



*Dedicated to Professor Ionel Haiduc
on the occasion of his 75th anniversary*

RATE EQUATIONS OF SOLID STATE REACTIONS. EUCLIDEAN AND FRACTAL MODELS

Eugen SEGAL*

University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry,
4-12 Bd. Regina Elisabeta, Bucharest, RO-70376, Roumania

Received June 2, 2011

The author suggests a comparative analysis of the classical Euclidean rate equations and the fractal ones. The fractal kinetic equations contain the fractal dimension, property which could be used as a kinetic characteristic of the investigated solid-state reacting system.

INTRODUCTION

In some previous notes, solid-gas decompositions limited by nucleation-growth phenomena were kinetically treated using euclidean as well as fractal models.¹⁻³ Rigorously valid equations were obtained for extreme values of the nuclei fractal dimension and approximate ones for the intermediate ones. The consideration of the fractal character proves to be important in order to establish the form of the kinetic equations. As shown, for the solid-gas decompositions limited by nucleation-growth phenomena, the fractal rate equations could account for the fractional values of the time exponent in the integral kinetic equation $\alpha \propto t^n$.

EUCLIDEAN RATE EQUATIONS⁴⁻¹¹

Surface controlled reaction or phase boundary controlled reaction^{4,5,11}

For fast diffusion through the product layer the chemical change is considered as phase boundary

controlled. Under such conditions the reaction rate is treated as being directly proportional to the surface area of the unreacted reactant.

$$\frac{d(V_0\alpha)}{dt} = kA \quad (1)$$

where V_0 is the initial volume of the reacting particle and α the degree of conversion or

$$\frac{d\alpha}{dt} = k \frac{A}{V_0} \quad (2)$$

The integral form of equation (2) is:

$$1 - (1 - \alpha)^n = \frac{k}{r_0} t \quad (3)$$

with values of $n = \frac{1}{3}, \frac{1}{2}$ and 1 for three, two and one dimensional geometry of the reacting particle.

* Corresponding author: esegal@gw-chimie.math.unibuc.ro

Diffusion controlled reactions

Jander equation

According to Jander¹² model the reaction rate of the component which is covered, A, in a system of spherical grains with comparable sizes is limited by the diffusion of the component, B, which covers through the product layer, AB. The model supposes that surface of the grain belongs to the reactant and that the concentrations of the diffusing component B at the interfaces A/AB and AB/B are constant.

For the kinetics of the reaction between reactante A and B under the form of compact powders Jander worked up the following integral equation:

$$\left[1 - (1 - \alpha)^{\frac{1}{3}}\right]^2 = \frac{2kD_0}{r_0^2} t \quad (4)$$

where k is the rate constant, D_0 the diffusion coefficient of the reactant B through the layer of product and r_0 is the initial radius of the reactant A.

Kroger and Ziegler equation¹³

$$\left[1 - (1 - \alpha)^{\frac{1}{3}}\right]^2 = \frac{2k}{r_0^2} \ln t \quad (5)$$

Zhuravlev, Lesotkin and Tempelman equation,¹⁴

$$\left[\frac{1}{(1 - \alpha)^{\frac{1}{3}}} - 1\right]^2 = \frac{2kD_0}{r_0^2} t \quad (6)$$

Ginstling and Braunshtein equation,¹⁵

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} = \frac{2kD_0}{r_0^2} t \quad (7)$$

Carter and Valensi equation,¹⁶⁻¹⁸

$$z - (z - 1)(1 - \alpha)^{\frac{2}{3}} - [1 + (z - 1)\alpha]^{\frac{2}{3}} = \frac{2kD_0}{r_0^2} t \quad (8)$$

where z is the ratio between the volumes: actual (real) and ideal (if no change occurs) of the product layer.

Anti Jander model could be treated as the reverse of Jander model. Accordingly the reaction

rate is limited by the diffusion of the component, A, through the product layer at the interface AB/B. **Anti Jander equation,**¹⁹

$$\left[(1 + \alpha)^{\frac{1}{3}} - 1\right]^2 = \frac{3kD_0}{r_0^2} t \quad (9)$$

Anti Ginstling Braunstein equation,²⁰

$$1 + \frac{2}{3}\alpha - (1 + \alpha)^{\frac{2}{3}} = kt \quad (10)$$

All the presented kinetic equations describe various nonreacted shrinking core models.

Another model is based on continous bulk absorption of the reactant, B, in the reactant, A, the whole volume of the system changing gradually to the volume of the product, AB.²¹⁻²² Under such conditions the degree of conversion is given by:

$$\alpha = 1 - \frac{6}{\pi^2} \sum_{n=1}^{n=\infty} \frac{1}{n^2} e^{-n^2 kt} \quad (11)$$

where k is the rate constant given by:

$$k = \frac{\pi^2 D_0}{r_0^2} \quad (12)$$

FRACTAL RATE EQUATIONS

Surface controlled reactions¹¹

As according to the fractal geometry the surface area of the reaction boundary, A , and the volume V_0 are given by:

$$A = ar_0^{D-1} \quad (13)$$

$$V_0 = br_0^D \quad (14)$$

a and b being constants,

$$\frac{d\alpha}{dt} = (1 - \alpha)^{\frac{D-1}{D}} \quad (15)$$

with the fractal dimension is within the range;

$$2 \leq D \leq 3$$

The integral form of equation (15) is:

$$1 - (1 - \alpha)^{\frac{1}{D}} = kt \quad (16)$$

For $D=2$ and $D=3$ equation (16) leads to the integral kinetic equations known as R_2 and R_3 .

Diffusion controlled reactions

For $2 \leq D \leq 3$: Ozao and Ochiai using the obvious relation:

$$\alpha = 1 - \left(\frac{r}{r_0}\right)^3 \quad (17)$$

obtained:

$$\frac{d\alpha}{dt} = [(1 - \alpha)^{\frac{2-D}{D}} - 1]^{-1} \quad (18)$$

and

$$-\frac{2}{D}\alpha - (1 - \alpha)^{\frac{2}{D}} + 1 = kt \quad (19)$$

Equation (19) with $D=3$ turns into:

$$-\frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} + 1 = kt \quad (20)$$

which is a variant of Ginstling-Braunstein equation.

Using relation (17) as well as the presented euclidean kinetic equations one obtains:

Jander fractal equation,

$$[1 - (1 - \alpha)^{\frac{1}{D}}]^2 = \frac{2kD_0t}{r_0^2} \quad (21)$$

Kroger and Ziegler fractal equation,

$$[1 - (1 - \alpha)^{\frac{1}{D}}]^2 = \frac{2k \ln t}{r_0^2} \quad (22)$$

Zhuravlev fractal equation

$$[(1 - \alpha)^{\frac{1}{D}} - 1]^2 = \frac{2kD_0t}{r_0^2} \quad (23)$$

Anti-Jander fractal equation,

$$[(1 - \alpha)^{\frac{1}{D}} - 1]^2 = \frac{2kD_0t}{r_0^2} \quad (24)$$

Anti Ginstling-Braunstein fractal equation,

$$1 + \frac{2}{D}\alpha - (1 + \alpha)^{\frac{2}{D}} = kt \quad (25)$$

The fractal kinetic equations are valid for the same systems which use euclidean rate equations.

Slightly different values of the exponents which result as consequences of the change of euclidean dimensions into fractal ones are to be noticed.

CONCLUSIONS

The fractal rate equations are more general with respect to the euclidean ones.

The fractal rate equations open the perspective of better quantitative treatment of the kinetic properties of solid-state reaction mixtures.

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