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A Theory of Surface Nucleation, its Relation to Erofeyev's Equation, and its Application to the Thermal Decomposition of Cobalt(II) Carbonate and Nickel Oxalate

ARNE ENGBERG

The Technical University of Denmark, Chemistry Department A, Building 207,
DK-2800 Lyngby, Denmark

A theory of surface nucleation has been developed for the thermal decomposition of solids. The nuclei were presumed to be randomly distributed on a certain number of lines, which again were randomly distributed over the surface of prismatic crystals. Hereby, were explained the non-integral and varying values for the apparent reaction order, which occurs in Erofeyev's equation. Thus, the decomposition of cobalt(II) carbonate could be described satisfactorily by a model of instantaneous nucleation of only a single pair of (opposite) crystal faces, while the decomposition of nickel oxalate, which is accompanied by a considerable induction period, first at the later stages followed the same kinetics as for the cobalt(II) carbonate.

Though dehydration of salt hydrates or calcination of carbonates may seem to be simple processes, the kinetics for those and other thermal decompositions have been shown to be far from simple. Depending on the experimental conditions (*e.g.* atmosphere, vapour pressure, and prehistory of the solid) the recorded reaction curve (degree of reaction *versus* time) may or may not exhibit a sigmoid shape. In the latter case the initial straight line and the succeeding decay period have been explained by the growth of a uniform product layer from the outside of the particles leaving a kernel of unreacted material. Consequently, the kinetics could be derived from the outer geometry of the particles as has been done for spheres [1] and parallelepipeds,[2] though it was found later that the size distribution of the particles should also be taken into consideration.[3–5] In case of a sigmoid curve the acceleratory period has been explained by the activation and growth of a limited number of growth nuclei located either on the surface [6,7] or in the volume.[10–17] The decay period can also be described in many cases – if not in all by reversible reactions – by the topochemical kinetics mentioned above.[1–5] Thus surface nucleation tends to be favoured. However, the expressions derived by Mampel,[7] extended by Delmon,[8] and reviewed by Young [9] have not been much used, probably because of their rather complicated nature. So far they have been overshadowed by the theories based on volume nucleation, including those of Avrami,[10–11] Erofeyev,[12] Prout-Tompkins,[13] and the versions of Garner's theory of linear branching chains.[14–17] While the Avrami-Erofeyev equation may be expected to describe satisfactorily such physical processes as recrystallizations and phase transitions, the assumption of volume nucleation appears unrealistic for chemical processes where gases are involved. Due to larger lattice vibrations caused by the partial potential, the probability of a chemical dissociation and, hence, of a nucleation should be larger at the surface. This may be the reason why deviations have been observed even in the allotropic transformation of tin [18] for the ultimate part of the reaction curve.

In the Avrami-Erofeyev equation, which reads

$$\alpha = 1 - e^{-Kt^m} \tag{1}$$

the exponent, $m = n + i$, is assumed to be the sum of the dimensionality, n, and the number of nucleation steps, i. Thus, an integral number should be expected for the slope, m, when $\ln[-\ln(1-\alpha)]$ is plotted against $\ln(t)$. In practice, however, broken or extremely low or high values may be found together with deviations from the straight line in the decay period. From the literature the initial and final values of m for following decompositions can be extracted: 2.5 – 3.1, 2.9 – 5.1 ($KMnO_4$),[19] 5.0, 3.2 (NiC_2O_4), [20] 0.7 – 1.9, 0.7 – 1.0 (MgC_2O_4),[21] and 1.48, 1.67 ($CoCO_3$).[22]

In the following it will be shown how m may be rationalized into meaningful values by allowance of a certain induction period, t_0, (the observed times, t_{obs}, being reduced by t_0; that is, $t = t_{obs} - t_0$) and how the decay period can be explained by surface nucleation.

While Avrami [10] supposed nucleation to be a first order process (to be derived, if all germs are nucleated with the same probability), Mampel [7] considered the extreme case of a constant nucleation rate. Here, the other extreme case, that of instantaneous nucleation, will be considered. The latter case not only leads to especially simple equations, but is presumed to represent the decomposition of solids in a dynamic vacuum more realistically than does a constant nucleation rate.

Instead of a random nucleation, as supposed by Avrami, Mampel, and Delmon, a distribution of the germs on certain lines will be assumed in harmony with the inference given by Young [23] for the decomposition of nickel oxalate and the observations made on calcite [24] and nickel sulphate hexahydrate.[25]

The basis of the growth nuclei on the surface has formerly been considered as circular in harmony with the observations on tin [18] and chrome alum [26] (with the nuclei growing inwards as hemispheres). However, a square basis will be assumed here in harmony with that observed on nickel sulphate hexahydrate.[25] In order to further facilitate the calculations the growth nuclei will be considered as hemicubes instead of the hemioctahedra that are observed.[25]

THE SURFACE REACTION

Consider a rectangular planar surface with sides b and c and containing a number of lines, l_0, running parallel to c, but randomly distributed over the surface. Furthermore let the basis of the growth nuclei be squares of sides $2k_gt$, orientated parallel to b and c, and with their centers located on the lines so that each line contains m_0 randomly distributed centers (see Fig. 1).

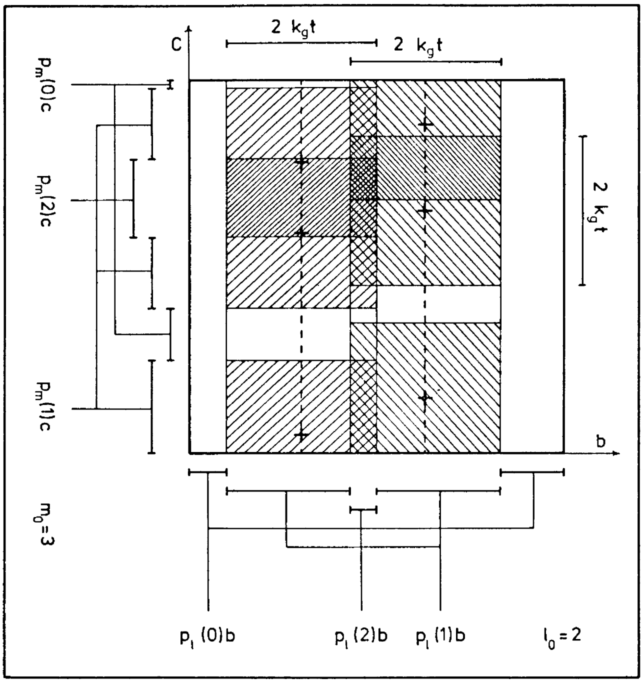

Fig. 1. Model for coverage of a crystal surface with growth nuclei. The centers of the growth nuclei (+) are located on two lines (- - -) running parallel to the side c.

Now, according to Mampel,[7] the probability that a given point on a growth line has been covered by i overlapping growth nuclei originating from the same line should be given by the Poisson formula

$$p_m(i) = (\mu^i/i!)e^{-\mu} = [(2k_gtm_0/c)^i/i!]e^{-(2k_gtm_0/c)} \tag{2}$$

where the average, μ, for the present case will equal the total length of the nuclei, $2k_gtm_0$, divided by the length of the line, c. The probability that a point on the surface has been covered by j overlapping growth lines is expressed in a similar way by

$$p_l(j) = [(2k_gtl_0/b)^j/j!]e^{-(2k_gtl_0/b)} \tag{3}$$

It will appear from Fig. 1 that the total area of the uncovered surface can be estimated by the sum of the areas for the rectangles of breadths $\mathrm{p}_1(j)b$ and hereto corresponding lengths $[\mathrm{p}_m(0)]^j c$. Thus, the degree of covered surface, θ, should amount to

$$\theta(t) = 1 - \sum_{j=0}^{l_0} p_1(j)[p_m(0)]^j \tag{4}$$

which on insertion of (2) and (3) gives

$$\theta(t) = 1 - \sum_{j=0}^{l_0} \frac{(2k_\mathrm{g}tl_0/b)^j}{j!} \mathrm{e}^{-(2k_\mathrm{g}tl_0/b)} \mathrm{e}^{-j(2k_\mathrm{g}tm_0/c)} \tag{5}$$

By introduction of a reduced time, u,

$$u = 2k_\mathrm{g}t/a \tag{6}$$

where a is the thickness of the crystal (normal to the surface under consideration), and the reduced number of germs, M, and lines, L,

$$M = m_0a/c \tag{7}$$

$$L = l_0a/b \tag{8}$$

eqn. (5) simplifies to

$$\theta(u) = 1 - \sum_{j=0}^{L} \frac{(Lu)^j}{j!} \mathrm{e}^{-Lu} \mathrm{e}^{-jMu} \tag{9}$$

The upper summation limit should not have been changed into L (unless $l_0 = L$ for $a = b$) but the error thus produced will be of minor importance.

For description of the acceleratory phase of the reaction the exponential terms in (9) can be expanded in a power series, yielding

$$\theta(u) = LMu^2[1 - \tfrac{1}{2}Mu - \tfrac{1}{2}M(L - \tfrac{1}{3}M)u^2 + \tfrac{1}{2}M^2(L - \tfrac{1}{12}M)u^3 + \cdots] \tag{9a}$$

Thus, $\theta(u)$ tends to approach LMu^2 at the very beginning, which is to be expected, when $LM = N$ represents the reduced number of growth nuclei in total and u^2 stands for the reduced area for a single growth nucleus.

If Mu is very small compared to unity, then eqn. (9) reduces to

$$\theta(u) = 1 - \mathrm{e}^{-LMu^2} = 1 - \mathrm{e}^{-Nu^2} \tag{9b}$$

to be expected for a completely random distribution of the germs. If on the other hand Mu is very large compared to unity, then eqn. (9) reduces to

$$\theta(u) = 1 - \mathrm{e}^{-Lu} \tag{9c}$$

to be expected for the growth from randomly distributed lines. Thus, the ratio M/L will be determining for the tendency of the germs to array themselves on a line.

THE VOLUME REACTION

Consider a rectangular parallelepiped as shown in Fig. 2, where the faces normal to the sides a, b, and c have reacted to the respective degrees of surface coverage, θ_a, θ_b, and θ_c. Provided that nucleation is instantaneous and that the growth nuclei are hemicubes (or just cylindrical with the axis normal to the surface), the degree of coverage for a plane parallel to the surface and at a certain distance below it will be independent of the depth when this is smaller than $k_g t$. Otherwise the degree of coverage will be zero. Hereby, the evaluation of the reacted volume has been greatly simplified. It will appear from Fig. 2 that there are three growth domains in the model crystal: I with growth from a single face, and II and III with interfering growth from two and three faces, respectively. For the first domain the reacted volume, v_I, is found as a sum of the areas, *e.g.* $(b-2k_g t)(c-2k_g t)$, multiplied by their respective degrees of coverage, θ_a, and the depth $k_g t$,

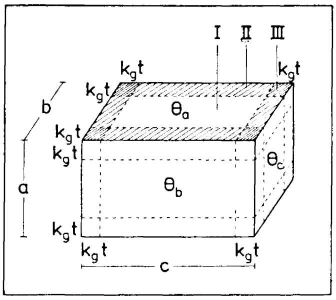

Fig. 2. Penetration of the growth layers from the various faces of the model crystal shown by dotted lines. Ingestion of the growth layers from either two or three faces are shown by the hatched areas, respectively.

$$v_\text{I} = 2k_g t\sum_{a}^{c}(b-2k_g t)(c-2k_g t)\theta_a \tag{10}$$

When the overlapping growth nuclei originate from more than one face, the resultant probability for an uncovered surface element should be the product of the individual probabilities for uncovering for the faces in question. Hence, for that part of domain II, where growth layers normal to a and b are overlapping, the total degree of covering, θ_ab, becomes

$$\theta_\text{ab} = 1-(1-\theta_a)(1-\theta_b) \tag{11}$$

In a similar way the degree of coverage, θ_{abc}, is obtained for domain III,

$$\theta_{abc} = 1-(1-\theta_a)(1-\theta_b)(1-\theta_c) \tag{12}$$

Consequently, the reacted volumes of domains II and III become

$$v_\text{II} = 4(k_g t)^2\sum_{a}^{c}(a-2k_g t)[1-(1-\theta_b)(1-\theta_c)] \tag{13}$$

$$v_\text{III} = 8(k_g t)^3[1-(1-\theta_a)(1-\theta_b)(1-\theta_c)] \tag{14}$$

By introduction of (6) and the elongations l_1 and l_2,

$$l_1 = b/a;\ l_2 = c/a \tag{15}$$

the degree of reacted volume, α, can be expressed by

$$\alpha = (v_{\mathrm{I}} + v_{\mathrm{II}} + v_{\mathrm{III}})/abc = (\theta_a + \theta_b/l_1 + \theta_c/l_2)u - (\theta_b\theta_c/l_1l_2 + \theta_a\theta_c/l_2 + \theta_a\theta_b/l_1)u^2 + (\theta_a\theta_b\theta_c/l_1l_2)u^3 \tag{16}$$

where θ_a, θ_b, and θ_c depend on u according to (9).

The universality of the expression given above will be shown in the following by the extremes that can be derived from it. The first one to be considered is that derived when the ratios θ_b/l_1 and θ_c/l_2 are either vanishing or identical with θ_a $(=\theta)$,

$$\alpha(u) = 1-(1-\theta u)^n \qquad (n = 1, 2, \text{ or } 3) \tag{16a}$$

which further simplifies for $\theta = 1$ to the well known expression for a n-dimensional phase boundary reaction. Thus, a low dimensionality of a reaction can be produced either by a preferential nucleation of some of the faces (θ_b or θ_c vanishing) or by a preferential growth of the dimensions (l_1 or l_2 large).

At this stage it must be emphasized that (16) should apply equally well for anisotropic reactions, provided that the geometric elongations defined in (15) have been replaced by the corresponding kinetic quantities

$$l_1 = (k_a/k_b)(b/a);\ l_2 = (k_a/k_c)(c/a) \tag{15a}$$

obtained by multiplication of the geometric elongations by the proper ratios of the anisotropic rate constants k_a, k_b, and k_c (for reactions along a, b, and c, respectively).

The second extreme to be mentioned is that occurring when the faces have been covered totally by the growth nuclei. By a reasonable large number of germs this may be realized even in an early stage of the process, whereafter the general topochemical expression [5] should be followed,

$$\alpha(u) = \frac{l_1 + l_2 + l_1l_2}{l_1l_2}u - \frac{1 + l_1 + l_2}{l_1l_2}u^2 + \frac{1}{l_1l_2}u^3 \tag{16b}$$

At the end of the reaction, when $2k_gt$ has grown larger than one of the dimensions corresponding to u larger than unity (when a is smallest dimension), at least one pair of the growth layers which originate from opposite faces, would have grown into each others. As the phenomenon has not been considered by the derivations, (16) should apply strictly for the previous period only (u less than unity). In practice, however, the equation may reproduce also the following period satisfactorily, especially for an apparent three-dimensional reaction. Thus, the transition ($u = 1$) should occur at a degree of reaction of at least $\alpha_{\mathrm{trans}} = 1 - e^{-3} = 0.95$ (corresponding to $ML = 1$) and usually at much higher values (*e.g.* $\alpha_{\mathrm{trans}} = 0.9998$ for $ML = 3$).

Greatest deviations should be expected for an apparent unidimensional reaction, where the transition may occur at a degree of reaction as low as 0.63. Therefore, the correct treatment shall be given for this type of reaction. Putting θ_b/l_1 and θ_c/l_2 equal to zero in (16) or n equal to unity in (16a) results in the description of the first period ($u \leq 1$; $k_gt \leq a/2$),

$$\alpha(u) = \theta u = \left[1 - \sum_{j=0}^{L} \frac{(Lu)^j}{j!} \mathrm{e}^{-Lu} \mathrm{e}^{-jMu}\right] u \tag{17a}$$

In the following period ($1 \leq u \leq 2$) the two growth layers have grown into each other within a layer of reduced thickness $u-1$ in the middle of the particle. Then, according to (11), the degree of covering within the overlap layer should amount to $2\theta - \theta^2$, provided that the surface coverages, θ, are identical for the two nucleation faces in question. As $2-u$ will represent the thickness of the other layers (the bread of the sandwich), the degree of reacted volume should be given by

$$\alpha(u) = \theta(2-u) + (2\theta - \theta^2)(u-1) = \theta u - \theta^2(u-1) \tag{17b}$$

When the growth layers have reached the opposite faces ($2 \leq u$), no further growth in thickness is possible, the growth being limited to the two other dimensions for completion of the reaction. The ultimate period is thus described by

$$\alpha(u) = 2\theta - \theta^2 \tag{17c}$$

By introduction of a cutting-off function $\mathrm{F}(x)$, defined as

$$\mathrm{F}(x) = \begin{cases} 0 \ (x \leq 0) \\ x \ (0 \leq x \leq 1) \\ l \ (l \leq x) \end{cases} \tag{18}$$

the kinetics for the three periods given above can be combined into the following expression,

$$\begin{aligned} \alpha(u) &= 2\theta\ \mathrm{F}(u/2) - \theta^2\ \mathrm{F}(u-1) \\ &= 2\left[1 - \sum_{j=0}^{L} \frac{(Lu)^j}{j!} \mathrm{e}^{-Lu} \mathrm{e}^{-jMu}\right] \mathrm{F}(u/2) - \\ &\quad \left[1 - \sum_{j=0}^{L} \frac{(Lu)^j}{j!} \mathrm{e}^{-Lu} \mathrm{e}^{-jMu}\right]^2 \mathrm{F}(u-1) \end{aligned} \tag{19}$$

REACTION OF HETEROSIZED PARTICLES

Besides overlap and ingestion of the growth nuclei described above the decay period of the reaction curve may be influenced by the diffusion of gaseous products and, when particulate samples are used, by the particle size distribution. As long as reactions of small particles in dynamic vacuum are discussed, the diffusion may be of minor importance. Therefore, the discussion will concentrate on the effect from the particle size distribution.

Let the sample consist of crystals with a pair of invariant nucleation faces, bc, and with the thickness, a, being distributed over a certain number of classes, such that the i-th class contains a number, n_i, of crystals of dimension a_i. Instead of (19) it can then be shown that

$$\alpha(u) = 2\theta \sum \frac{n_i a_i}{\sum n_i a_i} \mathrm{F}\left(\frac{u \sum n_i a_i}{2 a_i \sum n_i}\right) - \theta^2 \sum \frac{n_i a_i}{\sum n_i a_i} \mathrm{F}\left(\frac{u \sum n_i a_i - 1}{a_i \sum n_i}\right) \tag{20}$$

provided that the reduced time u is on basis of the mean dimension $\bar{a}$,

$$\bar{a} = \sum(n_i a_i / \sum n_i) \tag{21}$$

to be inserted in (6).

The expression can be simplified somewhat by introduction of the normalized frequencies, f_i, and the reduced dimensions, q_i,

$$f_i = n_i / \sum n_i \tag{22}$$

$$q_i = a_i / \bar{a} \tag{23}$$

whereby (20) reduces to

$$\alpha(u) = 2\theta \sum f_i q_i \,\mathrm{F}\left(\frac{u}{2q_i}\right) - \theta^2 \sum f_i q_i \,\mathrm{F}\left(\frac{u}{q_i} - 1\right) \tag{24}$$

RESULTS AND DISCUSSION

Some calculations have been made on a Wang model 700 desk computer using a program written for the purpose and based on (9) and (20) (or (24)). The program was designed to operate mainly with the number distributions determined by microscopy of a relatively low number of particles. For this reason and because of the low storage capacity of the computer (120 registers), the particle size distribution was assumed to be present as a ten-class histogram. In the calculations to be reported here approximations to the log-normal weight distribution were used. This is the distribution which to a greater extent was found obeyed for precipitates such as AgCl in photographic emulsions,[27] $BaSO_4$,[28] and $CuSO_4.5H_2O$.[29] Consequently, the corresponding number distribution should be given by

$$f_i = (\text{constant})\, q_i a^3 \exp\left[-(\ln q_i - \ln q_{\text{mode}})^2 / 2\sigma^2\right] \tag{25}$$

with the constant $= \exp[-2\sigma^2] / [\sigma(2\pi)^{\frac{1}{2}}]$

Table 1. Approximated number distributions for log-normal weight distributions with the frequency given in percentage.

σ	q/q_{mode}										$1/q_{\text{mode}}$
	0.4	0.5	0.6	0.7	0.8	0.9	1.1	1.3	1.5	1.7	
0.1				0.54	9.03	56.70	32.30	1.42	0.01		0.9602
0.2	0.04	0.89	5.39	14.17	21.24	32.70	19.52	5.01	0.89	0.15	0.8961
0.3	4.30	10.09	15.85	17.80	16.00	18.49	11.22	4.19	1.40	0.66	0.7919

σ	q/q_{mode}										$1/q_{\text{mode}}$
	0.2	0.3	0.4	0.5	0.7	0.9	1.1	1.5	1.9	2.5	
0.2			0.04	3.38	29.64	40.37	24.37	2.15	0.05		0.8891
0.3	0.02	0.53	4.90	19.66	33.74	23.40	14.58	2.84	0.31	0.02	0.7757
0.4	1.72	6.96	13.25	28.56	25.07	13.30	8.41	2.22	0.45	0.06	0.6546
0.5	10.82	17.28	17.96	24.32	15.69	7.30	4.74	1.42	0.39	0.08	0.5253

For the precipitates mentioned above σ was observed in the range of $0.2-0.5$. In Table 1 the histograms are given which have been used to reproduce (25). It will appear that two sets of class interval have been chosen in order to obtain reasonable approximations over the whole range of the dispersion.

The results in Fig. 3 are shown for the case in which the reaction is under the influence of particle size distribution alone ($M=L=\infty$). Apart from the mean size, whose influence has been eliminated by introduction of the reduced time u, the further influence – namely that from the dispersion – is seen to result in a retardation of the later stages of the reaction. In fact, for all relevant magnitudes of the dispersion only the upper halfs of the reaction curves will be affected by the particle size distribution, which is in agreement with earlier findings.[5] Although the curves may appear somewhat edged because of the coarseness in the histograms used, the duplicates (for $\sigma=0.2$ and 0.3) run close together, which indicate that the deviations from the master curves (those for the true log-normal distribution) are relatively small.

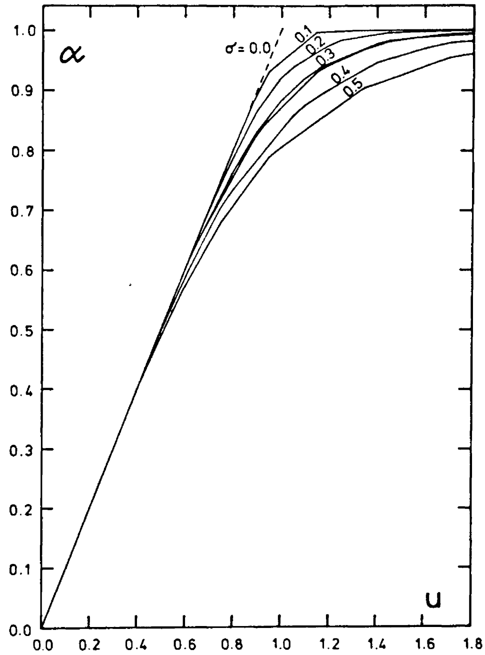

Fig. 3. Reaction curves for an apparent unidimensional reaction in the topochemical limit ($\theta=1$) for particles with approximated log-normal weight distributions (Table 1).

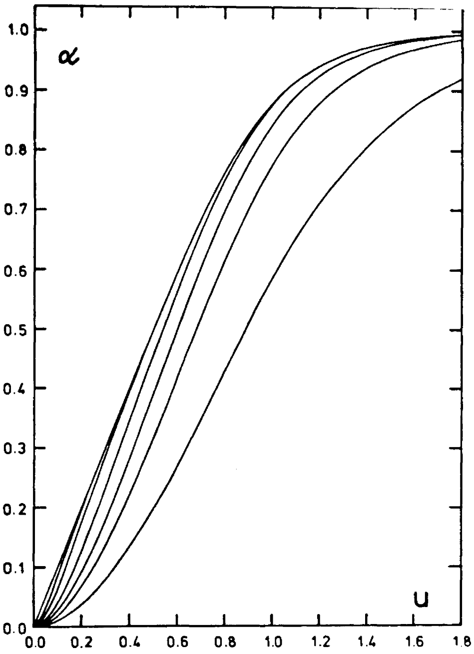

Fig. 4. Reaction curves for an apparent unidimensional reaction for particles with an approximated log-normal weight distribution ($\sigma=0.3$) and with solid ($M=\infty$) growth lines of following numbers: $L=\infty$, 20, 10, 5, 3, 2, 1 (for the curves from top to bottom).

When the reaction initiates from a limited number of growth lines, a more or less pronounced acceleratory period is found even if an infinite number of growth nuclei are present as shown in Fig. 4. The reaction curves begin as parabolas which can be realized by the approximation of (17a),

$$\alpha(u) = [1 - \mathrm{e}^{-Lu}]u + \cdots = Lu^2 + \cdots \tag{26}$$

but because of the growth overlap they soon approach the corresponding topochemical curve (*cf.* Fig. 3) until practical coincidence, the occurrence of which is determined by L. For many lines ($L > 20$) the coincidence occurs already in the first stages of the reaction ($\alpha \leq 0.2$), while few lines ($L < 4$) can remove the coincidence. It must also be emphasized that the infinite number of lines assumed in topochemical kinetics, in practice is satisfied, when L is in the order of 100. When L is larger than 10, the coincidence will occur within the first half of the reaction, which means that the two phenomena, growth from nucleation lines and particle size distribution, can be discussed independently of each other. All of the curves are remarkably close to straight lines when $0.2 < \alpha < 0.6$ but their slopes deviate somewhat from that of the interfacial reaction ($L = \infty$) within the limits of 10 % above ($L = 10$) and 20 % below ($L = 1$). Consequently, the rapid estimate of k_g/a obtained from the slope may be inaccurate, while a more reliable estimate must be gained from the ultimate part of the reaction where the influence from the growth lines has been reduced to a minimum.

According to (26) an estimate of L may be obtained from the initial slope of $[\alpha(u)]^{\frac{1}{2}}$, but an examination of Fig. 5 reveals that the predicted straight line is followed over a very narrow range ($0 < \alpha < 0.006$) when M is large. When M is small, however, $\mathrm{d}[\alpha(u)]^{\frac{1}{2}}/\mathrm{d}u$ is constant over a considerably larger part of

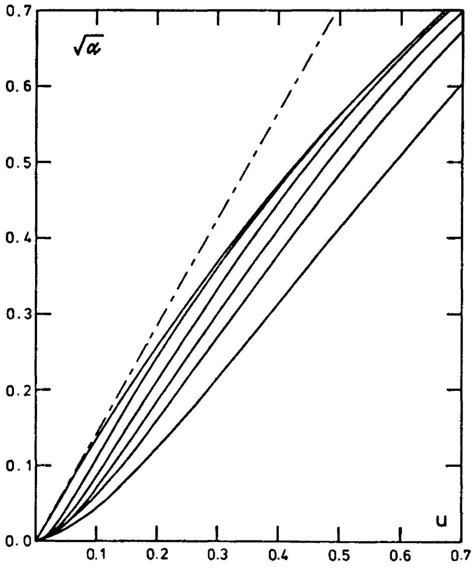

Fig. 5. The acceleratory period ($\alpha^{\frac{1}{2}}$ *versus* u) for one of the reaction curves in Fig. 4 ($L = 2$, $M = \infty$) together with curves for a decreasing number of nuclei, $M = \infty$, 10, 5, 3, 2, 1 (for the curves from top to bottom).

the curves, but the slope is somewhat dependent on M: 1.414 ($M=\infty$), 1.377 ($M=10$), 1.249 ($M=5$), 1.160 ($M=3$), 1.096 ($M=2$), 1.000 ($M=1$).

When the reaction curves are transformed into Erofeyev plots, nearly straight lines are produced and in such a way that each curve may be approximated by two lines bisecting each other at about 0.4. In Fig. 6 such curves have been drawn for the same material as presented in Fig. 4. The apparent reaction order given by the slope is dependent on L, but the variations are largely concentrated to the lower half of the reaction as can be realized from the following figures: 1.06, 1.63($L=\infty$); 1.32, 1.63($L=20$); 1.57, 1.63($L=10$); 1.68, 1.74($L=5$); 1.84, 1.91($L=3$); 1.96, 2.00($L=2$); 1.94, 1.89 ($L=1$). The first of these figures are valid for the region $0.05<\alpha<0.2$ while the second ones are valid for the region $0.5<\alpha<0.9$. This is just in accordance with the theory since the first reaction order should be affected by the number and distribution of the growth nuclei and thus vary between the topochemical limit (1) and the limit of a two dimensional growth of nuclei (2), while the final reaction order should be determined by the topochemical properties of the sample material.

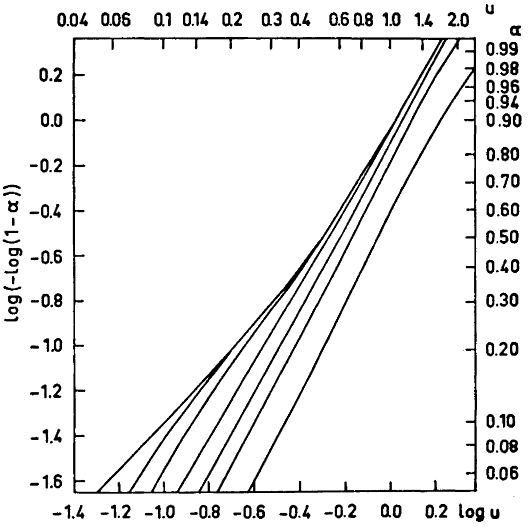

Fig. 6. Erofeyev plot ($\log[-\log(1-\alpha)]$ *versus* $\log u$) for the same reaction curves as in Fig. 4.

Although the above discussion has been limited to the apparent unidimensional reactions, it is also true that for other types of reactions a non-integral or varying reaction order may in general be explained by a surface nucleation.

Finally, some experimental results will be taken from the literature and related to the theory. For the thermal decomposition of commercial cobalt(II) carbonate Avramov and Janatchkova [22] found the Erofeyev equation to be obeyed with reaction orders ranging from 1.37 (at 220°C) to 2.54 (at 270°C) in dependence of temperature. The kinetics could have been described better by the Erofeyev equation if an induction period had been included. Thus, for the lowest temperature the initial reaction order (taken for the region $0.05 \leq \alpha \leq 0.20$) could be moved from 1.48 ($t_0 = 0$) to 1.67 ($t_0 = 5$) and 2.00 ($t_0 =$ 10 min), whereas the final reaction order of 1.67 (for the region $0.5 \leq \alpha \leq 0.9$) is scarcely changed. By the first movement the reaction is described by a constant reaction order, and by the second movement the initial reaction order assumes a meaningful value. The discrepancy between the slopes reported here (1.48) and those reported earlier (1.37) originates from the fact that Avramov and Janatchkova did not normalize α to unity for the maximum degree of reaction as done here. Their values for α were based on the reaction scheme

$$CoCO_3 + \tfrac{1}{6}O_2 \rightarrow \tfrac{1}{3}Co_3O_4 + CO_2 \quad (27)$$

Their final values amounting to 75–77 % indicate, however, that the sample material after drying at 130°C must have been a basic carbonate

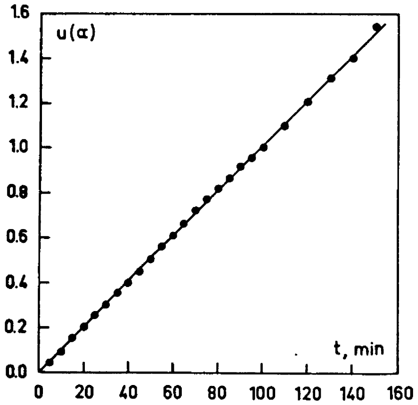

Fig. 7. The inverse reaction curve ($u(\alpha)$ *versus* t) for the decomposition of cobalt(II) carbonate at 220°C.

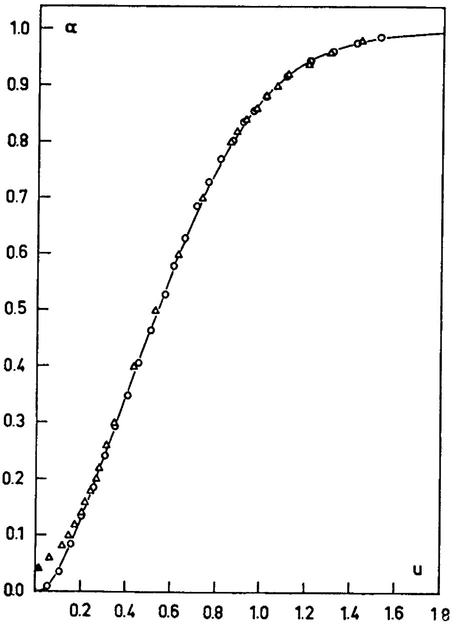

Fig. 8. Reduced reaction curves for the thermal decomposition of cobalt(II) carbonate at 220°C (○) and nickel oxalate at 240°C (△). $u = 2k_g(t_{obs} - t_0)/a$ with $t_0 = 0$ for cobalt(II) carbonate and $t_0 = 98$ min for nickel oxalate. The solid line represents an unidimensional reaction of log-normal weight distributed particles ($\sigma = 0.3$) with $L = 5$ and $M = 20$.

instead of the neutral one assumed. For instance, $2CoCO_3.Co(OH)_2.H_2O$ yields a weight loss of 77.60 % of the reaction scheme mentioned above.

In contrast to the theories of Avrami and Erofeyev the apparent two-dimensional growth in the acceleratory period and a smaller dimensionality in the later stages of the reaction can be explained easily by the present theory. The magnitudes of L, M, and $k=k_g/a$ were estimated in the following way. L was estimated by a comparison of the Erofeyev plot for the observed α with the corresponding theoretical curves in Fig. 6. A translation of the observed curve over the theoretical ones with respect to the time axis gave a practical coincidence of the curves when $L=5$ ($M=\infty$). A somewhat better fit was obtained when α was corrected by an amount $\alpha_0=0.02$ so that $\alpha_{corr}=(\alpha-\alpha_0)/(1-\alpha_0)$, the quantity α_0 being determined as the intercept of the smoothed curve from a α,t^2 plot. A still better fit was also obtained when M was finite, say $M=20$ ($15<M<100$). Furthermore the constant could have been obtained from the comparison mentioned above, as the translation will amount to log k. More accurately, however, k is found as the slope of the straight line obtained, when $u(\alpha)$ has been plotted against t, as shown in Fig. 7. In the present case the linear regression analysis yields $k=(1.013\pm0.012)\times10^{-2}$ min^{-1} with a negligible induction period $t_0=-0.16\pm0.15$ min, and a standard deviation on t of ±0.68 min (corresponding to 0.3 mm on the published curve). The goodness of the fit for the final results can also be realized from Fig. 8. The above mentioned correction by α_0 may be justified if excess water is present and given off rapidly. The observed increase of the reaction order for increasing temperatures may be explained by a lower activation energy for the nucleation than for the growth. Then growth will be more enhanced than nucleation by an increase in temperature with a resulting decrease in number of effective growth nuclei and, consequently (*cf.* Fig. 6), an increase of the reaction order.

When the experimental curves for higher temperatures were treated as above, $N=LM$ was found to decrease gradually from about 100 (220°C) down to 1 (270°C). The apparent activation enthalpy for k of 22.8 kcal/mol then became much closer to the thermodynamic value of 21.8 kcal/mol for bond breaking (removal of carbon dioxide without oxidation of the metal) than did Avramov and Janatchkova's value of 27.85 kcal/mol. If in addition the metal is allowed to oxidize, the latter deviates even more from the thermodynamic value, which amounts to only 9 kcal/mol.

Nearly the same kinetics as given above have been found for nickel oxalate, although without a considerable induction period. So, the thermal decomposition of the oxalate can not occur by just a bond breaking as in case of the carbonate but must pass through several steps before the ordinary growth nuclei can be formed, namely: (1) charge transfer (of an electron) from the surface anion to an anion vacant site, (2) dissociation of the anion radical into gaseous carbon dioxide, (3) diffusion of the vacant anion sites into the body of the crystal, and (4) migration of the trapped electrons to the cation sites under production of free metal. This scheme was already mentioned by Allen and Scaife [30] and later adopted by Jacobs and Kureishy [31] and others.[23,32–34] As the rather large anion will possess a low mobility, the third step should be the rate determining one until so many vacant sites are formed that the structure in the outer layer collapses under formation of metallic nuclei, after which the nuclei are expected to grow at normal rate.

When the induction period was eliminated by subtraction of an appropriate value for t_0 (98 min), the resulting reduced data for the reaction (240°C) in hydrogen [20] may be shown to fall on the same curve in Fig. 8 as that given for the cobalt carbonate. Following the curve for $L=5$ and $M=20$ the data indicate a pronounced tendency for the nuclei to align themselves on lines, a result which has already been observed by electron microscopy.[34] In the acceleratory period the experimental data for nickel oxalate appear somewhat high, however, which suggests that the growth nuclei first acquire their final number at a later stage. A more satisfactory description could be obtained by allowance of a certain α_0 (0.02). Together with a diminished induction period ($t_0=65.8$ min) this gave the best fit to (24) but not, however, without changes of L (2) and M (2). Even the deviations were reduced but they were not removed, indicating the aforementioned nucleation period.

CONCLUSION

From the kinetic model of surface nucleation followed by three-dimensional growth it turns out that Erofeyev's equation and the equation for the contracting rectangle (or sphere, envelope and line) are two of the extremes from a more general description. Thus, the apparent reaction order in Erofeyev's equation is affected by the number of nuclei and their possible alignment for the acceleratory phase and to a lesser extent by the particle geometry and size distribution for the decay period. Furthermore, if the number of nuclei depend on temperature and Erofeyev's method is used, the activation energy will not correspond to the interfacial reaction, as exemplified by the reaction of the cobalt carbonate. If only a few nuclei are present, several solutions for the constants k, L, and M may apply to the experimental data (*cf.* nickel oxalate) whereby the magnitudes of the constants can only be assigned within wide limits rather than with definite values. Then the correct solution must be obtained from, *e.g.*, microscopical examinations of the reaction. The aim of the present work, however, has been concentrated on obtaining a family of reasonable solutions to the observed kinetics, of which only one, of course, will be correct.

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