

A model is constructed to describe motion of a plane transformation front in a solid body, assuming arbitrary relations between the rates of various transport processes involved in the mass transfer of substances.

In modern technology one widely uses mass-transfer processes whose crucial stage occurs inside a solid body. Such processes include various modifications of surface layers of materials (by heat or chemical treatment, corrosion protection, oxidation), extraction of components from a new phase, certain catalytic reactions, processing of powder materials (reduction of ores, drying, annealing), etc. The study and practical realization of such processes are hindered largely by the unavailability of general macrokinetic models for their description.

Indeed, the rate of mass-transfer processes in condensate phases is, as a rule, determined not so much by the kinetics of the principal chemical or phase transformation as by the rate the slower material transport processes participating in a transformation. In theoretical studies one usually assumes that the rate of one of these processes is much lower than those of the others. In this case a transformation can be regarded as occurring within one of the characteristic macrokinetic regions: outer or inner diffusion region, adsorption or dissolution region; for the transformation rate on the whole one can then obtain rather simple relations, as already listed [1, 2]. In reality, however, the rates of those mass-transfer processes are quite often of the same order of magnitude and do limit the observable transformation kinetics to the same extent. As a consequence, one deals with a highly nonlinear problem of interaction between those processes. Such a problem will be considered here.

Any transformation regardless of its physicochemical nature will, for simplicity, be called "reaction" with a single "reactant" entering through the surface of the solid body (e.g., from the gaseous phase) and a single "product" leaving through that surface. For a study of the principal aspect of the problem, we will make several simplifying assumptions, the following being the major ones.

The reaction is localized within a narrow zone inside the solid body, a zone which can be regarded as the interface between different solid phases: one where transformation has already begun and one where it has not or has already ended. This assumption is valid when the rate of the reaction proper exceeds by far the characteristic rate of transfer by diffusion. An analysis of the diffusion equation, taking into account absorption of the reactant by the product, will readily demonstrate that in this case there always exists a narrow zone where the reactant concentration drops very fast to zero while the concentration gradient is much larger within this zone than outside it. When the reaction rate is lower than or of the same order of magnitude as the diffusion rate (which is particularly characteristic of heterogeneous transformations in porous bodies), then such a zone does not appear and the reaction proceeds uniformly throughout the volume of the body.

The system has plane symmetry, which means there exists a depthwise propagating simply connected plane reaction front parallel to the interface between the solid body and the outer phase. This assumption may not be valid during the initial stage of a heterogeneous process corresponding to surface nucleation and subsequent evolution of nuclei into a continuous plane front.

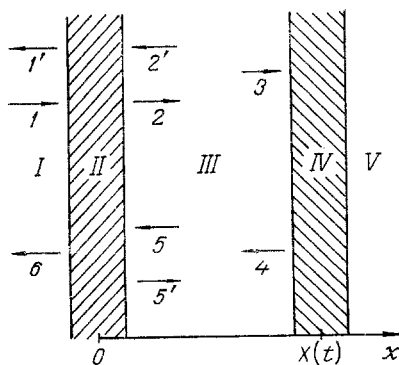


Fig. 1. Model of process.

The mixing process within the outer phase near the body surface and thus feed of the reactant to it and removal of the product from it occur much faster than the sorption-desorption processes and transport within the solid phase. This assumption is valid for rather many reactions in solid bodies; it implies that the characteristics of the outer phase can be regarded as the same at the body surface and far from it. Obvious exceptions are situations where formation of stagnation zones or other obstacles impede access for the outer phase to the reacting surface.

Finally, the heat effect of the reaction is assumed to be negligible and the diffusion coefficients as well as the kinetic parameters determining the rates of sorption, desorption, and dissolution in the solid phase are assumed to remain constant. This assumption implies either a weak concentration dependence of those quantities or low concentrations of the reactant and the product. There is no fundamental difficulty involved in extending this assumption to cases where nonuniform distribution of diffusion coefficients, heat effect of the reaction, and finite rate of mass transfer in the "solid body-outer phase" system must be taken into account.

The main components of the model are shown in Fig. 1. Components of the reactant (molecules, atoms, or ions) are adsorbed from the outer phase I into the surface layer II of the solid body and then desorbed in the opposite direction (fluxes 1 and 1'). From the surface layer they go into a solid solution (flux 2), the reverse process of desorption from that solution (flux 2') also being taken into consideration. In the solid phase III, constituting the part of the body in which the reaction has been completed, there occurs diffusion of the reactant with attendant rise of flux 3 toward the reaction front IV on which the reactant is then absorbed. Region V represents the part of the solid phase where the reaction has not yet begun. The emerging product of the reaction is removed from the reaction front by diffusion (flux 4) and is sorbed in the surface layer (flux 5). From there it is desorbed, either back into the solid phase (flux 5') or into the outer phase (flux 6). Diffusion of reactants present in the solid body and of other products forming phase III is completely disregarded. It must be noted, however, that there exist certain heterogeneous processes where this diffusion is not negligible. Examples of such processes are those where the reactant diffuses from the solid phase through a solid layer of reaction products to the body surface at which the reaction occurs.

We introduce fractions  $S$  and  $S'$  of the surface area of the surface layer occupied by the reactant and the reaction product, respectively, also the coefficient  $\alpha$  of reactant adsorption from the outer phase and the desorption rate constants  $\beta$ ,  $\beta'$  for the reactant and the reaction product, respectively. Using the Langmuir representations of independently adsorbed individual components, to be specific, we write the equations of kinetics of surface-layer occupation

$$\frac{\partial S}{\partial t} = \alpha(1 - S - S') - \beta S + \frac{\delta S}{\delta t}, \quad \frac{dS'}{dt} = -\beta' S' + \frac{\delta S'}{\delta t} \quad (1)$$

Here  $\delta S/\delta t$  and  $\delta S'/\delta t$  denote the total rates of surface-layer occupation by the reactant and the reaction product, respectively, through transfer from the solid phase. Coefficient  $\alpha$  is proportional to the partial pressure of the reactant from the outer phase (or to some power of it, when adsorption is coupled with dissociation, etc.), the partial pressure of the reaction product being, for simplicity, assumed to be zero so that its adsorption from the outer phase can be disregarded.

The surface concentrations of the reactant and the reaction product can be represented as  $f = s/l^2$  and  $f' = S'/l'^2$ . Assuming that the dissolution rates are proportional to these concentrations, while the rates of adsorption from the solid solution are proportional to the volume concentrations of the respective substances at the surface layer (at  $x = 0$ ), and considering that the total fluxes of the reactant and the reaction product from the solid phase to the surface layer must be equal to the corresponding diffusion fluxes, in accordance with the law of mass conservation, we have

$$\begin{aligned} \frac{\delta f}{\delta t} &= -k_1 f + k_2 l (1 - S - S') c_0 = D \frac{\partial c}{\partial x} \Big|_{x=0}, \\ \frac{\delta f'}{\delta t} &= -k'_1 f' + k'_2 l' (1 - S - S') c'_0 = D' \frac{\partial c'}{\partial x} \Big|_{x=0}, \\ c_0 &= c|_{x=0}, \quad c'_0 = c'|_{x=0} \end{aligned} \quad (2)$$

(here sorption from the solid solution takes into account partial contamination of the surface layer, unlike in other studies on this subject known to this author).

For the reactant at the reaction front  $x = X(t)$  we obviously have the condition of fast absorption. The condition for the concentration field of the reaction product follows from the requirement of material balance. We thus have the conditions

$$c = 0, \quad -D \frac{\partial c}{\partial x} = v D' \frac{\partial c'}{\partial x}, \quad x = X(t), \quad (3)$$

which are universal and must be satisfied for fast reaction of any order.

As to the reactant material balance (reactant entering from the outer phase and reactant already in the solid body), it yields the equation

$$\varphi \frac{dX}{dt} = -D \frac{\partial c}{\partial x} \Big|_{x=X(t)} \quad (4)$$

for the velocity of the moving reaction front, where  $\varphi$  is the effective concentration of the reactant in the original solid body multiplied by the appropriate stoichiometric factor.

Concentrations  $c(t, x)$  and  $c'(t, x)$  in the solid phase are found from the solutions to the corresponding diffusion equations, with relations (2) and (3) acting as boundary conditions imposed on those solutions. The characteristic time of concentration field relaxation on the  $0 < x < X(t)$  interval is of the order of  $X^2/D$  and  $X^2/D'$ , respectively, while the characteristic time of intrinsic reaction front propagation is of the order of  $(\varphi/c_0)X^2/D$  (these orders of magnitude follow directly from the diffusion equation and from Eq. (4), respectively). Since almost always  $c_0/\varphi \ll 1$  for reactions in condensate phases, the characteristic propagation time is much longer than the characteristic concentration relaxation time for either of the two components and thus quasisteady concentration distributions becomes established. These distributions, satisfying the aforementioned boundary conditions, are

$$c = c_0 \left( 1 - \frac{x}{X} \right), \quad c' = c'_0 + \frac{D}{vD'} c_0 \frac{x}{X}, \quad (5)$$

with Eqs. (2) yielding relations

$$\begin{aligned} c_0 &= \frac{k_1}{k_2 l (1 - S - S') + D/X} f, \\ c'_0 &= \frac{1}{k'_2 l' (1 - S - S')} \left[ k'_1 f' + \frac{D}{vX} \frac{k_1}{k_2 l (1 - S - S') + D/X} f \right] \end{aligned} \quad (6)$$

for the concentrations at the surface layer and relations

$$\frac{\delta f}{\delta t} = -\frac{\delta f'}{\delta t} = -\frac{k_1 D}{k_2 l (1 - S - S') X + D} f \quad (7)$$

for the rates of surface-layer occupation from the solid phase.

Expressions (5) and (6) close Eq. (4) for the reaction front coordinate, expression (7) closes the occupation equations (1). The result is a system of equations completely describing the process

$$\begin{aligned}\frac{dS}{dt} &= \alpha(1 - S - S') - \beta S - \frac{k_1 D}{D + k_2 l(1 - S - S')X} S, \\ \frac{dS'}{dt} &= -\beta' S' + \frac{k_1 D}{D + k_2 l(1 - S - S')X} S, \\ \frac{dX}{dt} &= \frac{k_1 D}{D + k_2 l(1 - S - S')X} \frac{S}{\varphi l^2}.\end{aligned}\quad (8)$$

These equations are self-adjoint with respect to quantities describing the rate of product transfer, which is quite logical from the standpoint of the requirement of material balance imposed on the system. Exceptions are the quantities  $\beta'$  and  $l'^2$  characterizing the possibility of surface-layer "poisoning" by the reaction product, on which the process kinetics on the whole can, according to Eqs. (8), depend very strongly.

It will be now convenient to introduce the dimensionless variables and parameters

$$\begin{aligned}\left\{ \begin{matrix} b \\ b' \end{matrix} \right\} &= \frac{1}{\alpha} \left\{ \begin{matrix} \beta \\ \beta' \end{matrix} \right\}, \quad \kappa = \frac{l'^2}{l^2}, \quad K = \frac{k_1}{\alpha}, \quad L = \frac{k_2}{\varphi l D}, \\ \tau &= \alpha t, \quad \xi = \varphi l^2 X,\end{aligned}\quad (9)$$

in which the system of equations (8) becomes

$$\begin{aligned}\frac{dS}{d\tau} &= 1 - (1 + b)S - S' - \frac{K}{1 + L(1 - S - S')\xi} S, \\ \frac{dS'}{d\tau} &= -b'S' + \frac{\kappa K}{1 + L(1 - S - S')\xi} S, \\ \frac{d\xi}{d\tau} &= \frac{K}{1 + L(1 - S - S')\xi} S.\end{aligned}\quad (10)$$

Parameters  $b$ ,  $b'$ , and  $K$  describe the ratio of the reactant and product desorption rates and the rate of reactant dissolution in the solid phase to the rate of its adsorption from the outer phase, while parameter  $L$  describes the relation between the rates of reactant adsorption from the solid solution and of reactant diffusion in the dissolved state.

As the initial conditions for Eqs. (10) it is logical to use the conditions

$$S = S' = \xi = 0, \quad \tau = 0, \quad (11)$$

corresponding to the process which begins at time  $t = 0$ . In principle, however, there is no difficulty to solve Eqs. (10) for any other initial conditions including those of periodicity in the pulse mode.

In the general case the solution to problem (10)-(11) cannot be expressed analytically but can be easily obtained numerically for a wide diversity of parameter values. Here are the results of a concise qualitative analysis of this problem.

At low values of the dimensionless time ( $\tau \ll (1 + b)^{-1}$ ,  $b'^{-1}$ ) we have approximately, retaining only the principal terms of the expansion in  $\tau$ ,

$$S \approx \tau, \quad S' \approx (\kappa K/2)\tau^2, \quad \xi \approx (K/2)\tau^2. \quad (12)$$

These relations describe the initial "induction" period of the reaction buildup. These relations, with definitions (9), indicate that the velocity of the moving reaction front

$$dX/dt \sim \alpha k_1 t \quad (13)$$

is equally limited by adsorption and dissolution of the reactant but does not depend on the rates of other mass-transfer processes.

In order to determine the trend of changes of the quantity  $dX/dt$  in subsequent instants of time, we will analyze the problem in the quasisteady approximation so that the derivatives of  $S$  and  $S'$  with respect to  $\tau$  can be disregarded. Then, with  $L\xi \ll 1$ , Eqs. (10) yield

$$S \approx \frac{b'}{\kappa K + b'(1+b+K)}, \quad S' \approx \frac{\kappa K}{\kappa K + b'(1+b+K)} \quad (14)$$

These values of  $S$  and  $S'$  depend largely on the rate constants of sorption-desorption processes. The effect of surface poisoning by the reaction product increases as  $\kappa$  increases and as  $b'$  decreases, being overall rather strong. At low values of  $b'$  we have  $S \sim b'$  and  $1 - S' \sim b'$ , which implies that the surface layer is almost completely occupied by the adsorbed reaction product.

When relations (14) hold true, then Eqs. (10) and conditions (11) yield

$$\xi \approx \frac{b'K\tau}{\kappa K + b'(1+b+K)} \quad (15)$$

and

$$\frac{dX}{dt} \sim k_1\beta' \left[ \kappa k_1 + \beta' \left( 1 + \frac{\beta + k_1}{\alpha} \right) \right]^{-1} \quad (16)$$

Accordingly, the velocity of the moving reaction front increases when  $\alpha$ ,  $k_1$ ,  $\beta'$  increase and  $\beta$  decreases but depends neither on the rate of reactant sorption from the solid solution nor on the rate of its diffusion to the reaction front.

By complete analogy, for  $L\xi \gg 1$  we have instead of relations (14) and (15) the relations

$$S \approx \frac{1}{1+b}, \quad S' \approx 0, \quad \xi \approx \left( \frac{2K\tau}{bL} \right)^{1/2}, \quad (17)$$

and thus the velocity of the moving reaction front

$$\frac{dX}{dt} \sim \left( \frac{\alpha k_1 D}{\beta k_2 t} \right)^{1/2} \quad (18)$$

in this case altogether ceases to depend on the kinetics of product desorption but begins to depend on the parameters  $D$  and  $k_2$ , increasing as the former increases and as the latter decreases. This dependence on  $D$  is a consequence of a lower effective rate of the heterogeneous process on the whole and, therefore, of a smaller flux of reaction product which could fill the surface layer. The dependence on  $k_2$  is a consequence of a larger rôle of the diffusion resistance over larger distances between the body surface and the reaction front.

As a function of time, the quantity  $dX/dt$  first increases linearly with  $t$ , then remains approximately constant for some period (this period becoming longer as  $b'$  decreases), and finally decreases proportionally to  $t^{-1/2}$  (relations (13), (16), and (18)).

It is in many cases possible to greatly simplify the system of equations (10) so that its solutions become quite straightforward in analytical form. When the value of  $K$  is low (the process is limited by the rate of reactant dissolution), for instance, one can discard the last terms in the first two of Eqs. (10) and those two equations will then altogether cease to depend on the third one. In this case

$$S \approx \frac{1}{1+b} [1 - \exp(-(1+b)\tau)], \quad S' \approx 0, \quad (19)$$

$$\left( 1 + \frac{L}{2}\xi \right) \xi \approx \frac{K}{1+b} \left\{ \tau - \frac{1}{1+b} [1 - \exp(-(1+b)\tau)] \right\}.$$

When  $L \ll 1$  (reactant adsorption from the solid solution is impeded relative to reactant diffusion), then  $L\xi \ll 1$  over a long period of time so that Eqs. (10) become linear and can be easily solved by standard methods. Without writing out the entire solution, because of its unwieldiness, we will only note that there exist two fundamentally different modes of process evolution. The first mode corresponds to real roots of the characteristic equation

$$\lambda^2 + (1+b+b'+K)\lambda + b'(1+b+K) + \kappa K = 0 \quad (20)$$

of the system of linear equations of occupation based on Eqs. (10) and is characterized by aperiodic variation of  $S$  and  $S'$ . The second mode corresponds to complex roots of Eq. (20) and is characterized by oscillatory variation of  $S$  and  $S'$  in time. The oscillatory mode is

realized, as can be easily demonstrated on the basis of Eq. (20), when the inequality

$$4xK > (1 + b + K - b')^2 \quad (21)$$

holds true.

It is evident that at any values of the other parameters there always exists a range of values of parameter  $b'$  (relative rate of product desorption into the outer phase) at which the oscillatory mode can be realized. In this case the velocity of the moving reaction front also oscillates, remaining positive. One easily establish analogous relations for the cases where the rate of mass transfer on the whole is limited by diffusion, adsorption from the outer phase, or desorption. Some of those relations are identical to already known ones [1, 2].

We will note that the results of this study can be very easily extended also to processes involving several reactants and reaction products. To each of them will be applicable an occupation equation of the (1) kind and a relation of the (2) kind for the flux from the solid phase, with contamination of the surface layer by all substances participating in the reaction taken into account. The concentrations of reactants at the reaction front must become zero, as before, while the relations between the diffusion fluxes of reactants and reaction products must correspond to the stoichiometric equation of the reaction as well as to conditions (3). The equation of motion for the reaction front can also be formulated in terms of one of those diffusion fluxes, similarly to what has been done in Eq. (4).

In conclusion, two side effects of possible significance in the theory of topochemical reactions are noteworthy. Firstly, it is not necessary, in principle, to prove the existence of a narrow front of such a reaction by the conventional method based on the concept of higher reactivity at that front. As has been said already, this would require a rate of the reaction proper much higher than the rate of reactant supply to the reaction front. Secondly, the existence of an induction period and of a maximum process rate on the whole can be deduced, in principle, without resorting to concepts about gradually evolving nucleation at the surface of a solid body, which has been usually considered to be necessary. This deduction remains valid also when a continuous plane reaction front has been formed at the very beginning.

#### NOTATION

$c$ , volume concentration,  $D$ , diffusion coefficient;  $f$ , surface concentration;  $b$ ,  $K$ ,  $L$ , dimensionless kinetic parameters defined by expressions (9);  $l$ , characteristic dimension determining the area  $l^2$  occupied by a molecule in the surface layer;  $k_1$ ,  $k_2$ , coefficients determining the rates of desorption and adsorption, respectively, from the solid solution;  $S$ , fraction of the area of the surface layer occupied by the adsorbed substance;  $t$ , time;  $x$ , space coordinate read depthwise in the solid body;  $X(t)$ , space coordinate of the reaction front;  $\alpha$ ,  $\beta$ , rate constants of adsorption and desorption, respectively, into the outer phase;  $\kappa$ ,  $\xi$ ,  $\tau$ , defined by expressions (9);  $\nu$ , stoichiometric factor; a prime sign ( $'$ ) refers to the reaction product; and subscript 0 refers to conditions at  $x = 0$ .

#### LITERATURE CITED

1. P. Barré, Kinetics of Heterogeneous Processes [Russian translation], Mir, Moscow (1976).
2. A. Ya. Rozovskii, Heterogeneous Chemical Reactions: Kinetics and Macrokinetics [in Russian], Nauka, Moscow (1980).