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DIFFUSION TO AN ABSORBING PARTICLE WITH MIXED KINETICS

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The concentration field in the neighborhood of a solid sphere in a Stokes stream with a first order chemical reaction taking place on the sphere surface is determined by the method of joining asymptotic expansions (in high Péclet number). Dependence of the total diffusion flux at the sphere surface on the chemical reaction rate is determined. It is shown that depending on the constant of chemical reaction rate a region of kinetic mode may be absent in the neighborhood of the forward stagnation point, while in that of the rear stagnation point there always exists a region of the diffusion mode of the process of chemical reaction. Saturation of the diffusion flux with increasing Péclet number is disclosed. Concentration distribution in the diffusion trail region is determined and its structure investigated.

The problem of diffusion on a reacting plane surface with mixed kinetics was reduced in [1] to solving an ordinary differential equation by the method of integral transformations. The diffusion on a sphere proves to be more complex, and a method similar to that in [2] does not permit the reduction of the problem to the solution of an ordinary equation. It is only suitable for estimating the total diffusion flux at the sphere surface.

1. Statement of the problem. Concentration distribution in the diffusion boundary layer. The convective diffusion of matter on a solid sphere in a Stokes stream of viscous incompressible fluid whose velocity away from the sphere is U. It is assumed that the Péclet number $P = aU / D$ is high (a is the sphere radius and D is the diffusion coefficient) and that a first order chemical reaction at constant rate k' takes place at the particle surface.

In the spherical system of coordinates r, θ attached to the particle the equation of convective diffusion and the boundary conditions are of the form

$$\frac{1}{\sin\theta}\left(\frac{\partial\psi}{\partial\theta}\frac{\partial c}{\partial r}-\frac{\partial\psi}{\partial r}\frac{\partial c}{\partial\theta}\right)=\varepsilon^3\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial c}{\partial\theta}\right)\right] \quad (1.1)$$

$$\left[\frac{\partial c}{\partial r}-kc\right]_{r=1}=0,\quad c|_{r\to\infty}\to 1$$

$$\left[\frac{\partial c}{\partial\theta}\right]_{\theta=0}=\left[\frac{\partial c}{\partial\theta}\right]_{\theta=\pi}=0,\quad \varepsilon=P^{-1/3},\quad k=\frac{k'a}{D}$$

where c is the concentration of matter, ψ is the stream function, and angle θ is measured from the direction of the oncoming stream.

The problem of concentration distribution is formulated in (1.1) in dimensionless variables with the sphere radius, the stream velocity, and concentration at infinity taken as reference quantities.

The dimensionless stream function of a Stokes flow past the particle is of the form

$$\psi = \left(r^2 - \frac{3}{2} r + \frac{1}{2r}\right) \frac{\sin^2\theta}{2} \tag{1.2}$$

The asymptotic analysis of problem (1.1), (1.2) shows [3] that when $\varepsilon \ll 1$ it is possible to discern in the particle neighborhood several characteristic regions with different mass transport mechanisms. These are: the external region e, the diffusion boundary layer d, and the diffusion trail region W which consists of zones $W^{(i)}$ $(i = 1, 2, 3, 4)$. In each of these zones Eq. (1.1) is approximated by the principal terms of expansions in the small parameter ε. Congruence of solutions in separate regions is achieved by asymptotic joining at their nominal boundaries.

In the outer region $e = \{r - 1 \gg \varepsilon,\ \varepsilon \ll \theta\}$ (here and below the inequalities in braces indicate the order of characteristic dimensions of a particular region) the right-hand side of Eq. (1.1) is negligibly small, diffusion and transport of matter are insignificant, and concentration is constant and equal to that at infinity, i.e. $c^{(e)} = 1$.

In the forward stagnation point region $b = \{r - 1 \leqslant \varepsilon,\ \pi - \theta \leqslant \varepsilon\}$ Eq. (1.1) can be somewhat simplified, but the terms that define diffusion in both the tangential and normal directions remain in it. Analysis shows that the effect of this region on concentration distribution in the diffusion boundary layer, as well as the contribution of that region to the magnitude of the total diffusion stream on the particle surface is small, hence it can be neglected in the calculation of the over-all mass transport between particle and stream to within the principal term of expansion in powers of ε.

The determining factor in the transport of the dissolved constituent to the particle surface is the process of convective diffusion in the diffusion boundary layer $d = \{r - 1 < O(\varepsilon),\ \theta > O(\varepsilon)\}$, which consists of convection along the particle surface and diffusion in the transverse direction.

Substituting variables

$$\xi = \varepsilon^{-1}\psi^{1/2}, \quad t = T(\theta) = \frac{\sqrt{3}}{8}\left[\pi - \theta + \frac{1}{2}\sin 2\theta\right]$$

and retaining the principal terms of expansions in parameter ε, for the concentration distribution in the diffusion boundary layer d from (1.1) and (1.2) we obtain the equation

$$\frac{\partial c^{(d)}}{\partial t} = \xi^{-1}\frac{\partial^2 c^{(d)}}{\partial \xi^2} \quad (0 < t \leqslant t_0) \tag{1.3}$$
$$c^{(d)}|_{t=0} = 1, \quad \left[\eta(t)\frac{\partial c^{(d)}}{\partial \xi} - \varepsilon k c^{(d)}\right]_{\xi=0} = 0, \quad c^{(d)}|_{\xi\to\infty} \to 1$$
$$\eta(t) = \frac{\sqrt{3}}{2}\sin T^\circ(t), \quad t \equiv T[T^\circ(t)], \quad t_0 = t(0) = \frac{\sqrt{3}\pi}{8}$$

A solution of Eq. (1.3) of the diffusion boundary layer with the condition of total absorption of matter at the sphere surface $(k = \infty)$ was obtained in [1]. It can be written as follows:

$$c_*^{(d)}(\xi, t) = \Gamma^{-1}(1/3)\,\gamma(1/3,\ \xi^3 / 9t) \tag{1.4}$$

$$\gamma(^1/_3, x) = \int_0^x e^{-\tau}\tau^{-2/3}d\tau,\ \Gamma\left(\frac{1}{3}\right) = \gamma\left(\frac{1}{3}, \infty\right)$$

We introduce the substitution $z = {}^2/_3\, \xi^{3/2}$ and seek the solution of the complete problem (1.3) in the form $c^{(d)} = c_*^{(d)} - u$; for the unknown function u we obtain the equation

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial z^2} + \frac{1}{3z}\frac{\partial u}{\partial z}; \quad u\,|_{t=0} = 0, \quad u\,|_{z\to\infty} = 0 \tag{1.5}$$

$$\left[z^{1/3}\frac{\partial u}{\partial z} - \left(\frac{2}{3}\right)^{1/3}\varepsilon k\eta^{-1}(t)\,u - 2^{1/3}\Gamma^{-1}\left(\frac{1}{3}\right)\,t^{-1/3}\right]_{z=0} = 0$$

whose solution is sought in the form

$$u(z,t) = \frac{2^{-1/3}}{\Gamma(^2/_3)}\int_0^t \Phi(\lambda)(t-\lambda)^{-2/3}\exp(-\varkappa^2)\,d\lambda \tag{1.6}$$

$$(0 < t \leqslant t_0), \quad \varkappa = {}^1/_2\, z\,(t-\lambda)^{-1/2}$$

Function (1.6) satisfies the equation and the first two boundary conditions (1.5) for any function $\Phi(x)$ in the interval $0 < t \leqslant t_0$ has the following properties [4]:

$$\lim_{z\to 0} u = \frac{2^{-1/3}}{\Gamma(^2/_3)}\int_0^t \Phi(\lambda)(t-\lambda)^{-2/3}d\lambda$$

$$\lim_{z\to 0}\left(-z^{1/3}\frac{\partial u}{\partial z}\right) = \Phi(t) \tag{1.7}$$

The last of boundary conditions (1.5) and the properties (1.7) imply that function $\Phi(x)$ is a solution of the integral equation

$$\eta(x)\Phi(x) + k^*\int_0^x \Phi(\lambda)(x-\lambda)^{-2/3}d\lambda + \alpha\mu(x) = 0 \tag{1.8}$$

$$\mu(x) = \eta(x)\,x^{-1/3}, \quad k^* = 3^{-1/3}\Gamma^{-1}(^2/_3)\,k\varepsilon; \quad \alpha = 2^{1/3}\Gamma^{-1}(^1/_3)$$

The case in which functions $\mu(x)$ and $\eta(x)$ are simultaneously some constants was considered in [4].

Function $\eta(x)$ in Eq. (1.8) has the following properties:

$$x \to 0, \quad \eta(x) \to 3^{2/3}2^{-1/3}x^{1/3}$$
$$x \to t_0, \quad \eta(x) \to 3^{2/3}2^{-1/3}(t_0 - x)^{1/3}$$

and in the neighborhood of point $x = 0$ it can be represented by the series

$$\eta(x) = \sum_{n=0}^{\infty} a_n(x)^{(2n+1)/3}; \quad a_0 = 3^{2/3}2^{-1/3}, \quad a_1 = {}^1/_5, \ldots \tag{1.9}$$

Because of this we seek a solution of Eq. (1.8) of the form

$$\Phi(x) = \sum_{n=0}^{\infty} b_n x^{(2n-1)/3} \tag{1.10}$$

Substituting expression (1.10) into Eq. (1.8) and equating coefficients at like powers of x with allowance for (1.9), we obtain the recurrent formula

$$b_n = -\left(\alpha a_n + \sum_{k=1}^{n} a_k b_{n-k}\right)(a_0 + k^* B_n)^{-1} \tag{1.11}$$

$$B_n = B\left(1/3, 2/3(n+1)\right), \quad B(p, q) = \int_0^1 \tau^{p-1}(1-\tau)^{q-1} d\tau = \Gamma(p)\Gamma(q)\Gamma^{-1}(p+q)$$

where $B(p, q)$ is the beta function.

For the first two terms of series (1.10) we have

$$b_0 = -\frac{\alpha a_0}{a_0 + k^* B_0}, \quad b_1 = \frac{\alpha a_1}{a_0 + k^* B_1} + \frac{\alpha a_0 a_1}{(a_0 + k^* B_0)(a_0 + k^* B_1)}$$

There exists a neighborhood of point $x = 0$, where the series (1.10), (1.11) is convergent.

To prove this it is sufficient to construct a series dominating (1.10). We represent the series in the form

$$\eta(x) = a_0 x^{1/3} + v(x), \quad v(x) = \sum_{n=1}^{\infty} a_n x^{(2n+1)/3}$$

$$\Phi(x) = b_0 x^{-1/3} + y(x), \quad y(x) = \sum_{n=1}^{\infty} b_n x^{(2n-1)/3}$$

then from formula (1.8) we obtain for the determination of function y the following integral equation:

$$\eta(x) y(x) + k^* \int_0^x y(\lambda)(x-\lambda)^{-2/3} d\lambda + F(x, \eta(x)) = L(y, \eta(x)) = 0$$

$$F(x, \eta(x)) = \frac{\alpha k^* B_0}{a_0 + k^* B_0}\left[\eta(x) x^{-1/3} - a_0\right]$$

Since series (1.9) is convergent, hence by Abel's test of convergence (substituting $x^0 = x^{1/3}$) the series

$$\eta^*(x) = \sum_{n=0}^{\infty} |a_n| x^{(2n+1)/3} \tag{1.12}$$

is also convergent.

Let us consider the series

$$y^*(x) = \sum_{n=1}^{\infty} b_n^* x^{(2n-1)/3}; \tag{1.13}$$

$$a_0 b_n^* = -\alpha |a_n| - \sum_{k=1}^{n} |a_k| b_{n-k}^*, \quad b_0^* = b_0$$

which can be obtained by equating to zero the integral term in equation $L(y, \eta^*(x)) = 0$, and is an expansion in powers of $x^{1/3}$ of the expression

$$y^*(x) = -F(x, \eta^*(x))[\eta^*(x)]^{-1}$$

Hence the series (1.13) is convergent for at least such x for which series (1.12) is convergent and the inequality

$$\frac{1}{|a_0|}\sum_{n=1}^{\infty} |a_n| x^{2n/3} < 1 \quad \left(\text{or } \frac{\eta^*(x) x^{-1/3}}{2|a_0|} < 1\right)$$

is satisfied.

Since series (1.13) is convergent, the series

$$\sum_{n=1}^{\infty} |b_n^*| \, x^{(2n-1)/3}$$

which dominates the input series (1.10) is also convergent in the same interval.

Equation (1.9) was analyzed by numerical methods. For isolating the singularity in the neighborhood of point $x = 0$ the representation in the form of series (1.10) was used. Derived results are discussed in Sect. 3.

In what follows the complete solution for the diffusion boundary layer in terms of function Φ is used in the form

$$c^{(d)}(\xi, t) = \frac{1}{\Gamma(1/3)} \gamma\left(\frac{1}{3}, \frac{\xi^3}{9t}\right) - \frac{1}{2^{1/3}\Gamma(2/3)} \int_0^t \Phi(\lambda)(t-\lambda)^{-2/3} \exp\left[-\frac{\xi^3}{9(t-\lambda)}\right] d\lambda \tag{1.14}$$

2. Concentration distribution in the diffusion trail. Let us consider the diffusion trail region W consisting of four characteristic zones: the convection boundary layer $W^{(1)}$, the inner zone $W^{(2)}$, the rear stagnation point zone $W^{(3)}$, and the mixing zone $W^{(4)}$ [3].

Contribution of the diffusion trail zone, whose boundary corresponds to $\theta \sim \varepsilon$, to the over-all diffusion flux to the particle surface is relatively small $\sim O(\varepsilon)$. However the concentration field in the trail plays an important part in the mass exchange of particles moving in the trail of the preceding particle [5, 6].

For convenience we introduce in the diffusion trail region an additional boundary condition (of symmetry) $[\partial c / \partial\theta]_{\theta=0} = 0$. In this case it is equivalent to the condition of boundedness of solutions in $W^{(2)}$ on the axis of the stream.

Estimate of separate terms of Eqs. (1.1) and (1.2) in the convection boundary layer region $W^{(1)} = \{\varepsilon \ll r - 1, \ \varepsilon^3 \ll \psi \ll \varepsilon^2\}$ shows that the right-hand side of the equation can be neglected. Thus the condensation depends only on the stream function and is the same as in the diffusion boundary layer. The formula for concentration in $W^{(1)}$ is determined by joining with solution (1.14) for $\theta \to 0$ and $\xi = \text{const}$, and is of the form

$$c^{(1)}(\xi) = c^{(d)}(\xi, t_0) \quad (t_0 = \sqrt{3}\,\pi / 8) \tag{2.1}$$

To investigate the trail inner zone $W^{(2)} = \{\varepsilon \ll r - 1 \ll \varepsilon^{-1}, \ \psi \ll \varepsilon^3\}$ and the mixing zone $W^{(4)} = \{\varepsilon^{-1} \ll r, \ \psi \ll \varepsilon^2\}$, in which transport is small, we use for convective diffusion the equation in variables

$$\frac{\psi_\theta}{\sin\theta} \frac{\partial c}{\partial r} = \varepsilon^3 \left\{\psi_\theta^2 \frac{\partial^2 c}{\partial \psi^2} + (\psi_{\theta\theta} + \operatorname{ctg}\theta\,\psi_\theta) \frac{\partial c}{\partial \psi}\right\} \tag{2.2}$$

taking into account that in these regions the first term in parentheses in the right-hand side of Eq. (1.1) can be neglected. In this equation all coefficients must be expressed in terms of r and ψ using for ψ the expression in (1.2).

The rear stagnation point zone $W^{(3)} = \{\theta \ll \varepsilon, \ r - 1 \ll \varepsilon\}$ in which radial and tangential transport are significant, and the inner trail zone $W^{(2)}$ will be considered together.

The equation and the boundary condition for $W^{(2)}$ in variables $y = r - 1$, and $\zeta = \varepsilon^{-3}\psi$ are of the form

$$\frac{\partial c^{(2)}}{\partial y} = 2\frac{\partial}{\partial \zeta}\zeta\frac{\partial c^{(2)}}{\partial \zeta} \tag{2.3}$$

$$\zeta^{1/2}\frac{\partial c^{(2)}}{\partial \zeta}\bigg|_{\zeta=0} = 0, \quad c^{(2)}|_{\zeta\to\infty} = c^{(1)}|_{\xi\to 0} \to \varepsilon^{1/2}A\zeta^{1/3}$$

$$A = 3^{1/3}[\Gamma^{-1}(1/3)t_0^{-1/3} + 2^{-1/3}\Phi(t_0)]$$

where the equation is obtained from (2.2) and the boundary condition at infinity ($\zeta \to 0$) defines the condition of joining with the solution in the convection boundary layer zone $W^{(1)}$. In deriving this condition it was taken into account that

$$u(\xi, t_0) \to u(0, t_0) + \frac{\partial u}{\partial \xi}\bigg|_{\xi=0}\xi = -\left(\frac{3}{2}\right)^{1/3}\Phi(t_0)\xi, \quad \xi \to 0$$

$$u(0, t_0) = \int_0^{t_0}\Phi(\lambda)(t_0 - \lambda)^{-2/3}d\lambda = 0$$

where the integral is zero due to the properties of Eq. (1.8) and the derivative $[\partial u/\partial\xi]_{\xi=0}$ follows from the second property of function u (1.7).

The equations and boundary conditions for $W^{(3)}$ in variables $Y = \varepsilon^{-1}(r - 1)$ and $S = \varepsilon^{-1}\theta$ are as follows:

$$\frac{3}{2}Y^2\frac{\partial c^{(3)}}{\partial Y} - \frac{3}{2}YS\frac{\partial c^{(3)}}{\partial S} = \frac{\partial^2 c^{(3)}}{\partial Y^2} + \frac{1}{S}\frac{\partial}{\partial S}S\frac{\partial c^{(3)}}{\partial s} \tag{2.4}$$

$$\left[\frac{\partial c^{(3)}}{\partial Y}Y^2 - \varepsilon k c^{(3)}\right]_{Y=0} = 0, \quad \frac{\partial c^{(3)}}{\partial S}\bigg|_{S=0} = 0$$

$$c^{(3)}|_{S\to\infty} = c^{(d)}(\xi(\theta, r), t(\theta))|_{\theta\to 0} \to \varepsilon\frac{\sqrt{3}}{2}AYS$$

The last boundary condition is the condition of joining with the boundary layer solution (1.14). The statement of problems (2.4) and (2.3) must be supplemented by the condition

$$c^{(3)}(Y \to \infty) = c^{(2)}(y \to 0) \tag{2.5}$$

of congruence of solutions in zones $W^{(2)}$ and $W^{(3)}$.

Below we shall need the following statement.

Let the solution of the boundary value problem contain a small parameter ε be sought in region Ω with two regions $\sigma_1 = \{0 \leqslant Y < O(\varepsilon),\ 0 \leqslant s \leqslant s_0\}$ and $\sigma_2 = \{O(\varepsilon) \leqslant y,\ 0 < s \leqslant s_0\}$ (with coordinates $Y = \varepsilon^{-1}y$ in σ_1 and y in σ_2) that correspond to different asymptotic expansions v_i, $i = 1, 2$ (inner and outer, respectively) of the unknown function $v(y, s, \varepsilon)$. We assume that the boundary condition for v when $y = 0$ does not contain ε and is of the form

$$y = 0, \quad H(v, s) = \sum_{k=1} H_{\gamma_k}(v, s) = 0, \quad 0 < \gamma_1 < \gamma_2 < \ldots < \gamma_n \ldots \tag{2.6}$$

$$H_{\gamma_k}(\lambda, v, s) = \lambda^{\gamma_k}H_{\gamma_k}(v, s)$$

where H_{γ_k} are operators homogeneous with respect to v, and γ_k are arbitrary numbers, not necessarily integers.

Let one of the boundary conditions (at infinity) for $v(y, s, \varepsilon)$ be of order unity, and let it be possible to have in σ_2 a solution of the form

$$\varepsilon \to 0, \quad v_2 \to \varepsilon^p v_* (y, s) + o(\varepsilon^p), \quad p > 0 \tag{2.7}$$

The boundary condition for v_2 with $y = 0$ is then

$$y = 0, \quad H_{\gamma_1}(v_2, s) = 0 \tag{2.8}$$

This statement is proved by substituting $v(y, s, \varepsilon)$ into boundary condition (2.6) and passing to limit with $\varepsilon \to 0$ using formula (2.7).

In the considered case $\gamma_1 = 1$ and, consequently, the boundary condition for $c^{(2)}$ is the same as that in (1.1). For the most important case of the diffusion boundary layer $k \geqslant O(\varepsilon^{-1})$ from this we obtain

$$c^{(2)}|_{y=0,\ \theta=\mathrm{const}} = 0 \tag{2.9}$$

which is accurate to within $O(\varepsilon)$.

The solution of problem (2.3), (2.9) of concentration distribution in $W^{(2)}$ is sought in the form [5]

$$c^{(2)}(y, \zeta) = (2\varepsilon)^{1/2} A y^{1/2} F(x), \quad x = -\frac{\zeta}{2y}; \quad x \in (-\infty, 0] \tag{2.10}$$

and for the determination of function $F(x)$ we have

$$xF_{xx}'' + (1 - x)F_x' + {}^1/_2 F = 0$$

$$(-x)^{1/2} F_x'|_{x=0} = 0, \quad F|_{x \to -\infty} \to [-x]^{1/2}, \quad x \in (-\infty, 0]$$

where the prime denotes differentiation with respect to x. For the concentration distribution in $W^{(2)}$ we finally obtain

$$c^{(2)} = (2\varepsilon)^{1/2} \Gamma({}^3/_2) A y^{1/2} \Phi(-{}^1/_2, 1, -\zeta / 2y) \tag{2.11}$$

$$\Phi(a, c, x) = 1 + \sum_{k=1}^{\infty} \frac{a(a+1)\ldots(a+k-1)}{c(c+1)\ldots(c+k-1)} \frac{x^k}{k!}$$

where $\Phi(a, c, x)$ is a degenerate hypergeometric function.

Formulas (2.5) and (2.11) yield for concentration in the rear stagnation point zone $W^{(3)}$ the following boundary condition:

$$c^{(3)}|_{Y \to \infty} \to \varepsilon 2^{1/2} \Gamma({}^3/_2) A Y^{1/2} \Phi(-{}^1/_2, 1, -{}^3/_8 Y S^2) \tag{2.12}$$

Problem (2.5), (2.12) was analyzed by numerical methods in [3, 7] for $k = \infty$. It was shown that the contribution of zone $W^{(3)}$ to the total diffusion flux on the sphere is of order ε, i.e. it introduces a correction only in the third term of the expansion of solution of the diffusion boundary layer in series in ε. This occurs also here, and we shall not analyze this zone.

Let us now consider the mixing zone $W^{(4)} = \{\varepsilon^{-1} \leqslant r, \psi \leqslant \varepsilon^2\}$, in which, as in $W^{(2)}$, the diffusion along streamlines can be neglected. Concentration $c^{(4)}$ satisfies the following equation and boundary conditions:

$$\frac{\partial c^{(4)}}{\partial \rho} = \frac{1}{\xi} \frac{\partial}{\partial \xi} \xi \frac{\partial c^{(4)}}{\partial \xi}, \quad \rho = \varepsilon \frac{r}{2} \tag{2.13}$$

$$\frac{\partial c^{(4)}}{\partial \xi}\bigg|_{\xi=0} = 0, \quad c^{(4)}|_{\xi\to\infty} = 1$$

$$c^{(4)}|_{\rho\to 0} = [c^{(3)}(\xi) + c^{(2)}(\zeta, y) - A\xi]_{y\to\infty} =$$
$$[c^{(3)}(\xi) - A\xi + 2\Gamma(^3/_2)\, A\rho^{1/2}\Phi(-{}^1/_2, 1, -\xi^2/4\rho)]_{\rho\to 0}$$

where the initial condition is determined by the joining of solution in the mixing zone with solutions in zones $W^{(1)}$ and $W^{(2)}$. The solution of problem (2.13) is of the form

$$c^{(4)}(\xi, \rho) = \mathbf{B}(\xi, \rho) * [c^{(3)}(\xi) - A\xi] + 2A\Gamma(^3/_2)\,\rho^{1/2}\Phi(-{}^1/_2, 1, -\xi^2/4\rho) \tag{2.14}$$

$$\mathbf{B}(\xi, \rho) * u(\xi) = \int_0^\infty \frac{\xi^*}{2\rho}\exp\left(-\frac{\xi^2+\xi^{*2}}{4\rho}\right) I_0\left(\frac{\xi\xi^*}{2\rho}\right) u(\xi^*)\, d\xi^*$$

3. Diffusion flux on the sphere surface. Discussion of results. Using the integral equation (1.8) for function Φ, we obtain for the local diffusion flux j on the sphere surface the equation

$$j(t) = [\partial c^{(d)}/dr]_{r=1} = \varepsilon^{-1}\eta(t)\,[\partial(c_*^{(d)} - u)/\partial\xi]_{\xi=0}$$

From formula (1.4) for $c_*^{(d)}$ with allowance for the property (1.7) we obtain for the relation between functions Φ and j

$$\Phi(x) = \frac{2^{1/3}}{\Gamma(^1/_3)\, x^{1/3}} - \varepsilon\left(\frac{2}{3}\right)^{1/3}\eta^{-1}(x)\, j(x) \tag{3.1}$$

Substituting this expression into Eq. (1.8) for $\Phi(x)$ we obtain the following integral equation for the local diffusion flux:

$$j_*(x) = 1 - k^*\mathbf{G}(x) * j_*(x), \quad j_*(x) = j(x)k^{-1} \tag{3.2}$$

$$\mathbf{G}(x) * w(x) = \int_0^x w(\lambda)\,\eta^{-1}(\lambda)\,(x-\lambda)^{-2/3}\, d\lambda$$

Let us now investigate the two limit cases of $k^* \gg 1$ and $k^* \ll 1$. For the local flux j the first case relates to a fixed ε and $k\to\infty$, while the second corresponds to fixed k and $\varepsilon\to 0$.

In the first case in the zero approximation we have the equation

$$\mathbf{G}(x) * j^\circ(x) = \frac{3^{1/3}B_0}{\varepsilon\Gamma(^1/_3)}, \quad B_0 = \Gamma\left(\frac{1}{3}\right)\Gamma\left(\frac{2}{3}\right)$$
$$(k\to\infty,\ \varepsilon = \mathrm{const})$$

whose solution is of the form

$$j^\circ(x) = \varepsilon^{-1}\frac{3^{1/3}}{\Gamma(^1/_3)}\,\eta(x)\, x^{-1/3} \tag{3.3}$$

which corresponds to the limit diffusion flux defined by the concentration $c_*^{(d)}$ (1.4).

The next following approximation with respect to parameter k^{-1} is determined by Abel's equation

$$\mathbf{G} * j^1 = -\varepsilon^{-1}3^{1/3}\Gamma(^2/_3)\, j^\circ \tag{3.4}$$

whose solution is

$$j = j^\circ - (k^*)^{-1}\frac{3^{1/3}}{2\pi}\eta(x)\frac{d}{dx}\int_0^x j^\circ(\lambda)(x-\lambda)^{-2/3}d\lambda$$

$$(k^* = 3^{-1/3}\Gamma^{-1}(2/3)k\varepsilon)$$

The computation of integral (3.5) yields for the total flux the formula

$$I = 2\pi\int_0^\pi \sin\tau j(\tau)d\tau = I_0[1 - 0.46(k^*)^{-1}], \quad I_0 = \frac{2\pi 3^{4/3}t_0^{2/3}}{\varepsilon\Gamma(1/3)} \tag{3.6}$$

where I_0 is the limit flux on the sphere when $k = \infty$.

In the second limit case ($\varepsilon \to 0$) the integral equation (3.2) shows that the local diffusion flux over the whole surface of the sphere (except in the region of the rear stagnation point $\sigma = |t_0 - x| < O(e^{-1/\varepsilon})$) in the principal approximation with respect to parameter ε is

$$j(x) = k \quad (\varepsilon \to 0,\ k = \mathrm{const}) \tag{3.7}$$

which means that when $k \ll P^{1/3}$ the mode of the reaction process over the whole surface of the sphere is close to kinetic.

Since $G * 1 \to \infty$ when $x \to t_0$, there exist in the vicinity of the rear stagnation point a region of the boundary layer kind $\sigma = \{|t_0 - x| \ll e^{-1/\varepsilon}\}$, in which the local diffusion flux rapidly changes from unity to zero. Hence a region of the reaction diffusion mode always exists in the neighborhood of the rear stagnation point. The effect of region σ on the total flux is insignificant. Hence we have

$$\mathrm{Sh} = k, \quad \mathrm{Sh} = I / 4\pi \quad (\varepsilon \to 0,\ k = \mathrm{const}) \tag{3.8}$$

It is seen that the formulas for diffusion fluxes are independent of the Péclet number. This means that in the case of finite rate of surface reaction the Sherwood number with increasing Péclet number tends to a constant value, shown in (3.8).

This phenomenon may be considered to be the saturation of the diffusion flux and is explained by that with increasing Péclet number the diffusion flux increases until the surface reaction becomes the limiting factor of the diffusion process.

Solution of the integral equation (1.8) for intermediate values of k^* was obtained by numerical methods. Function $\Phi(x)$ is presented for several values of k^* in Fig.1 by solid lines *1*, *2*, and *3* which correspond to $k^* = 0.1$, 1, and 10, respectively. The first two terms of series (1.10) were used in numerical computations, and the unknown function was represented as $\Phi(x) = b_0x^{-1/3} + b_1x^{1/3} + \varphi(x)$. Function $\varphi(x)$ and its derivatives have no singularities along the segment $[0, t_0]$.

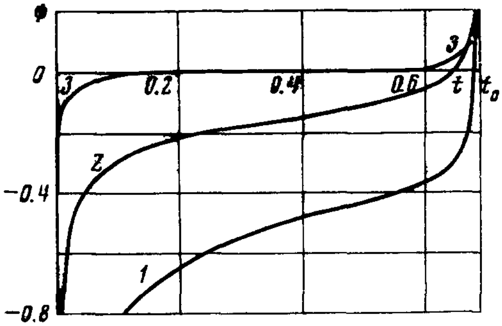

Fig.1

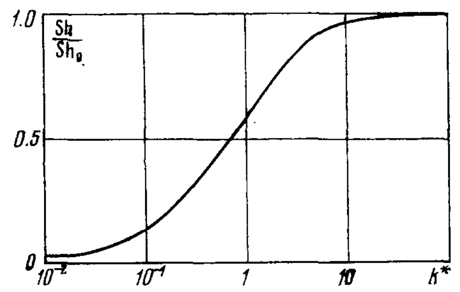

Fig.2

The obtained results make it possible to determine the total flux on the sphere surface. For the mean Sherwood number we have

$$\frac{\mathrm{Sh}}{\mathrm{Sh}_0} = -2^{5/3}3^{-1/3}\pi^{-2/3}\Gamma\left(\frac{1}{3}\right)\left[(b_0+\alpha)t_0^{2/3} + \frac{1}{2}b_1 t_0^{4/3} + \frac{2}{3}\int_0^{t_0}\varphi(\tau)\,d\tau\right] \tag{3.9}$$

where $\mathrm{Sh}_0 = I_0 / 4\pi$ is the Sherwood number for the limit flux on the sphere.

Dependence of the mean Sherwood number on parameter k^* is shown in Fig. 2. Note that the numerical solution of the integral equation for $\varphi(x)$ shows the relative contribution of that function to the mean Sherwood number to be fairly small. Thus for $k^* = 0.1$ it amounts to 30% and rapidly diminishes with increasing k^*, dropping to not more than 10% when $k^* = 1$. Owing to this, it is possible to represent in a wide range of values of k^* the dependence of total flux on the reaction rate constant by the approximate formula

$$\frac{\mathrm{Sh}}{\mathrm{Sh}_0} = \frac{k^*}{a_0 / B_0 + k^*} + \frac{3^{1/3}\pi^{2/3}\Gamma(2/3)\,k^*}{20\Gamma^2(1/3)(a_0/B_0+k^*)(a_0/B_1+k^*)}$$

The results obtained in Sect. 1 make it possible to draw certain conclusions about the reaction modes at the sphere surface.

We would point out that the conclusions reached in [2] about the existence in the vicinity of the forward stagnation point of a region of kinetic reaction mode at any finite rate of the latter is not generally valid. In fact, (1.10), (1.11), and (1.8) imply that at the forward stagnation point

$$c^{(d)}\Big|_{\substack{r=a\\ \theta=\pi}} = -\frac{b_0 B_0}{2^{1/3}\Gamma(2/3)} = \frac{1}{1+2^{1/3}3^{-1}\Gamma(1/3)\,kP^{-1/3}}$$

and, consequently, $j = kc^{(d)} \neq kc\,|_{r\to\infty} = k$, which means that in the general case a kinetic mode is absent. When $k \ll P^{1/3}$ we have $j = k + O(\varepsilon)$, and this shows that then the reaction in the neighborhood of point $\theta = \pi$ is fairly close to the kinetic mode. As previously noted, a region of the diffusion reaction mode always exists in the neighborhood of the rear stagnation point.

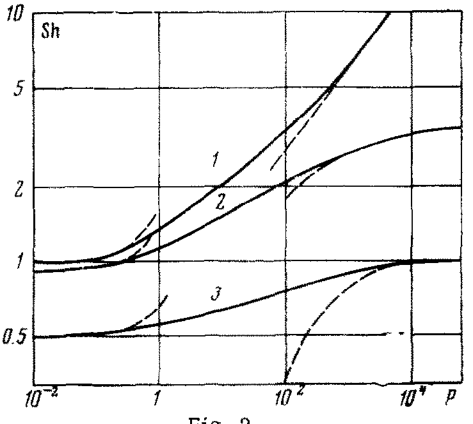

Fig. 3

The present investigation shows that the solution derived in [1] for the limit flux on a particle is applicable only when $k^* \gg 1$, i.e. $k \gg P^{1/3}$. This means that at fairly high Péclet numbers the limit flux is not realized until very high rates of surface reaction are reached.

These results may be compared, as in [2], with those obtained in [8] for low Péclet numbers. The dependence of the Sherwood number on the Péclet number is shown in Fig. 3, where the dash lines relate to low (according to [8] in a particular case of Stokes flow) and high Péclet numbers and several values of the constant of the reaction rate. Curves *1*, *2*, and *3* relate to $k = \infty$, 10, and 1.0, respectively. The possibility of interpolation for intermediate values of Peclet numbers and any chemical reaction rates can be seen from Fig.3, where some examples of interpolation are indicated by solid lines. The phenomenon of diffusion flux saturation with increasing Peclet number is also apparent in Fig.3.

We note in conclusion that the results obtained above can be extended to cases of more complex flow fields (see, e.g., [9]).

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