mott's description of the decomposition of metallic azides [7]. These laws are derived from assumptions based on an infinite volume of the “reacting” solid, and on bulk nucleation (which is realistic for nucleation-growth processes in bulk materials such as crystallization of metals as described by Kolmogorov [8]).

However, it is a matter of fact that in general gas-solid reactions do not fulfill these conditions, since nuclei appear at the surface of the particles as it has been shown for copper sulfate pentahydrate dehydration [9], alums dehydration [10] or lithium sulfate monohy-

drate dehydration [11]. Thus how to interpret sigmoidal $\alpha(t)$ curves avoiding models based on bulk nucleation?

Garner and Hailes [12] have introduced the concept of branching nucleation which allows to simulate the first accelerating period of the reaction. In order to interpret the following decelerating period, Prout and Tompkins [13] have proposed a mechanism in which the threadlike nuclei meet which leads to the branches interruption. This mechanism conducts to the well-known Prout–Tompkins equation (often referred to as B1). Nevertheless two criticisms could be addressed to this equation: firstly non-branching nucleation is not taken into account; and secondly this theory considers that the fractional extent is proportional to the nuclei number without taking into account the way of development of the growing nuclei. So even if the Prout–Tompkins equation could mathematically describe some experimental curves, its physical meaning remains uncertain for application in kinetic analysis (notably due to its indeterminate nature at small and large values of the extent of decomposition as previously discussed by Brown [14] and Bohn [15]).

In fact two kinds of models with surface nucleation may be distinguished according to the way in which the growth proceeds: if the nuclei develop at the same rate in all directions of space, i.e. the growth is isotropic, the Mampel's [16,17] model (based on the overlapping theory proposed by Johnson and Mehl [18] and used by Avrami) must be used, whereas if the growth is anisotropic, i.e. very fast development of the nuclei along the surface compared to the bulk, then specific models must be established.

Bianchet and Rigotti [19] proposed a model for decomposition of solids by taking into account a surface nucleation occurring on plates, followed by inward growth. Two growth rates are considered (one for

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Nomenclature

Notations

A	Pre-exponential factor (s^{-1})
ΔC	Difference of concentration of the diffusing species at both interfaces (mol m^{-3})
D	Diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
E_a	Apparent activation energy (J mol^{-1})
$g(r)$	Mathematical function of the particle size distribution
G_D	Geometrical factor
h	Length of a cylindrical particle (m)
J_K	Flux of diffusing species k ($\text{mol m}^{-2} \text{s}^{-1}$)
l_0	Constant length (= 1 m)
n_0	Initial amount of solid reactant (mol)
N_0	Initial number of particle
N	Number of particles without any nucleus at time t
r_e	External interface radius (m)
$r_g(\tau, t)$	Rate of growth of one nucleus appearing at time τ (mol s^{-1})
r_i	Internal interface radius (m)
r_0	Initial radius of a particle (m)
R	Ideal gas constant (= $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
s_e	External interface surface area (m^2)
s_i	Internal interface surface area (m^2)
$s_p(\tau, t)$	Active area (m^2)

s_0	Initial surface area of a particle (m^2)
$S_L(\tau)$	Free surface for nucleation (m^2)
S_m	Space function ($\text{m}^2 \text{ mol}^{-1}$)
t	Time (s)
t_f	Time necessary to totally transform one particle (s)
T	Temperature (K)
V_A	Solid reactant volume (m^3)
V_B	Solid product volume (m^3)
V_{mA}	Molar volume of solid reactant ($\text{m}^3 \text{ mol}^{-1}$)
V_{mB}	Molar volume of solid product ($\text{m}^3 \text{ mol}^{-1}$)
V_0	Initial solid reactant volume (m^3)
x	Solid product thickness (m)
z	Expansion coefficient
α	Fractional extent of the powder
α_p	Fractional extent of a particle
γ	Areic frequency of nucleation ($\text{nuclei m}^{-2} \text{ s}^{-1}$)
ν_B	Stoichiometric coefficient related to solid product
ν_j	Stoichiometric coefficient related to gas j
ξ	Extent of reaction (mol)
ξ_i	Extent of reaction with regard to the constituent i (mol)
τ	Date of appearance of a nucleus (s)
ϕ	Areic reactivity of growth ($\text{mol m}^{-2} \text{ s}^{-1}$)
ω	Reduced rate of reaction
$d\alpha/dt$	Rate of reaction (s^{-1})
$d\xi/dt$	Absolute speed of reaction (mol s^{-1})

the normal growth and one for the tangential growth) thus allowing to consider anisotropic growth (when the tangential component is much bigger than the normal component) or an isotropic growth. This model was applied to the dehydration of crystals of 11-aminoundecanoic acid dihydrate [20]. By fitting to experimental curves obtained in isothermal and isobaric conditions, the authors were able to determine three parameters: a nucleation rate (expressed in min^{-1}), a normal growth rate (with a rate-determining step located at the internal interface) and a third parameter including in particular the tangential growth rate, a shape factor and the density of nucleation sites.

More recently, Ogasawara and Koga [21] have combined induction period, surface reaction and phase boundary reaction to interpret the thermal dehydration of ferrous oxalate dihydrate.

Models based on surface nucleation and anisotropic growth of the nuclei have already been used to analyze the kinetics of certain reactions such as the dehydration of lithium sulfate monohydrate [22], the reduction of U_3O_8 on UO_2 by H_2 [23], the dehydroxylation of kaolinite [24] and the oxidation of copper nanoparticles [25]. However the general principles of the calculation of the rate of reaction leading to eighteen laws according to the assumptions done for the rate-determining step and the direction of growth were never presented. The present article aims to describe precisely these principles and assumptions and to detail the calculation of the rate equations.

2. Assumptions for kinetic modeling

A chemical solid-gas reaction can be written



where A and B are the solid reactant and the solid product respectively, G_j are the gas involved in the reaction, ν_B is the stoichiometric coefficient related to the solid B (the stoichiometric coefficient related to the solid A is chosen equal to 1 by convention) and ν_j are the algebraic stoichiometric coefficient of the gas j ($\nu_j < 0$ for the gas reactant and $\nu_j > 0$ for the gas product).

The chemical reaction represented by Eq. (1) takes place according

to a mechanism involving a set of elementary steps during which reactive intermediates are created and/or consumed.

For a given reaction one can define an extent of reaction ξ_i with regards to the constituent i. If the reaction occurs in a steady-state regime, each ξ_i are equal during the reaction and it is possible to define the extent of reaction ξ by $\xi = \xi_1 = \xi_2 = \dots = \xi_i$. The absolute speed of reaction corresponds to the derivative of the extent of reaction with respect to time, i.e. $d\xi/dt$ (expressed in moles of reactant transformed per unit of time). If the reaction balance is written by giving the stoichiometric coefficient 1 to the solid reactant phase, and if n_0 represents the initial amount of reactant then the reaction can be characterized by the fractional extent α and by the rate of reaction $d\alpha/dt$:

$$\alpha = \frac{1}{n_0} \xi \quad (2)$$

$$\frac{d\alpha}{dt} = \frac{1}{n_0} \frac{d\xi}{dt} \quad (3)$$

The kinetic rate of the reaction will be calculated taking into account the growth of all the nuclei appeared at the surface of the particles. Rigorously the rate of the whole reaction corresponds to the sums of the contributions of both processes of nucleation and growth. Nevertheless since the nucleation leads in practice to very small amounts of product, its contribution to the measured reaction rate can be neglected, thus the rate of the whole reaction will be directly obtained by calculating the rate of growth.

Nucleation of the new solid phase is supposed to occur homogeneously at the surface of the particles and to be followed by a very fast (quasi instantaneous) two-dimensional growth: once a nucleus appears, the particle becomes covered with a very thin layer of product. The growth then proceeds perpendicularly to the surface of the particles. However all the nuclei do not appear at the particles surfaces at the same time, which means that during the transformation, the powder is a mixture of unreacted, partially and fully transformed particles, as it is shown in Fig. 1 in the case of spherical, cylindrical and plate-like particles. Each particle is in fact transformed in the same way, but begins to transform only after a period which corresponds to the time

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