LITERATURE CITED

1. O. Kreisher, Scientific Principles of Drying Technology [in Russian], Moscow (1961).
2. V. G. Petrov-Densiov and L. A. Maslennikov, Processes of Heat and Moisture Transfer in Industrial Insulation [in Russian], Moscow (1983).
3. G. N. Dul'nev and Yu. P. Zarichnyak, Thermal Conductivity of Mixtures and Composite Materials [in Russian], Leningrad (1974).
4. A. V. Lykov, Heat and Mass Transfer (Handbook) [in Russian], Moscow (1978).

STEADY-STATE TWO-DIMENSIONAL DIFFUSION OF A RADIOACTIVE IMPURITY IN A CHANNEL WITH SORBING WALLS

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We consider the analytical solution of the problem of steady-state diffusion of a radioactive impurity in a gas-filled channel of finite length with sorbing walls, with allowance for surface diffusion. The conditions under which the two-dimensional problem becomes one-dimensional are found.

The study of diffusion of impurity components in gas-filled porous media is of great importance in developing a whole range of technologies associated with processes of drying, absorption, desorption, and heterogeneous catalysis, as well as in solving radioecological problems. The simplest model of capillary-porous media in the form of a set of cylindrical capillaries allows the discussion to be confined to diffusion in a single capillary. Further analysis is carried out, as a rule, on the assumption that the bulk and adsorption phases are in equilibrium in each cross section of the capillary, which allows the problem to be reduced to a one-dimensional formulation with the introduction of an effective diffusion coefficient, which makes allowance for the effect which both absorption and diffusion on the surface of the capillary have on the total diffusion flux [1-3]. In the case of steady-state diffusion of a radioactive impurity as well as in the case of unsteady-state diffusion of a stable impurity, however, the local equilibrium in an element of length of the channel may be disrupted substantially and as a result the contributions of volume and surface diffusion to the total diffusion flux through the capillary are redistributed considerably. In our study we find the parameter that specifies the degree of such nonequilibrium in the case of steady-state diffusion of a radioactive impurity and examine the conditions for the transition to the one-dimensional formulation.

Let us consider a cylindrical channel of length L and radius r_0, filled with a motionless inert gas. Suppose that the concentration of the radioactive impurity is maintained at c_0 at the beginning of the channel and is zero at the end of the channel. In accordance with the geometry of the problem we chose a cylindrical coordinate system, directing the z axis along the axis of the channel. Then steady-state diffusion of this impurity in the channel, complicated by adsorption on the channel walls and diffusion along the channel surface, can be described by the system of equations

$$\varepsilon \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial c}{\partial \rho} - gc(x, \rho) = 0, \tag{1}$$

$$\varepsilon \frac{d^2 c_{\mathrm{s}}}{dx^2} - pc_{\mathrm{s}}(x) - s\left(\frac{\partial c}{\partial \rho}\right)_{\rho=1} = 0, \tag{2}$$

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$$\beta_0 \left[\frac{\partial c}{\partial \rho} + tc(x, \rho) \right]_{\rho=1} = tc_s(x), \tag{3}$$

$$c(0, \rho) = c_0, \quad c(1, \rho) = 0, \quad 0 < c(x, 0) < \infty, \tag{4}$$

where $\varepsilon = (r_0/L)^2$, $g = \lambda r_0^2/D$, $p = \lambda r_0^2/D_s$, $t = v_t r_0/4D$; $b = \beta r_0^2/D_s$, $S = \beta_0 b/l$, and $\beta_0 = v_t n_0 \sigma^2/4\beta$ is Henry's adsorption coefficient.

Equations (1) and (2) describe the balance of the number of particles in an element of volume and in an element of surface of the channel. By means of the boundary condition (3) the radial diffusion flux on the channel wall is represented as the resultant of two fluxes: the flux of molecules incident on the wall from the gaseous phase and the flux of desorbed molecules. The assumption is that the molecules incident on the wall have an equilibrium (Maxwellian) velocity distribution and the adsorption isotherm is linear. The problem (1)-(4) can also be considered as a mathematical model of steady-state two-dimensional diffusion of an impurity which enters into a first-order chemical reaction. The solution of this problem has the form

$$c(x, \rho) = c_0 \left\{ \frac{\operatorname{sh}[(g/\varepsilon)^{1/2}(1-x)]}{\operatorname{sh}[(g/\varepsilon)^{1/2}]} - t \sum_{n=1}^{\infty} C_n I_0(\beta_n \rho) \sin(\pi n x) \right\}, \tag{5}$$

$$c_s(x) = \beta_0 c_0 \left\{ \frac{\operatorname{sh}[(p/\varepsilon)^{1/2}(1-x)]}{\operatorname{sh}[(p/\varepsilon)^{1/2}]} + b \sum_{n=1}^{\infty} C_n \frac{\beta_n}{\gamma_n^2} I_1(\beta_n) \sin(\pi n x) \right\}, \tag{6}$$

where

$$C_n = \frac{2\pi n \varepsilon (p-g)/\beta_n^2}{t\gamma_n^2 I_0(\beta_n) + (\gamma_n^2 + b)\beta_n I_1(\beta_n)}, \tag{7}$$

$$\beta_n^2 = g + \varepsilon(\pi n)^2, \quad \gamma_n^2 = p + \varepsilon(\pi n)^2, \tag{8}$$

and I_0 and I_1 are Bessel functions of order zero and order one, respectively. Clearly, the deviation from equilibrium between the gaseous and adsorbed phases is characterized by the radial diffusion flux at the channel wall, i.e., the quantity $(\partial c/\partial \rho)_{\rho=1}$. From (5)-(7) we see that the radial diffusion flux is exactly zero only in two cases: when the decay constant λ is zero and when the diffusion coefficient D in the gaseous phase is equal to the surface diffusion coefficient D_s. In both cases the dependence of the bulk concentration c on the radial coordinate disappears because the coefficient C_s becomes zero. Otherwise, the equilibrium between the gaseous and adsorbed phases is disrupted to one degree or another.

Let us find the conditions under which the problem becomes quasi-one-dimensional, i.e., the dependence of the concentration on the radial coordinate is weak. In this case one should expect that an expression of the form

$$c(x, \rho) = A(x) + B(x)\rho^2 \tag{9}$$

will be a good approximation of the exact solution of the problem. If we set $\rho = 1$ in Eq. (1), then the resulting condition together with conditions (2) and (3) specifies the algebraic relation between A(x) and B(x). When this relation is taken into account and Eq. (9) is substituted into Eq. (1) and we confine our discussion to terms of order zero in ρ and solve the resulting differential equation for A(x) with the boundary conditions $A(0) = c_0$ and $A(1) = 0$, we obtain

$$c(x, \rho) = c_0 \frac{\operatorname{sh}[(g+a)^{1/2}(1-x)/\varepsilon^{1/2}]}{\operatorname{sh}[(g+a)^{1/2}/\varepsilon^{1/2}]} \left(1 + \frac{a}{4}\rho^2\right), \tag{10}$$

where

$$a = \frac{4(p-g)t}{(p-g)(2+t) + 4t + 2b}. \tag{11}$$

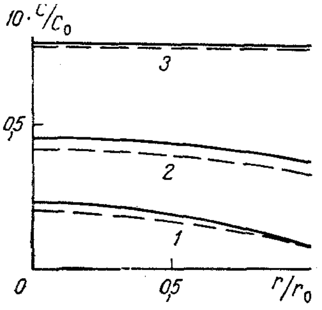

Fig. 1

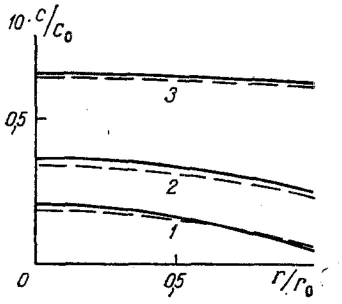

Fig. 2

Fig. 1. Concentration versus radial coordinate at p = 10 [solid curves represent the exact solution (5) and dashed curves represent the quasi-one-dimensional approximation (10)]: 1) b = 10, 2) $b = 10^4$, 3) $b = 10^5$.

Fig. 2. Concentration versus radial coordinate with condition (14) not satisfied (solid and dashed lines as in Fig. 1): 1) $b = 10^3$, p = 10; 2) $b = 10^2$ and p = 1; 3) $b = 10^2$ and p = 0.1.

The dimensionless numerical density of the impurity in the adsorbed phase is found in this case from the boundary condition (3). Expression (10) is a good approximation of the exact solution of problem (1)-(4) on condition that there is a weak dependence on the radial variable, i.e., when $a \ll 4$, or allowing for Eq. (11) and the explicit form of the parameters in it,

$$\frac{8D}{v_t r_0}+\frac{4D_s}{\lambda r_0^2(1-D_s/D)}+\frac{8D\beta}{v_t r_0\lambda(1+D_s/D)}\gg 1. \tag{12}$$

Usually $D_s < D$ and, therefore, all terms in condition (12) are positive. Furthermore, since $D/v_t r_0 \sim \mathrm{Kn}$, where Kn is the Knudsen number, and the formulation of the problem corresponds to a viscous regime, the first term in condition (12) is much smaller than unity. Condition (12), therefore, in actual fact breaks up into two conditions:

$$\lambda r_0^2/D_s \ll 1, \tag{13}$$

$$\beta/\lambda \gg \mathrm{Kn}^{-1}. \tag{14}$$

If at least one of these conditions is satisfied the problem becomes quasi-one-dimensional and its solution is described well by Eq. (10).

Condition (13) is violated, e.g., when the surface diffusion coefficient D_s is zero. In this case from Eq. (2) we have $-D\left(\frac{\partial n}{\partial r}\right)_{r=r_0} = \lambda n_s(x)$, i.e., radial diffusion flux exactly balances the radioactive decay of the impurity atoms in the adsorbed phase. In this case satisfaction of condition (14), which in fact means no radioactive decays during adsorption, thus results in negligible radial fluxes on the wall, i.e., the problem remains quasi-one-dimensional.

Calculations performed with formulas (5) and (10), with the assumption that $t = 10^3$, $\varepsilon = 10^{-4}$, $p/g = 10^4$, confirmed the above. Figures 1 and 2 show the radial distribution of the impurity concentration of the radioactive impurity in the cross section of the channel at x = 0.01 for various values of the parameters p and b. Figure 1 corresponds to the fixed value p = 10 [condition (13) is not satisfied] and Fig. 2 corresponds to the fixed value $\beta/\lambda = b/p = 10^2$ [condition (14) is not satisfied]. From Figs. 1 and 2 we see that as one of the conditions, (13) or (14), is satisfied the problem becomes quasi-one-dimensional and at the same time the approximate expression (10) provides a more and more adequate description of the behavior of the exact solution (5).

As already mentioned, two-dimensionality should lead to a redistribution of the contributions of volume and surface diffusion to the total diffusion flux. The nature of this redistribution can be assessed from the quasi-one-dimensional solution (10). In this case the ratio of the total flux J_g in the gaseous phase to the total flux J_s over the surface of the channel does not depend on the longitudinal coordinate x and has the form

$$J_s/J_g = \frac{3t}{b}\left(1 - \frac{2}{6-a}\right), \tag{15}$$

while in the purely one-dimensional case (which is realized, e.g., at $\lambda = 0$) this ratio is 2t/b. From a comparison of this value with (15) it follows that when the two-dimensionality is taken into account, i.e., when there is not local equilibrium between the bulk and adsorbed phases, the contributions are redistributed to the benefit of the gaseous phase.

NOTATION

L, channel length, r_0, channel radius; x, ρ, dimensionless longitudinal and radial coordinates; c, numerical density of the admixture in a gaseous phase; n_0, the total number of particles in a gaseous phase; c_s, dimensionless numerical density of the admixture in the adsorption phase (degree of occupation); σ, diameter of the adsorbate molecules; λ, constant of radioactive decay; D, D_s, diffusion coefficient in the gaseous phase and over the channel surface, respectively; v_i, thermal velocity of the admixture molecules in the gaseous phase; $1/\beta$, adsorption time; J_s, total diffusion flow over the channel surface; J_g, total diffusion flow in the gaseous phase.

LITERATURE CITED

1. G. A. Aksel'rud and M. A. Al'tshuler, Introduction to the Capillary-Chemical Technology [in Russian], Moscow (1983).
2. Yu. G. Frolov, Course of Colloidal Chemistry [in Russian], Moscow (1982).
3. D. P. Timofeev, Usp. Khim., 29, No. 3, 401 (1960).

MACROKINETICS OF INTERMETALLIC COMPOUND FORMATION IN THE DIFFUSION ZONE

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A macrokinetic model is developed for reaction diffusion in binary metallic systems for situations when the phase composition of the diffusion zone does not correspond to the equilibrium phase diagram.

Investigation of the formation of intermetallides and silicides during diffusion mass transfer with solid phase transformations is associated with the development of integral circuit technology, the perfection of methods of superposing protective coatings on metals, etc. It is established experimentally that the phase composition of the diffusion zone during the annealing of thin-film and bulk diffusion pairs of the metal—metal (Ni—Al, Co—Al, Cr—Al, Au—Al, Cu—Sn, etc.) and metal (Co, Ni, Pd, Pt, Cr, Ti, V, W, Mo, Nb, Ta, Zr, etc.)-silicon types does not correspond to an isothermal section of the equilibrium phase diagram [1-3]. For instance, only Ni_2Si out of the six equilibrium phases (Ni_3Si, Ni_5Si_2, Ni_2Si, Ni_3Si_2, NiSi, $NiSi_2$) is formed in the Ni—Si system at the annealing temperature 200-350°C [4], while only Pd_2Si of the four phases (Pd_3Si, Pd_5Si_2, Pd_2Si, PdSi) [5] is formed in the Pd-Si pair at 200-600°C, and which grow until exhaustion of one of the initial elements. The absence of thin interlayers of the remaining phases is confirmed by using scanning electron microscopy [3-5]. Analogous facts, the absence of intermediate compounds, are observed during growth of $MoSi_2$, $TiSi_2$, $NbSi_2$, WSi_2 during silicon saturation of infusible metals

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