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CONVECTIVE DIFFUSION TO A REACTING PARTICLE IN A FLUID. NONLINEAR SURFACE REACTION KINETICS

A. D. POLYANIN and YU. A. SERGEEV
Institute for Problems in Mechanics of the U.S.S.R., Academy of Sciences, 117526 Moscow, U.S.S.R.

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Abstract — The paper is concerned with convective diffusion to a spherical particle in a uniform Stokes flow at large Péclet numbers in the case of a chemical reaction occurring on the particle surface with the rate being finite and arbitrarily dependent on concentration. Integral equations for the local diffusion flow and the surface concentration are obtained and a numerical method of their solution is developed based on the use of the appropriate asymptotics in the neighbourhood of the forward stagnation point. The effect of the reaction rate constant and the reaction kinetics on the total diffusion flux to the particle surface is studied. A simple approximate formula is suggested allowing determination of the mean Sherwood number with adequate accuracy.

A chain of reacting particles is considered and a corresponding integral equation is obtained for the local diffusion flux on their surface. A qualitative analysis of mass transfer for the chain of spheres is performed and it is shown that interaction of the diffusion wakes and boundary layers of particles in this kind of the ordered systems results in a substantial decrease in the mass transfer rate. Approximate expressions are obtained for integral fluxes to the chain particles.

The proposed method is extended to an arbitrary three-dimensional flow around particles (or drops) of arbitrary shape.

NOMENCLATURE

A,	constant defined by (17);
A_n,	constants in Acrivos and Chambre's equilibrium equation;
a,	sphere radius;
a_n,	factors in the series-expansion of function $\eta(t)$;
$B(p,q)$,	beta-function;
b,	forward stagnation point region;
b_n,	factors in the series-expansion of function $\Phi(t)$;
C,	reagent concentration close to the surface;
C_0,	surface concentration under conditions of complete absorption;
c,	reagent concentration in flow;
c_0,	substance concentration far from a sphere;
C_*,	concentration distribution in a diffusion boundary layer under conditions of complete absorption;
D,	diffusivity;
d,	diffusion boundary layer region;
e,	outer region;
f,	function determined by the mechanism of surface reaction;
G,	operator defined by equation (35);
G_v,	operator defined by equation (52);
g_0,	$= [g_{\xi\xi} g_{\mu\mu} g_{\chi\chi}]_{\xi=0}$;
$g_{\xi\xi}$, $g_{\mu\mu}$, $g_{\chi\chi}$,	components of metric tensor;
I,	dimensionless total flux;
I^*,	dimensional total flux;
I_0,	dimensionless total flux under conditions of complete absorption; modified Bessel function;
$I_\Sigma^{(m)}$,	total diffusion flux to the first m particles of the chain;
i,	instantaneous number of the point of division of the interval $[0, t_0]$;
j,	local diffusion flux;
j^0,	local limiting diffusion flux;
K^*,	$= 3^{-1/3}\Gamma^{-1}(2/3)\varepsilon k$;
k,	dimensionless constant of the surface reaction rate;
k',	dimensional constant of the surface reaction rate;
L,	plate length;
l,	distance between particles;
m,	number of the sphere in a chain;
N,	number of divisions of interval $[0, t_0]$;
n,	number of the point of division of the interval $[0, t_0]$;
Pe,	$= aUD^{-1}$, Péclet number;
p,	number of the point (line) of incidence;
q,	root of equation (11);
r,	radial coordinate;
S,	$= \varepsilon^{-1}\theta$;
S,	particle surface area;
Sh,	mean Sherwood number;
Sh_0,	mean Sherwood number under conditions of complete absorption;
t,	$= \sqrt{\frac{3}{8}}[\pi - \theta + \frac{1}{2}\sin 2\theta]$;
t_0,	$= \pi\sqrt{\frac{3}{8}}$;
U,	fluid velocity far from the particle;
u,	$= c^{(d)} - c_*^{(d)}$;
W,	diffusion wake region;
$W^{(i)}$,	diffusion wake subregions;
X,	$= \varepsilon^{-1}(\pi - \theta)$;
x,	coordinate running along the plate;
Y,	$= \varepsilon^{-1}(r - 1)$;
z,	$= \frac{2}{3}\xi^{3/2}$;

Greek symbols

α,	$= 2^{1/3}\Gamma^{-1}(\frac{1}{3})$;
ε,	$= Pe^{-1/3}$;
ζ,	$= \frac{1}{2}z(t-\lambda)^{-1/2}$;
η,	$= \sqrt{\frac{3}{2}}\sin\theta$;
θ,	angular coordinate;
κ,	order of reaction;
μ_p,	coordinate of the point (line) of incidence;
ν,	kinematic viscosity of liquid;
ξ,	$= \varepsilon^{-1}\psi^{1/2}$;
(ξ,μ,χ),	coordinate system for a three-dimensional flow in Section 2;
Π,	RHS of Acrivos and Chambre's difference equation;
ρ,	$= \frac{1}{2}\varepsilon r$;
τ,	$= (m-1)\tau_0 + \tau_m$;
τ_0,	$= \pi\sqrt{\frac{3}{8}}$;
τ_m,	$= t(\theta_m)$;
τ_m^0,	$= \tau_m(0)$;
$\Phi(t)$,	kernel of integral equation;
Ψ,	stream function analog for a three-dimensional flow;
ψ,	stream function;
ω,	$= \frac{1}{3}\cdot 2^{1/3}\Gamma(1/3)k\varepsilon$.

Superscripts

(b),	forward stagnation point region;
(d),	diffusion boundary layer;
(e),	outer region;
(i),	subregions of the region W, $i = 1, 2, 3, 4$.

Subscript

m,	number of the sphere in the chain.

1. INTRODUCTION

ONE OF the main objectives of the physico-chemical hydrodynamics is to determine the total flux of the substance dissolved in a liquid to a reacting particle. In this respect the problems involving the finite rate of the surface reaction which present themselves, for example, in the case of the integral-order reactions and in the case of the Langmuir surface fractional-order reaction kinetics [1] are of considerable interest.

The problem of diffusion to a flat plate in a viscous incompressible fluid flow at large Reynolds numbers was earlier considered in the diffusion boundary layer approximation for the first order reaction in [2] and for the arbitrary surface reaction kinetics in [3, 4].

The problem of convective diffusion to a spherical particle moving in a gas at small Péclet numbers for the linear and arbitrary kinetics was considered respectively in [5, 6] by the method of matched asymptotic expansions.

In the present paper, by using the method of the matched asymptotic expansions, the distribution of concentration near a sphere in translational Stokes flow has been obtained for large Péclet numbers in the case of a chemical reaction occurring on the sphere surface with the rate which depends arbitrarily on the reagent concentration close to the surface. An important feature of this problem, which is absent in the flat plate case [2–4], is that concentration in the vicinity of the forward stagnation point of the sphere differs from a non-depleted concentration in the main flow. Because of this, fairly general results, which were obtained by Acrivos and Chambre [4] and which were based on the additional inference that concentrations at infinity and at the point of incidence are equal, as well as their method of numerical integration of the corresponding integral equation for the surface concentration cannot be directly applied in the present case.

2. STATEMENT OF THE PROBLEM. CONCENTRATION DISTRIBUTION IN A DIFFUSION BOUNDARY LAYER

Consideration is given to the steady state convective diffusion of substance to a solid sphere of radius a in a uniform Stokes flow of an incompressible fluid having the velocity U and concentration c_0 far from the sphere. It is presumed that there is a chemical reaction on the sphere surface occurring with the finite rate $k'c_0 f(C/c_0)$, where k' is the reaction rate constant, C is the reagent concentration at the surface. The function f is determined by the particular reaction mechanism on the sphere surface. Thus, for the κ-order reaction $f(C) = C^\kappa$.

In spherical coordinates, r and θ, fixed with respect to the particle, the dimensionless equation of the steady state convective diffusion and the boundary conditions are of the form

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

$r = 1, \partial c/\partial r - kf(c) = 0; r \to \infty, c \to 1; \theta = 0, \partial c/\partial\theta = 0; \theta = \pi, \partial c/\partial\theta = 0; \varepsilon^{-3} = Pe = aUD^{-1}, k = k'aD^{-1}$, $f(0) = 0$. Here c is the substance concentration, ψ is the stream function, Pe the Péclet number, D the diffusion coefficient; the angle θ is measured from the flow direction. The scales in equation (1) are taken to be the sphere radius, the rate and the concentration at infinity.

The dimensionless Stokes stream function for a sphere is of the form

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

We shall hereafter assume that, as usual, the Péclet number for fluids is large, i.e. $\varepsilon \ll 1$. An asymptotic analysis of the problem (1), (2) at $\varepsilon \to 0$ for the case of complete absorption on the sphere surface $c(r = 1) = 0$ $(k = \infty)$ was carried out by Sin and Newman [7] and for the case of the linear kinetics, $f(C) = C$, by Polyanin and Sergeev [8].

At $\varepsilon \ll 1$, the flow in the vicinity of the particle can be divided into several characteristic regions with different mechanisms of mass transfer [7]. These are: the outer region e, the region of the forward stagnation point b, the diffusion boundary layer d and the region of the diffusion wake W, the latter, in turn, being composed of the subregions $W^{(i)}$ $(i = 1, 2, 3, 4)$. In each of these regions, equation (1) is replaced by an approximate one by isolating the principal terms of the expansion in the small parameter ε. Agreement between the solutions for separate regions is ascertained by asymptotic matching at their arbitrary boundaries.

In the outer region $e = \{r - 1 > 0(\varepsilon), 0(\varepsilon) < \theta\}$ (here and subsequently, inequalities within braces indicate the order of characteristic dimensions for the region considered) the RHS of equation (1) is negligibly small and diffusion plays a minor part in substance transfer. Here, concentration retains its constant value equal to that at infinity, i.e. $c^{(e)} = 1$.

In the region of the forward stagnation point $b = \{r - 1 < 0(\varepsilon), \pi - \theta < 0(\varepsilon)\}$ equation (1) can be slightly simplified, but it will retain the terms which describe diffusion both in the tangential and in the radial directions. It will be shown later (see Section 5) that this region does not affect the distribution of concentration in the diffusion boundary layer and in the diffusion wake of the particle.

Convective diffusion in the diffusion boundary layer, $d = \{r - 1 < 0(\varepsilon), 0(\varepsilon) < \theta\}$, which is composed of the convection along the sphere surface and the lateral diffusion, predominates in the process of the dissolved component transfer to the particle surface.

Employing substitutions $\xi = \varepsilon^{-1}\psi^{1/2}$, $t = T(\theta) = \sqrt{\frac{3}{8}}[\pi - \theta + \frac{1}{2}\sin 2\theta]$ and retaining the principal terms of expansion in ε, we obtain from equations (1), (2) the following equation and boundary conditions for the concentration distribution in the diffusion boundary layer

$$\left(\frac{\partial}{\partial t} - \xi^{-1}\frac{\partial^2}{\partial \xi^2}\right)c^{(d)} = 0 \quad (0 < t \leq t_0),$$

$$\xi = 0, \quad \eta(t)\partial c^{(d)}/\partial \xi - \varepsilon k f(c^{(d)}) = 0;$$

$$\xi \to \infty, \quad c^{(d)} \to 1; \quad t = 0, \quad \xi \neq 0, \quad c^{(d)} = 1; \quad (3)$$

$$\eta(t) = \frac{\sqrt{3}}{2}\sin T^0(t), \quad t \equiv T[T^0(t)],$$

$$t_0 = t(0) = \frac{\pi\sqrt{3}}{8}.$$

Here, the last boundary condition at $t = 0$ is the condition of incidence [2].

Solution of the diffusion boundary layer equation (3) under the condition of complete substance absorption on the sphere surface (k $= \infty$) was obtained in [2] as:

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

$$(\tfrac{1}{3}, x) = \int_0^x e^{-\tau}\tau^{-2/3}\mathrm{d}\tau, \quad \Gamma(\tfrac{1}{3}) = \gamma(\tfrac{1}{3}, +\infty). \quad (4)$$

Following [8], we perform the substitution $z = 2/3\xi^{3/2}$ and seek the solution of the problem (3) in the form $c^{(d)} = c_*^{(d)} + u$; in so doing, we obtain for the unknown function u the following equation and the boundary conditions

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial z^2} + \frac{1}{3z}\frac{\partial u}{\partial z}, \quad (5)$$

$$z = 0, \quad -z^{1/3}\frac{\partial u}{\partial z} + (\tfrac{2}{3})^{1/3}\frac{k\varepsilon}{\eta(t)}f(u) - \frac{2^{1/3}}{\Gamma(\frac{1}{3})t^{1/3}} = 0, \quad (6)$$

$$z \to \infty, \quad u \to 0; \quad t = 0, \quad u = 0. \quad (7)$$

The solution of equation (5) is sought in the form

$$u(z, t) = \frac{2^{-1/3}}{\Gamma(\frac{2}{3})}\int_0^t \Phi(\lambda)(t - \lambda)^{-2/3}\exp(-\zeta^2)\mathrm{d}\lambda, \quad (8)$$

$$\zeta = \tfrac{1}{2}z(t - \lambda)^{-1/2} \quad (0 < t \leq t_0).$$

The function (8) satisfies equation (5) and boundary conditions (7) for any kernel $\Phi(t)$, and over the interval $0 < t \leq t_0$ it has the following properties [9]:

$$\lim_{z \to 0} u = L_*\Phi \equiv \frac{2^{-1/3}}{\Gamma(\frac{2}{3})}\int_0^t \Phi(\lambda)(t - \lambda)^{-2/3}\mathrm{d}\lambda, \quad (9)$$

$$\lim_{z \to 0}[z^{1/3}\partial u/\partial z] = -\Phi(t).$$

It follows from (6) and (9) that the function $\Phi(t)$ is the solution of the integral equation

$$\eta(t)\Phi(t) + 2^{1/3}\Gamma(\tfrac{2}{3})K^*f(L_*\Phi) - \alpha\eta(t)t^{-1/3} = 0, \quad (10)$$

$$K^* = 3^{-1/3}\Gamma^{-1}(\tfrac{2}{3})\varepsilon k, \quad \alpha = 2^{1/3}\Gamma^{-1}(\tfrac{1}{3}).$$

The function $\eta(t)$ in the vicinity of the point $t = 0$ has the series expansion

$$\eta(t) = \sum_{n=0}^{\infty} a_n t^{(2n+1)/3}; \quad a_0 = 3^{2/3}2^{-1/3}, \quad a_1 = \tfrac{1}{5}, \ldots$$

and the property $t \to t_0$, $\eta(t) \to a_0(t - t_0)^{1/3}$.

If the function $f(x)$ is continuous, then $\Phi(t) \to \alpha q t^{-1/3} + O(t^{-1/3})$ at $t \to 0$, where q is the root of the equation

$$H(q, \omega) \equiv q + \omega f(q) - 1 = 0, \quad (11)$$

$$(\omega = \tfrac{1}{3} \cdot 2^{1/3}\Gamma(\tfrac{1}{3})k\varepsilon).$$

Here and subsequently, unless otherwise specified, the validity of the following inequalities is assumed: $f(1) > 0$; $f'_x > 0$ at $x > 0$. By virtue of the fact that $H(0, \omega) \leq 0$, $H(1, \omega) \geq 0$, $H'_q > 0$ $(0 \leq \omega \leq \infty)$, the above properties mean that equation (11) has a single non-negative root q, $0 \leq q \leq 1$. The above inequalities hold, for example, when the reactions are of the order $\kappa > 0$.

If the function $f = f(x)$ can be expanded into a Taylor series converging in a neighbourhood of the point $x = q$, then, similarly to the linear kinetics case [8], the solution of equation (10) can be represented in the form of a locally converging series

$$\Phi(t) = \sum_{n=0}^{\infty} b_n t^{(2n-1)/3}, \quad b_0 = \alpha q. \quad (12)$$

In particular, the coefficient b_1 can be written in the following form [$B(p, q)$ is the beta function]

$$b_1 = a_1\alpha(1-q)\{a_0 + K^*B(1/3, 4/3)[\partial f/\partial x]_{x=q}\}. \tag{13}$$

The coefficients b_0 and b_1 will further be used to evaluate the total diffusion flow to the particles.

With the aid of the function Φ, the concentration distribution in the diffusion boundary layer may be given as

$$c^{(d)}(\xi, t) = \Gamma^{-1}(1/3)\gamma(1/3, \xi^3/9t)$$
$$+ \frac{2^{-1/3}}{\Gamma(2/3)}\int_0^t \Phi(\lambda)(t-\lambda)^{-2/3}\exp\left[-\frac{\xi^3}{9(t-\lambda)}\right]d\lambda. \tag{14}$$

3. CONCENTRATION DISTRIBUTION IN A DIFFUSION WAKE

Consider the diffusion wake region W adjacent to the diffusion boundary layer region d and the sphere surface in the neighbourhood of the point $\theta = 0, r = 1$. It was shown in [7] that the region Wconsists of four distinctive zones: the convective boundary layer region $W^{(1)}$, the inner wake region $W^{(2)}$, the rear stagnation point region $W^{(3)}$ and the mixing region $W^{(4)}$.

The diffusion wake region, the boundary of which corresponds to $\theta \sim \varepsilon$, contributes but slightly to the integral diffusion flow to the particle surface. However, the concentration field in W will play an important part in mass transfer of the particles that move in the diffusion wake of the first particle [10, 11] (see Sections 9, 10).

Estimation of separate terms of equations (1), (2) in the convective boundary layer region of the wake

$$W^{(1)} = \{O(\varepsilon) < r - 1,\ O(\varepsilon^3) < \psi < O(\varepsilon^2)\}$$

shows that the RHS of these equations may be neglected. Therefore, the concentration depends on the stream function alone and retains the constant value along the stream lines which is equal to the value at the exit from the diffusion boundary layer. The concentration expression in $W^{(1)}$ is determined by matching with solution (14) and has the form

$$c^{(1)}(\xi) = c^{(d)}(\xi, t(\theta))\big|_{\theta\to 0,\ \xi=\text{const.}} = c^{(d)}(\xi, t_0). \tag{15}$$

In order to investigate the inner wake region

$$W^{(2)} = \{O(\varepsilon) < r - 1 < O(\varepsilon^{-1}),\ \psi < O(\varepsilon^3)\}$$

and the mixing region

$$W^{(4)} = \{O(\varepsilon^{-1}) < r,\ \psi < O(\varepsilon^2)\},$$

in which the radial trans fer is of no consequence, let us write the convective diffusion equation in terms of the variables r, ψ taking into account the fact that for these regions the first term in brackets on the RHS of equation (1) may be neglected

$$\frac{\psi_\theta}{\sin\theta}\frac{\partial c}{\partial r} = \varepsilon^3\left\{\psi_\theta^2\frac{\partial^2 c}{\partial\psi^2} + (\psi_{\theta\theta} + \cot\theta\,\psi_\theta)\frac{\partial c}{\partial\psi}\right\}. \tag{16}$$

Here all of the coefficients should be expressed in terms of r and ψ with the use of expression (2) for ψ.

The region of the rear stagnation point

$$W^{(3)} = \{\theta < O(\varepsilon),\ r - 1 < O(\varepsilon)\},$$

in which the transfer in both the radial and the tangential directions is substantial, and the inner wake region $W^{(2)}$ will be considered simultaneously.

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

$$\frac{\partial c^{(2)}}{\partial y} = 2\frac{\partial}{\partial\zeta}\zeta\frac{\partial c^{(2)}}{\partial\zeta}. \tag{17}$$

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

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

Here the equation has been obtained from equation (16), while the boundary condition at infinity ($\zeta \to \infty$) expresses the condition of matching with the solution in the convective boundary layer region $W^{(1)}$ equation (15).

In the derivation of the above boundary condition, the asymptotics

$$\xi \to 0,\ u(\xi, t_0) \to -(3/2)^{1/3}\Phi(t_0)\xi$$

was taken into account which follows from equation (10) and from the second property of the function Φ equation (9).

The equation and the boundary conditions for $W^{(3)}$ in terms of the variables $Y = \varepsilon^{-1}(r - 1)$, $S = \varepsilon^{-1}\theta$ will be of the form

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

$$\left[\frac{\partial c^{(3)}}{\partial Y} - \varepsilon k f(c^{(3)})\right]_{Y=0} = 0, \quad \frac{\partial c^{(3)}}{\partial S}\bigg|_{S=0} = 0, \tag{18}$$

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

The last boundary condition is the condition of matching with the solution (14) for the boundary layer. The formulation of the problem (18), as well as of the problem (17), must be supplemented with the condition of the conformity of solutions in the regions $W^{(2)}$ and $W^{(3)}$:

$$c^{(3)}(Y \to \infty) = c^{(2)}(y \to 0). \tag{19}$$

Let us now show the manner in which two boundary-value problems (17)–(19) can be split up and each reduced to a successive solution. Let us assume that we have obtained the solution for $W^{(2)}$. Then, it follows from the last boundary condition (17) at $\zeta \to \infty$ (ζ is further replaced by the variable $s = \varepsilon^{-3/2}\theta$) that in this region the solution can be given in the form $c^{(2)} = \sqrt{\varepsilon}\,w(y, s)$, $y = r - 1$.

By assuming that the solution for the full problem has been found, we shall write it in terms of the variables y and s, i.e. $c(y, \theta, \varepsilon) \equiv v(y, s, \varepsilon)$. At $\varepsilon \to 0$ (s

$=$const.), the solution of the full equation (by definition) goes over into $c^{(2)}$, i.e. the following holds

$$\varepsilon \to 0, v(y, s, \varepsilon) \to \sqrt{\varepsilon}\, w(y, s) + O(\sqrt{\varepsilon}). \quad (20)$$

We assume here that the boundary condition for concentration on the particle boundary is of the form

$$y = 0, F(c) = \sum_{k=1} F_{\gamma_k}(c) = 0, \quad (21)$$

$$F_{\gamma_k}(\lambda c) = \lambda^{\gamma_k} F_{\gamma_k}(c); \quad 0 < \gamma_1 < \gamma_2 < \ldots,$$

where F_{γ_k} are the operators homogeneous in c which are independent of the angle θ and the parameter ε.

Multiplying the boundary condition (21) by $\varepsilon^{-\gamma_1/2}$, employing the representation (20) and taking the limit as $\varepsilon \to 0$, $s=$const., yield the following boundary condition for concentration in the inner wake region

$$y = 0, \quad F_{\gamma_1}(c^{(2)}) = 0. \quad (22)$$

Having obtained the concentration distribution in the inner diffusion wake region $W^{(2)}$, and having written it in terms of the variables Y, S, we, letting ε approach zero in $c^{(2)}(Y, S, \varepsilon)$, will obtain from (19) the boundary condition for the rear stagnation point region $W^{(3)}$ at $Y \to \infty$.

In the case of the κ-order surface reaction, at $\kappa < 1, \gamma_1 = \kappa$, $\gamma_2 = 1$; $F_\kappa = kc^\kappa$, $F_1 = \partial c/\partial y$; at $\kappa > 1$, $\gamma_1 = 1$, $\gamma_2 = \kappa$, $F_1 = \partial c/\partial y$, $F_\kappa = kc^\kappa$, while at $\kappa = 1$, $\gamma_1 = 1$, $F_1 = \partial c/\partial y - kc$.

When the boundary condition includes the parameter ε or other quantities connected with it by any relations, the procedure of obtaining the boundary condition for $W^{(2)}$ remains the same and consists in isolation of the higher-order term of expansion in ε from (21) on having substituted (20) into (21).

The case, which is most important for the diffusion boundary layer, is characterized by $k\varepsilon \sim 1$. Then, for $0 < \kappa < 3$ the above procedure yields

$$y = 0, \quad c^{(2)} = 0. \quad (23)$$

The solution of the problem (17), (23) is of the form [8]:

$$c^{(2)} = (\pi\varepsilon)^{1/2} 2^{-1/2} A y^{1/2} \Phi(-1/2, 1, -\zeta/2y), \quad (24)$$

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

Equations (24) and (19) give the boundary condition for concentration in a neighbourhood of the rear stagnation point:

$$Y \to \infty, c^{(3)} \to \varepsilon\pi^{1/2} 2^{-1/2} A Y^{1/2} \Phi(-1/2, 1, -3/2YS^2).$$

The problem (18) with the latter boundary condition was studied by numerical methods at $k = \infty$ [7].

The contribution of this region into the integral flow to the sphere is insignificant, therefore, it will not be analyzed here.

Consider now the mixing region

$$W^{(4)} = \{O(\varepsilon^{-1}) < r,\ \psi < O(\varepsilon)\},$$

in which, just as in $W^{(2)}$, diffusion along the stream lines may be neglected. The concentration $c^{(4)}$ satisfies the following equation and boundary conditions

$$\frac{\partial c^{(4)}}{\partial \rho} = \frac{1}{\xi} \frac{\partial}{\partial \xi} \xi \frac{\partial c^{(4)}}{\partial \xi} \quad (\rho = \tfrac{1}{2}\varepsilon r,\ \xi = \varepsilon^{-1}\psi^{1/2}), \quad (25)$$

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

$$c^{(4)}(\rho \to 0) = [c^{(1)}(\xi) + c^{(2)}(\zeta, y) - A\xi]_{y \to \infty}.$$

Here the initial condition is determined by matching the solution in the mixing region $W^{(4)}$ with the solutions in the regions $W^{(1)}$ and $W^{(2)}$.

The solution of the problem (25) is of the form

$$c^{(4)}(\xi, \rho) = \int_0^\infty \frac{\xi^*}{2\rho} \exp\left\{-\frac{\xi^2 + \xi^{*2}}{4\rho}\right\} \times I_0\left(\frac{\xi\xi^*}{2\rho}\right) c^{(1)}(\xi^*) \mathrm{d}\xi^*. \quad (26)$$

Here, I_0 is the modified Bessel function and $c^{(1)}(\xi)$ is determined from equation (15).

The expressions for concentration distribution in the diffusion wake regions $W^{(2)}$ and $W^{(3)}$ show that the distribution of concentration in them differs from that in the case of complete absorption ($k = \infty$) by the proportionality factor A alone (17) which includes an additional term with $\Phi(t_0) < 0$ being responsible for the increase of concentration in these regions as compared with the limiting case $k = \infty$. It is seen from equation (24) that on the flow axis $\zeta = 0$ at $r - 1 < 0(\varepsilon^{-1})$ the concentration is of order $\sqrt{\varepsilon}$ and increases in proportion to the square root of the distance up to the body surface.

4. CONCENTRATION DISTRIBUTION IN THE VICINITY OF THE FORWARD STAGNATION POINT. UNIFORM APPLICABILITY OF THE DIFFUSION BOUNDARY LAYER SOLUTION

It follows from the results of Section 3 (at $k = \infty$ [7]) that the diffusion boundary layer approximation is not uniformly applicable as to the parameter $\varepsilon \ll 1$ over the entire flow region. In particular, a special analysis is required for the rear stagnation point region since here both the normal and tangential substance transfer along the particle surface is substantial. This leads to the following additional questions: (1) whether the diffusion boundary layer approximation is valid in the region of the forward stagnation point (in view of the fact that the Jacobian of the transformation from the coordinates r, θ into the Mises variables ψ, θ vanishes at the forward stagnation point) and (2) whether any error results from the additional boundary condition $c^{(d)}(t = 0) = 1$ (condition of incidence [2]) [equation (1)] in the actual concentration distribution over the flow.

In order to perform the analysis, let us introduce into

$$b = \{r - 1 < O(\varepsilon),\ \pi - \theta < O(\varepsilon)\}$$

the prolate coordinates

$$Y=\varepsilon^{-1}(r-1),\ X=\varepsilon^{-1}(\pi-\theta). \tag{27}$$

Expressing equation (1), with regard for (2), in terms of the variables X, Y and retaining the higher-order terms of expansion in ε, X, $Y=0(1)$, we obtain the equation and boundary conditions for the region of the forward stagnation point

$$\frac{3}{2}Y\left(-Y\frac{\partial c^{(b)}}{\partial Y}+X\frac{\partial c^{(b)}}{\partial X}\right)=\frac{\partial^2 c^{(b)}}{\partial Y^2}+\frac{1}{X}\frac{\partial}{\partial X}X\frac{\partial c^{(b)}}{\partial X}, \tag{28}$$

$$Y=0,\ \partial c^{(b)}/\partial Y-\varepsilon kf(c^{(b)})=0;\ Y\to\infty,\ c^{(b)}\to 1,$$

$$X=0,\ \partial c^{(b)}/\partial X=0.$$

In order to complete the formulation of the problem (28), it is necessary to add the condition of matching with the boundary layer solution (14)

$$c^{(b)}(X\to\infty)=c^{(d)}(\theta\to\pi),\ Y=\text{const}. \tag{29}$$

For the explicit form of the concentration expression in the diffusion boundary layer at an arbitrary boundary with the region b to be obtained, we shall employ the asymptotics for the kernel $\Phi(t)\to\alpha qt^{-1/3}+O(t^{-1/3})$ at $t\to 0$, where q is the root of equation (11). In view of the above, we can obtain from (14)

$$c^{(d)}(\theta\to\pi)\to J(\xi,t)+O(t^{2/3}), \tag{30}$$

$$J=\frac{\alpha q}{2^{1/3}\Gamma(2/3)}\int_0^t\lambda^{-1/3}(t-\lambda)^{-2/3}$$

$$\times\exp\left[-\frac{\xi^3}{9(t-\lambda)}\right]\mathrm{d}\lambda.$$

The expression for J can be put into a more simplified form. The properties (9) of the functions in the form of (8) show that $J(\xi,t)$ is the solution of the boundary-value problem

$$\xi\frac{\partial J}{\partial t}=\frac{\partial^2 J}{\partial\xi^2}, \tag{31}$$

$$t=0,\ J=0;\ \xi\to\infty,\ J\to 0;\ \xi=0,\ J=q.$$

The first two boundary conditions are due to the representation (8), while the last one has been obtained by direct computation of the integral (30) at $\xi=0$. A direct check shows that the function

$$J(\xi,t)=q+\Gamma^{-1}(1/3)(1-q)\gamma(1/3,\xi^3/9t)$$

is the solution of the problem (31).

Using the substitution (27) and taking the limit as $\varepsilon\to 0$, we obtain the matching condition in the form

$$X\to\infty,\ c^{(b)}\to q+\Gamma^{-1}(1/3)(1-q)\gamma(1/3,Y^3/2). \tag{32}$$

It can be easily verified that the solution of the problem (28), (32) does not depend on the coordinate X and coincides exactly with the asymptotics (32). The equality $q=0$ corresponds to the case of limiting absorption.

It is seen from equation (32) that concentration in the region b depends only on the coordinate Y and increases rapidly from its value at the particle surface $c(0)=q$ up to the concentration in the outer region. Concentration in the region b is determined only by the boundary condition at $X\to\infty$. This means that the solution for the diffusion boundary layer (14) is uniformly applicable over the entire region $\theta>0(\varepsilon)$.

The concentration and the local diffusion flux at the forward stagnation point $\theta=\pi$, $r=1$ (at $t=0$) are determined by

$$C(0)=q,\ j(0)=k\omega^{-1}(1-q). \tag{33}$$

where q is the root of equation (11).

It follows from equations (11) and (33) that the diffusion flux in the vicinity of the forward stagnation point increases with k and decreases with increase in the reaction order κ.

In the particular case of the first-order reaction, $\kappa=1$, we have

$$C(0)=(1+\omega)^{-1},\ j(0)=k(1+\omega)^{-1},$$
$$\omega=1/3\cdot 2^{1/3}\Gamma(1/3)k\varepsilon.$$

Hence, $j=kc^{(b)}\neq kc|_{r\to\infty}=k$, and in the general case the kinetic regime in the vicinity of the forward stagnation point are absent. Note, that in the case of convective diffusion to a flat plate [2–4] the neighbourhood of the forward stagnation point is always the region for the kinetic reaction regime. For a solid sphere, the kinetic condition in the region of the forward stagnation point exist only at $k\ll Pe^{1/3}$.

5. EQUATIONS FOR THE LOCAL DIFFUSION FLUX AND THE SURFACE CONCENTRATION

Using the integral equation for Φ(10), we shall now obtain similar equations for the local diffusion flux $j=[\partial c^{(d)}/\partial r]_{r=1}$ and the surface concentration $c(r=1,\theta)\equiv C(t)$.

Equation (14) and the properties (9) give the relationship between the kernel and the local flux j

$$\Phi(t)=\frac{2^{1/3}}{\Gamma(1/3)t^{1/3}}-\varepsilon\left(\frac{2}{3}\right)^{1/3}\eta^{-1}(t)j(t).$$

Substituting this expression into equation (10) and taking the equality $j=kf(C)$ into account yield the following integral equations for the local diffusion flux and the surface concentration

$$j(t)=kf(1-k^{-1}K^*G*j), \tag{34}$$

$$C(t)=1-K^*G*f(C), \tag{35}$$

$$G*w\equiv\int_0^t w(\lambda)\eta^{-1}(\lambda)(t-\lambda)^{-2/3}\,\mathrm{d}\lambda.$$

At $K^*\to\infty$ (which corresponds to $Pe=\text{const.}$, $k\to\infty$), equations (34) and (35), with the equality $f(0)=0$ taken into account, yield

$$j^0=\varepsilon^{-1}3^{1/3}\Gamma^{-1}(1/3)\eta(t)t^{-1/3},\ C^0=0. \tag{36}$$

This solution corresponds to the case of complete absorption which is specified by the concentration distribution (4).

At $K^* \to 0$ (which corresponds to $Pe \to \infty$, $k =$ const.), the integral equations (34) and (35) show that in the principal approximation over the parameter K^* the local diffusion flux and the surface concentration are constant over the entire sphere surface

$$j(t) = kf(c)\big|_{r\to\infty} = kf(1),\; C = c\big|_{r\to\infty} = 1. \quad (37)$$

From this it follows that at $k \ll Pe^{1/3}$ the conditions for the reaction to occur throughout the entire sphere surface (except for a small region in the neighbourhood of the point of outflow $\theta = 0$) are close to the kinetic conditions. The explanation of this result lies in the fact that with increase in the Péclet number the diffusion flux can increase only until the surface reaction becomes a limiting stage in the diffusion process.

6. NUMERICAL SOLUTION OF THE INTEGRAL EQUATION FOR THE LOCAL DIFFUSION FLUX

In order to obtain a numerical solution of the integral equation (34), let it be written down with account for (36) as

$$j(t) = kf\left(1 - \frac{1}{\Gamma(1/3)\Gamma(2/3)} \times \int_0^t \frac{j(\lambda)}{j^0(\lambda)}\lambda^{-1/3}(t-\lambda)^{-2/3}\,\mathrm{d}\lambda\right).$$

Partition the interval $[0, t_0]$ into N equal parts $[(i-1)\Delta t, i\Delta t]$, $\Delta t = t_0/N$, $i = 1, \ldots, N$. The above equation will be approximated by the following system of algebraic equations for the function $j(i)$ (from now on the number of i is indicated as the argument of the function $j(i\Delta t)$):

$$j(n) = kf\left\{1 - \frac{1}{\Gamma(1/3)\Gamma(2/3)}\left[\frac{1}{2}\left(\frac{j(n)}{j^0(n)} + \frac{j(n-1)}{j^0(n-1)}\right) \times n^{-1/3} + \sum_{i=1}^{n-1}\left(\frac{1}{2}\left(\frac{j(i)}{j^0(i)} + \frac{j(i-1)}{j^0(i-1)}\right)\frac{1}{i^{1/3}(n-i)^{2/3}}\right)\right]\right\}.$$

In writing down a numerical scheme to evaluate the integral, it was taken into account on the RHS of this equation that the functions $j(t)$ and $j^0(t)$ have no singularities over the interval $[0, t_0]$. The value of $j(0)$ is determined by equation (33). The function $j^0(t)$ is determined according to equation (36).

Hence, the problem of determining the value of $j(n)$ reduces to the solution of the transcendental equation.

It should be noted that the above numerical method for the solution of the integral equation (34) is more simple than that used by Acrivos and Chambre [4] since it does not involve the computation of derivatives.

The results of numerical solution of equation (34) are presented in Fig. 1, where dashed, solid and dashed–dotted lines show the local flux distribution over the particle surface for the 1/2-, 1- and 2-order reactions, respectively. Curves 1, 2 and 3 correspond to $K^* = 0.1$, 1, ∞.

Figure 2 illustrates the effect of the reaction rate constant for the same reaction orders on the dimensionless total flux I to the particle. Here

$$I = \frac{I^*}{aDc_0} = 2\pi\int_0^\pi \frac{\partial c}{\partial r}\bigg|_{r=1}\sin\theta\,\mathrm{d}\theta,$$

$$I_0 = (3\pi)^{5/3}\left[2\varepsilon\Gamma(1/3)\right]^{-1},$$

where I^* is the dimensional total flux, I_0 is the dimensionless total flux provided there is complete substance absorption on the sphere surface.

7. CERTAIN FEATURES IN DETERMINATION OF SURFACE CONCENTRATION

Consider now in more detail the equation for the surface concentration (35). If the concentration on the LHS of equation is supposed to be prescribed, then equation (35) may be looked upon as the Abel equation for the unknown function $f(C)$. Solving equation (35) for $f(C)$ and introducing the derivative under the integral sign, we shall transform equation (35) to

$$kf(C) = j^0(t)\left\{[1 - C(0)] - t^{1/3}\int_0^t \frac{\mathrm{d}C}{\mathrm{d}\lambda}(t-\lambda)^{-1/3}\,\mathrm{d}\lambda\right\}, \quad (38)$$

where j^0 is the local diffusion flux provided there is complete absorption of the dissolved substance on the particle surface ($k = \infty$) (36).

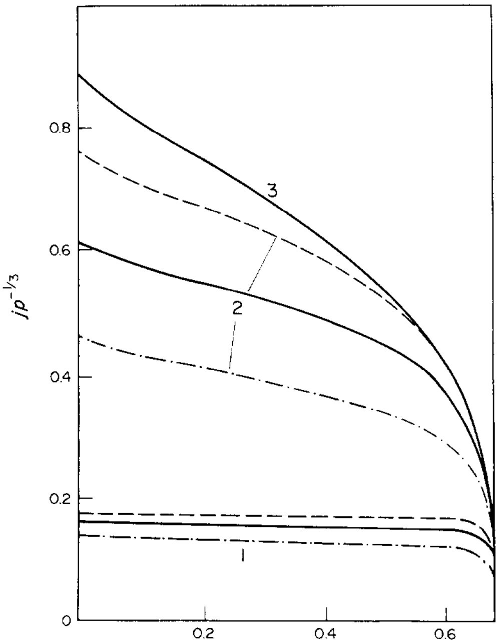

FIG. 1. Local diffusion flux to the particle surface. – – –, surface reaction of the 1/2 order; ——, first-order reaction; – · – · –, second order reaction. Curves 1, 2, 3 correspond to $K^* = 0, 1$, 1, and ∞.

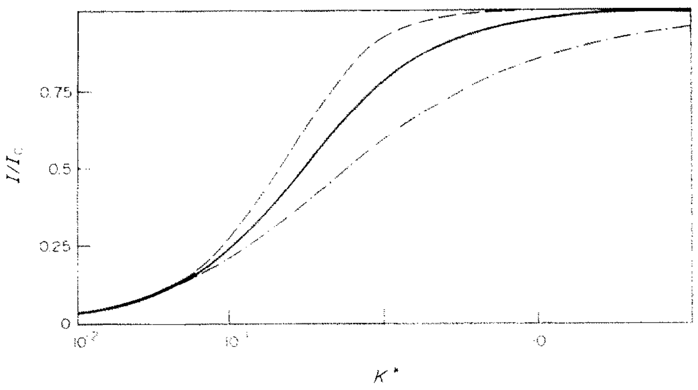

FIG. 2. Dependence of the total diffusion flux on K^*. – – –, reaction of the 1/2 order; ——, first-order reaction; · · · ·, second-order reaction.

Equation (38) will coincide with the equation obtained by Acrivos and Chambre, but derived by another method [see equation (6) of ref. 4], if we omit the terms in square brackets which are due to the difference between the concentration at the point of incidence and the non-depleted concentration in the flow far from the particle, $C(t=0) \neq c(r=\infty)=1$. The proviso was made in [4] that in the limiting case of complete absorption, $c(r=1)=0$ ($k=\infty$), the integral on the RHS of the derived equation should be looked upon as the Stiltjes integral. However, in the present case, as it follows from (38), the integral in Acrivos and Chambre's equation at any k should always be regarded as the Stiltjes integral.

Moreover, in their method of numerical integration of the respective integral equation (equation (11) of [4]) Acrivos and Chambre assume that the surface concentration at the point of incidence is known and equal to the non-depleted concentration $c(t=0)=1$. It can easily be shown with the aid of equation (38) that in the general case the RHS of the difference equation (11) of [4] should have the form

$$\Pi = \frac{2}{3}n^{-1/3}[1-C(0)] + C(0)\{n^{2/3}-(n-1)^{2/3}\} + \sum_{k=1}^{n-1} C(k)A_{n-k}, \quad (39)$$

where A_n are some constants independent of concentration, $n=1, 2, \ldots$.

Equation (39) differs substantially from equation (11) of [4] and coincides with the latter only in special cases when the equality $C(0)=1$ is valid. As shown earlier, for a Stokes flow around a sphere, the concentration at the forward stagnation point (33) is governed by equation (11) (it can also be obtained directly from equation (38)) and can differ greatly from the non-depleted concentration. In particular, at $kPe^{-1/3} \gg 1$, the inequality $C(0) = q \ll 1$ holds.

It should be noted that in a general case, depending on the kinetics of the reaction $f=f(x)$, equation (1) may simultaneously have several roots corresponding to different reaction conditions on the particle. This phenomenon is a typical one for the problems of the combustion theory [1].

It will be shown later (see Section 11) that in the case of a flat plate in a viscous incompressible liquid flow at large Reynolds numbers, which was considered by Acrivos and Chambre in [4], the limiting equality $C(0)=1$ does hold for any k and arbitrary form of the function f. The only mode of reaction for any f ($k \neq \infty$) and its nil effect on the concentration at the point of incidence in this singular case are due to the following two reasons: (1) inapplicability of the expression used in this work for the stream function and obtained in the approximation of the hydrodynamic boundary layer in the vicinity of the point of incidence; and (2) inadequacy of the diffusion boundary layer approximation in the vicinity of the forward stagnation point of the plate. Both reasons are similar in character and stem from the fact that the Reynolds numbers $Re_x = xU\nu^{-1}$ and the Péclet numbers $Pe_x = xUD^{-1}$ (x is the coordinate running along the plate) are small in the vicinity of the forward stagnation point of the plate.

Note, that in the case of the Stokes flow around a sphere the diffusion boundary layer approximation is a correct one and uniformly applicable in the vicinity of the forward stagnation point (see Section 4).

8. APPROXIMATE EXPRESSION FOR THE MEAN SHERWOOD NUMBER

The results of numerical integration of equation (34) show that the mean Sherwood number can be approximately determined from the algebraic (transcendental) equation

$$Sh = kf\left(1-\frac{Sh}{Sh_0}\right), \quad Sh = \frac{I}{S}, \quad (40)$$

where $Sh_0 = I_0S^{-1}$ is the mean Sherwood number per particle provided there is complete absorption of the substance on its surface $c(r=1,\theta)=0$ ($k=\infty$), S is the particle surface area. The solution of equation (40) can be written in the form $Sh=(1-q)Sh_0$, where q is the root of the equation $H(q, kSh_0^{-1})=0$ (11).

A check of the validity of the above formula has shown that in the case of a Stokes flow around a sphere the maximum deviation of the root of equation (40) from the results obtained by numerical integration of equation (34) is observed at $K^* \simeq 0.1$ ($\kappa = 1/2, 1, 2$) and does not exceed 15 %.

Let us now show that it is also advisable to use equation (40) to determine the mean Sherwood number at small and moderate Péclet and Reynolds numbers.

1. At small Péclet and Reynolds numbers in the case of a uniform flow around a sphere for any velocity constant k and arbitrary form of the function f, equation (40) yields a correct (exact) result at least for the first three terms of the asymptotic-series expansion of the Sherwood number in a small Péclet number! This is proved by direct substitution of the expression for the mean Sherwood number Sh_0, obtained for the case of complete absorption ($k = \infty$) [12], into equation (40) with subsequent series expansion in a small Péclet number, and finally, by comparison with the data of [6].

2. For particles of any shape at an arbitrary f equation (40) yields a correct asymptotic result in the case of small and large reaction rate constants, $k \to 0$ and $k \to \infty$, for arbitrary Péclet and Reynolds numbers.

3. The validity of equation (40) at the finite Péclet and Reynolds numbers was tested with the aid of the results of [13] obtained by numerical methods for the problem of mass transfer of a spherical particle involving heterogenous chemical reaction of the first order, $f(x) = x$. It follows from the Table in [13] (p. 130) that in this case too equation (40) provides very good results (to within 5 %).

The considerations given above show that equation (40) (recall the assumption that $f(1) > 0$; $f'_x > 0$ at $x > 0$ — the reason for equation (40) to have a single root) may be used to approximately determine the mean Sherwood number for any k and f over the whole range of the Péclet numbers ($0 \le Pe \le \infty$) for laminar flow around particles of an arbitrary shape. In this case, for equation (40) to be used, it is required to know only one single constant, Sh_0, which is determined from the solution of a substantially simpler auxiliary problem subject to the condition of complete absorption of the dissolved substance on the particle surface (note that Sh_0 can also be determined experimentally).

9. MASS TRANSFER OF A CHAIN OF SPHERES. EQUATION FOR THE LOCAL DIFFUSION FLUX

Consider now convective diffusion to a chain of spheres of equal radius. The spheres are assumed to be arranged one after the other on the axis of a uniform Stokes flow and the dimensionless distance between the spheres satisfies the condition $1 \ll l \ll Pe^{1/3}$ (here, as before, the sphere radius is taken for the characteristic length scale).

The condition $l \ll Pe^{1/3}$ means that mass transfer of each subsequent sphere m is controlled by concentration distribution in the convective boundary layer region of the diffusion wake $W^{(1)}_{m-1}$ of the preceding sphere [10, 11]. Owing to the condition that $1 \ll l$ the flow field in the vicinity of each sphere is determined by equation (2) to within $O(l^{-1})$. The case of rather a loose chain of particles at $l \ge O(Pe^{1/3})$ which corresponds to the interaction of the boundary layers d_m with the mixing regions of the diffusion wake $W^{(4)}_{m-1}$ is not considered here and can be analyzed in the manner similar to [10].

The concentration in the convective boundary layer region of the diffusion wake $W^{(1)}_m$ of the mth sphere retains constant values along the stream lines. These are equal to concentration at the exit from the diffusion boundary layer d_m. Hence, once the solution $c^{(d)}_m = c^{(d)}_m(\xi, \tau_m)$ in the diffusion boundary layer of the mth particle is known (here ξ and $\tau_m = t(\theta_m)$ are determined in equation (3), θ_m is reckoned from the point of outflow), then the distribution of concentration in the convective boundary layer region $W^{(1)}_m$ is determined by the expression $c^{(1)}_m(\xi) = c^{(d)}_m(\xi, \tau^0_m)$, $\tau^0_m = \tau_m(0)$.

The concentration distribution in the diffusion boundary layer of the mth particle is determined from the solution of (3) where the "initial" condition at $t = 0$, $c = 1$ is replaced by the condition determined from the concentration distribution in the convective boundary layer region $W^{(1)}_{m-1}$ of the $(m-1)$th sphere.

By analogy with the results of [10, 11] it is possible to obtain the recurrent system of the boundary-value problems which determines the concentration distribution in the diffusion boundary layer of the mth sphere ($m = 1, 2, \ldots$) in the form

$$\left(\frac{\partial}{\partial \tau_m} - \xi^{-1}\frac{\partial^2}{\partial \xi^2}\right)c^{(d)}_m = 0 \quad (\xi = \varepsilon^{-1}\psi^{1/2}), \quad (41)$$

$$\xi = 0,\ \eta_m(\tau_m)\partial c^{(d)}_m/\partial \xi - k\varepsilon f(c^{(d)}_m), = 0;$$

$$\xi \to \infty,\ c^{(d)}_m \to 1;\ \tau_m = 0,$$

$$c^{(d)}_m = c^{(d)}_{m-1}(\xi, \tau^0_{m-1});\ c^{(d)}_0 \equiv 1.$$

Here the function $\eta_m = \eta_m(\tau_m)$ is prescribed parametrically

$$\eta_m = \frac{\sqrt{3}}{2}\sin\theta_m,\ \tau_m = \frac{\sqrt{3}}{8}(\pi - \theta_m + 1/2\sin 2\theta_m). \quad (42)$$

Substitution of

$$\tau = (m-1)\tau_0 + \tau_m,\ \tau_0 = \tau^0_m = \pi\frac{\sqrt{3}}{8} \quad (43)$$

reduces the system of equations (41), (42) to a single boundary-value problem

$$\left(\frac{\partial}{\partial \tau} - \xi^{-1}\frac{\partial^2}{\partial \xi^2}\right)c = 0;\ \tau = 0,\ c = 1;$$

$$\xi \to \infty,\ c \to 1; \quad (44)$$

$$\xi = 0,\ \eta(\tau)\partial c/\partial \xi - k\varepsilon f(c) = 0,$$

$$c^{(d)}_m(\xi, \tau_m) = c(\xi, (m-1)\tau_0 + \tau_m),$$

where $\eta(\tau)$ is the periodic function with the period τ_0, $\eta(\tau + \tau_0) = \eta(\tau)$, which is determined by the equality $\eta(\tau) = \eta_1(\tau_1)$ (42) over the interval $0 \le \tau_1 = \tau \le \tau_0$.

Equation (44) is similar to (3), therefore using the procedure of Section 2.5 we obtain the following equation for the local diffusion flux to the particles

$$j(\tau) = kf\left(1 - \frac{\varepsilon}{3^{1/3}\Gamma(2/3)}\int_0^{\tau} j(\lambda)\eta^{-1}(\lambda)(\tau-\lambda)^{-2/3}\,\mathrm{d}\lambda\right) \tag{45}$$

$$j_m(\tau_m) = j((m-1)\tau_0 + \tau_m).$$

In order to evaluate the contribution of interaction of the diffusion wakes and boundary layers of the particles into mass transfer between the chain and the fluid, consider first the solution of the problem (45) under the condition of complete substance absorption on the surfaces of spheres.

Taking into account that $f(0)=0$, we obtain the following expression for the local diffusion flux to the surface of the mth sphere

$$j_m(\tau) = \varepsilon^{-1}3^{1/3}\Gamma^{-1}(1/3)\eta(\tau)\tau^{-1/3},$$
$$\tau = (m = 1)\tau_0 + \tau_m(\theta_m) \tag{46}$$

Expressions for the total diffusion flux I_m to the mth particle and the sum of fluxes $I_\Sigma^{(m)}$ to the first m particles of the chain are as follows [10, 11]

$$I_m = 2\pi\int_0^{\pi} j_m(\theta_m)\sin\theta_m\,\mathrm{d}\theta_m = I_\Sigma^{(m)} - I_\Sigma^{(m-1)}, \tag{47}$$

$$I_\Sigma^{(m)} = 2\pi\varepsilon^{-1}3^{4/3}\Gamma\left(\frac{1}{3}\right)\left[\sum_{i=1}^{m}\tau_i^0\right]^{2/3} = I_0 m^{2/3},$$

$$I_0 = (3\pi)^{5/3}[2\varepsilon\Gamma(1/3)]^{-1}.$$

It should be noted that the diffusion flux to the second particle is only 0.63 of the flux to the first particle. This is indicative of the important effect of diffusion interaction between the reacting particles.

10. QUALITATIVE ANALYSIS OF MASS TRANSFER OF THE CHAIN OF SPHERES

Solution of equation (45) for the periodic function $\eta(\tau)$ at an arbitrary reaction law f calls for a further numerical analysis. Here, we shall confine ourselves to the qualitative analysis of mass transfer of a chain of spheres.

If we consider a body consisting of spheres located closely one after the other on a common axis passing through their centers and if we assume that the fluid velocity field near the body surface is locally periodic with period 2 and is governed, in the vicinity of each sphere, by the principal term of expansion in $r-1$ of the stream function of the Stokes flow around a single sphere (2), then the equation for the local diffusion flux (written down in the approximation of the diffusion boundary layer) will coincide exactly with equation (45). By using this analogy with a single body, we, in order to approximately determine the total diffusion flux to an arbitrary chain of spheres, shall avail ourselves of equation (40) which, as has been already shown, yields rather good results for a single particle.

In the present case Sh (Sh_0) is the mean Sherwood number for the whole chain of particles, S is the total surface of particles. Taking into account that for the chain composed of m spheres the following equalities are valid: $S_m = 4\pi m$, $Sh_{0m} = I_{0\Sigma}^{(m)}S_m^{-1}$, $I_{0\Sigma}^{(m)} = I_0 m^{2/3}$ (see equation (47)), we obtain from equation (40) the following formulae for the diffusion fluxes

$$I_\Sigma^{(m)} = I_0\sigma(m),\ I_m = I_0[\sigma(m) - \sigma(m-1)], \tag{48}$$

$$\sigma(m) = [1 - q(m)]m^{2/3},$$

where $q=q(m)$ is the root of equation $H(q, 4\pi I_0^{-1}km^{1/3})=0$ (11).

For the linear kinetics $f(x)=x$ we have

$$\sigma(m) = 4\pi km(I_0 + 4\pi km^{1/3})^{-1}. \tag{49}$$

It is seen from equations (48) and (49) that interaction of the diffusion wakes and the boundary layers of the chain particles can lead to a noticeable decrease in the mean mass transfer rate of the system. Then the following relations hold:

$$I_1 > I_2 \ldots \geq I_m,\ \lim_{m\to\infty} I_m = 0\ (k > 0,\ Pe^{-1} > 0).$$

At $k \to \infty$ ($Pe, m=\text{const.}$) equations (48) pass over into equation (47), while at $Pe \to \infty$ (k, $m=\text{const.}$), $I_m \to 4\pi k$, which corresponds to the kinetic conditions of absorption on the spheres.

As it follows from equations (48), at $m \to \infty$ the following asymptotic expressions hold

$$I_\Sigma^{(m)} \approx I_0 m^{2/3},\ I_m = \frac{2}{3}I_0 m^{-1/3}\ (m \to \infty) \tag{50}$$

Comparison of these expressions with equations (47) shows that far from the beginning of the chain ($m \gg 1$) mass exchange of the particle with the surrounding fluid is close to the limiting conditions of complete absorption on its surface (provided there is complete absorption on the preceding particles). This means that at $1 \ll l \ll Pe^{1/3}$ far particles in the chain are less "sensitive" to the reaction kinetics f. This situation is quite similar to the case of convective diffusion to a flat plate in which the principal term of the asymptotic expansion for the local flux j far from the beginning of the plate is independent of the velocity constant k and coincides with the respective expression for the limiting local diffusion flux in the case of complete absorption $k = \infty$ [2].

The limiting equations (50) can be also obtained directly from the analysis of equation (45). By assuming that at $m \to \infty$, $j_m \to 0$ and for this reason, neglecting the LHS of equation (45), we, with regard for $f(0)=0$, arrive at equation (46) from which equations (47) do follow.

From a physical point of view this phenomenon can be explained as follows. The region of the diffusion wake behind the first particle W_1 which forms the initial (incidence) condition for the diffusion boundary layer of the second particle is strongly depleted due to reaction on its surface. Therefore, concentration at the stream lines in the vicinity of the second sphere surface which arrives from the region of the diffusion wake W_1

will be lower than respective concentration in the vicinity of the first sphere. Thus, reaction in the neighbourhood of the forward stagnation point of the second sphere proceeds under the conditions close to the mode of complete absorption. It is directly seen from equation (45) since by virtue of the properties of the function $\eta(\tau)$ the following equalities should hold: $j_2(\theta_2=\pi)=0$, $c_2(\theta_2=\pi)=0$. More accurate estimates can be obtained if it is remembered that the concentration in the region $W_1^{(2)}$ is of the order of $\sqrt{\varepsilon}$ (24) (recall that the concentration distribution in the inner region of the diffusion wake $W_1^{(2)}$ was not allowed for in the derivation of equation (45)), therefore, $c_2(\pi) \sim \sqrt{\varepsilon} \ll 1$.

The diffusion wake behind the second sphere, W_2, is even more depleted as compared with the diffusion wake W_1 of the first sphere and leads to a further decrease of concentration in the region of the diffusion boundary layer of the third sphere. In this case, an increase of the surface area is observed in the vicinity of the forward and rear stagnation points. The surface area operates in a nearly diffusion mode as compared with the preceding spheres. At a distance from the beginning of the chain ($m \gg 1$) depletion of the solution will finally lead to a drop in the rate of convective substance supply down to the values which are small as compared with the reaction rate and it will limit the rate of the whole process. This, in turn, will lead to the equality

$$m \to \infty,\ \mathrm{Max}^{S_m}\ C_m \to 0,$$

i.e. to the condition of complete absorption.

It should be noted that although the above analysis is a purely qualitative one, in all likelihood, equations (48) and (49) can be used for rough quantitative estimations at small m. It is, therefore, of interest to compare approximate equations (48) with the results of numerical integration of equation (45).

11. SOME GENERALIZATIONS

In the general case of a three-dimensional flow around particles (or drops) of an arbitrary shape it is possible to show that when the analog of the stream function Ψ near the body surface is presented in the form

$$\Psi = \xi^n \varphi(\mu, \chi) \quad (\xi \to 0),$$

where ξ, μ, χ is a special system of coordinates fixed with respect to the body surface $\xi=0$ and the stream lines [11], the integral equation for the local diffusion flux and the surface concentration are of the form ($g_{\xi\xi}=1$)

$$j(t) = kf(1 - \varepsilon G_\nu * j), \tag{51}$$

$$C(t) = 1 - k\varepsilon G_\nu * f(C), \tag{52}$$

$$G_\nu * w = \frac{\nu^{1-2\nu}}{\Gamma(1-\nu)} \int_0^t w(\lambda)\eta^{-1}(\lambda)(t-\lambda)^{\nu-1}\,\mathrm{d}\lambda,$$

$$t = t(\mu, \mu_p) = \frac{1}{n}\left| \int_{\mu_p}^{\mu} |\varphi(\tau)|^{1/n} \sqrt{g_0(\tau)}\,\mathrm{d}\tau \right|, \quad p = 1,2,\ldots, \tag{53}$$

$$\nu = (n+1)^{-1},\ \varepsilon = Pe^{-1/(n+1)}, \qquad g_0 = [g_{\xi\xi} g_{\mu\mu} g_{\chi\chi}]_{\xi=0}.$$

Here, $n=1$ for liquid particles and $n=2$ for solid particles. The function $\eta(t)$ is prescribed parametrically from the expression

$$\eta(\mu) = |\varphi(\mu)|^{1/n} \tag{54}$$

with the aid of equation (53); μ_p are the critical points (lines) of incidence on the body surface $\varphi(\mu_p)=0$ in the vicinity of which the normal velocity of liquid is directed toward the body surface; equation (51) is valid up to singular points (lines) of outflow which are closest to μ_p (in the neighbourhood of which the normal velocity of fluid is directed away from the surface). The coordinate χ is omitted throughout since equations (51)–(54) depend on it only parametrically.

It follows from equations (51)–(54) that in the general case the surface concentration and the local diffusion flux at singular points or lines of incidence μ_p ($p = 1, 2, \ldots$) is determined by equations (11), (33) at $\omega = k(1-q)j^{-1}$ (∞, p), where $j(\infty, p)$ is the local flux at the points μ_p for limiting absorption.

For the axisymmetric and two-dimensional problems $\partial/\partial\chi = 0$ and the system of coordinates ξ and μ coincides with the orthogonal coordinate system usually used in the boundary layer theory and fixed with respect to the body surface.

In the case of a flat plate of length L ($Pe = LUD^{-1}$) in a longitudinal laminar (boundary layer) flow, when the coordinate ξ is running across, and μ along, the plate we have

$$n = 2,\ \sqrt{g_0} = 1,\ \eta(t) = \gamma t^{-1/3},\ \gamma = \text{const}. \tag{55}$$

It is seen from equations (51) and (55) that at the forward stagnation point of the plate the following limiting equalities hold

$$x \to 0,\ C \to 1,\ j \to k \quad (k < \infty).$$

The latter means that in this case the conditions for the incident flux to be nondepleted at the forward stagnation point do hold.

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DIFFUSION CONVECTIVE POUR UNE PARTICULE EN REACTION DANS UN FLUIDE CINETIQUE NON LINEAIRE DE REACTION EN SURFACE

Résumé—La diffusion convective pour une particule sphérique dans un écoulement de Stokes, à grand nombre de Peclet, est étudié dans le cas d'une réaction chimique sur la surface de la particule avec une vitesse dépendant arbitrairement de la concentration. Des équations intégrales pour la diffusion locale et la concentration à la surface sont obtenues et une méthode numérique de résolution est développée par utilisation d'asymptotiques appropriées au voisinage du point d'arrêt. L'effet de la vitesse de réaction constante et de la cinétique de réaction sur le flux total de diffusion à la surface de la particule est étudié. Une formule approchée simple est suggérée pour déterminer le nombre de Sherwood moyen avec une précision convenable.

On considère une chaine de particules et l'équation intégrale correspondante est obtenue pour le flux local de diffusion sur leur surface. On analyse qualitativement le transfert massique pour la chaine de sphères et on montre que l'intéraction des ondes de diffusion et des couches limites des particules dans ce type de système conduit à une diminution sensible du transfert massique. Des expressions approchées sont obtenues pour les flux globaux sur les particules en chaine. La méthode proposée est étendue à un écoulement tridimensionnel arbitraire autour de particules (ou gouttes) de forme arbitraire.

KONVEKTIVE DIFFUSION AN EINEM CHEMISCH REAGIERENDEN TEILCHEN IN EINEM FLUID: NICHTLINEARE REAKIONSKINETIK AN DER OBERFLÄCHE

Zusammenfassung—Dieser Bericht beschäftigt sich mit konvektiver Diffusion an einem runden Teilchen in einer gleichmäßigen, schleichenden Strömung bei hohen Peclet-Zahlen, wobei eine chemische Reaktion an der Teilchenoberfläche stattfindet, deren Geschwindigkeit endlich ist und willkürlich von der Konzentration abhängt. Es werden Integralgleichungen für den örtlichen Diffusionsstrom und die Konzentration an der Oberfläche aufgestellt und eine numerische Methode, welche auf der Verwendung geeigneter Asymptoten in der Umgebung des vorderen Staupunktes basiert, zu ihrer Lösung entwickelt. Der Einfluß der Reaktionsgeschwindigkeits- Konstanten und der Reaktionskinetik auf den gesamten Diffusionsstrom zur Teilchenoberfläche wird untersucht. Eine einfache Näherungsgleichung wird vorgeschlagen, die die Bestimmung der mittleren Sherwood-Zahl mit hinreichender Genauigkeit ermöglicht. Eine Reihe reagierender Teilchen wird betrachtet und eine entsprechende Integralgleichung für den örtlichen Diffusionsstrom an ihrer Oberfläche aufgestellt. Eine qualitative Analyse des Stoffübergangs wird durchgeführt und gezeigt, daß die Wechselwirkung zwischen der Diffusionsnachlauf-Strömung und den Grenzschichten der Teilchen bei dieser Systemanordnung einen substantiellen Rückgang der Stoffübergangsgeschwindigkeit bewirkt. Näherungsausdrücke für die integralen Ströme zu den Teilchen der Reihe werden aufgestellt. Die vorgeschlagene Methode wird auf eine beliebige dreidimensionale Strömung um Teilchen oder Tropfen mit beliebiger Oberfläche ausgedehnt.

КОНВЕКТИВНАЯ ДИФФУЗИЯ К РЕАГИРУЮЩЕЙ ЧАСТИЦЕ В ЖИДКОСТИ. НЕЛИНЕЙНАЯ КИНЕТИКА ПОВЕРХНОСТНОЙ РЕАКЦИИ

Аннотация—Рассматривается конвективная диффузия к сферической частице в однородном стоксовом потоке при больших числах Пекле в случае, когда на ее поверхности протекает химическая реакция, скорость которой конечна и произвольным образом зависит от концентрации. Получены интегральные уравнения для локального диффузионного потока и поверхностной концентрации и разработан численный метод их решения, использующий соответствующие асимптотики в окрестности передней критической точки. Исследуется зависимость полного диффузионного потока на поверхность частицы от константы скорости и кинетики реакции; приведена простая приближенная формула, позволяющая с достаточно высокой точностью определять среднее число Шервуда.

Рассмотрена цепочка реагирующих частиц и получено соответствующее интегральное уравнение для локального диффузионного потока на их поверхности. Проведен качественный анализ массообмена цепочки сфер и показано, что взаимодействие диффузионных следов и погранслоев частиц в упорядоченных системах такого рода приводит к существенному торможению интенсивности процесса массообмена. Получены приближенные выражения для интегральных потоков на частицы цепочки.

Предложенный метод обобщается на случай произвольного трехмерного обтекания частиц (или капель) любой формы.