Kinetics of solid state reactions with a positive feedback between the reaction and fracture

1. A quantitative model for movement of the fracture front

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A model describing the steady-state kinetics of thermal decomposition in the solid phase occurring with a decrease in the solid phase volume and accompanied by fracture in the reaction zone is suggested. The model is based on the concept of positive feedback between the reaction and fracture. The rate of the fracture front and the size of the product fragments formed were calculated.

Key words: solid state reactions, localization of the reaction, reaction zone, diffusion, mechanical stress, fracture, positive feedback.

Reaction localization at the interface between the reagents and the products is one of the characteristic features of chemical reactions in the solid phase.[1] It is generally assumed that processes of thermal decomposition

$$\mathbf{A}_s \rightarrow \mathbf{B}_s + \mathbf{C}_g, \qquad (1)$$

e.g., dehydration of crystal hydrates and decomposition of carbonates and sulfites, occur in the reaction zone.[2,3] Structural discrepancies and/or differences in molar volumes of the starting reagent and reaction products bring about mechanical stress in the reaction zone, which can relax either by plastic deformation or by fracture in the reaction zone.[4] Fracture of the solid reagent is the most common way of stress relaxation in the solid phase for the reaction type in question.[5,6] Initially, the reaction starts at the original surface $\mathbf{A}_s$; as the component **C** is removed to the gas phase, the reaction slows down due to diffusion hindrance.[7] Fracture of the surface layer depleted of component **C** removes the diffusion hindrance, since it forms a new reaction surface. Thus, positive feedback is established between the reaction and fracture: the reaction propagates to some depth in the solid reagent and causes mechanical stress, which at some critical moment leads to the fracture of the solid reagent in the reaction region and to its rapid termination in the mechanically destroyed solid. Since the reaction is heterogeneous, autocatalysis makes the process localize at the interface separating the solid reagent and the product, *i.e.*, the formation of a reaction front occurs. The positive feedback described above plays the role of reaction autocatalysis. The reaction is localized in the region where fracture occurs. The characteristic width of such a region is determined by the condition that the elastic energy accumulated in it is sufficient to form a new surface upon fracture. For this process to occur, it is necessary that other ways of relaxation of mechanical stress do not compete considerably with fracture. For the reagent not to relax as a whole body, its size should exceed noticeably the diffusion profile width. The absence of fracture in small crystals has been observed experimentally for the decomposition of barium hydrooxalate.[6] The crystals of $Ba(HC_2O_4)_2 \cdot H_2O$ with linear dimensions not exceeding 50 μm underwent dehydration without cracking, whereas larger crystals cracked on dehydration. Plastic deformation can play the role of another channel for relaxation. Competition between plastic deformation and fracture may explain the autolocalization of topochemical reactions. Plastic deformation can prevent the onset of fracture over the entire original surface of a solid and not allow it to be destroyed subsequently. As a result, the reaction virtually stops due to diffusion hindrance. If fracture has nevertheless started at some place of the original surface, it can continue, since it leads to the formation of efficient stress concentrators which remove hindrance to the development of new cracks. Thus, the reaction will proceed at the boundary of the once formed and growing fracture zone (nucleus).

A study of the dehydration of silicate glue[8] can serve as an evident experiment qualitatively confirming this scheme. It is evident in the microphotographs reported previously[8] that the regions of the dehydration product (dehydration nuclei) are fracture zones. A comparison of the kinetics of water evolution with microscopic obser-

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vations shows unambiguously that the fracture observed is not just a side effect of the dehydration process, but it is the fracture that determines the kinetics, *i.e.*, the formation of fracture zones (nuclei) concludes the induction period, and the process accelerates considerably after that.

Models describing the steady-state regime of a process with positive feedback between a reaction which has a surface stage and fracture have been suggested previously.[9,10] These models consider a reaction of the type (1), which occurs in an infinite isotropic body at a flat reaction front moving at a constant rate v and results in a decrease in the solid phase volume. The models differ in the assumed fracture geometry. In one case,[10] a system of parallel cracks spaced at an equal distance h from each other is considered; in the other case,[9] the assumption is made that the fragments splitting off have random shapes with characteristic size h.

In both cases, it is concluded that the steady-state process is unambiguously described by the dimensionless parameter kh_0/D. To summarize the results, let us introduce unified designations: k is the rate constant of the surface reaction (cm s^{-1}); $h_0 = 9\gamma/(E\beta^2)$ is the characteristic size of fracture; γ is the specific surface energy of fracture (erg cm^{-2}); E is the Young's modulus; $\beta = \Delta V/V$ is the bulk shrinkage due to the reaction (the relative decrease in the solid phase volume, where V is the original volume of the solid reagent and ΔV is the decrease in this volume upon complete transformation); D is the diffusion coefficient of the molecules of compound **C** in the solid reagent. The models give qualitatively similar results in the two limiting cases corresponding to small and large values of this parameter.

It has been shown[9] that over the entire range of the kh_0/D parameter, $vh/D \approx 0.9$. In the limit $kh_0/D >> 1$

$$h \approx 1.2h_0,$$

and in the limit $kh_0/D << 1$

$$h \approx h_0^{1/3}(D/k)^{2/3}.$$

It has been found[10] that $vh/D \approx 7$ for all magnitudes of kh_0/D. At $kh_0/D >> 1$

$$h \approx 100h_0,$$

while at $kh_0/D << 1$

$$h \approx 7h_0^{1/3}(D/k)^{2/3}.$$

The purpose of the present work is to create a model based on the crack geometry observed experimentally.

Model of movement of the fracture front

The development of separate cracks has been observed in experiments on the dehydration of silicate glue.[8] Each new crack nucleates at the edge of a previous crack and moves away from the latter in a perpendicular direction, *i.e.*, in the direction of movement of the reaction front. The crack then moves along the edge of the previous crack (*i.e.*, along the reaction front) and for a markedly longer distance. In this way, relaxation in the entire region between the old and new cracks occurs. This pattern is observed at the reaction front of the nucleus and is visible on the the original surface of the reacting body; however, such a geometry of the cracks is also possible in the bulk. In other words, we assume that the relaxation of stress in the reaction zone can occur by splitting off fragments of the reagent in the form of plates coplanar to the reaction front (Fig. 1).

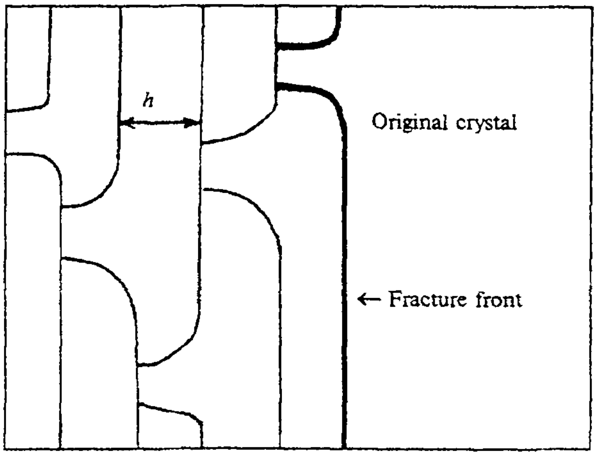

Fig. 1. Schematic representation of the assumed geometry of cracks.

In order to derive an approximate model, let us assume that the longitudinal size of the plates is infinite. This distinguishes the diffusion problem in this model from those described previously:[9,10] in our case, the problem of diffusion in a semi-space with a stepwise moving border is being considered.

Let us consider a process which occurs between two subsequent split-offs, when the boundary remains immobile. Then account of the preceding diffusion is reduced to introducing the initial condition

$$C(x, t = 0) = C^0(x),$$

corresponding to a concentration profile which remains in the semi-space under consideration at the split-off moment ($t = 0$). The concentration changes according to the following diffusion Eq. (the subscripts indicate the corresponding partial derivatives)

$$C_t = DC_{xx}, \qquad (2)$$

while at the boundary the condition corresponding to desorption is fulfilled:

$$DC_x = kC, \ x = 0. \qquad (3)$$

The solution is sought in the form

$$C(x,t) = \int_0^\infty G(x,x')C^0(x')\mathrm{d}x'. \tag{4}$$

The Green function can be obtained using the Laplace transformation over time

$$S(x,p) = \int_0^\infty \exp(-pt)C(x,t)\mathrm{d}t.$$

This transforms Eq. (2) to

$$DS_{xx} - pS = -C^0(x),$$

while condition (3) changes to

$$DS_x = kS,\ x = 0.$$

This problem is solved by the method of Green's functions:

$$S(x) = -\int_0^\infty g(x,x')C^0(x')\mathrm{d}x', \tag{5}$$

while the corresponding problem on $g(x,x')$ (δ is the Dirac delta-function)

$$Dg_{xx} - pg = \delta(x-x')$$

with a boundary condition

$$Dg_x = kg,\ x = 0$$

has a nondivergent solution

$$g = -\frac{1}{2\sqrt{pD}}\left(\exp\left(-|x-x'|\sqrt{\frac{p}{D}}\right) + \frac{\sqrt{pD}-k}{\sqrt{pD}+k}\exp\left(-(x+x')\sqrt{\frac{p}{D}}\right)\right).$$

Applying the reverse Laplace transformation to Eq. (5), one obtains Eq. (4), where G is a prototype of $-g$, *i.e.*,

$$G = \frac{1}{2\sqrt{\pi Dt}}\left(\exp\left(-\frac{(x-x')^2}{4Dt}\right) + \exp\left(-\frac{(x+x')^2}{4Dt}\right)\right) -$$
$$-\frac{k}{D}\exp\left(\frac{k}{D}(x+x') + \frac{k^2t}{D}\right)\mathit{erfc}\left(\frac{k\sqrt{t}}{\sqrt{D}} + \frac{x+x'}{2\sqrt{Dt}}\right),$$

where

$$\mathit{erfc}(z) = \frac{2}{\sqrt{\pi}}\int_z^\infty \exp(-y^2)\mathrm{d}y$$

is an additional error integral. For a sequence of diffusion and fracture cycles to describe a "steady-state" reaction, it is necessary that these cycles be identical. To guarantee this, it is sufficient to establish the identity of the starting conditions in two consecutive cycles. Assuming the duration of a cycle to be τ and the thickness of the splitting layer to be h, one obtains

$$C(x+h,\pi) = C^0(x).$$

Taking Eq. (4) into account, one obtains an integral equation for $C^0(x)$:

$$C^0(x) = \int_0^\infty G(x+h,x')C^0(x')\mathrm{d}x'. \tag{6}$$

Thus, the expression for $C^0(x)$ satisfying the condition of identity of cycles is the eigenfunction of the $G(x+h,x')$ kernel taken at $t = \tau$. The existence of such own functions at any positive h and τ follows from their physical meaning.

The determination of the diffusion problem parameters, h and τ, requires two conditions, which have to be obtained from an analysis of the fracture problem. The first condition is the conservation of energy upon fracture, *i.e.*, the energy liberated due to the relaxation of mechanical stress is consumed for the formation of a new surface. The second condition is related to the mechanical stability of the solid. This implies that in a real situation, a stressed layer always contains stress concentrators, since the longitudinal size of plates is not infinite but is limited by a network of cracks. Hence splitting occurs immediately as soon as the stressed state satisfies the energetic condition for fracture.

If W_0 and W_1 are the energies of the plate before and after splitting, respectively, and S is the plate area, it can be shown that

$$W_0 - W_1 = 2S\gamma. \tag{7}$$

However, certain corrections should be made in this approximate expression. In an ideal case, Eq. (7) is valid for one-dimensional strips of width h that are separated from a semi-plane, *i.e.*, for the problem from which one dimension has been excluded, rather than for two-dimensional plates. When considering two dimensions normal to the direction of front movement, it is essential to note that during crack propagation, full stress relaxation along two directions simultaneously is impossible. During the initial crack propagation, the plate can relax along only one direction (normal to the crack front), and it is only at the end of splitting that the plate can relax as a whole, *i.e.*, along two directions. Since the start of fracture has to be considered for the description of the critical state, W_1 will indicate the energy of a plate relaxed along only one of the two longitudinal directions (the deformations along the second direction remain unchanged).

Another correction is related to the finiteness of the longitudinal plate size. The network of cracks confining the plates relaxes a part of the mechanical stress even before they split off, hence decreasing the initial energy W_0. Assuming that the elastic energy that is liberated is consumed for the formation of the surface of the network of cracks noted above (with the same energy consumption for fracture, γ), we obtain the simplest way of estimating this correction, *i.e.*, by using the full surface of the plate, including the surface of the edges:

$$2S \rightarrow 2\alpha S,\ \alpha \approx 1 + 2h/L,$$

where L is the characteristic longitudinal size of the plates. Generally speaking, it is possible to determine the magnitude of α by solving the problems according to the elasticity and fracture theories, but because of their complexity, α will be considered as a phenomenological parameter. Thus, we obtain the condition for energy conservation in the final form:

$$W_0 - W_1 = 2\alpha S\gamma. \qquad (8)$$

To calculate the energy of a stressed plate, it is necessary to know the components of the tensors of deformation, ε_{ij}, and stress, σ_{ij}. We are considering plane-stressed states, since the stress in the direction normal to the plate surface is absent. Deformation is caused by isotropic bulk shrinkage and is uniformly distributed in the plane of the plate, therefore the deformation tensor has only diagonal components depending only on the x coordinate. Hence, the stress tensor, which depends on the deformation tensor according to the Hooke's law, also has only diagonal components. According to the condition of plane stress, there are just two of these components.

In the initial state, the stresses and deformations along both directions in the plane of the plate are equal. Let the deformation in the plane of the plate be $\beta'\varepsilon_0$, where $\beta' = 1 - (1-\beta)^{1/3}$ is the linear shrinkage (at $\beta << 1$, the following approximation can be used: $\beta' = \beta/3$) and ε_0 is a value that can vary from 0 to 1. Then, calculating the corresponding stress according to the Hooke's law, one can obtain the following expression for the energy:

$$W_0 = S\int_0^h \frac{\sigma_{ij}\varepsilon_{ij}}{2}\mathrm{d}x = S\frac{E\beta'^2}{9(1-\nu)}\int_0^h \varepsilon_0^2\mathrm{d}x, \qquad (9)$$

where ν is the Poisson modulus. Let us assume for definiteness that the local shrinkage depends linearly on the local degree of transformation. This relates to the situation in which the reaction zone is a solid solution of the reaction product in the original reagent. Thus,

$$\varepsilon_0 = 1 - C(x)$$

(the concentration is normalized to the starting value, so that $C \rightarrow 1$ at $x \rightarrow \infty$).

As a result, if a split-off plate is allowed to relax while keeping the deformation along one of the directions in its plane unchanged, the plate will shrink and bend (into a cylindrical surface) along the other direction. This shrinkage and bending will also be uniform, as they are caused by originally uniform stress. If the deformation caused by shrinkage and bending is $\beta'(1+\nu)\varepsilon_1$, the W_1 energy is expressed as follows:

$$W_1 = S\frac{E\beta'^2}{2(1-\nu^2)}\int_0^h\left[(\varepsilon_0-\varepsilon_1)^2(1+\nu)^2+\varepsilon_0^2(1-\nu^2)\right]\mathrm{d}x. \qquad (10)$$

Uniform shrinkage and bending can be represented in the form

$$\varepsilon_1 = 1 - \langle C\rangle + (h/2 - x)/R,$$

which is analogous to the pattern of deformations in a rod subjected to uniform compression along its axis and bending with a constant curvature radius. The relaxation parameters, $\langle C\rangle$ and R, can be determined from the condition of minimum energy W_1. It follows from the $\partial W_1/\partial\langle C\rangle = 0$ and $\partial W_1/\partial R = 0$ conditions that

$$\langle C\rangle = \frac{1}{h}\int_0^h C\mathrm{d}x,$$

$$\frac{1}{R} = \frac{12}{h^3}\int_0^h (1 - C(x))(h/2 - x)\mathrm{d}x.$$

Substituting expressions (9) and (10) into Eq. (8) and changing somewhat the expression for h_0 (it differs from that defined above only in the dimensionless coefficients)

$$h_0 = \frac{4\alpha\gamma(1-\nu)}{(1+\nu)E\beta'^2},$$

one obtains

$$\Delta \equiv \int_0^h\left[\varepsilon_0^2 - (\varepsilon_0-\varepsilon_1)^2\right]\mathrm{d}x = h_0. \qquad (11)$$

This equation is one of the two conditions determining h and τ. It signifies the conservation of energy upon fracture. To obtain an expression for the second condition, *i.e.*, mechanical stability, one has to analyze the behavior of the $\Delta(h,\tau)$ function, which is proportional to the energy (with a constant proportionality coefficient, $S\frac{E\beta'^2(1+\nu)}{2(1-\nu)}$) liberated upon relaxation of a plate of thickness h after the next reaction cycle of duration τ. It can be easily shown that Δ is a monotone increasing function of τ, as at any depth the degree of transformation in the reaction zone and the related stress increase with time to approach a certain limit, and the greater the initial stress, the higher the energy liberated upon relaxation. It can be shown further that at any τ, the Δ function has a maximum at a certain h. In fact, let the characteristic width of the diffusion profile (and stress profile) be d by the moment τ. Then at $h << d$, the stress is described with good precision by a linear function of x in the range of x from 0 to h. Using the formulas for $\langle C\rangle$, $1/R$, and ε_1 presented above, one can obtain

$$\varepsilon_1 \approx \varepsilon_0,$$

whence it follows that

$$\Delta \approx \int_0^h \varepsilon_0^2\mathrm{d}x \approx \varepsilon_0^2(x=0)h,$$

i.e., at $h << d$, Δ increases proportionally to h. In the other limit, at $h >> d$, relaxation almost does not occur when a plate is split off, since the stressed layer is much thinner than the plate. Calculating the values of $\langle C\rangle$ and $1/R$ for this limit, one obtains $\Delta \sim 1/h$. Thus, for any d (and hence for any τ), the Δ function has a maximum at a certain $h \sim d$. It follows from the above considerations that the value of Δ, which is everywhere smaller than h_0

at the start of each cycle (otherwise the condition of fracture would be fulfilled at the very start of the cycle), increases with time. At some moment τ, at h corresponding to the maximum Δ, this maximum reaches h_0, and a plate of thickness h is split off according to the condition of mechanical stability. Thus, the condition of mechanical stability coincides with the condition of maximum Δ:

$$\partial\Delta/\partial h = 0.$$

Differentiation of Eq. (11) gives a simple result (the terms corresponding to differentiation of the integrand become zero because of the form of deformations determined by the condition of the minimum elastic energy W_1)

$$\varepsilon_0^2(h) - (\varepsilon_0(h) - \varepsilon_1(h))^2 = 0. \qquad (12)$$

Thus, the problem reduces to solving a system of three equations, *i.e.*, (6), (11), and (12). To perform a numerical solution, the Eq.s were brought to dimensionless form by the following substitutions:

$$\frac{x}{2\sqrt{D\tau}} = \chi,\ k\sqrt{\frac{\tau}{D}} = \theta,\ \frac{h}{2\sqrt{D\tau}} = x_0,\ \frac{kh_0}{D} = P.$$

In order to improve the accuracy of calculations over the entire ranges of θ and P, the value $f = 1 - C$ was used instead of concentration C. In addition, for convenience of calculations, integral Eq. (6) was reformulated to a concentration profile at the end of the cycle. Taking all the changes into account, the system assumes the form

$$f(\chi) = \int_0^\infty K(\chi,\chi')f(\chi' + x_0)\mathrm{d}\chi' +$$
$$+ erfc(\chi) - \exp(2\theta\chi + \theta^2)erfc(\chi + \theta), \qquad (13)$$

where

$$K = \frac{1}{\sqrt{\pi}}\{\exp[-(\chi - \chi')^2] + \exp[-(\chi + \chi')^2]\} -$$
$$- 2\theta\exp[2\theta(\chi + \chi') + \theta^2]erfc(\chi + \chi' + \theta),$$

$$f^2(x_0) - (f(x_0) + 2\langle f\rangle - 3M)^2 = 0, \qquad (14)$$

$$2x_0\theta(4\langle f\rangle^2 + 3M^2 - 6\langle f\rangle M) = P, \qquad (15)$$

where

$$6fc = \frac{1}{x_0}\int_0^{x_0} f\mathrm{d}\chi,$$
$$M = \frac{2}{x_0^2}\int_0^{x_0} \chi f\mathrm{d}\chi.$$

Results and Discussion

The system was solved by iterations with a starting profile $f(\chi) = 0$ and a given t. In each iteration, Eq. (13) defines a new $f(\chi)$ profile based on the profile and x_0 obtained in the previous iteration, while Eq. (14) serves as the condition determining x_0 for the $f(\chi)$ obtained. Calculations showed that in all cases, condition (14) is fulfilled only in one point corresponding to one of the two possible roots, namely, $2\langle f\rangle = 3M$, hence the thickness of the split-off part is determined unambiguously. The sequence of iterations converges rather quickly to the limit to provide $f(\chi)$ and x_0 corresponding to a given duration of the cycle, θ. Equation (15) determines the P parameter for the cycle. Thus, this procedure indirectly gave the dependences of the cycle duration, the thickness of the plates split off, and the diffusion profile in the reaction zone on the dimensionless parameter P, which characterizes the ratio of the process constants. It is important to note that the values of P and x_0 determined after the first iteration were only a few percent different from the values to which the sequence of iterations converged. The main changes in the intermediate results corresponded only to the "tail" of the $f(\chi)$ profile located beyond $\chi = x_0$, which gradually becomes exponential, as occurs in the problem with a uniformly moving border. This allows one to assume that the sequence of iterations approximately reflects the sequence of cycles of the kinetics described, starting from the initial reagent surface. Hence from the start of the reaction, the rate of movement of the fracture front and the size of product fragments differ only slightly from the stationary values.

It is convenient to represent the calculation results as dependences of the dimensionless process characteristics, h/h_0 and vh/D (where $v = h/\tau$ is the mean rate of the front), on P. These characteristics can easily be expressed through the parameters introduced for the calculation: $h/h_0 = 2x_0\theta/P$ and $vh/D = 4x_0^2$. The calculation results (Fig. 2) show the existence of two modes corresponding to large and small P values. At $P >> 1$, h approaches its minimum value ($\sim 3.6h_0$), whence it follows that $kh/D >> 1$. The meaning of the latter condition is simple: it states that a reaction occurring in some region with a characteristic size h and involving surface and bulk steps is limited by diffusion. This is clear from the fact that h^2/D is the characteristic time of diffusion on the h scale, and h/k is the characteristic time of a reaction, which is limited by a surface step, in a bulk with characteristic size h. In this limit, cycles between fracture events involve widening of the diffusion profile to a critical width, while the mean rate of the front is determined by diffusion for a distance $\sim h_0$.

At $P << 1$, the dependence $h/h_0 \sim 1/P^{2/3}$ was obtained, *i.e.*, $kh/D \sim P^{1/3}$, and hence $kh/D << 1$. In contrast to the previous case, this means that the reaction is limited by the surface step. It is thus clear that the condition $P^{1/3} << 1$ is a more correct description of this limit. Although in this case the diffusion itself is not the limiting stage in the sense mentioned above, the result still depends on D, since diffusion determines the reaction zone width.

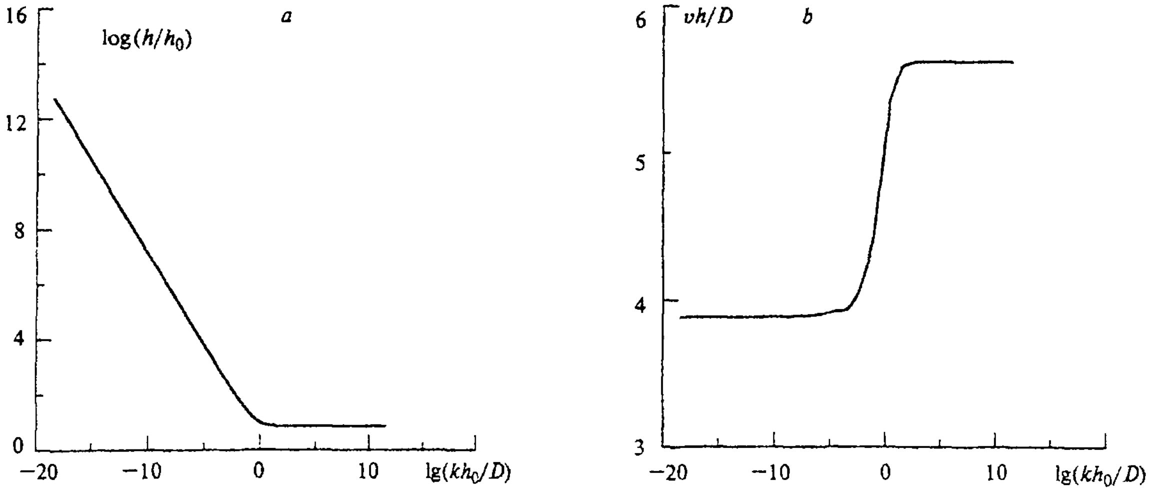

Fig. 2. Calculated dependences of h/h_0 (*a*) and vh/D (*b*) on the dimensionless parameter kh_0/D.

Thus, simulation in the two limiting cases gave the following results:
at $kh_0/D >> 1$,

$$h = 3.6h_0,\ vh/D = 5.6;$$

and at $kh_0/D << 1$,

$$h = 2.2h_0^{1/3}(D/k)^{2/3},\ vh/D = 3.9.$$

It is evident that the calculation results are qualitatively similar to those derived from the earlier models,[9,10] *i.e.*, the averaged process characteristics (v and *h*) are almost insensitive to the fracture pattern selected.

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