

bed itself (see [7, 9], for example). For the formulation of such models it is necessary to accumulate test data on heat exchange, as well as on the concentrations of particles and their fractional composition in the space above a bed and the dependences of these characteristics on various physical and hydrodynamic factors.

#### NOTATION

D, outside diameter of tube of the heat-exchange sensor; d, particle diameter; g, free-fall acceleration; h, height above the gas-distribution grid; H, H<sub>0</sub>, bed height and initial bed height; H<sub>c</sub>, critical height of the separation zone; j, mass of solid particles falling into a "bucket" per unit time; R, residue of particles on a sieve with a mesh d<sub>i</sub>; S, horizontal cross-sectional area of a "bucket"; u, u<sub>0</sub>, velocities of filtration and of the onset of fluidization; α, α<sub>∞</sub>, α<sub>b</sub>, coefficients of external heat exchange in the space above the bed, in pure air, and in the fluidized bed, respectively; ε, ε<sub>0</sub>, porosities of the bed at filtration velocities u and u<sub>0</sub>, respectively; λ<sub>f</sub>, coefficient of thermal conductivity of the fluidizing gas; ν<sub>f</sub>, kinematic viscosity of the gas; ρ<sub>s</sub>, ρ<sub>f</sub>, densities of the particles and the gas, respectively; Ar = gd<sup>3</sup>(ρ<sub>s</sub>/ρ<sub>f</sub> - 1)/ν<sub>f</sub><sup>2</sup>; Nu<sub>∞</sub> = α<sub>∞</sub>D/λ<sub>f</sub>; Re = uD/ν<sub>f</sub>; Re<sub>c</sub> = ud<sub>c</sub>/ν<sub>f</sub>.

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#### MASS TRANSFER IN A DISPERSE MATERIAL WITH ABSORPTION BY PARTICLES

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The general principles of an average macroscopic description of diffusion mass transfer in disperse media containing surface and bulk sources are elucidated in [1]. In this investigation the mentioned principles are applied to an analysis of diffusion in the gaps between nonconducting particles on whose surfaces absorption and liberation of the diffusing impurity are possible. Such a problem is of direct interest in studying mass transfer processes in suspensions that evaporate and dissolve or grow because of particle condensation and crystallization [2], in granular systems with absorption and heterogeneous chemical reactions [3], in inhomogeneous materials, and particularly, metals with discrete elements of a new phase [4], in certain biological systems [5]. An analogous problem was examined earlier in [6] where certain simplifying phenomenological representations were utilized. In order to obtain the fundamental results in an analytic easily discernible form, we limit ourselves below to an analysis of diffusion in moderately concentrated systems containing spherical particles of identical size. The kinetics of the surface transformations is considered linear while the system itself is spatially homogeneous in macroscopic respects.

We write down the fundamental governing relationships that characterize diffusion in a system with non-conducting particles when the diffusing substance either does not generally penetrate the particle bulk or is not contained within them with a homogeneous concentration. In this case there is a single macroscopic diffusion equation [1]

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$$\partial(\epsilon c_0)/\partial t = -\nabla q + h, \quad (1)$$

where the mean impurity flux and surface source intensity are written in the form

$$q(t, \mathbf{R}) = -D_0 \left( \nabla(\epsilon c_0) - n \int_{|\mathbf{R}-\mathbf{R}'|=a} c_0^*(t, \mathbf{R}|\mathbf{R}') n' d\mathbf{R}' \right), \quad (2)$$

$$h(t, \mathbf{R}) = -kn \int_{|\mathbf{R}-\mathbf{R}'|=a} [c_0^*(t, \mathbf{R}|\mathbf{R}') - c_*] d\mathbf{R}'.$$

The integration here is over the locations  $\mathbf{R}'$  of the center of a liberated (test) particle such that the point  $\mathbf{R}$  is on its surface. The quantity  $c_*$  that represents the mean impurity concentration at the surface of a fixed test particle is determined from the solution of a special problem on the perturbations induced by the latter in a mean field of concentration  $c_0$ . In conformity with the general method [1] a Fourier transform in the time must be applied to formulate this problem and the transformed quantities from (2) must be represented in the form of linear combinations of the Fourier transforms of scalar and vector quantities that completely describe the average concentration field at this point. For  $\epsilon = \text{const}$  the most general form of these linear relationships is

$$q = -D\nabla c_0, \quad h = K(c_* - c_0) - Lc_0, \quad (3)$$

where  $D$ ,  $K$ , and  $L$  are certain, unknown as yet, complex coefficients that depend on the physical parameters and the Fourier variable  $\omega$ . Consequently, the transformed diffusion equation (1) takes the form

$$\Delta c_0 = s^2 c_0 - m^2 c_* = s^2 (c_0 - C_*),$$

$$s^2 = \frac{K + L + i\epsilon\omega}{D}, \quad m^2 = \frac{K}{D}, \quad C_* = \left( \frac{m}{s} \right)^2 c_* \quad (4)$$

(the notations for the appropriate originals are kept for the Fourier transforms).

Setting  $c_*^*(\omega, \mathbf{R}|\mathbf{R}') = c_0(\omega, \mathbf{R}) + \varphi(\omega, \mathbf{r})$ , where  $\mathbf{r} = \mathbf{R} - \mathbf{R}'$ , the test particle problem can be formulated in the approximation of a moderately concentrated medium thus [1]

$$\Delta\varphi - s^2\varphi = 0, \quad r > a; \quad \varphi \rightarrow 0, \quad r \rightarrow \infty;$$

$$-n'\nabla(c_0 + \varphi) = \sigma(c_* - c_0 - \varphi), \quad r = a; \quad \sigma = k/D. \quad (5)$$

Let us note that although the problem (5) agrees exactly with that investigated in [6], the relationships (2) differ from those used in the paper mentioned. This is related firstly to the fact that a method [1] for the strict description of mean concentration fields in phases of a heterogeneous disperse medium in the presence of local concentration discontinuities of the particle surfaces was not known. Consequently, it turned out to be necessary formally to continue the concentration field defined outside the particles into the region within them, for which a purely heuristic assumption was used that a value of the concentration equal to its mean on its surface should be ascribed to the center of each particle. Secondly, under such an assumption there was no sense in trying for excess mathematical accuracy of the theory, and consequently, the integrals with respect to the locations  $\mathbf{R}'$  of the center of the test particle such that  $|\mathbf{R} - \mathbf{R}'| = a$  would be replaced by simple integrals with respect to the particle surface with center at the point  $\mathbf{R}$ .

The field  $c_0(\omega, \mathbf{R})$  whose linear scale  $l$  should be much greater than  $a$  figures in the boundary condition of the test particle surface in (5). (This is a certain condition for the applicability, in principle, of continual methods to the description of diffusion in disperse and generally heterogeneous media.) Consequently, it is natural to represent  $c_0(\omega, \mathbf{R}) = c_0(\omega, \mathbf{R}' + \mathbf{r})$  in the domain  $r \sim a$  in the form of a Taylor expansion in powers of the components  $\mathbf{r}$ . Assuming, for simplicity, that  $c_0(\omega, \mathbf{R})$  depends only on one such component, by selecting the polar axis in the direction  $\nabla c_0(\omega, \mathbf{R})$  and introducing the appropriate polar angle  $\theta$  we write

$$c_0(\omega, \mathbf{R}) \approx c'_0 + E'z + M'z^2 + N'z^3 + T'z^4, \quad z = r \cos \theta. \quad (6)$$

Substituting (6) into (4), we arrive at the equalities

$$M' = \frac{s^2}{2} (c'_0 - C_*), \quad N' = \frac{s^2}{6} E', \quad T' = \frac{s^4}{24} (c'_0 - C_*). \quad (7)$$

The coefficients in (6) are defined in the usual way in terms of values of  $c_0$  and its derivatives at the point  $R'$  and are independent of  $r$ . Let us note that terms with  $N'$  and  $T'$  were not taken into account in the theory before, although as follows from the analysis presented below, in the long run they do not result in corrections that vanish within the limits of the accuracy taken in the final relationships. It is convenient to convert the series (6) into an expansion in the Legendre polynomials  $P_j(\cos \theta)$ . Taking (7) into account, we have

$$c_0 \approx \left[ c'_0 + \frac{s^2 a^2}{6} \left( 1 + \frac{s^2 a^2}{20} \right) (c'_0 - C_*) \right] P_0 + \left( 1 + \frac{s^2 a^2}{10} \right) a E' P_1 + \frac{s^2 a^2}{3} \left( 1 + \frac{s^2 a^2}{14} \right) (c'_0 - C_*) P_2 + \frac{s^2 a^2}{15} a E' P_3, \quad P_j = P_j(\cos \theta), \quad c_0 = c_0(\omega, R' + a). \quad (8)$$

Using an analogous expansion for  $c_0(\omega, R - r)$  with coefficients defined at the point  $R$ , we obtain the relationships

$$\begin{aligned} c'_0 P_0 &\approx \left[ c_0 + \frac{s^2 a^2}{6} \left( 1 + \frac{s^2 a^2}{20} \right) (c_0 - C_*) \right] P_0 - \left( 1 + \frac{s^2 a^2}{10} \right) a E P_1, \\ a E' P_1 &\approx - \frac{s^2 a^2}{3} \left( 1 + \frac{s^2 a^2}{10} \right) (c_0 - C_*) P_0 + \left( 1 + \frac{3s^2 a^2}{10} \right) a E P_1, \\ c'_0 P_2 &\approx \frac{s^2 a^2}{15} \left( 1 + \frac{s^2 a^2}{14} \right) (c_0 - C_*) P_0 - \frac{2}{5} \left( 1 + \frac{s^2 a^2}{7} \right) a E P_1, \end{aligned} \quad (9)$$

which are required for evaluation of the integrals in (2). Only components that do not vanish under the integration mentioned are retained in (9). It is seen from (6) that the quantity  $|sa|$  is of the order  $a/l$ , i.e., can be considered as a small parameter of continual theory. The accuracy of the theory is determined by the number of components taken into account in (6) or (8); all the results are written below to the accuracy of quantities of the order of  $s^4 a^4 \sim m^4 a^4$  inclusive without additional commentary.

We seek the solution of the problem (5) in the form

$$\varphi(\omega, r) = \sum_{j=0}^{\infty} B_j \left( \frac{a}{r} \right)^{1/2} K_{j+1/2}(sr) P_j(\cos \theta), \quad (10)$$

where  $K_\alpha(x)$  is the Macdonald function. Within the framework of the accuracy taken, the first three terms in the series (10) must be taken into account. Using the boundary conditions from (5) as well as the expansion (8), we arrive at the following expressions for the coefficients in (10) after sufficiently awkward calculations:

$$B_0 K_{1/2}(sa) = (1 + \sigma a + sa)^{-1} \left\{ \left[ \sigma a \left( 1 + \frac{m^2 a^2}{6} \left( 1 + \frac{s^2 a^2}{20} \right) \right) - \frac{m^2 a^2}{3} \left( 1 + \frac{s^2 a^2}{10} \right) \right] c_* - \left[ \sigma a \left( 1 + \frac{s^2 a^2}{6} \left( 1 + \frac{s^2 a^2}{20} \right) \right) - \frac{s^2 a^2}{3} \left( 1 + \frac{s^2 a^2}{10} \right) \right] c'_0 \right\}, \quad (11)$$

$$B_1 K_{3/2}(sa) = \left( 2 + \sigma a + \frac{s^2 a^2}{1 + sa} \right)^{-1} \left[ 1 - \sigma a + \frac{s^2 a^2}{10} (3 - \sigma a) \right] a E',$$

$$B_2 K_{5/2}(sa) = \left[ 3 + \sigma a + \frac{s^2 a^2 (1 + sa)}{3 + 3sa + s^2 a^2} \right]^{-1} \left[ 2 - \sigma a + \frac{s^2 a^2}{14} (4 - \sigma a) \right] \frac{s^2 a^2 c'_0 - m^2 a^2 c_*}{3}.$$

Taking (9) and (11) into account, the expansions (8) and (10) define completely the components in the Fourier transforms of the relationships (2) that do not vanish during integration with the accuracy needed. Integrating, we obtain linear relationships of the same kind as in (3). Identifying the relationships mentioned (which is a condition for the self-consistency of the theory being developed), we arrive at a system of three complex transcendental equations to determine the quantities  $D$ ,  $K$ , and  $L$  introduced in (3). In dimensionless form we have

$$\begin{aligned} \beta = \frac{1}{z} = 1 - \rho &\left[ 1 + \frac{1 - \delta z + (3 - 2\delta z) s^2 a^2 / 5}{2 + \delta z + s^2 a^2 (1 + sa)^{-1}} + \right. \\ &\left. + \frac{\delta z + (4\delta z - 5) s^2 a^2 / 15}{1 + \delta z + sa} + \frac{2}{15} \frac{s^2 a^2 (\delta z - 2)}{3 + \delta z + s^2 a^2 (1 + sa)(3 + 3sa + s^2 a^2)^{-1}} \right], \end{aligned} \quad (12)$$

$$x = 3\rho\delta \left( \frac{1+sa}{1+\delta z+sa} + \frac{xz}{3} f \right), \quad y = \rho\delta z(y+p)f,$$

$$f = \frac{1-\delta z + 2(2-\delta z)s^2a^2/15}{1+\delta z+sa} - \frac{1-\delta z + (2-\delta z)s^2a^2/5}{2+\delta z+s^2a^2(1+sa)^{-1}} +$$

$$+ \frac{s^2a^2}{15} \frac{2-\delta z}{3+\delta z+s^2a^2(1+sa)(3+3sa+s^2a^2)^{-1}}, \quad sa = [z(x+y+p)]^{1/2}.$$

The time scale  $\tau$  and the following dimensionless quantities

$$\tau = a^2/D_0, \quad \delta = ka/D_0, \quad x = K\tau, \quad y = L\tau, \quad z^{-1} = \beta = D/D_0, \quad p = i\varepsilon\omega\tau \quad (13)$$

are introduced here.

The quantity  $\tau$  has the meaning of a relaxation time of the concentration field at the level of individual particles. The smallness of  $|sa|$  means that the characteristic times of variation of the mean concentration should be much greater than  $\tau$ ; i.e., within the framework of the continual description we should take  $\omega\tau \ll 1$ . Moreover, since  $z \sim \beta \sim 1$  it is necessary that  $x \ll 1$ . Let us define the small parameters

$$\mu = \frac{3\rho\delta}{\beta_0 + \delta}, \quad \kappa = \left( \mu + \frac{p}{\beta_0} \right)^{1/2} \sim \mu^{1/2} \quad (14)$$

and let us represent the unknown systems (12) in the form

$$\beta = \beta_0 \left[ 1 + \rho\beta_2\kappa^2 + \mu \left( \sum_0^2 \beta^{(i)} \kappa^i + \beta_{\mu}\mu \right) \right],$$

$$x = \beta_0\mu \left[ 1 + \sum_1^4 x_i\kappa^i + \mu \left( \sum_0^2 x^{(i)}\kappa^i + x_{\mu}\mu \right) \right], \quad (15)$$

$$y = \frac{\mu p}{3} \left( \sum_0^2 y^{(i)}\kappa^i + y_{\mu}\mu \right).$$

The meaning of the quantity  $\beta_0$  in (14) becomes clear from the first expansion in (15). In general the coefficients in (15) are on the order of one. Certain of the coefficients in the expansions for  $\beta$  and  $y$  vanish identically, which is taken into account at once in writing these expansions. For  $\rho \geq 0.1$  it is required, for the parameter  $\mu$  to be small compared with one, that  $\delta \ll 1$ , i.e., a heterogeneous transformation is realized in the kinetic regime. If the latter proceeds in the diffusion regime expressed ( $\delta \ll 1$ ), it is necessary that the inequality  $\rho \ll 1$  be satisfied, i.e., the disperse system under consideration be rarefied.

To obtain analytic representations of the coefficients in (15), the original equations (12) must be expanded in powers of the parameters (14). In principle, these calculations are simple but quite awkward. We present the result of the calculations only here:

$$\beta_0 = 1 - \rho \frac{3\beta_0}{2\beta_0 + \delta}, \quad \beta^{(0)} = -\frac{1}{3\beta_0}, \quad \beta^{(1)} = \frac{1}{3(\beta_0 + \delta)},$$

$$\beta^{(2)} = -\frac{\beta_0}{3(\beta_0 + \delta)^2}, \quad \beta_{\mu} = \frac{(3/2)x_1 - 1}{9(\beta_0 + \delta)},$$

$$\beta_2 = \frac{\beta_0 - \delta}{(2\beta_0 + \delta)^2} + \frac{5\beta_0 - 4\delta}{15\beta_0(\beta_0 + \delta)} + \frac{2(2\beta_0 - \delta)}{15\beta_0(3\beta_0 + \delta)} + \frac{-3\beta_0 + 2\delta}{5\beta_0(2\beta_0 + \delta)}; \quad (16)$$

$$x_1 = \frac{\delta}{\beta_0 + \delta}, \quad x_i = (-1)^{i+1} \frac{\delta\beta_0^{i-1}}{(\beta_0 + \delta)^i}, \quad i = 2, 3, 4,$$

$$x^{(0)} = x_1^2 \left( \frac{1}{2} + 2\beta^{(0)} \right) + y^{(0)}, \quad x^{(1)} = \frac{x_1}{2} \left[ x_2 + \frac{\beta_0 y^{(0)}}{3} + \right.$$

$$\left. + \frac{4\delta\beta^{(1)} + (\delta - 3\beta_0)\beta^{(0)} - 2\beta_0 x_1}{\beta_0 + \delta} \right] + \frac{2\beta_0}{2\beta_0 + \delta} y^{(1)}, \quad (17)$$

$$x^{(2)} = x_1 \left[ \beta^{(2)} + \frac{x_3}{2} + \frac{\beta_0 y^{(1)}}{6} - \frac{3\beta_0 - \delta}{2(\beta_0 + \delta)} \right] + x_2 \left[ \frac{5x_2}{2} + \right.$$

$$\begin{aligned}
& + \frac{\beta_0 y^{(0)}}{3} - \frac{2\beta_0 - \delta}{3\beta_0(\beta_0 + \delta)} \Big] + \gamma \frac{\beta_0 + \delta}{\beta_0} + y^{(1)} \left( x_1 + \frac{x_2}{2} \right), \\
x_\mu = x_1 \left( \beta_\mu + \frac{y^{(1)}}{2} \right) & + \frac{\beta_0 - 3\delta}{9\beta_0(\beta_0 + \delta)^2} - \frac{\delta}{3(2\beta_0 + \delta)} \left( y^{(1)} + \frac{3}{2\beta_0 + \delta} \right) + y^{(0)}(x^{(0)} - \beta^{(0)}); \\
y^{(0)} = \frac{\beta_0 - \delta}{2\beta_0 + \delta}, \quad y^{(1)} = -\frac{\beta_0 - \delta}{\beta_0 + \delta}, \quad y^{(2)} = \gamma \frac{\beta_0 + \delta}{\beta_0}, \\
y_\mu = y^{(0)} \left( \beta^{(0)} + \frac{y^{(0)}}{3} \right) & + \frac{x_1 y^{(1)}}{2} - \frac{\delta}{2\beta_0 + \delta} \left( y^{(1)} + \frac{1}{2\beta_0 + \delta} \right).
\end{aligned} \tag{18}$$

Here

$$\gamma = \frac{2(2\beta_0 - \delta)}{15(\beta_0 + \delta)} + \frac{\beta_0^2(\beta_0 - \delta)}{(\beta_0 + \delta)^3} - \frac{2\beta_0 - \delta}{5(2\beta_0 + \delta)} + \frac{\beta_0(\beta_0 - \delta)}{(2\beta_0 + \delta)^2} + \frac{2\beta_0 - \delta}{15(3\beta_0 + \delta)}. \tag{19}$$

The relationships (16)-(19) completely determine the expansions (15) and, therefore, the complex quantities  $D$ ,  $K$ , and  $L$  in the Fourier transform (4) of the average diffusion equation, as calculated from (14), as well. Applying the inverse Fourier transform, we easily obtain the equation itself; the mentioned quantities are here generally replaced by linear operators with differentiation and integration with respect to the time.

In a stationary diffusion process  $p = 0$ ,  $D = D_s$ ,  $K = K_s$ , where  $D_s$  and  $K_s$  are real positive quantities, and  $L = 0$ . We have

$$D_s = \beta_s D_0, \quad K_s = x_s / \tau, \quad \beta_s = \beta_0 \{ 1 + \mu [\beta^{(0)} + \rho \beta_2 + \beta^{(1)} \sqrt{\mu} + (\beta^{(2)} + \beta_\mu) \mu] \}, \tag{20}$$

$$x_s = \beta_0 \mu \{ 1 + x_1 \sqrt{\mu} + \mu [x_2 + x^{(0)} + (x_3 + x^{(1)}) \sqrt{\mu} + (x_4 + x^{(2)} + x_\mu) \mu] \},$$

where the parameter  $\mu$  is defined in (14), and the coefficients of (20), in (16)-(19).

The dependences of the effective coefficients  $\beta_s$  and  $x_s$  on  $\delta$  for different  $\rho$  are presented in Fig. 1.

In addition to the quantity  $D_s$  characterizing the intensity of the "transit" diffusion, it is expedient to consider the coefficient  $D_s^\circ$  describing the intensity of diffusion to individual particles and thereby characterizing the effective mass transfer between the disperse and continuous phases (components) of the system. Such a coefficient can be introduced by equating the quantity  $K_s(c_0 - c_x)$ , which is the mass flux density between the phases, to the diffusion flux to  $n$  particles, calculated in a standard manner, that corresponds to the previous value of the heterogeneous reaction rate constant  $k$  and the effective diffusion coefficient  $D_s^\circ$ . We consequently arrive at the equation obtained in [6]

$$D_s^\circ = \left( \frac{3\rho}{x_s} - \frac{1}{\delta} \right)^{-1} D_0. \tag{21}$$

Substituting  $x_s$  here from (20), we obtain under stationary conditions

$$\begin{aligned}
D_s^\circ = \beta_0 \left\{ 1 + 3\rho \left[ x_2 + x^{(0)} + \frac{\beta_0}{\beta_0 + \delta} (x_1 + 3\rho(x_2 + x^{(0)})^2) \right] + \right. \\
\left. + \sqrt{\mu} \left[ 1 + 3\rho \left( x_3 + x^{(1)} + \frac{2\beta_0(x_2 + x^{(0)})}{\beta_0 + \delta} \right) \right] + 3\rho\mu(x_4 + x^{(2)} + x_\mu) + \mu \sqrt{\mu} \left( \frac{\beta_0}{\beta_0 + \delta} \right)^2 \right\} D_0.
\end{aligned} \tag{22}$$

Dependences of the quantity  $\beta_s^\circ = D_s^\circ / D_0$  on  $\rho$  for different  $\delta$  are presented in Fig. 2, where appropriate dependences of the coefficient  $\beta_s = D_s / D_0$  are also shown.

Easily obtained for the kinetic mode ( $\delta \ll 1$ ) are  $D_s \approx (1 - 3\rho/2)D_0$  and  $D_s^\circ \approx D_0$  on  $K_s \approx 3\rho k/a$ . In the diffusion mode  $D_s \approx (1 - \rho)D_0$  and  $D_s^\circ \approx (1 + \sqrt{3\rho})D_0$  or  $K_s \approx 3\rho(1 + \sqrt{3\rho})D_0 a^{-2}$ . These results are in agreement with those obtained earlier [6].

Let us now examine nonstationary diffusion processes whose continual description is possible by using an average diffusion equation of the type (1) if the characteristic frequency of variation of the mean concentration satisfies the inequality  $\omega\tau \ll 1$ . In the general case when the relationship between the parameters  $|p|$  and  $\mu$  is arbitrary the application of the inverse Fourier transform to equation (4) with  $D$ ,  $K$ , and  $L$  defined according to (13)-(19) will result in the appearance of quite awkward integrodifferential operators. We limit ourselves

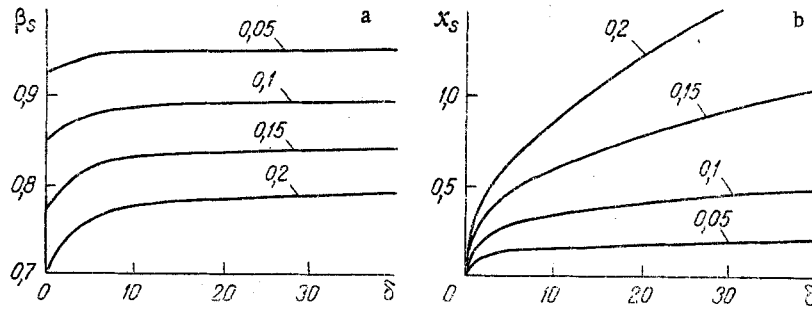


Fig. 1. Dependence of the relative diffusion coefficient (a) and the parameter  $x_s$  characterizing the interphasal mass transfer under stationary conditions (b) on  $\delta$  for different  $\rho$  (numbers on the curves).

here to an analysis of the situation in the two limit cases  $\mu \gg |p|$  and  $\mu \ll |p|$ , when the expression for  $x$  from (14) can be simplified somewhat. Setting  $|p| \leq \mu^2$  for definiteness, we obtain to the accuracy taken in (15):

$$\beta \approx \beta_s + i\rho\beta_2\varepsilon\tau\omega, \quad y \approx i(1/3)y^{(0)}\mu\varepsilon\tau\omega, \quad x \approx x_s + i(0.5x_1\sqrt{\mu} + x_2\mu)\varepsilon\tau\omega. \quad (23)$$

Substituting the representations for  $D$ ,  $K$  and  $L$  following from (13) and (23) into (4) multiplied by  $D_s$ , expanding  $D^{-1}$  in a power series in  $p$  (and limiting ourselves to just the first two terms in this expansion within the limits of the accuracy taken), and then performing the inverse Fourier transformation, we obtain an equation for the mean concentration

$$\left(1 + \frac{1}{3}y^{(0)}\mu\right)\varepsilon\frac{\partial c_0}{\partial t} - \rho\varepsilon^2\frac{\beta_2}{\beta_0}\tau\frac{\partial^2 c_0}{\partial t^2} = D_s\Delta c_0 + K_s(c_* - c_0) + \left[\frac{1}{2}x_1\sqrt{\mu} + (x_2 - \rho\beta_2)\mu\right]\frac{\partial(c_* - c_0)}{\partial t}. \quad (24)$$

Therefore, the nonstationary diffusion process in a heterogeneous medium of the kind under consideration differs, for comparatively low frequencies, from the diffusion in a homogeneous medium in the following respects. Firstly, the effective "capacity" of the space between the particles changes: increases for  $y^{(0)} > 0$  ( $\beta_0 > \delta$ ) and diminishes in the opposite case. Secondly, a relaxation term appears in the expression for the mass flux between the phases per unit volume of mixture: the latter starts to depend on not only the stationary moving force  $c_* - c_0$  but also on its rate of change  $\partial(c_* - c_0)/\partial t$  (it is clear that  $\partial c_*/\partial t = dc_*/dt$ ). Both these effects were mentioned in [6]. Thirdly, and finally, a relaxation term appears with the second derivative with respect to the time, whose sign is determined by the sign of the coefficient  $\beta_2$  defined in (16). The dependences of  $\beta_2$  on  $\delta$  for one of the values of  $\rho$  are presented in Fig. 3. It is seen that this coefficient is positive for small and negative for large  $\delta$ , while the equation (24) itself belongs, respectively, to the elliptic or hyperbolic type. An elliptic equation for a diffusion type process in a heterogeneous medium has been obtained earlier in [7], while hyperbolic equations for such a process were examined in [8, 9], say. The presence of a term with  $\partial^2 c_0/\partial t^2$  in the diffusion equation alters the properties of its solution substantially as compared with those for an equation of parabolic type.

In the second limit case we have by setting  $\mu \leq |p|^2$

$$\beta \approx \beta_s + i\rho\beta_2\varepsilon\tau\omega, \quad y \approx i(1/3)y^{(0)}\mu\varepsilon\tau\omega, \quad (25)$$

$$x \approx \mu\beta_0 \left[ 1 + x_2\mu + \frac{x_1}{V i\rho\beta_0\varepsilon\tau\omega} \left( \frac{\mu\beta_0}{2} + i\varepsilon\tau\omega \right) \right] + ix_2\mu\varepsilon\tau\omega.$$

In this case the average diffusion equation is

$$\left(1 + \frac{1}{3}y^{(0)}\mu\right)\varepsilon\frac{\partial c_0}{\partial t} - \rho\varepsilon^2\frac{\beta_2}{\beta_0}\tau\frac{\partial^2 c_0}{\partial t^2} = D_s\Delta c_0 + \frac{\mu\beta_0}{\tau} \left[ (1 + x_2\mu)(c_* - c_0) + \right. \quad (26)$$

$$\left. + x_1 \int_{-\infty}^t \left\{ \left( \frac{\mu\sqrt{\beta_0}}{2} + \frac{\varepsilon}{V\beta_0}\tau\frac{\partial}{\partial t} \right) (c_* - c_0) \right\}_{t=t'} \frac{dt'}{V\tau(t-t')} \right] + (x_2 - \rho\beta_2)\mu\varepsilon\frac{\partial(c_* - c_0)}{\partial t}.$$

The relationships (25) and the equation (26) describe comparatively high-frequency diffusion processes. In this case still another important effect appears: the intensity of the interphasal mass transfer depends on the process history, i.e., ceases to be local in time.

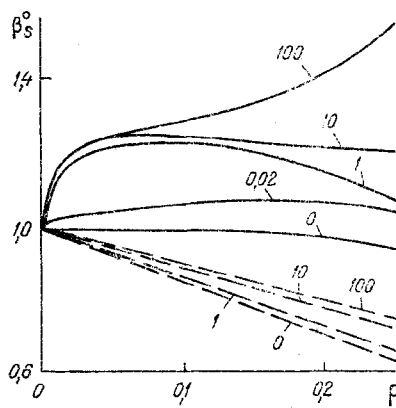


Fig. 2. Dependence of the dimensionless effective diffusion coefficient to individual particles on  $\rho$  for different  $\delta$  (numbers at the curves); analogous dependences for  $\beta_s$  are shown by the dashed curves.

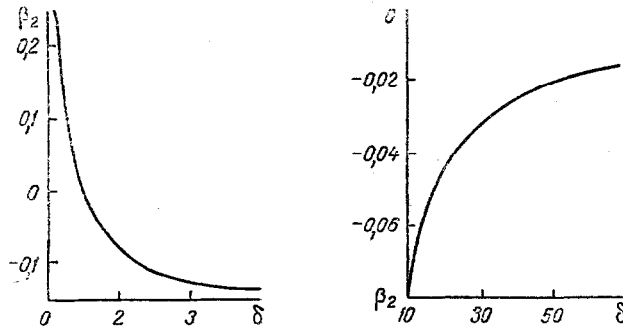


Fig. 3. The quantity  $\beta_2$  as a function of  $\delta$ ,  $\rho = 0.05$ .

The possibility of the appearance of hereditary integrals in the averaged diffusion and heat conduction equations has been mentioned in [10] as well as in [7, 11].

Extension of the results to broader frequency ranges is not a complication in principle but the appropriate equations have a more complicated form than (24) or (26). It is also easy to write simplified forms of the average equation that are valid in particular situations. For instance, in the limiting kinetic mode of the progress of transformations on the particle surfaces ( $\delta \rightarrow 0$ ) for any frequencies satisfying the general condition of applicability of continual theory, we obtain the elliptic equation

$$\varepsilon \frac{\partial c_0}{\partial t} - \frac{67\rho\varepsilon^2}{180(1-3\rho/2)^2} \tau \frac{\partial^2 c_0}{\partial t^2} = D_0 \left(1 - \frac{3\rho}{2}\right) \Delta c_0. \quad (27)$$

In the limiting diffusion mode ( $\delta \rightarrow \infty$ ) we have

$$\varepsilon \frac{\partial c_0}{\partial t} = \varepsilon D_0 \Delta c_0 + \frac{3\rho D_0}{a^2} (c_* - c_0) + \frac{\sqrt{3\rho}}{2} \varepsilon \frac{\partial (c_* - c_0)}{\partial t} \quad (28)$$

for the low frequencies

$$\varepsilon \frac{\partial c_0}{\partial t} = \varepsilon D_0 \Delta c_0 + \frac{3\rho D_0}{a^2} \left[ c_* - c_0 + \int_{-\infty}^t \left\{ \left( \frac{3\rho}{2} + \varepsilon \tau \frac{\partial}{\partial t} \right) (c_* - c_0) \right\}_{t=t'} \frac{\partial t'}{\sqrt{\tau(t-t')}} \right] \quad (29)$$

for the high frequencies. If  $\delta$  grows from zero while remaining small as compared with unity, then the source term due to interphasal mass transfer becomes substantial in (27). If  $\delta$  diminishes from a large quantity while remaining greater than one, the term with the second derivative then starts to play a part in (28) and (29), where (28) turns out to be hyperbolic here.

The characteristic relaxation times for the disperse systems of moderate concentration are approximately an order less than  $\tau = a^2/D_0$ . For instance, if we speak of diffusion in a heterogeneous material with a solid continuous phase for  $a \sim 10^{-6}$ - $10^{-5}$  m and  $D_0 \sim 10^{-15}$ - $10^{-13}$  m<sup>2</sup>/sec, then  $\tau$  varies between 10 and  $10^5$  sec, i.e., the relaxation phenomena due to heterogeneous phenomena at the interphasal boundary are actually capable of influencing the progress of real diffusion processes substantially.

The correspondence between the developed representations and the data of experiment is naturally set up in application to specific diffusion processes in specific systems, which requires independent analysis of diverse problems. However, the adequacy of these representations apparently does not, on the whole, raise doubt and is confirmed fully by results achieved during semiempirical insertion of terms with the second derivative of an unknown function and with memory integrals into the familiar parabolic diffusion equation [8-11]. The prospects for utilizing the hyperbolic equation to describe the concentration curves observed during chemical-thermal treatment processes for heterogeneous metals have recently been communicated in [12].

#### NOTATION

$a$ , particle radius;  $c_0$ ,  $c_*$ , mean concentration in gaps between particles and its equilibrium value;  $C_*$ , effective equilibrium concentration;  $h$ , source density;  $k$ , reaction rate constant;  $E$ ,  $M$ ,  $N$ ,  $T$ , expansion coefficients;  $n$ , numerical particle concentration;  $q$ , mass flux;  $R$ ,  $R'$ , radius-vectors of the test particle point and center;  $r = R - R'$ ;  $t$ , time;  $\epsilon$ , bulk concentration of the continuous phase;  $\rho = 1 - \epsilon$ ;  $\tau = a^2/D_0$ , relaxation time;  $\varphi$ , perturbation of the mean concentration;  $\omega$ , frequency (the Fourier transform variable). The subscript  $s$  refers to the stationary state.

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