

Influence of Crystal Habit and Particle Size Distribution on the Decomposition of a Solid

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The topochemical kinetics has been derived for the decomposition of rectangular prismatic crystals with a certain particle size distribution. It is shown that narrow rectangular and Gaussian size distributions can result in approximately the same kinetics. For these distributions, the degree of reaction has been tabulated for selected values of a reduced time, the crystal length ratios, and a distribution parameter. The reduced theoretical decomposition curves are shown to agree with the experimental ones for vacuum dehydration of copper(II) chloride dihydrate.

The thermal decomposition of a solid is a complex process¹ involving several stages such as nucleation,²⁻⁴ breaking of bonds,⁵⁻⁷ desorption, diffusion,⁸ and heat transfer.⁹

When bond breaking is the rate determining step, the degree of reaction may be given by

$$\alpha(t) = 1 - (1 - k_n t)^n \quad (1)$$

where the rate constant k_n is dependent on temperature and mean particle diameter. Deviations from the simple rate law, which is valid for unisized cubes or spheres ($n=3$), quadratic plates ($n=2$) or needles ($n=1$), will occur for other crystal habits and for samples with a particle size distribution.

Hume and Colvin¹⁰ have considered the decomposition of a rectangular parallelepiped while Eckhardt and Flanagan¹¹ considered a monoclinic crystal. The influence of particle size distribution has been discussed by Trambouze and Imelik,¹² who considered spherical particles with a Gaussian and a log-normal size distribution. The present work deals with the size distribution of rectangular parallelepipeds.

THEORY

Let us consider a sample of N prismatic crystals each with the edge lengths a_j , b_j , c_j . Then the degree of reaction at time t may be calculated from the volume, $V(t)$, of unreacted material by

$$\alpha(t) = 1 - \frac{V(t)}{V(0)} \quad (2)$$

When the reaction at the surface boundary is the rate determining step, the thickness of product layer is proportional to time.

Thus the volume of unreacted material for an anisotropic decomposition can be written as

$$V(t) = \sum_{j=1}^N (a_j - 2k_a t)(b_j - 2k_b t)(c_j - 2k_c t) \quad (3a)$$

where k_a , k_b , k_c denote the individual rate constants for the three main directions. Introducing the overall rate constant $k = \sqrt[3]{k_a k_b k_c}$ and the "kinetic" edge lengths $a_j^* = \frac{k}{k_a} a_j$, $b_j^* = \frac{k}{k_b} b_j$, $c_j^* = \frac{k}{k_c} c_j$ we obtain

$$V(t) = \sum_{j=1}^N (a_j^* - 2kt)(b_j^* - 2kt)(c_j^* - 2kt) \quad (3b)$$

which is identical to the expression for an isotropic reaction with a rate constant k for a crystal of dimensions a^* , b^* , c^* . Therefore the mathematical problem is reduced to a discussion of the isotropic decomposition.

By working out eqn. (3b) and using eqn. (2), the degree of reaction can be given in terms of initial volume V_0 , surface area A_0 , and sum of edge lengths L_0 . The result is

$$\alpha(t) = \frac{A_0}{V_0} kt - \frac{L_0}{V_0} (kt)^2 + \frac{8N_0}{V_0} (kt)^3 \quad (4)$$

Thus the rate constant k may be calculated from the initial slope of the decomposition curve, when the volume-specific surface area A_0/V_0 is known. However, this method is very inaccurate due to the rapid change of slope of the decomposition curve. The rate constant should therefore be calculated from the decomposition curve over its whole range. This may be brought about by polynomial regression analysis or by fitting the experimental data to a master curve, where the degree of reaction

$$\alpha(u) = \frac{A_0 a_m}{2V_0} u - \frac{L_0 a_m^2}{4V_0} u^2 + \frac{N_0 a_m^3}{V_0} u^3 \quad (5)$$

is expressed in terms of a time parameter

$$u = 2kt/a_m \quad (6)$$

and a_m , the mean of the edge length a_j .

The master curve according to eqn. (5) is seen to be independent of the rate constant and therefore of the temperature but dependent on the specific surface area. A more universal master curve is obtained by expressing α in terms of the parameter

$$x = 2kt/a_0 \quad (7)$$

where the cubic mean edge length

$$a_0 = 6V_0/A_0 \tag{8}$$

is defined as the edge length of a cube with the same specific surface area as the sample. The degree of reaction then becomes

$$\alpha(x) = 3x - \frac{9L_0V_0}{A_0^2}x^2 + \frac{216N_0V_0^2}{A_0^3}x^3 \tag{9}$$

In the following we shall discuss the influence of crystal habit and particle size distribution on the coefficients in eqn. (5) and (9). For the first moment we will consider the crystals to be uniform in shape, which means that the length ratios $l_1=b_i/a_i$ and $l_2=c_i/a_i$ are the same two for all crystals. In this case the initial volume may be written as

$$V_0 = l_1l_2a_m^3 \sum_{i=1}^N q_i^3 \tag{10}$$

where the reduced edge length q_i is defined as a_i/a_m . By dividing the sample into n fractions, where the i -th fraction consists of ΔN_i crystals with q_i ranging from $q_i - \Delta q/2$ to $q_i + \Delta q/2$, the initial volume may be written as

$$V_0 = l_1l_2a_m^3 \sum_{i=1}^n \frac{\Delta N_i}{\Delta q} q_i^3 \Delta q - \frac{1}{2} l_1l_2a_m^3 (\Delta N_1 q_1^3 + \Delta N_n q_n^3) \tag{11}$$

When the total number of crystals N is sufficiently large and Δq is small, the sum in eqn. (11) may be replaced by an integral. Let further the frequency $\Delta N_i/\Delta q$ be given by the function $G(q)$, whereby

$$V_0 = l_1l_2a_m^3 \int_0^\infty G(q) q^3 dq \tag{12}$$

Similarly we find

$$A_0 = 2(l_1+l_2+l_1l_2)a_m^2 \int_0^\infty G(q) q^2 dq \tag{13}$$

$$L_0 = 4(1+l_1+l_2)a_m \int_0^\infty G(q) q dq \tag{14}$$

$$N_0 = \int_0^\infty G(q) dq \tag{15}$$

Rectangular particle size distribution

In this case $G(q)$ is simply a constant, say g , within the range $1-s \leq q \leq 1+s$ and zero otherwise. By integration of eqns. (12)–(15) we get

$$V_0 = 2l_1l_2a_m^3s(1+s^2) \tag{16}$$

$$A_0 = 4(l_1+l_2+l_1l_2)a_m^2s(1+s^2/3) \tag{17}$$

$$L_0 = 8(1+l_1+l_2)a_ms \tag{18}$$

$$N_0 = 2s \tag{19}$$

which on insertion in eqns. (5) and (9) give us

$$\alpha(u) = \frac{(l_1+l_2+l_1l_2)(1+s^2/3)}{l_1l_2(1+s^2)}u - \frac{1+l_1+l_2}{l_1l_2(1+s^2)}u^2 + \frac{1}{l_1l_2(1+s^2)}u^3 \tag{20a}$$

$$\alpha(x) = 3x - \frac{9(1+s^2)(1+l_1+l_2)l_1l_2}{(1+s^2/3)^2(l_1+l_2+l_1l_2)^2} x^2 + \frac{27(1+s^2)^2l_1^2l_2^2}{(1+s^2/3)^3(l_1+l_2+l_1l_2)^3} x^3 \quad (20b)$$

If the edge length a_j represents the smallest of three characteristic edge lengths a_j , b_j , c_j for a crystal, then the smallest crystals are decomposed completely at the limiting time t_{lim} , defined by

$$2kt_{lim} = a_m(1-s) \quad (21)$$

The corresponding limits of u and x are given by

$$u_{lim} = \frac{2kt_{lim}}{a_m} = 1-s \quad (22)$$

and the relation

$$x = \frac{2kt}{a_0} = \frac{(l_1+l_2+l_1l_2)(1+s^2/3)}{3l_1l_2(1+s^2)} u \quad (23)$$

For times greater than t_{lim} the volumes of unreacted material for the smallest crystals are calculated according to eqn. (3b) to be negative. Consequently eqns. (20a) and (20b) should be applied only for values of x , u , and t less than their limiting values. Therefore the distribution function $G(q)$ should only be related to the number of crystals not being decomposed totally, whereby $G(q)$ is to be nonzero within the range $u \leq q \leq 1+s$, when u is greater than u_{lim} . Hence, the degree of reaction should be calculated from

$$\begin{aligned} V(u) &= \int_u^{1+s} ga_m^3(q-u)(l_1q-u)(l_2q-u)dq \\ &= ga_m^3 \left[\frac{l_1l_2(1+s)^4}{4} - \frac{(l_1+l_2+l_1l_2)(1+s)^3}{3} u + \frac{(1+l_1+l_2)(1+s)^2}{2} u^2 \right. \\ &\quad \left. - (1+s)u^3 + \left(\frac{1}{2} - \frac{l_1+l_2}{6} + \frac{l_1l_2}{12} \right) u^4 \right] \quad (24) \end{aligned}$$

and eqns. (2) and (16) giving

$$\begin{aligned} \alpha(u) &= 1 - \frac{(1+s)^4}{8s(1+s^2)} + \frac{(l_1+l_2+l_1l_2)(1+s)^3}{6l_1l_2s(1+s^2)} u - \frac{(1+l_1+l_2)(1+s)^2}{4l_1l_2s(1+s^2)} u^2 \\ &\quad + \frac{1+s}{2l_1l_2s(1+s^2)} u^3 - \frac{6+l_1l_2-2l_1-2l_2}{24l_1l_2s(1+s^2)} u^4 \quad (25) \end{aligned}$$

and in the special case of cubes:

$$\alpha(u) = 1 - \frac{(1+s-u)^4}{8s(1+s^2)} \quad (26)$$

The expression in terms of x are more complicated and computations of $\alpha(x)$ are performed most conveniently by first calculating related value of u according to eqn. (23).

Gaussian particle size distribution

If the distribution function is given by

$$G(q) = g \exp \left[-\frac{3}{2} \left(\frac{q-1}{s} \right)^2 \right]$$

eqn. (12) becomes

$$V_0 = l_1 l_2 a_m^3 g \int_0^\infty \exp \left[-\frac{3}{2} \left(\frac{q-1}{s} \right)^2 \right] q^3 dq \quad (27)$$

Introducing $y = \sqrt{\frac{2}{3}} \left(\frac{q-1}{s} \right)$ we get

$$V_0 = \sqrt{\frac{2}{3}} s l_1 l_2 a_m^3 g \left[\int_{-\sqrt{3/2}/s}^\infty e^{-y^2} dy + \sqrt{6} s \int_{-\sqrt{3/2}/s}^\infty e^{-y^2} y dy + 2s^2 \int_{-\sqrt{3/2}/s}^\infty e^{-y^2} y^2 dy + \sqrt{\left(\frac{2}{3}\right)^3 s^3} \int_{-\sqrt{3/2}/s}^\infty e^{-y^2} y^3 dy \right] \quad (28)$$

For narrow distributions, where s is small, the expression may be approximated by changing the lower integration limit to $-\infty$. Then the four integrals take the values of $\sqrt{\pi}$, 0 , $\sqrt{\pi}/2$, and 0 , respectively, whence the volume

$$V_0 = \sqrt{\frac{2\pi}{3}} s g a_m^3 l_1 l_2 (1+s^2) \quad (29)$$

Similarly we obtain

$$A_0 = 2 \sqrt{\frac{2\pi}{3}} s g a_m^2 (l_1 + l_2 + l_1 l_2) (1+s^2/3) \quad (30)$$

$$L_0 = 4 \sqrt{\frac{2\pi}{3}} s g a_m (1 + l_1 + l_2) \quad (31)$$

$$N_0 = \sqrt{\frac{2\pi}{3}} s g \quad (32)$$

Insertion of these quantities into eqn. (9) yields an expression identical to (20b). Thus narrow Gaussian and rectangular particle size distributions will result in approximately the same kinetics.

When the standard deviation related to the Gaussian distribution is denoted by σ , then according to eqn. (22) $\sigma = s/\sqrt{3}$. For cubical particles eqn. (20a) then reduces to

$$1-\alpha = (1-u) \left[\frac{a(1-u)^2 + 3\sigma^2}{1+3\sigma^2} \right] \quad (33)$$

which is identical to the expression derived for spheres by Trambouze and Imelik.¹²

which are the coefficients in eqn. (20b) for the rectangular distribution parameter s equal to zero. This equation should hold for the reduced time u less than any of the quantities $1-s_a$, $l_1(1-s_b)$, and $l_2(1-s_c)$. Within this region a sample of crystals of completely nonuniform shape and size may decompose with just the same kinetics as that of a single crystal. Therefore the largest deviations from the rate expression for a single crystal should occur for samples of size distributed crystals when the crystals are uniform.

RESULTS AND DISCUSSION

A FORTRAN-4 computer program RECTA has been written for computation of the degree of reaction according to eqns. (20b) and (25). Herein the degree of reaction has been defined as a function, *recta* (l_1 , l_2 , s , x), of the length ratios, l_1 and l_2 , the particle distribution parameter, s , and the reduced time, x . The calculations have been performed on an IBM-7094 computer at NEUCC in Lyngby and an example of the results are given in Table 1 and Fig. 1. (A complete table can be obtained by writing to the author).

The reduced decomposition curve turns out to be more sensitive towards alterations of the length ratios than to alterations in the particle size distribution. Thus the influence of the particle size distribution can be detected only for $\alpha > 0.5$, while the influence of length ratios may be detected already at $\alpha = 0.2$. It is further seen that both factors will exert their greatest influence on the α, x curve, when $x \approx 0.6$, corresponding to $\alpha = 0.9$. Therefore reliable

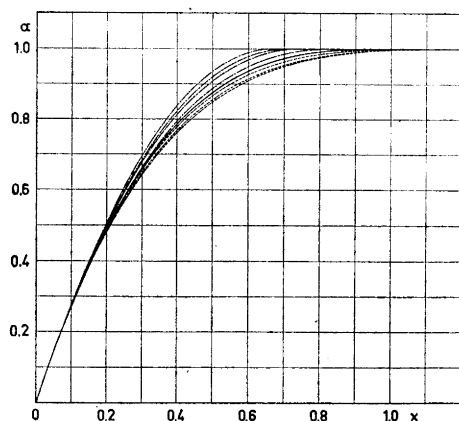


Fig. 1. Reduced, theoretical decomposition curves for samples of rectangular prismatic crystals with a rectangular size distribution. Curves for *recta* ($l_1, l_2, 0, x$) are drawn in full for $l_2=1$ and dot and dashed for $l_2=2, 4, 8, \text{ and } 128$ (at top), while *recta* ($l_1, 1, s, x$) are shown interrupted for $s=0.3, 0.5, \text{ and } 1.0$ (at bottom).

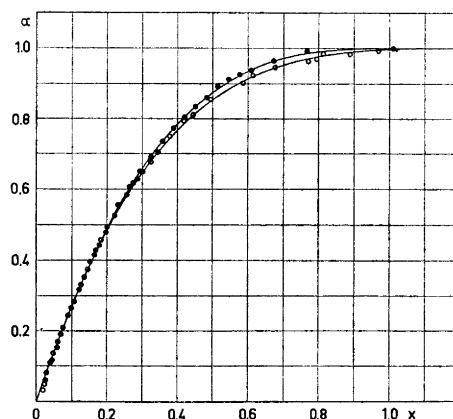


Fig. 2. Reduced, experimental decomposition curves for copper(II) chloride dihydrate. Filled circles: Single crystal data unfilled circles: Polycrystalline data. Fully drawn curves represent *recta* ($l_1, 1, s, x$) with $s=0.0$ (upper curve) and 0.5 (lower curve).

values of l_1 , l_2 , and s cannot be obtained from the reduced decomposition curve, unless this has been determined for the entire range of α .

In the following the theory will be illustrated by experimental α, x curves for the vacuum dehydration of crystals of copper(II) chloride dihydrate. Single crystals as well as polycrystalline material have been investigated by a method described previously.¹³ As the kinetics will later be discussed in details, this paper presents results only from the decomposition of one single crystal ($0.82 \times 0.52 \times 5.6$ mm) and of one 0.5–1.0 mm sieve fraction with the microscopically determined $s=0.6$. The influence of the particle size distribution is demonstrated in Fig. 2, where the single crystal data are seen to be well represented by recta (1, 1, 0, x), whereas the polycrystalline data concentrate about recta (1, 1, 0.5, x). The overall rate constant at 25°C is found to be 1.42×10^{-3} cm h⁻¹ for the single crystal and 1.41×10^{-3} cm h⁻¹ for the sieve fraction.

It has thus been shown that the kinetics of the vacuum dehydration of copper(II) chloride dihydrate may be explained by the topochemically derived rate expression, which is valid for decompositions, where neither nucleation nor diffusion is the rate determining step. For such cases the application of the theory to polycrystalline solids yields the same rate constants as those obtained for single crystals.

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