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ON A SELFSIMILAR SOLUTION OF THE PROBLEM OF NON-LINEAR DIFFUSION KINETICS OF A TOPOCHEMICAL REACTION WITH A SURFACE OF VARYING ACTIVITY*

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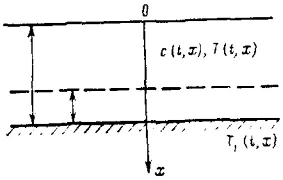
In the framework of the one-dimensional model, the macrokinetics of growth of the solid product layer formed in the course of exo- or endothermic topochemical reactions at the boundary separating the solid and mobile reagents occupying half-spaces are studied. The mobile reagent (gas or liquid), the temperature and concentration of which are assumed constant, diffuses through this layer to the reaction front propagating into the bulk of the solid reagent. The concentration and temperature fields are connected at the reaction front by an arbitrary non-linear law of microkinetics. The aging or poisoning of the reaction surface affects its activity with time /1—3/. Assuming that the activity varies according to the "inverse root" law, we obtain the selfsimilar solution of the problem, which can be used to determine the corrosion resistance of materials and to analyse the microkinetics of growth of a polymer layer on an activated filler when filled polymers are prepared by gas phase polymerization.



The phenomenological picture of the development of a topochemical reaction between a gas or liquid and a solid, localised on the boundary separating the solid reagent or catalyst from the solid reaction products, is governed strictly by the reaction kinetics as well as by diffusion of the mobile reagent through the growing layer of solid reaction product /1/. The picture may be complicated by the influence of the heat transfer processes in the phases in contact when the thermal effect of the reaction becomes apparent, and by the variation with time of the activity of the solid reagent (aging) or poisoning of the catalyst /2, 3/.

The figure shows schematically the positions of the regions at $t \neq 0$. The region $x < 0$ is occupied by the mobile reagent. The high effective transport coefficients of this reagent ensure that the values of temperature and concentration are kept constant at the boundary $x = 0$. Of most interest is the transport in the region $0 \leqslant x \leqslant \delta(t)$ occupied by the solid reaction product, heat conducting and diffusively permeable by the mobile reagent. The heat and mass exchange between the reaction surface $x = \delta(t)$ and the surface of the mobile reagent $x = 0$ takes place across this layer. The dashed line depicts, for the value of the coordinate $x = \delta(t) - \delta_1(t)$, the initial position of the boundary surface separating the solid and mobile reagent. The reagents come into direct contact at the instant $t = 0$ when the reaction products layer has zero thickness, i.e. $\delta(0) = 0$. The layer of the consumed solid reagent $\delta_1(t)$ will also have zero thickness $\delta_1(0) = 0$ at the initial instant. In subsequent states the layer of solid product will "wedge" itself between the reagents, filling the region vacated by the consumed solid reagent, and displacing at the same time, in the opposite direction, the bulk of the mobile reagent. All this shows that strictly speaking the reference system in question is not inertial. However, since the rates of layer growth achieved in practice are quite low, we shall neglect the related transport and dynamic effects.

It should be noted that the bulk of solid reagent is not permeable by the mobile reagent. In this connection the heat between the solid and mobile reagent takes place at the reaction surface $x = \delta(t)$ because of the initial temperature and heat emission (absorption) differences.

Assuming that the catalyst surface is uniformly accessible, we shall formulate the problem in question mathematically, using a reference system attached to the mobile phase - solid reaction products boundary as follows:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}, \quad t \geqslant 0, \quad 0 \leqslant x \leqslant \delta(t); \quad \delta(0) = 0 \tag{1}$$

$$c\,|_{x=0} = 1, \quad -D\frac{\partial c}{\partial x}\Big|_{x=\delta(t)} = \varkappa\frac{d\delta}{dt}$$

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$$\begin{gathered}
- D\frac{\partial c}{\partial x}\bigg|_{x=\delta(t)} = k(t)\, F\left(c|_{x=\delta(t)},\, T|_{x=\delta(t)}\right) \\
\frac{\partial T}{\partial t} = a\frac{\partial^2 T}{\partial x^2}, \quad t \geqslant 0, \quad 0 \leqslant x \leqslant \delta(t), \quad T|_{x=0} = T_0 \\
- r\rho_0 D\bigg|_{x=\delta(t)} = \lambda\frac{\partial T}{\partial x}\bigg|_{x=\delta(t)} - \lambda_1\frac{\partial T_1}{\partial x}\bigg|_{x=\delta(t)} \\
T|_{x=\delta(t)} = T_1|_{x=\delta(t)} \\
\frac{\partial T_1}{\partial t} = a_1\frac{\partial^2 T_1}{\partial x^2}, \quad t \geqslant 0, \quad \delta(t) \leqslant x < \infty; \quad T_1|_{t=0} = T_\infty \\
T_1|_{x\to\infty} \to T_\infty \\
\varkappa = \frac{\rho}{\rho_0}\frac{\mu_0\nu_0}{\mu_0\nu_0 + \mu_1\nu_1}
\end{gathered}$$

Here c is the dimensionless concentration of the mobile reagent in the solid reaction product, T is the temperature, D is the coefficient of diffusion of the mobile reagent in the solid product, r is specific heat of reaction, λ, a are the thermal conductivity and diffusivity, μ are the molecular weights of the reagents, and ν are the stoichiometric coefficients. The subscripts zero and one refer to the mobile and solid reagent respectively, and quantities without the subscript refer to the solid reaction product. In the case when the solid support is not a reagent but a catalyst, we must write $\nu_1 = 0$.

In the kinetic boundary condition F is a dimensionless function of the boundary concentration and temperature, and the activity of the reaction surface, which varies with time, is defined by the multiplier $k(t)$. The variation can be caused by a change in the phase and chemical composition of the surface, and its structure. Strictly speaking, the variation should be described by its kinetic equation reflecting the processes of formation and blocking of active centres of the basic reaction /2, 3/.

The time-dependent law of decrease in activity of the reaction surface is determined by the source of supply of the harmful impurity poisoning the active centres of the basic reaction. It is often used in the form of an exponential or power function of time /1/. If the diffusion is the rate determining process for the chemisorption of the harmful impurity, unlike the main reaction which takes place in a mixed, diffusion-kinetic mode, we can use the approximation $k(t) \sim 1/\delta(t)$, reflecting the fact that the diffusion resistance to the transport of the harmful impurity increases with increasing thickness of the solid reaction product layer. We shall seek the law of the reaction surface in the form

$$\delta(t) = 2\beta\sqrt{Dt} \tag{2}$$

where β is a dimensionless constant to be determined.

We shall consequently write the law of change in activity in the form

$$k(t) = \frac{2\beta\alpha D}{\delta(t)} \tag{3}$$

where α is a known dimensionless constant. Introducing the selfsimilar Boltzmann variable /4/

$$\xi = x/\sqrt{Dt}$$

we reduce the boundary value problem (1) for the concentration of the mobile reagent $u(\xi) = c(t, x)$ and dimensionless temperatures of the solid product $\theta(\xi) = T(t, x)/T_0$ and solid reagent $\theta_1(\xi) = T_1(t, x)/T_0$, to the form

$$\begin{gathered}
\frac{d^2u}{d\xi^2} + \frac{\xi}{2}\frac{du}{d\xi} = 0, \quad 0 \leqslant \xi \leqslant 2\beta \\
u|_{\xi=0} = 1, \quad -\frac{du}{d\xi}\bigg|_{\xi=2\beta} = \varkappa\beta, \quad -\frac{du}{d\xi}\bigg|_{\xi=2\beta} = \alpha f\left(u|_{\xi=2\beta},\, \theta|_{\xi=2\beta}\right) \\
\frac{d^2\theta}{d\xi^2} + L\frac{\xi}{2}\frac{d\theta}{d\xi} = 0, \quad 0 \leqslant \xi \leqslant 2\beta \\
\theta|_{\xi=0} = 1, \quad -\frac{du}{d\xi}\bigg|_{\xi=2\beta} = \Lambda\frac{d\theta}{d\xi}\bigg|_{\xi=2\beta} - \Lambda_1\frac{d\theta_1}{d\xi}\bigg|_{\xi=2\beta} \\
\theta|_{\xi=2\beta} = \theta_1|_{\xi=2\beta} \\
\frac{d^2\theta_1}{d\xi^2} + L_1\frac{\xi}{2}\frac{d\theta_1}{d\xi} = 0, \quad 2\beta \leqslant \xi < \infty \\
\theta_1|_{\xi\to\infty} \to \theta_\infty \\
\left(f(u, \theta) = F(c, T),\ L = \frac{D}{a},\ L_1 = \frac{D}{a_1},\right. \\
\left.\Lambda = \frac{\lambda T_0}{r\rho_0 D},\ \Lambda_1 = \frac{\lambda_1 T_0}{r\rho_0 D},\ \theta_\infty = \frac{T_\infty}{T_0}\right)
\end{gathered} \tag{4}$$

The solution of (4) for the concentration and temperature fields is

$$\begin{gathered}
u = 1 - \sqrt{\pi}\,\varkappa\beta\exp\beta^2\operatorname{erf}\frac{\xi}{2} \\
\theta = 1 + \frac{1}{\Delta}\left[\varkappa\beta\sqrt{\frac{\pi}{L_1}}\operatorname{erfc}(\sqrt{L_1}\,\beta) - (1 - \theta_\infty)\Lambda_1\exp(-L_1\beta^2)\right]\sqrt{\frac{\pi}{L}}\operatorname{erf}\frac{\sqrt{L}\,\xi}{2}
\end{gathered} \tag{5}$$

$$\theta_1 = \theta_\infty + \frac{1}{\Delta}\left[\varkappa\beta\sqrt{\frac{\pi}{L}}\operatorname{erf}(\sqrt{L}\,\beta) + (1-\theta_\infty)\Lambda\exp(-L\beta^2)\right]\sqrt{\frac{\pi}{L_1}}\operatorname{erfc}\frac{\sqrt{L_1}\,\xi}{2}$$
$$\Delta = \sqrt{\frac{\pi}{L}}\Lambda_1\operatorname{erf}(\sqrt{L}\,\beta)\exp(-L_1\beta^2) + \sqrt{\frac{\pi}{L_1}}\Lambda\operatorname{erfc}(\sqrt{L_1}\,\beta)\exp(-L\beta^2)$$

The constant β determining the law of motion of the reaction front (2) can be found from the solution of the following transcendental equation obtained from the kinetic condition in /4/:

$$\chi\beta = \alpha f(u|_{\xi=2\beta}, \theta|_{\xi=2\beta}) \tag{6}$$

In the general case when the function $f(u,\theta)$ is arbitrary, the question of the existence of a solution of (6) remains open. In the case of Arrhenius dependence on the temperature and power dependence on the concentration, we can show that a solution exists. Indeed, in the case (6) will be written in the form

$$\varkappa\beta = \alpha u^n|_{\xi=2\beta}\exp\left(-\frac{A}{\theta|_{\xi=2\beta}}\right) \tag{7}$$

where n is the order of the reaction A is the dimensionless activation energy. When $\beta = 0$ the left hand side of (7) is zero and the right hand side is positive in accordance with solution (5). When β increases, the left hand side increases monotonically and the right hand side tends to zero, since the power multiplier is bounded. For this reason the graphs depicting the dependence of the left and right hand side of (7) on β have at least one intersection. The non-uniqueness of the solution caused by the possible non-monotonic character of the right-hand side is very possible, especially in the case of an exothermic reaction.

To obtain the depth of penetration of the reaction front into the solid reagent $\delta_1(t)$, we shall write the relations expressing the mass balance and stoichiometry of the process as follows:

$$\rho\frac{d\delta}{dt} = -D\frac{\partial c}{\partial x}\bigg|_{x=\delta(t)}\rho_0 + \rho_1\frac{d\delta_1}{dt}$$
$$\nu_0\frac{\rho_1}{\mu_1}\frac{d\delta_1}{dt} = -D\frac{\partial c}{\partial x}\bigg|_{x=\delta(t)}\frac{\rho_0}{\mu_0}\nu_1 \tag{8}$$

From this we can obtain an expression for $\varkappa$ used in writing the boundary conditions in (1), and the relation

$$\delta_1(t) = \frac{\rho}{\rho_1}\frac{\mu_1\nu_1}{\mu_0\nu_0 + \mu_1\nu_1}\delta(t) \tag{9}$$

Equation (6) can serve as the basis for formulating and solving various types of inverse problems such as that of determining the kinetic constant α and estimating the diffusion and thermophysical characteristics of bodies in contact. The constant β, governing the rate of growth of the solid reaction product, must, of course, be determined experimentally.

It should be noted that although a selfsimilar solution (2), (5), (6), (9) of the direct or inverse problem of diffusion kinetics is possible only when the activity varies as given by (3), the expressions obtained can also be used for approximate integral estimates when $k(t)$ has a different form.

Indeed, integrating the Stefan condition from (1) over time from zero to some averaging time τ, we obtain

$$\varkappa\delta(\tau) = \int_0^\tau k(t) f(u|_{\xi=2\beta}, \theta|_{\xi=2\beta})\,dt \tag{10}$$

It can be shown that when the mechanism of the basic reaction is sufficiently slow $(\alpha \ll 1$, and hence $\beta \ll 1)$

$$f(u|_{\xi=2\beta}, \theta|_{\xi=2\beta}) \approx f(1,1)$$

Then

$$\frac{\varkappa}{f(1,1)}\delta(\tau) = \int_0^\tau k(t)\,dt \tag{11}$$

In solving the inverse problem, (11) can be regarded as an integral equation for determining $k(t)$ from the experimentally obtained $\delta(\tau)$. In solving the direct problem we can obtain from (11) an estimate for the value of $\langle\beta\rangle$ averaged over time τ in (2) and (5).

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SCATTERING OF A LONGITUDINAL WAVE BY A SPHERICAL CAVITY WITH A FLUID IN AN ELASTIC POROUS SATURATED MEDIUM*

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The diffraction of a plane longitudinal harmonic wave propagating in an unbounded elastic porous permeable fluid-saturated medium, by a spherical cavity with a fluid is examined. The Frenkel-Biot model /1—3/ is used to describe the dynamics of the porous saturated elastic medium.

The equations describing the space of harmonic waves in a saturated porous medium have the form

$$\omega^2\rho_{11}\mathbf{U} + \omega^2\rho_{12}\mathbf{V} = i\omega b\,(\mathbf{V} - \mathbf{U}) - N\Delta\mathbf{U} - \nabla\,[(A + N)\,\nabla\mathbf{U} + Q\nabla\mathbf{V}], \quad b = \eta\Phi^2F\,(\omega)/K \tag{1}$$

$$\omega^2\rho_{12}\mathbf{U} + \omega^2\rho_{22}\mathbf{V} = i\omega b\,(\mathbf{U} - \mathbf{V}) - \nabla\,(Q\nabla\mathbf{U} + R\nabla\mathbf{V})$$

Here $\mathbf{U}$ and $\mathbf{V}$ are, respectively, the displacement vectors of the solid and liquid phases in the pores, ρ_{11} and ρ_{22} are the coefficients of dynamic density, ρ_{12} is the mass coupling coefficient between the liquid and solid phases, A, N, Q, R are elastic constants, η is the dynamic viscosity of the fluid, Φ is the bulk porosity, K is the permeability, and ω is the angular frequency; the function $F(\omega)$ describes the deviation in the pores from Poiseuille flow /2/.

We represent the displacement vectors of the solid and liquid phases as the sum of displacement vectros in the incident and scattered waves, i.e.,

$$\mathbf{U} = \mathbf{\Pi} + \mathbf{u}, \quad \mathbf{V} = \boldsymbol{\pi} + \mathbf{v}$$

A plane travelling wave with the displacements $\mathbf{\Pi}$ in the solid and $\boldsymbol{\pi}$ in the liquid phases satisfies system (1). Therefore, because of the linearity of this system, the fields $\mathbf{u}$ and $\mathbf{v}$ of the scattered waves satisfy them. Introducing the spherical coordinates r, θ, φ with origin at the centre of a spherical cavity of radius a and polar axis coincident with the direction of incident wave propagation, we determine the complex amplitudes of the scattered wave displacement potentials by the following relationships:

$$\mathbf{u} = \nabla\Lambda + \nabla\times(\Psi\mathbf{e}_\varphi), \quad \mathbf{v} = \nabla B + \nabla\times(\chi\mathbf{e}_\varphi) \tag{2}$$

where $\mathbf{e}_\varphi$ is the unit vector in the equatorial direction, and the factor $\exp(-i\omega t)$ is omitted everywhere.

Substituting (2) into (1) applying the divergence operation to the system of equations, we reduce it to the form

$$q_{1k}\Delta\Lambda + q_{k2}\Delta B + \varkappa^2(\gamma_{1k}\Lambda + \gamma_{k2}B) = 0; \quad k = 1, 2$$

$$q_{11} = A + 2N, \quad q_{12} = Q/H, \quad q_{22} = R/H, \quad H = A + 2N + 2Q + R$$

$$\varkappa^2 = \omega^2\rho/H, \quad \rho = \rho_1(1 - \Phi) + \rho_2\Phi, \quad \gamma_{11} = (\rho_{11} + ib/\omega)/\rho$$

$$\gamma_{12} = (\rho_{12} - ib/\omega)/\rho, \quad \gamma_{22} = (\rho_{22} + ib/\omega)/\rho$$

where ρ_1 and ρ_2 are the densities of the solid and liquid phase material in the pores.

Performing the substitution $\Lambda = \Lambda_1 + \Lambda_2$, $B = m_1\Lambda_1 + m_2\Lambda_2$, we require that Λ_1 and Λ_2 satisfy the Helmholtz equations

$$\Delta\Lambda_i + \varkappa^2\xi_i\,\Lambda_i = 0 \tag{3}$$

For this it is necessary that ξ_1 and ξ_2 should be the roots of the following dispersion equation:

$$(q_{11}q_{22} - q_{12}^2)\,\xi^2 - (\gamma_{11}q_{22} + \gamma_{22}q_{11} - 2\gamma_{12}q_{12})\,\xi + (\gamma_{11}\gamma_{22} - \gamma_{12}^2) = 0 \tag{4}$$

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