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GENERAL KINETIC EQUATION FOR SOLID STATE REACTIONS

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Abstract

A general kinetic equation is suggested in order to describe solid state decompositions or, more generally, solid state reactions and transformations on the basis of some existing general equations. This differential equation can be expressed as: $d\alpha/dt=k[(1-\alpha)^q]^x\{[1-(1-\alpha)^{1-q}]/(1-q)\}^y$, where α represents the degree of conversion, k is the rate constant while q, x and y are characteristic parameters for a given mechanism.

Keywords: general rate equation, kinetic parameters, solid-state decompositions

Introduction

In the literature many papers have been dedicated to the derivation of kinetic equations describing solid state reactions and transformations [1–11]. As the number of particular kinetic equations has considerably increased, some attempts have been made in the last decades with the aim of deriving general rate equations suitable for describing the relatively high number of particular cases [3, 5–8].

In order to describe solid state reactions controlled by the movement of phase boundaries, by simple nucleation as well as by nucleation followed by nuclei growth and diffusion, Šesták and Berggren [6] suggested the following general equation:

$$d\alpha / dt = k(1-\alpha)^n\alpha^m[-\ln(1-\alpha)]^p \qquad (1)$$

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A critical analysis of Eq. (1) due to Gorbachev [8] shows that for isothermal conditions it can be transformed into three equations each being characterized by two exponents. Two of these equations are widely used and can be expressed as

$$d\alpha/dt = k(1-\alpha)^n[-\ln(1-\alpha)]^p \tag{2}$$

and

$$d\alpha/dt = k(1-\alpha)^n\alpha^m \tag{3}$$

Based on the well known theory of nucleation and nucleus growth, Ng proposed the following general equation for solid state decomposition kinetics [7]

$$d\alpha/dt = k\alpha^{1-a}(1-\alpha)^{1-b} \tag{4}$$

where a and b are parameters lying between zero and unity respectively. It is also important to notice that for $a=1-m$ and $b=1-n$ Eq. (4) becomes identical with Eq. (3).

Taking into account the importance of the above presented problem, this paper is dedicated to the identification of a more general kinetic equation which includes most of the expressions used to describe solid state reactions with heterogeneous decompositions as particular cases.

The general equation

Although Eqs (1)–(4) can be employed to derive several particular rate equations from literature, there are a number of mechanisms, e.g. D3 and D4, for which the corresponding rate equations cannot be obtained on the basis of the existing general equations [3, 6, 7]. Taking this problem into consideration the central objective of this paper is to find, by using a formal approach, a general form of a rate equation which is applicable to most of the kinetic expressions used in solid state reactions. It should be emphasized that in our attempt, instead of deducing the required general equation by employing the existing mechanistic theories, we prefer to try an alternative formal approach by exploiting the existing general equations, i.e. Eqs (2) and (3). Even though this procedure can be considered very unusual, the results obtained prove the utility of the proposed alternative method.

In order to derive the general equation we should analyse in detail Eqs (2) and (3). First let us rewrite these equations in the following equivalent forms

$$d\alpha/dt = k[(1-\alpha)^1]^n[-\ln(1-\alpha)]^p \tag{5}$$

and

$$d\alpha/dt = k[(1-\alpha)^2]^{(n+m)/2}[\alpha/(1-\alpha)]^m \tag{6}$$

Secondly, it is important to notice in connection with Eqs (5) and (6) that

$$\int_0^\alpha \mathrm{d}\alpha/(1-\alpha)^1 = [-\ln(1-\alpha)] \qquad (7)$$

and

$$\int_0^\alpha \mathrm{d}\alpha/(1-\alpha)^2 = [\alpha/(1-\alpha)] \qquad (8)$$

The generalization of these findings is obvious and consequently we can write the general equation as

$$\mathrm{d}\alpha/\mathrm{d}t = k[(1-\alpha)^q]^x[h(\alpha)]^y \qquad (9)$$

where

$$h(\alpha) = \int_0^\alpha \mathrm{d}\alpha/(1-\alpha)^q \qquad (10)$$

whereas q, x and y are suitable parameters that characterize a given mechanism. After performing the integration in Eq. (10) one obtains

$$h(\alpha) = [1-(1-\alpha)^{1-q}]/(1-q) \qquad q \neq 1 \qquad (11)$$

or

$$h(\alpha) = [-\ln(1-\alpha)] \qquad q = 1 \qquad (12)$$

Since

$$\lim[1-(1-\alpha)^{1-q}]/(1-q) = [-\ln(1-\alpha)] \qquad q \rightarrow 1 \qquad (13)$$

in the following we will consider that

$$h(\alpha) = [1-(1-\alpha)^{1-q}]/(1-q) \qquad (14)$$

without leaving out of consideration that for $q=1$ relationship (14) is in fact relationship (12).

Bearing in mind relationship (14), Eq. (9) can be transcribed into the form

$$\mathrm{d}\alpha/\mathrm{d}t = k[(1-\alpha)^q]^x\{[1-(1-\alpha)^{1-q}]/(1-q)\}^y \qquad (15)$$

which represents the general kinetic equation for solid state reactions we have been looking for. From Eq. (15) the corresponding differential conversion function, $f(\alpha)$, can be expressed as

$$f(\alpha) = [(1-\alpha)^q]^x\{[1-(1-\alpha)^{1-q}]/(1-q)\}^y \tag{16}$$

Finally, let us notice that for $q=1$; $x=n$ and $y=p$ Eq. (15) becames Eq. (2) while for $q=2$; $x=(m+n)/2$ and $y=m$ the general equation turns into Eq. (3).

Applications and discussion

Relationship (16) has been applied in order to derive several particular forms of it describing solid state reactions and transformations. Table 1 lists the most usual mechanisms as known from the literature.

Besides the form of $f(\alpha)$, the values corresponding to q, x and y and the symbols characteristic of the mechanisms and the type of the α–t curve, that is (A) for acceleratory, (S) for sigmoid-shaped and (D) for deceleratory, are given.

The conversion functions corresponding to mechanisms listed in Table 1 represent the starting point for discussion. First it is important to notice that the amount of reactant at a given time is proportional to $(1-\alpha)$, the fraction of the unreacted reactant, while the amount of product is proportional to α representing the fraction of the transformed reactant. On the other hand, many rate equations include a number of functions, i.e. $[-\ln(1-\alpha)]$ and $[1-(1-\alpha)^{1/3}]$, which increase with increasing α. Consequently, we consider that the amount of product is also related to these functions. Moreover, for qualitative considerations, we will assume that the amount of product is related to these functions, i.e. the higher the values of these functions the more product is formed.

Taking into account the above-mentioned observations and the data presented in Table 1, we can infer the following:

1. For mechanisms 1 and 2, which produce acceleratory α–t curves, the reaction rates are various functions of the amount of product and do not depend on the amount of reactant.
2. In the case of the mechanisms producing sigmoid-shaped α–t curves the reaction rates are various functions of the amount of reactant as well as of the amount of product.
3. For the D1 and D2 mechanisms the reaction rates change inversely the amount of product and do not depend on the amount of reactant.
4. The D3 and D4 diffusional mechanisms are characterized by rate equations for which the reaction rates change directly with the amount of reactant and inversely to the amount of product.
5. For all the diffusional mechanisms $y=-1$. Consequently, one has to take into account this condition when searching for new mechanisms describing reactions controlled by diffusion.

Table 1 Usual mechanisms from literature and the corresponding values for q, x and y

No.	Mechanism*		Type of α–t curve	$f(\alpha)$	q	x	y	Observations
1	P1	Power law	(A)	$\alpha^{(m-1)/m}$	2	$0.5(m-1)/m$	$(m-1)/m$	m=1; 2; 3 and 4
2	E1	Exponential law	(A)	α	2	1/2	1	
3	An	Avrami-Erofeev	(S)	$(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}$	1	1	$(n-1)/n$	n=3/2; 2; 3 and 4
4	B1	Prout-Tompkins	(S)	$\alpha(1-\alpha)$	2	1	1	
5	R2	Contracting surface	(D)	$(1-\alpha)^{1/2}$	1/2	1	0	
6	R3	Contracting volume	(D)	$(1-\alpha)^{2/3}$	2/3	1	0	
7	Fn	nth order reaction	(D)	$(1-\alpha)^n$	n	1	0	n=0; 1; 2 and 3
8	D1	1-D diffusion	(D)	$1/\alpha$	2	−1/2	−1	
9	D2	2-D diffusion	(D)	$[-\ln(1-\alpha)^{-1}$	1	0	−1	
10	D3	3-D diffusion	(D)	$(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	2/3	1	−1	
11	D4	Ginsling-Brounshtein	(D)	$(1-\alpha)^{1/3}[1-(1-\alpha)^{1/3}]^{-1}$	2/3	1/2	−1	

Conclusions

A new general equation (Eq. (15)) describing the kinetics of solid state reactions and particularly the kinetics of heterogeneous decompositions has been presented. This equation was applied successfully in obtaining a number of particular rate equations taken from the literature.

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