Comparison of relation (10) with the quantity $f(\zeta_0)$ [see formula (5)], shows that when $Re > 10$, the best agreement is when $\alpha = 0.72$.

NOTATION

r, θ, spherical coordinates; ψ, flow function; v_r, v_θ, velocity components; ζ, vorticity; C, concentration; $\mu = \mu_d/\mu_c$, ratio of viscosities of the dispersed and continuous phases; U, velocity of steady motion of liquid; a, radius of sphere; ν, kinematic viscosity of medium; D, coefficient of diffusion; k, mass-transfer coefficient; $Nu = 2ka/D$, Nusselt number; $Pe = 2Ua/D$, Peclet number; $Re = 2Ua/\nu$, Reynold's number; $Pr = \nu/D$, Prandtl number. Indices: 1, drop; 2, solid sphere; d, dispersed phase; c, continuous phase; s, point of flow separation; 0, values at the surface of the sphere.

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UNSTEADY MASS TRANSFER WITH A HETEROGENEOUS CHEMICAL REACTION DURING LAMINAR FLOW PAST A SPHERE

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Unsteady mass transfer toward a solid sphere is investigated in the region of Peclet numbers $1 \leq Pe \leq 1000$. Diffusion flow in the presence of a first-order chemical reaction is calculated and the relaxation time of the steady regime as a function of the Peclet number is determined.

The process of mass transfer between a moving spherical particle and a continuous flow was investigated earlier in a quasistationary approximation for limiting cases of small and large Peclet (Pe) values. In [1, 2] solutions were obtained for small Pe values by the method of joining asymptotic expansions [3]. Although theoretically this method is suitable only for $Pe < 1$, the results of such calculations were used sometimes also for $Pe > 1$. Solutions obtained in an approximation of the theory of a diffusion boundary layer are known for large Pe (see, for example, [4, 5]). In the transition region of Peclet numbers ($1 < Pe \sim 100$), when the diffusion boundary layer has still not formed and the contribution to the magnitude of the diffusion flow from the molecular and convective terms in the transfer equation is commensurable, the field of concentrations cannot be determined by a single one of the approximate methods. In [6] the problem of steady mass transfer was solved for the particular case of evaporation of water drops by the finite-difference method for $0 < Pe \lesssim 200$. In this article we will consider the most general case when the transfer process is unsteady and a chemical reaction occurs on the surface of the particle.

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For axisymmetric flow past a particle the equation of convective transfer can be written in the form

$$\frac{\partial z}{\partial \tau} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial z}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial z}{\partial \theta}\right) - \frac{\mathrm{Pe}}{2}\left(V_r\frac{\partial z}{\partial r} + \frac{V_\theta}{r}\frac{\partial z}{\partial \theta}\right). \tag{1}$$

The velocity components V_r and V_θ are determined in terms of the stream function by the formulas

$$V_r = -\frac{1}{r^2 \sin\theta}\frac{\partial \psi}{\partial \theta};\ V_\theta = \frac{1}{r \sin\theta}\frac{\partial \psi}{\partial r}.$$

Equation (1) is considered with the following boundary conditions. On the surface of the sphere in the case of pure mass transfer

$$z|_{r=1} = 0, \tag{2}$$

and for mass transfer accompanied by a chemical reaction

$$H\left.\frac{\partial z}{\partial r}\right|_{r=1} = z|_{r=1}.^{*} \tag{3}$$

Far from the sphere

$$z|_{r\to\infty} = 1. \tag{4}$$

It is assumed that at the initial instant the concentration of matter in the environment surrounding the particle is everywhere constant and equal to c_1, i.e.,

$$z|_{\tau=0,\, r>1} = 1. \tag{5}$$

The formulated problem is considered for a particle moving at $\mathrm{Re} \leq 40$. For $\mathrm{Re} \ll 1$ a Stokes velocity field is assigned. For $1 < \mathrm{Re} \leq 40$, the values of the stream function obtained by numerical integration of the Navier–Stokes equations, which are tabulated in [7], are used.

The intensity of mass transfer is characterized by the value of the total diffusion flow

$$I = 2\pi D a c_1 \int_0^\pi \left(\frac{\partial z}{\partial r}\right)_{r=1} \sin\theta d\theta. \tag{6}$$

The values of the local and average Sherwood numbers are of interest for mass transfer without a chemical reaction:

$$\mathrm{Sh}_\theta = 2\left(\frac{\partial z}{\partial r}\right)_{r=1}, \tag{7}$$

$$\mathrm{Sh} = \frac{1}{2}\int_0^\pi \mathrm{Sh}_\theta \sin\theta\, d\theta. \tag{8}$$

The problem was solved by the net-point method. The transformation $r = \exp x$ was introduced with respect to the radial coordinate, which made it possible to obtain with a uniform step with respect to x a crowding of the coordinate lines near the surface where the concentration gradients are large. The algorithm chosen was one of the variants of the predictor–corrector type schemes. In the first two half-steps with respect to time we used the method of variable directions [8] with unilateral difference quotients in first-order deriva-

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*Since in the presence of a chemical reaction the concentration of matter on the surface of the particle is a function of angle θ, in Eqs. (1) and (3) the dimensionless concentration is determined as $z = c/c_1$. When $H \to 0$ (diffusion regime of absorption of matter) boundary condition (3) changes to (2).

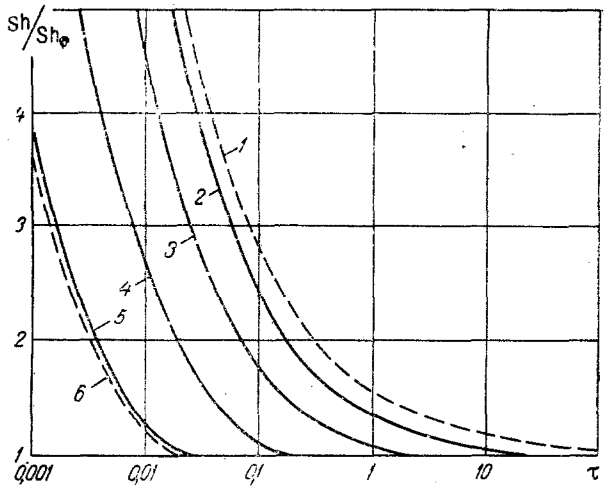

Fig. 1. Sh/Sh_0 vs τ for various Pe and Re << 1.

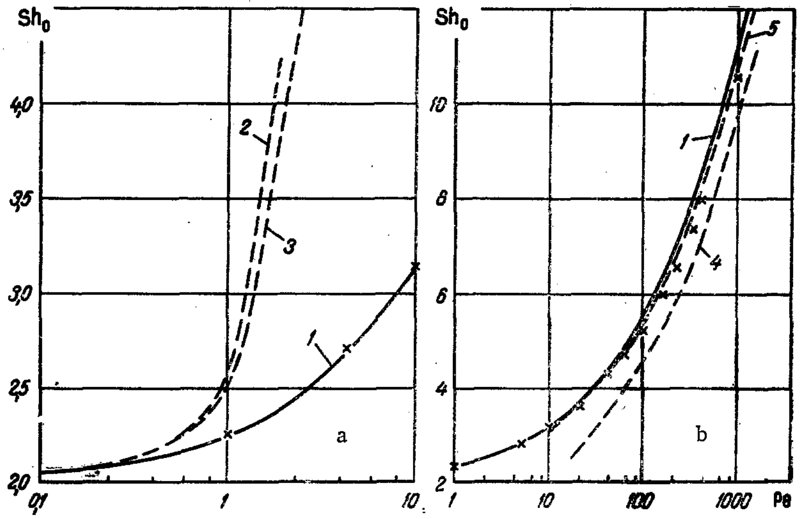

Fig. 2. Sh_0 vs Pe: the points denote calculations made in this article; 1) by Eq. (10); 2) according to data in [1]; 3) according to data in [2]; 4) by Eq. (11); 5) by Eq. (12).

tives. At the next step correction was accomplished according to an explicit scheme in which the first-order derivatives were approximated by central difference quotients. The given scheme provides uniform stability with respect to steps Δx, $\Delta\tau$, and the Pe number.

The calculations were made on an M-222 computer with net N_r = 25-40, N_θ = 24. Boundary condition (4) was set at different distances from the surface of the particle depending on the Pe value. For Pe ~ 1 the outer boundary was chosen at a distance of about 100 radii of the sphere. For Pe ~ 100-1000 this distance was reduced to 12-8 radii of the sphere, respectively.

It is known that at the initial instant the coefficients of mass transfer are considerably greater than in the case of a steady regime. However, in practice one often uses a quasistationary approximation, assuming that the relaxation time τ_r, i.e., the time during which a steady distribution of concentrations is established around the particle, is negligibly small in comparison with the total time of the process. It has been shown in [9] that for the case of unsteady mass transfer with a motionless medium (Re = 0) the value of the Sherwood number only upon lapse of time $\tau_r \approx 100$ approximates to its steady-state value Sh_0 = 2 with an error of about 5%. According to [9] the intensity of transfer is determined by the formula

$$\mathrm{Sh} = 2\left(1 + \frac{1}{\sqrt{\pi\tau}}\right). \tag{9}$$

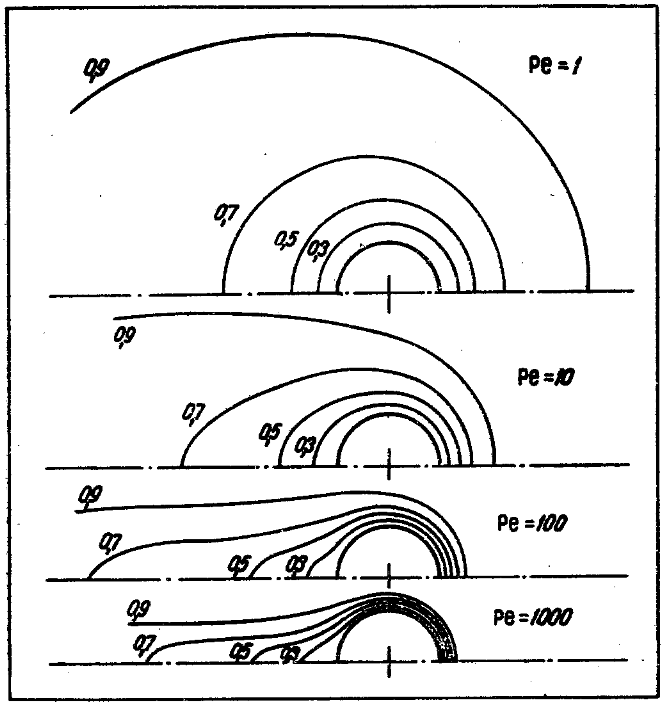

Fig. 3. Field of concentrations around sphere for various Pe.

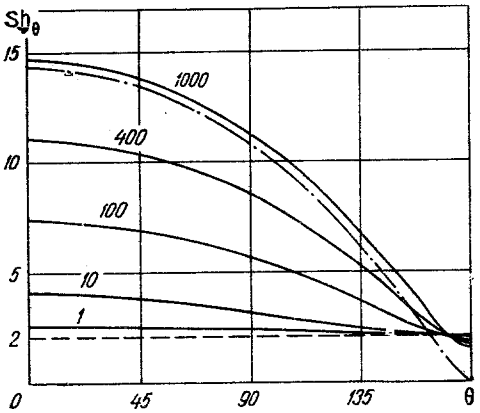

Fig. 4. Local values of the Sherwood number in a Stokes regime. The values of the Pe number are denoted by figures; the dashed-dot line was plotted by Eq. (13) for Pe = 1000; θ, deg.

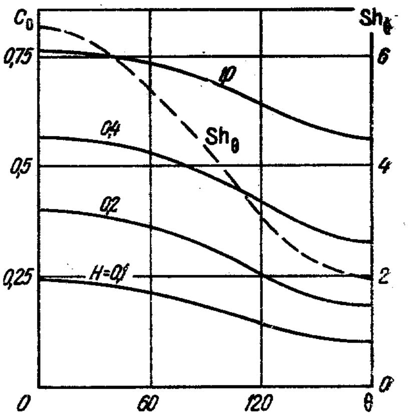

Fig. 5. Mass transfer of a sphere with a first-order chemical reaction on the surface (Re = 20, Sc = 1). Solid curves: values of the surface concentration c_0 for various H.

The relaxation time of the diffusion process for a moving particle depends substantially on the Pe number. Figure 1 shows Sh/Sh_0 as a function of τ for a Stokes flow regime for different Pe values. Curves 2, 3, 4, and 5 correspond to values Pe = 1, 10, 100, and 1000. Curve 1 was plotted for Pe = 0 in conformity with (9) and curve 6 for Pe = 1000 on the basis of the data of Konopliv and Sparrow [10], in which the problem of unsteady transfer was solved for large Pe in an approximation of the diffusion boundary layer. As we see from the graph, with an increase of Pe the relaxation time drops noticeably. For instance, $\tau_r \approx 10$ for Pe = 1, and $\tau_r \approx 0.02$ for Pe = 1000. For large Pe, according to [10], $\tau_r \sim 1/Pe^{2/3}$.

Figure 2 presents the calculation of the steady-state Sherwood number for a Stokes flow regime when $1 \leq Pe \leq 1000$. For small Pe (Fig. 2a) the results of the numerical calculations

TABLE 1. Calculation of Mass Flow toward a Chemical Reacting Sphere

Pe	Re	Sh_0	H	I/I_0		
				Exact calculation	Calculation by Eq. (14)	Calculation by Eq. (15)
20	20	4,281	0,1 0,2 0,4 1,0	0,829 0,707 0,544 0,321	0,821 0,701 0,542 0,320	0,824 0,700 0,539 0,318
40	40	5,363	0,5	0,432	0,435	0,427
100	«1	5,384	0,2 0,5 1,0	0,659 0,432 0,274	0,640 0,418 0,267	0,650 0,426 0,271

are compared with the solutions obtained by the method of joining asymptotic expansions [1, 2] (curves 2 and 3). Curve 1 is plotted according to the Brauer interpolation formula [11]

$$Sh_0 = 2 + \frac{0.333 Pe^{0,840}}{1 + 0.331 Pe^{0,507}}. \tag{10}$$

As follows from Fig. 2a, the approximate solutions [1, 2] can be used only when $Pe \lesssim 0.5$. In Fig. 2b, where calculations for $Pe \leq 1000$ are given, curve 4 is plotted according to the formula

$$Sh_0 = 0.991 \sqrt[3]{Pe}, \tag{11}$$

obtained in [1, 4] by diffusion boundary-layer methods. In [12] the expression

$$Sh_0 = 0.922 + 0.991 \sqrt[3]{Pe} \tag{12}$$

was obtained by using a more accurate expression for the stream function near the particle's surface, which is represented in Fig. 2b by curve 5. It should be noted that although Eq. (12) already when $Pe > 10$ gives a satisfactory accuracy for Sh_0, the diffusion boundary layer still does not exist for such low Pe. This is seen directly from Fig. 3 where the concentration fields around the particle are shown for various Pe. Even when $Pe = 1000$ the main drop of concentrations in the front part of the sphere is concentrated at a distance of about 0.2 of the radius, which, strictly speaking, does not permit considering the diffusion boundary layer to be completely formed. However, despite this the local values of Sh_0 when $Pe = 1000$ are in satisfactory correspondence (except for the rear region of the sphere) with calculations by the equation

$$Sh_\theta = 1.25 \frac{\sin\theta \, Pe^{1/3}}{\left(\theta - \frac{\sin 2\theta}{2}\right)^{1/3}}, \tag{13}$$

obtained in an approximation of the boundary layer [4] (see Fig. 4).

The results of calculating mass transfer of a chemically reacting sphere are shown in Fig. 5, where for $Re = 20$, $Sc = 1$, and various values of complex H the distribution of the surface concentration as a function of angle θ is presented. The considerable difference of concentrations between the front and rear parts of the surface of the sphere is a consequence of the fact that different regions of the sphere's surface are not equally accessible in a diffusion respect. This is confirmed by the character of the distribution of the local value of the Sherwood number for mass transfer without a chemical reaction (dashed line in Fig. 5).

In [13] an approximate method was proposed for calculating a diffusion flow toward a reacting surface, according to which the effect of the chemical reaction on the mass-transfer coefficients is disregarded (method of equally accessible surface). In conformity with this method the total diffusion flow on the sphere can be determined by the equation

$$I = I_0 \frac{1}{\mathrm{Sh}_0} \int_0^{\pi} \frac{\mathrm{Sh}_{0,\theta} \sin\theta \, d\theta}{2 + \mathrm{Sh}_{0,\theta} H} . \tag{14}$$

The averaged method of equally accessible surface is often used for practical calculation. In this case,

$$I = I_0 \frac{2}{2 + \mathrm{Sh}_0 H} . \tag{15}$$

The results of the exact solution for some values of the parameters are compared with the approximate calculations of Eqs. (14) and (15) in Table 1. The divergence in the values of the total mass flow calculated by the exact and approximate methods does not exceed 2%.

NOTATION

Pe = $2Ua/D$, Peclet number; Re = $2Ua/\nu$, Reynolds number; Sc = ν/D, Schmidt number; c, relative mass concentration of component being transported; c_0, c_1, concentrations on the surface of the sphere and in the incident flow, respectively; $z = (c - c_0)/(c_1 - c_0)$, dimensionless concentration; r, radial coordinate; θ, angular coordinate; t, time; $\tau = Dt/a^2$, dimensionless time (Fourier number); a, radius of the sphere; D, diffusion coefficient; ν, coefficient of kinematic viscosity; U, velocity of incident flow; V_r, V_θ, radial and tangential velocity components; ψ, stream function; K, rate constant of first-order chemical reaction; Da = Ka/D, Damkohler number; H = 1/Da; I, total mass flow on sphere; I_0, flow in a purely diffusion regime; Sh_θ, local value of Sherwood number; Sh, average Sherwood number; Sh_0, Sherwood number in steady regime; x, transformed radial coordinate; Δx, step with respect to x; $\Delta\tau$, step with respect to τ; N_r, N_θ, number of steps with respect to the radial and angular coordinate, respectively; τ_r, relaxation time of diffusion process.

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