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New kinetic equations in order to describe solid–gas decompositions

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Abstract

Some kinetic equations describing heterogeneous decompositions in solid–gas systems are derived. Except for one equation obtained via the "reaction order" model the other equations describe sigmoid curves. The values of the degree of conversion corresponding to the maximum reaction rate α_{max} are calculated for each derived kinetic equation.

INTRODUCTION

In order to describe the occurrence in time of the solid–gas decompositions $A(s) \rightarrow B(s) + C(g)$, the general equation has been introduced [1–3]

$$V(t) = \int_0^t v(t, y)\left(\frac{dN}{dt}\right)_{t=y} dy \qquad (1)$$

where $v(t, y)$ is the volume of a nucleus which began to grow at the moment y ($y < t$), dN/dt is the rate of nucleation, and t is the time. The volume $v(t, y)$ is given by the formula [1–3]

$$v(t, y) = \sigma(r(t, y))^{\lambda} \qquad (2)$$

where $r(t, y)$ is the linear dimension of a nucleus which began to grow at the moment y, σ is a factor of form and $\lambda = 1$, 2 or 3 for the unidimensional, bidimensional and three dimensional growth respectively. For a constant rate of growth of a given nucleus

$$\frac{dr}{dt} = k_g \qquad (3)$$

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and it follows that

$$r(t,y)=k_g(t-y) \tag{4}$$

From relationships (2) and (4) one obtains

$$v(t,y)=\sigma k_g^{\lambda}(t-y)^{\lambda} \tag{5}$$

One of the equations which describes the rate of nucleation, corresponds to the one stage nucleation and has the form

$$\frac{\mathrm{d}N}{\mathrm{d}t}=k_1(N_0-N) \tag{6}$$

where N_0 is the number of potential nuclei, N is the number of nuclei at the moment t and k_1 the nucleation rate constant.

From eqn. (6) through integration with $N=0$ at $t=0$, we obtain

$$N=N_0(1-\exp(-k_1t)) \tag{7}$$

or introducing this result in eqn. (6)

$$\frac{\mathrm{d}N}{\mathrm{d}t}=k_1N_0\exp(-k_1t) \tag{8}$$

Equation (8) as well as other rate equations for nucleation will be considered in the following.

From $V(t)$ and V_0 (the total volume of the solid reaction product) the current value of the degree of conversion $\alpha(t)$ is given by

$$\alpha(t)=\frac{V}{V_0} \tag{9}$$

CRITICAL CONSIDERATIONS CONCERNING THE FORM OF $v(t,y)$

Elementary physical considerations show that $v(t,y)$ should satisfy the two limit conditions

$$\lim_{y\to t} v(t,y)=0 \tag{10}$$

$$\lim_{t\to\infty} v(t,y)=\text{finite} \tag{11}$$

As one can easily verify, $v(t,y)$ given by eqn. (5) does not satisfy condition (11) as

$$\lim_{t\to\infty} \sigma k_g^{\lambda}(t-y)^{\lambda}=\infty \tag{12}$$

This inconsistent result which does not account for the fact that a nucleus cannot have an infinite size, is due to the neglect of the nuclei overlap during growth. The growing nuclei, at a given moment overlap; thus the use of eqn. (5) which supposes that the nuclei develop independently of each other is not justified.

These observations impose the search for another analytical form for $v(t, y)$.

As, due to the overlap of the nuclei, the notion of linear growth becomes meaningless, we will try to obtain directly the volume of the nucleus by using, as a first approximation, an equation of the form

$$\frac{\mathrm{d}y}{\mathrm{d}t} = k_v\left(1 - \frac{v}{q}\right) \tag{13}$$

where k_v is the rate constant of the volume growth of the nucleus and the meaning of q is soon going to be discovered.

From eqn. (13) through integration for $v = 0$ at $t = 0$, one obtains

$$v(t) = q\left(1 - \exp\left(-\frac{k_v}{q}t\right)\right) \tag{14}$$

Taking into account this last result, eqn. (13) takes the form

$$\frac{\mathrm{d}v}{\mathrm{d}t} = k_v \exp\left(-\frac{k_v}{q}t\right) \tag{15}$$

Equation (15) through variable separation and integration leads to

$$\int_y^t \mathrm{d}v = \int_y^t k_v \exp\left(-\frac{k_v}{q}t\right) \mathrm{d}t \tag{16}$$

and

$$v(t, y) = q\left(\exp\left(-\frac{k_v}{q}y\right) - \exp\left(-\frac{k_v}{q}t\right)\right) \tag{17}$$

which is the expression reached instead of eqn. (5). Equation (17) satisfies the conditions (10) and (11). Indeed for $t \to y$ eqn. (17) leads to $v(t, y) = 0$ and

$$\lim_{t\to\infty} q\left(-\frac{k_v}{q} - t\right) - \exp\left(-\frac{k_v}{q}t\right) = q \exp\left(-\frac{k_v}{q}y\right) = \text{finite} \tag{18}$$

From eqn. (14)

$$\lim_{t\to\infty} v(t) = q \tag{19}$$

Thus q represents the maximum volume of a nucleus which began to grow at $t = 0$.

In the following some applications are given of the general formula (1) in which $v(t, y)$ is given by relationship (17). In order to perform the calculations various forms of the rate of nucleation will be used. As far as the current value of the degree of conversion $\alpha(t)$ is concerned this is given by

$$\alpha(t) = \frac{V(t)}{V(\infty)} \tag{20}$$

Such an expression could not be used for $v(t, y)$ given by eqn. (5), because in this case

$$V(\infty) = \infty \tag{21}$$

has been obtained.

APPLICATIONS

Because many $\alpha(t)$ curves for isothermal conditions exhibit sigmoidal forms, the values $t_{\max}$ and $\alpha_{\max}$ for the maximum value of $-\mathrm{d}\alpha/\mathrm{d}t$ are determined from the conditions

$$\left(\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2}\right)_{\alpha_{\max}, t_{\max}} = 0 \tag{22}$$

Instantaneous nucleation

In this case all the nuclei appear at $t = 0$, so that

$$N = N_0 \tag{23}$$

In such conditions

$$V(t) = N_0 q\left(1 - \exp\left(-\frac{k_v}{q}t\right)\right) \tag{24}$$

Because

$$V(\infty) = N_0 q \tag{25}$$

it follows that

$$\alpha = 1 - \exp\left(-\frac{k_v}{q} - t\right) \tag{26}$$

Introducing the notation

$$\frac{k_v}{q} = k \tag{27}$$

eqn. (26) takes the integral and differential forms

$$-\ln(1 - \alpha) = kt \tag{28}$$

$$-\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1 - \alpha) \tag{29}$$

this equation belonging to the "reaction order" model.

Linear law of nucleation (*one stage nucleation*)

$$\frac{\mathrm{d}N}{\mathrm{d}t}=k_1N_0 \tag{30}$$

In such conditions

$$V(t)=\int_0^t q\left(\exp\left(-\frac{k_v}{q}y\right)-\exp\left(-\frac{k_v}{q}t\right)\right)k_1N_0\,\mathrm{d}y \tag{31}$$

After performing the calculations, relationship (31) turns into

$$V(t)=\frac{k_1N_0q^2}{k_v}\left[1-\exp\left(-\frac{k_v}{q}t\right)-\frac{k_v}{q}t\exp\left(-\frac{k_v}{q}t\right)\right] \tag{32}$$

For $t\rightarrow\infty$ from eqn. (32) one obtains

$$V(\infty)=\frac{k_1N_0q^2}{k_v} \tag{33}$$

Relationships (20), (32) and (33) lead to the isothermal kinetic equation

$$\alpha=1-\exp(-kt)(1+kt) \tag{34}$$

where

$$k=\frac{k_v}{q} \tag{35}$$

In order to determine $\alpha_{\max}$ and $t_{\max}$ the following equations should be considered:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k^2t\exp(-kt) \tag{36}$$

and

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2}=\exp(-kt)k^2(1-kt) \tag{37}$$

From the condition (22) one obtains

$$t_{\max}=\frac{1}{k} \tag{38}$$

By introducing this result in eqn. (34), for $t=t_{\max}$ we obtain

$$\alpha_{\max}=1-\frac{2}{\mathrm{e}}=0.264 \tag{39}$$

Two stage nucleation

$$\frac{dN}{dt} = k_{II}N_0t \tag{40a}$$

$$V(t) = \int_0^t q\left(\exp\left(-\frac{k_v}{q}y\right) - \exp\left(-\frac{k_v}{q}t\right)\right)N_0k_{II}y\,dy \tag{40b}$$

Taking into account notation (35), after performing the calculations eqn. (40) turns into

$$V(t) = \frac{N_0k_{II}q}{k^2}\left(1 - \exp(-kt)\left(\frac{(kt)^2}{2} + kt + 1\right)\right) \tag{41}$$

and

$$V(\infty) = \frac{N_0k_{II}q}{k^2} \tag{42}$$

In such conditions

$$\alpha = 1 - \exp(-kt)\left(\frac{(kt)^2}{2} + kt + 1\right) \tag{43}$$

$$\frac{d\alpha}{dt} = \exp(-kt)\frac{k^3t^2}{2} \tag{44}$$

$$\frac{d^2\alpha}{dt^2} = \exp(-kt)k^3t\left(1 - \frac{kt}{2}\right) \tag{45}$$

Condition (22) leads to

$$1 - \frac{kt_{max}}{2} = 0 \tag{46}$$

and

$$t_{max} = \frac{2}{k} \tag{47}$$

Introducing this result in eqn. (43) for $t = t_{max}$ one obtains

$$\alpha_{max} = 1 - \frac{5}{e^2} = 0.325 \tag{48}$$

Three stage nucleation

$$\frac{dN}{dt} = N_0 k_{III} t^2 \tag{49}$$

$$V(t) = \int_0^t q\left(\exp\left(-\frac{k_v}{q}y\right) - \exp\left(-\frac{k_v}{q}t\right)\right) N_0 k_{III} y^2 \, dy \tag{50}$$

After performing the calculation and taking into account notation (35), eqn. (50) turns into

$$V(t) = \frac{N_0 k_{III} q}{k^3}\left(2 - \exp(-kt)\left(\frac{(kt)^3}{3} + (kt)^2 + 2kt + 2\right)\right) \tag{51}$$

As

$$V(\infty) = \frac{2N_0 k_{III} q}{k^3} \tag{52}$$

from relationship (51) and (52) we obtain

$$\alpha = 1 - \exp(-kt)\left(\frac{(kt)^3}{6} + \frac{(kt)^2}{2} + kt + 1\right) \tag{53}$$

In order to evaluate α_{max} and t_{max} we have to consider the equations

$$\frac{d\alpha}{dt} = \exp(-kt)\frac{k^4 t^3}{6} \tag{54}$$

and

$$\frac{d^2\alpha}{dt^2} = \exp(-kt)\frac{k^4 t^2}{2}\left(1 - \frac{kt}{3}\right) \tag{55}$$

The condition (22) leads to

$$t_{max} = \frac{3}{k} \tag{56}$$

By introducing this result in relationship (53) for $t = t_{max}$ one obtains

$$\alpha_{max} = 1 - \frac{13}{e^3} = 0.353 \tag{57}$$

Exponential nucleation (nucleation rate given by relationship (8))

For this case

$$V(t) = \int_0^t q\left(\exp\left(-\frac{k_v}{q}y\right) - \exp\left(-\frac{k_v}{q}t\right)\right) k_1 N_0 \exp(-k_1 y) \, dy \tag{58}$$

After performing the detailed calculation one obtains

$$\alpha = 1 + \frac{k}{k_1}\exp(-(k_1 + k)t) - \frac{k + k_1}{k_1}\exp(-kt) \tag{59}$$

$$t_{\max} = \frac{1}{k_1}\ln\frac{k_1 + k}{k} \tag{60}$$

$$\alpha_{\max} = 1 - \frac{a + 1}{a^{(a/a-1)}} \tag{61}$$

where k is given by eqn. (27) and

$$a = \frac{k_1 + k}{k} \tag{62}$$

As $a \in (1, +\infty)$, it follows that

$$\alpha_{\max}(a \rightarrow 1) = 1 - \frac{2}{e} = 0.264 \tag{63}$$

$$\alpha_{\max}(a \rightarrow \infty) = 0 \tag{64}$$

thus $\alpha_{\max} \in (0, 0.264)$.

COMPARISON WITH EXPERIMENT

The proposed kinetic equations can be used in order to work out experimental curves. When working sigmoid curves, the model should be chosen in such a way that the difference between $\alpha_{\max}(\text{exp})$ and $\alpha_{\max}(\text{calc})$ should be as low as possible.

As an example the reaction

$Pb(NO_3)_2(s) \rightarrow PbO(s) + 2NO_2(g) + 0.5O_2(g)$

will be considered. According to the data given in ref. 4, for two temperatures T_1 and T_2 the authors obtained

$T_1 = 673.15$ K $\alpha_{\max} \approx 0.33$ $t_{\max} = 76.6$ min

$T_2 = 688.15$ K $\alpha_{\max} \approx 0.33$ $t_{\max} = 30.8$ min

These results are described by the two-stage nucleation model for which $\alpha_{\max} = 0.323$ was obtained.

One has to state that in ref. 4 the authors use three kinetic models, the Prout–Tompkins model [1–3], the "reaction order" model with $n = 1$ and the contracting sphere model. Only the first of these three models corresponds to a sigmoid curve. The rate equation is given by

$$\frac{d\alpha}{dt} = k\alpha(1 - \alpha) \tag{65}$$

and

$$\alpha_{\max} = 0.50 \tag{66}$$

Thus there is a high difference with respect to the experimental value.

From eqn. (47) we obtain $k(T_1) = 4.47 \times 10^{-4}\ \mathrm{s}^{-1}$ and $k(T_2) = 1.08 \times 10^{-3}\ \mathrm{s}^{-1}$, with the following values for the Arrhenius activation parameters: $A = 1.68 \times 10^4\ \mathrm{s}^{-1}$ and $E = 227\ \mathrm{kJ\ mol}^{-1}$.

CONCLUSIONS

New kinetic equation describing solid gas decompositions have been proposed. It has been shown that

(1) eqn. (5) for $v(t, y)$ does not satisfy condition (11);

(2) the new relationship for $v(t, y)$ (eqn. (17)) satisfies condition (11);

(3) except in the case of instantaneous nucleation the curves (α, t) are of sigmoid form;

(4) comparison between one of the elaborated models and experiment shows good agreement.

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