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INFLUENCE OF THE TEMPERATURE DISTRIBUTION ON CHEMICAL DEPOSITION IN INTERNAL PROBLEMS

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The issue of uniform deposition of a substance for the two-stage kinetics of a heterogeneous chemical reaction is investigated based on the molecular-kinetic approach.

Problems concerning the uniform course of a heterogeneous chemical reaction which leads to the deposition of reactant molecules (or their parts) on the internal surfaces of the system, in particular, in the case of flow of a reactant gas in porous media and individual channels, arise in many chemical-engineering problems. They include both problems connected with the manufacture of different elements of microelectronic devices [1], for which the condition of uniformity of the film formed on the surface is of importance, and problems in which the deposition of a layer of a substance on the channel walls (or on the pore walls in the case of a porous body) as a result of the chemical reaction is undesirable, for example, the problems of filtration of gases through finely porous bodies. In the latter case, the deposition of a substance on the walls of the pores can lead to their clogging, which results in deterioration of the technological process. We note that in the isothermal case the channels (pores) will be clogged more intensely near the ends facing the gas phase with reactant molecules, which can lead to totally blocked channels. A uniform deposition along the entire channel length can be realized on creation of an assigned temperature distribution along the channel wall. Some questions of uniform deposition of a substance in cylindrical channels with free-molecular gas flow have been considered in [2]. However, in [2], a one-stage scheme of deposition was used (disregarding the fact that the reactant molecules were in the intermediate state of physical adsorption). In the work proposed, we consider chemical deposition for internal problems with a two-stage scheme of a heterogeneous chemical reaction. It is shown that the temperature distribution which is necessary for a uniform deposition of molecules along the channel surface substantially depends on the relation between the energy of activation of the heterogeneous chemical reaction and the energy of desorption of the unreacted molecules of the reactant from the channel (pore) surface.

Let us consider chemical deposition from the gas phase in accordance with the scheme of [3]. This scheme assumes that in collision of a molecule of the reactant gas AB_χ with the surface we have a reaction resulting in the transition of one reaction product (A) to a bound state (c) and in the formation of gas molecules (B) desorbed from the surface:

$$AB_\chi\,(g) \to A\,(c) + \chi B\,(g)\,. \tag{1}$$

The thickness distribution of the layer of a substance, which is assumed to be solid, along the channel is determined by the resultant flux of the molecules deposited on the channel wall. The problem is considered in the quasistationary approximation. Next we assume that by the beginning of the desorption process the entire internal surface of the channel is already coated with the substance layer consisting of the deposited particles. The film thickness is considered to be much smaller than the channel radius throughout the process, so that a change in the probability of molecular transition from one element of the channel surface to another due to the growth in the thickness of the deposited layer can be neglected. The molecules entering the channel and leaving the surface are assumed to be distributed according to the cosine law. The rate of growth of the deposited-film thickness is determined as

$$v = \frac{dh}{dt} = n^{-1} J\,. \tag{2}$$

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Here J is the density of the resultant flux of the deposited molecules into the film, which can be represented in the form

$$J = J_1 + J_2 - j_A , \tag{3}$$

where j_A is the flux density of the evaporating particles of the component A, which is determined by the expression

$$j_A = G_A \exp\left\{-\frac{Q_A}{R_g T}\right\}; \tag{4}$$

Q_A is the heat of evaporation of the component A.

The values of J_1 and J_2 for the case of the free-molecular regime of gas flow in a cylindrical capillary are found from the equations

$$J_1 = \gamma\left[\int_0^1 I_r K_1(|x - x'|)\, dx' + N_r(0)\, K(x) + N_r(1)\, K(1-x)\right], \tag{5}$$

$$I_r = (1-\gamma)\left[\int_0^1 I_r K_1(|x - x'|)\, dx' + N_r(0)\, K(x) + N_r(1)\, K(1-x)\right], \tag{6}$$

$$J_2 = \alpha_A\left[\int_0^1 (j_A + I_A)\, K_1(|x - x'|)\, dx'\right], \tag{7}$$

$$I_A = (1-\alpha_A)\left[\int_0^1 (j_A + I_A)\, K_1(|x - x'|)\, dx'\right], \tag{8}$$

where x is the dimensionless coordinate directed along the channel axis ($x = X/L$) and the functions K and K_1 describe the probabilities of transition of a particle from one element of the channel surface to another. For a cylindrical channel they have the form [4, 5]

$$K(x) = \frac{l^2 x^2 + 2}{2\,(l^2 x^2 + 4)^{1/2}} - \frac{l}{2} x, \quad K_1(x) = -\frac{dK(x)}{dx}, \quad l = \frac{L}{R}. \tag{9}$$

The values $N_r(0)$ and $N_r(1)$ are the flux densities of the reactant molecules entering the channel through its ends at $x = 0$ and $x = 1$; I_r and I_A are the flux densities of the molecules of the reactant and the component A which are elastically reflected from the channel wall; α_A is the condensation coefficient of the particles of the component A.

Let us consider the physical meaning of the members of system (5)–(8) using Eq. (5) as an example. The quantity J_1 characterizes the flux density of the reactant molecules reacting on the channel surface. Under the specified assumptions, it is equal to the flux density of the particles deposited on the surface. The member in the square brackets in (5) determines the flux density of the reactant molecules incident on the surface element in the vicinity of the point x. The above flux consists of the reactant molecules which come to the given element of the surface both from the remainder of the channel surface after elastic reflection (which is assumed to be diffuse) and through the channel ends (without intermediate collision with the channel surface).

The coefficient γ characterizes a part of collisions of the reactant molecule with the surface that lead to a heterogeneous chemical reaction as a result of which a molecule (an atom) is built into the condensed phase. In the case of the two-stage scheme of the chemical reaction which accounts for the reactant molecule being in the intermediate

state of physical adsorption, to determine the value of γ in the heterogeneous chemical reaction of first order within the framework of the Langmuir absorption theory we can write the expressions

$$\gamma N_r = \beta N_r \left(1 - \frac{n_a}{n_0} - \frac{n_b}{n_0}\right) - k_d n_a \,, \tag{10}$$

$$\gamma N_r = k_r n_a \,, \tag{11}$$

where n_a and n_b are the number concentrations of the adsorbed molecules of the reactant and the buffer (or admixture) gas respectively and k_r and k_d are the rate constants of the chemical reaction and the desorption of the reactant molecules, which have the form

$$k_r = k_{r0} \exp\left\{- Q_r/R_g T\right\} , \tag{12}$$

$$k_d = k_{d0} \exp\left\{- Q_d/R_g T\right\} . \tag{13}$$

In the case of a rather low concentrations of the adsorbed molecules n_a and n_b, (10) and (11) yield an expression for γ which coincides with the expression used in [6]:

$$\gamma = \frac{\beta}{1 + \dfrac{k_d}{k_r}} = \frac{\beta}{1 + \dfrac{k_{d0}}{k_{r0}} \exp\left\{- (Q_d - Q_r)/R_g T\right\}} . \tag{14}$$

The problem of uniform deposition in a channel in the free-molecular regime of flow lies in obtaining the temperature distribution for which a constant value of the quantity J ($J = J_0$) is realized.

It should be noted that in a number of cases the reevaporation of deposited molecules is very low in chemical deposition and it can be neglected. Let us consider this case. It corresponds to the conditions $J_2 = J_A = j_A = 0$ and $J_1 = J$. From (5)–(8) we obtain

$$J + I_r = \int_0^1 I_r K_1 \left(\left| x - x' \right|\right) dx' + N_r (0)\, K (x) + N_r (1)\, K (1 - x) . \tag{15}$$

Approximating K_1 and K by exponential functions [4], differentiating (15) twice, and combining the obtained expression with the initial one, we have

$$\frac{d^2 I_r}{dx^2} = l^2 J - \frac{d^2 J}{dx^2} . \tag{16}$$

The solution of (16) has the form

$$I_r = l^2 \int \left(\int J (x)\, dx\right) dx - J + ax + b . \tag{17}$$

The constants a and b are found by substitution of (17) into (15).

Let us consider the case which is symmetric relative to the reactant gas ($N_r(0) = N_r(1) = N_r$). Here, with account for (12)–(14) and the above assumptions, we obtain the following temperature distribution $T(x)$ along the channel, resulting in a uniform deposition of the substance on the channel wall (which corresponds to the condition $J = J_0 = \text{const}$):

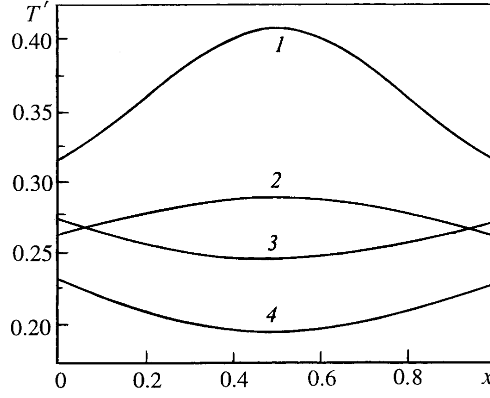

Fig. 1. Dimensionless-temperature distributions which are necessary for a uniform chemical deposition in a cylindrical channel for $l = 10$ and different relations between Q_r and Q_d. Curves 1 and 2 correspond to $Q_r > Q_d$, $k_{d0}/k_{r0} = 1$, and $\beta = 1$; curves 3 and 4 correspond to $Q_r < Q_d$, $k_{d0}/k_{r0} = 600$, and $\beta = 0.36$; curves 1 and 4 correspond to $N_r/J_0 = 30$; curves 2 and 3 correspond to $N_r/J_0 = 50$.

$$T(x) = \frac{Q_r - Q_d}{R_g \ln \left\{ \frac{k_{r0}}{k_{d0}} \left(\beta \left[\frac{N_r}{J_0} - \frac{l}{2} - \frac{l^2 x (1-x)}{2} \right] - 1 \right) \right\}} . \tag{18}$$

Figure 1 presents the distributions of the dimensionless temperature $T' = \frac{T(x)}{|Q_r - Q_d|/R_g}$ along the channel; they lead to a uniform chemical deposition for the cases $Q_r < Q_d$ and $Q_r > Q_d$. For $Q_r < Q_d$ we have taken the values of the parameters k_{d0}/k_{r0} and β used in [6] for the initial stage of the reaction of SiH_2Cl_2 decomposition on the surface of Si, which results in the chemisorption of SiCl molecules: $k_{d0}/k_{r0} = 600$ and $\beta = 0.36$ (in [6], the value of $Q_d - Q_r$ was set equal to 3.8 kcal/mole). For the case $Q_r > Q_d$ we have taken the following values of the parameters: $k_{d0}/k_{r0} = 1$ and $\beta = 1$. It is seen in Fig. 1 that the function $T'(x)$ has a maximum at the center of the channel for $Q_r > Q_d$ and a minimum for $Q_r < Q_d$.

We note that the effective coefficient γ_e determined by the ratio of the number of reactant molecules reacted on the channel wall in a unit time to the number of reactant molecules entering the channel in a unit time for the case of a uniform heterogeneous chemical reaction along the channel length has the form (when $N_r(0) = N_r(1) = N_r$)

$$\gamma_e = \frac{LJ_0}{RN_r} . \tag{19}$$

It follows from (19) that the quantity γ_e is proportional to the factor $l = L/R$.

The foregoing shows that the temperature distribution which is necessary for a uniform chemical deposition of the substance in the channel substantially depends on the relation between the activation energy of the heterogeneous chemical reaction and the desorption energy of the unreacted molecules of the reactant. In the one-stage approach (without considering the molecule being in the intermediate state of physical adsorption), the temperature distribution leading to a uniform chemical deposition along the channel is characterized by the maximum at the center of the channel [2]. It should be noted that, with allowance for [7], the results obtained for a single channel can quite simply be applied to a porous body described by the dusty-gas model.

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NOTATION

T, temperature; n_0, number of adsorption centers per unit surface; L, length of the channel; R, radius of the channel; $l = L/R$; t, time; h, thickness of the film; v, rate of growth of the film thickness; J_0, flux density of reacting (chemisorbed) molecules in uniform chemical deposition; G_A, k_{d0}, and k_{r0}, preexponential factors which are assumed to be constant quantities; Q_d and Q_r, heats of desorption of reactant molecules and of the heterogeneous chemical reaction respectively; n, number of molecules per unit volume of the condensate; β, sticking coefficient of reactant molecules; N_r, flux density of reactant molecules incident on the surface; n_a and n_b, number concentrations of the adsorbed molecules of the reactant and the buffer (admixture) gas respectively; R_g, gas constant. Subscripts: d, desorption; r, reaction; a, adsorbed; b, buffer; A, component; p, particle; g, gas; e, effective.

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