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NONSTATIONARY CONVECTIVE HEAT AND MASS TRANSFER IN A FLUID AT HIGH PECLET NUMBERS

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The diffusion flux on the surface of a drop in a stationary Stokes flow (Rybchinskii—Adamar velocity field) was determined in [1] with the help of a Laplace transformation with respect to time for the case of nonstationary diffusion with the reaction turned on suddenly. In [2-5], the self-similar variable $\xi\delta^{-1}(t, \eta)$ (ξ and η are the normal and tangential coordinates fixed to the surface of the body, t is time, δ is the thickness of the diffusion boundary layer), which permitted reducing the starting equation of convective diffusion to a first order partial differential equation for a boundary layer of thickness δ and to an ordinary differential equation for the concentration, was used to analyze nonstationary boundary-layer problems. Two new variables (simplifying the initial problem), which were also determined by solving a first-order partial differential equation, were introduced in [5-9]. The introduction of new variables permitted studying a number of nonstationary problems, described by the equation of convective diffusion with time dependent coefficients [2-5, 7-9], for which the method in [1] cannot be used.

In the present paper, we propose a general method for solving nonstationary problems of this type, based on introducing three new independent coordinates (related to the initial coordinates by a nonsingular transformation) and permitting studying the corresponding equation in a unified form.

It is shown that in the general case of initial and boundary conditions, the solution of the boundary-layer equation has a strong discontinuity (propagating with a finite velocity) and the corresponding solution on one side of the discontinuity is determined only by the initial conditions, while on the other side (at the entrance to the diffusion bound-

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ary layer) only by boundary conditions. At the same time, in the vicinity of the discontinuity, the approximation of the diffusion boundary layer itself is no longer valid and there exists a thin region (of the order of $\mathrm{Pe}^{-1/2}$, Pe is Peclet's number), in which the concentration varies continuously and rapidly. The boundary value problem for determining the concentration near the discontinuity is formulated.

1. Description of the Method. Equations for the New Variables. We will examine the three-dimensional problem of nonstationary convective diffusion toward the surfaces of drops (or liquid films) in a laminar flow of incompressible fluid. We assume that the flow field is known from a solution of the appropriate hydrodynamic problem.

For the analysis, as in [9, 20], we will introduce the local orthogonal coordinate system ξ, η, and λ fixed to the (moving) reacting surface and the flow field in its vicinity. For this purpose, it is necessary to give the orientation of the unit vectors at any point M lying near the surface and to indicate how the curvilinear coordinates are measured. It is assumed that at any time a single (external) normal can be drawn toward any point on the reacting surface and that there exists a region in which these normals do not intersect. The vector normal to the surface, passing through the point M, determines the direction of the unit vector $\mathbf{e}_\xi$ and the magnitude of the coordinate ξ, i.e., the value $\xi = 0$ corresponds to the reacting surface and $g_{\xi\xi} = 1$($g_{\xi\xi}$, $g_{\eta\eta}$, $g_{\lambda\lambda}$ are the components of the metric tensor). The direction of the unit vector $\mathbf{e}_\eta$ is determined by the direction of the projection of the velocity vector of the fluid at the point M on a plane perpendicular to $\mathbf{e}_\xi$, while the unit vector $\mathbf{e}_\lambda$ is chosen so that the system of vectors $\mathbf{e}_\xi$, $\mathbf{e}_\eta$, and $\mathbf{e}_\lambda$ forms an orthogonal right-handed triad. In such a system of coordinates, the velocity vector of the fluid at each point at any time t has the form $\mathbf{u} = \{u_\xi, u_\eta, 0\}$. For convenience, we do not yet fix the origin of the coordinates and the metric ($g_{\eta\eta}$ and $g_{\lambda\lambda}$); we will indicate these separately for each specific case.

We will call the point of inflow (outflow) the critical point, lying on the surface of the particle, near which the normal component of the fluid velocity is directed toward (away from) the surface, while the streamline, leaving it, is the inflow (outflow) trajectory.

In the general case of an incompressible fluid in a system of coordinates ξ, η, and λ ($g_{\xi\xi} = 1$), the dimensionless equation of the nonstationary convective diffusion in the approximation of a diffusion (thermal) boundary layer has the form [9, 10]

$$\frac{\partial c}{\partial t} + \frac{1}{\sqrt{g}}\left(\frac{\partial \Phi}{\partial \xi}\frac{\partial c}{\partial \eta} - \frac{\partial \Phi}{\partial \eta}\frac{\partial c}{\partial \xi}\right) = \mathrm{Pe}^{-1}\frac{\partial^2 c}{\partial \xi^2}, \tag{1.1}$$

$$g = g(t, \eta, \lambda),\ \Phi = \xi\Omega(t, \eta, \lambda),\ 0 < t,\ \xi < \infty,\ \eta^- < \eta < \eta^+,$$

$$u_\xi = -\sqrt{\frac{g_{\xi\xi}}{G}}\frac{\partial \Phi}{\partial \eta},\quad u_\eta = \sqrt{\frac{g_{\eta\eta}}{G}}\frac{\partial \Phi}{\partial \xi},\quad G = g_{\xi\xi}g_{\eta\eta}g_{\lambda\lambda}$$

$$(\eta^- < \eta < \eta^+,\ \Omega > 0;\ \Omega(\eta^-) = \Omega(\eta^+) = 0;\ g = [G]_{\xi=0}),$$

where c is the concentration (temperature); t is the time; g and Ω are known functions of the coordinates and time, determined by the shape of the body and the local velocity field of the fluid near its surface; Pe is the Peclet number; the values η^- and η^+ correspond to neighboring inflow and outflow trajectories. We note that the representation (1.1) in the boundary layer for the analog of the stream function Φ (linearity with respect to ξ) in problems of mass transfer of droplets (bubbles) in the presence of a viscous laminar flow past the droplets is valid for most fluids (such as water), while in thermal problems (with potential flow past the droplets), it is valid for media such as liquid metals [11]. The coordinate λ enters into Eq. (1.1) only parametrically, so that in what follows the dependence of the functions used in this work on λ is not indicated.

Neglecting for the moment the initial and boundary conditions for Eq. (1.1), we introduce the new variables

$$\omega = \omega(t, \eta),\ \zeta = \sqrt{\mathrm{Pe}}\,\xi f(t, \eta),\ \tau = \tau(t, \eta) \tag{1.2}$$

in such a way that the equation of convective diffusion in these variables would have the simplest form. For this, we require that the functions (1.1) satisfy the following system of first order partial differential equations

$$\mathbf{L}\omega = 0,\quad \mathbf{L}f = g^{-1/2}\Omega'_\eta f,\quad \mathbf{L}\tau = f^2,\quad \mathbf{L} = \mathbf{L}(t, \eta) = \partial/\partial t + g^{-1/2}\Omega\partial/\partial\eta, \tag{1.3}$$

whose general solution has the form

$$\omega = \omega(t, \eta), \quad f = B(\omega) \exp\left\{ \int\limits_{\eta^*}^{\eta} \left(\frac{\partial}{\partial \eta} \ln \Omega \right)_{(t)} d\eta \right\}, \tag{1.4}$$

$$\tau = \int\limits_{\eta^-}^{\eta} \sqrt{g}\, \Omega^{-1} f^2 d\eta + A(\omega),$$

where ω is any first integral of the equations (or arbitrary function of it)

$$\eta_t' = g^{-1/2}\Omega \qquad (\mathrm{L}\omega = 0), \tag{1.5}$$

while the function in the integrand in expressions (1.4) is expressed in the variables η and ω (in the integration, ω is viewed as a parameter); in the second integral, the quantity marked by the index (t) is a partial derivative of $\ln \Omega(t, \eta)$ with respect to η, written in the variables η, ω [9]; A and B are arbitrary functions that depend only on ω; η^* ($\eta^- < \eta^* < \eta^+$) is arbitrary.

Equation (1.1) after the substitutions (1.2)-(1.5) reduces to the usual equation of heat conduction with constant coefficients

$$\partial c/\partial \tau = \partial^2 c/\partial \zeta^2, \; c = c(\omega, \zeta, \tau). \tag{1.6}$$

It is evident that Eq. (1.6) does not depend on the coordinate ω, which here is completely analogous to the cyclical variables in analytical mechanics. The corresponding initial and boundary conditions for Eq. (1.6) must be written in the variables (1.3) and (1.4), which reduces the starting boundary-value problem to the usual problem of heat conduction, depending on the parameter ω.

The general expressions for the new variables (1.4) contain arbitrary functions $A(\omega)$ and $B(\omega)$ and, in this case, the form of the variable ω is also determined to within an arbitrary function (a function of ω). In order for the transformation $(t, \eta, \xi) \to (\omega, \zeta, \tau)$ not to be singular, the Jacobian

$$J = \frac{\partial(\omega, \zeta, \tau)}{\partial(f, \eta, \xi)} = \sqrt{\mathrm{Pe}}\, f^3 \frac{\partial \omega}{\partial \eta}$$

must not vanish in the region in which Eq. (1.1) is defined, so that from the properties of the function Ω (1.1) and the relations (1.4) and (1.5), it follows that the transformation (1.2)-(1.5) is not singular for $|B(\omega)| > 0$.

The specific form of the arbitrary functions, entering into (1.4) and (1.5), is chosen from considerations of convenience, determined by the type of initial and boundary conditions (see Sec. 2). It should be emphasized, however, that for Eq. (1.1) and all types of initial and boundary conditions, it is possible to use a nonsingular transformation of variables (1.2)-(1.5) (chosen by giving the explicit form of the functions A, B, and ω) fixed once and for all, which in the final analysis, by way of complicating (sometimes considerably) the intermediate calculations, will lead to the same results.

2. Choice of Variables. Initial and Boundary Conditions.

When the function Ω can be represented as a product of two factors (which corresponds to nonstationary rectilinear motion of spherical droplets in a viscous incompressible fluid and spheres in a perfect fluid)

$$\Omega(t, \eta) = U(t)\sigma(\eta), \; g = g(\eta), \tag{2.1}$$

it is convenient to choose the variables f and ω (1.2)-(1.5) in the form ($B(\omega) = \sigma^{-1}(\eta^*) = \mathrm{const}$)

$$f = \sigma(\eta), \quad \omega = \int\limits_{\eta^*}^{\eta} \sqrt{g}\, \sigma^{-1} d\eta - \int\limits_{0}^{t} U dt. \tag{2.2}$$

Here, the variables (2.2), τ will determine the nonsingular transformation with Jacobian $J = \sqrt{\mathrm{Pe}}\, g\, \sigma^2(\eta) > 0$ ($\eta^- < \eta < \eta^+$), which coincides with the Jacobian for Mie's transformation of the corresponding stationary problem with $U(t) = \mathrm{const}$; the expression for τ (1.4) is written out below, since its specific form will depend on the type of initial and boundary conditions. It should also be noted that for (2.1) the possibility of introducing a new (additional), third variable in the region $\omega > 0$ [by a method different from that proposed by (1.2-(1.5)] was indicated in [7], although it was not used therein, since a self-similar problem was being examined.

If the function Ω depends only on the linear combination of t and η [which corresponds to wave processes on the free surface of the fluid film [3, 4] (see Sec. 5)]

$$\Omega(t,\ \eta) = \Omega(z),\ z = \eta - \varkappa t,\ g \equiv 1, \tag{2.3}$$

it is convenient to choose the variables f and ω in the form

$$f = u(z) = \Omega(z) - \varkappa, \quad \omega = \eta - z - \varkappa \int\limits_0^z u^{-1}(z')\,dz'. \tag{2.4}$$

The transformation (2.4) will be nonsingular for $J = -\sqrt{\mathrm{Pe}}\,\Omega u^2 \neq 0$.

In order to obtain expressions (2.2) and (2.4) for the function f, it is most convenient, without using the general equations (1.4), to make use of the second equation in (1.3) directly.

From these particular examples, it is evident that the choice of variable f is mainly determined by the velocity field of the fluid near the reacting surface, while the choice of the variable ω is determined by the velocity field and the equation of convective diffusion (1.1), and at the same time, in both cases, the choice does not depend on the initial and boundary conditions.

We note that if the right side of Eq. (1.1) included a source $q = q(t, \eta, \lambda)$, then the final equation (1.6) after transformations (1.2)-(1.5) would have on the right side the term qf^{-2}.

For Eq. (1.1), as in [8], we will distinguish two types of problems, for which the time-like variable τ is chosen differently. In this case, the form of the variable τ will be determined by the requirement that for the appropriate initial or boundary condition, τ should vanish. For this choice of τ, the initial problem (1.1) will be reduced to the heat conduction equation with the usual initial boundary condition for $\tau = 0$. In what follows, it is shown that the solution of Eq. (1.1) in the case of arbitrary initial and boundary conditions, can be obtained by a simple combination of these partial solutions.

The first type of problem corresponds to the motion of a reacting body with a variable velocity (from the stationary state) in a fluid with nonuniform concentration; it is assumed that for $t \leqslant 0$ the concentration distribution in the flow is determined by the solution of the corresponding stationary equation of convective diffusion (for example, by the solution in [11]). At the same time, during the course of the entire process, the boundary condition on the inflow trajectory is imposed [8, 9]

$$\eta = \eta^- \qquad (\text{case } \alpha). \tag{2.5}$$

In this case, the equation for determining τ (equation for determining the specific form of the function $A(\omega)$) is obtained by substituting (2.5) into the general expression for τ (1.4) followed by setting it equal to zero, i.e., $\tau(\eta = \eta^-) = 0$. It follows from this equation that $A(\omega) = 0$ and the variable τ (responsible for the boundary condition) has the form

$$\tau_\alpha = \tau_\alpha(t, \eta) = \int\limits_{\eta^-}^{\eta} \sqrt{g}\, f^2 \Omega^{-1}(\omega, \eta')\, d\eta' = \int\limits_{-\infty}^{t} f^2(\omega, t')\, dt'. \tag{2.6}$$

Here and in what follows, all quantities relating to the first and second type of problems are denoted by indices α and β, respectively; the second representation for τ_α was obtained by a simple transformation from the variable of integration η to the variable t taking into account the relation $\omega = \omega(t, \eta)$ and the properties of the function Ω; in the integration, ω is viewed as a parameter.

The second type of problem corresponds to chemical reactions that suddenly begin on the surface of the particle and in this case it is assumed that for

$$t = 0 \qquad (\text{case } \beta) \tag{2.7}$$

the initial concentration distribution in the flow is given.

In this case, the equation for determining τ (the variable responsible for the initial condition) has the form $\tau(t = 0) = 0$ and leads to the following expression

$$\tau_\beta = \tau_\beta(t, \eta) = \tau_\alpha - \tau_\alpha(0, S(\omega)) = \int_0^t f^2(\omega, t')\,dt', \tag{2.8}$$

$$S(\omega(0, \eta)) \equiv \eta.$$

If the function Ω can be represented in the form (2.1), then

$$\tau_\alpha = \int_{\eta^-}^{\eta} \sqrt{g}\,\sigma(\eta')U^{-1}(t(\omega, \eta'))\,d\eta', \quad \tau_\beta = \int_0^t \sigma^2(\eta(\omega, t'))\,dt', \tag{2.9}$$

and in the case (2.3) and (2.4)

$$\tau_\alpha = \int_{\eta^-}^{\eta} \frac{u(z(\omega, \eta'))}{u(z(\omega, \eta')) + \varkappa}\,d\eta', \quad \tau_\beta = \int_0^t u^2(z(\omega, t'))\,dt'. \tag{2.10}$$

Using the results in Secs. 1 and 2, we now obtain the solution of several nonstationary problems (in cases α and β), not examined previously [1-9].

3. Nonuniform Starting Concentration Distribution. Let us examine nonstationary convective diffusion toward a drop (bubble) in a stationary Stokes flow (Rybchinskii—Adamar stream function)

$$\xi = r - 1,\ \eta = \pi - \theta,\ g = 2\Omega = 1 - \mu^2,\ \mu = \cos\,\theta = -\cos\eta \tag{3.1}$$

with a nonuniform concentration distribution outside it and the reaction turned on suddenly on the surface at $t = 0$

$$t = 0,\ c = q(\mu),\ \xi = 0,\ c = 0 \qquad (q(-1) = 1), \tag{3.2}$$

where r and θ form a spherical coordinate system fixed to the center of the drop; θ is measured from the direction of the oncoming flow (i.e., from the outflow trajectory); q is an arbitrary function that depends only on the angle θ; the characteristic scales are: the radius of the drop a, the characteristic velocity $U = U_\infty(\beta + 1)^{-1}$ (U_∞ is the velocity of the oncoming flow, β is the ratio of the viscosities of the drop and the fluid surrounding it), and c_∞ is the concentration on the axis of symmetry far from the drop. We also assume that on the oncoming trajectory $\mu = -1$ the concentration distribution is given by Levich's stationary solution [11]. The solution of this problem will determine the characteristic times t_0 for the concentration to reach a steady-state regime [11], depending on the nonuniformity of the initial distribution $t_0 = t_0(q)$.

Using the expressions (2.1), (2.2), and (2.8), taking into account (3.1), gives the following equation for the variables (1.2) and (1.3):

$$f = \frac{1}{2}(1 - \mu^2), \quad \omega = -t + \ln\left(\frac{1 + \mu}{1 - \mu}\right), \tag{3.3}$$

$$\tau_\beta = \tau_\alpha - \tau_\alpha(S(\omega)), \quad \tau_\alpha = \frac{1}{6}(2 - \mu)(1 + \mu)^2, \quad S(\omega) = \mathrm{th}\left(\frac{\omega}{2}\right).$$

In this case, the initial problem (1.1), (3.1), and (3.2) is reduced to Eq. (1.6) with the boundary conditions

$$\tau_\beta = 0,\ c = q(S(\omega)),\ \zeta = 0,\ c = 0\ (\zeta \to \infty,\ c \to q(S)), \tag{3.4}$$

whose solution has the form (D is the diffusion coefficient)

$$c = q\left(\mathrm{th}\,\frac{\omega}{2}\right)\mathrm{erf}\left(\frac{\sqrt{\mathrm{Pe}}\,(r - 1)\,f(\mu)}{2\sqrt{\tau_\alpha(\mu) - \tau_\alpha\left(\mathrm{th}\,\frac{\omega}{2}\right)}}\right), \quad \mathrm{Pe} = \frac{aU}{D}. \tag{3.5}$$

We note that for $q(\mu) \equiv 1$ Eq. (3.5) transforms into the results in [1, 2, 6] for the outer problem. It is evident that for $t \to +\infty$ solution (3.5) enters into a steady-state regime [11].

4. Nonstationary Diffusion with Mixed Kinetics. Let us now examine the problem of stationary convective diffusion toward a particle with a chemical reaction occurring on its surface at a finite rate kc; k is the dimensionless rate constant. In this case, the following boundary conditions occur on the surface of the particle and far away from it for the concentration (uniform concentration is assumed far from the particle):

$$\xi = 0,\ \partial c/\partial\xi - kc = 0,\ \xi \to \infty,\ c \to 1. \tag{4.1}$$

For both types of initial and boundary conditions (2.5), (2.7), transforming to variables (1.2)-(1.5), we arrive at Eq. (1.6) with the corresponding initial and boundary conditions

$$\tau = 0,\ c = 1,\ \zeta \to \infty,\ c \to 1,\ \zeta = 0,\ f(\tau,\ \omega)\partial c/\partial\zeta - k\mathrm{Pe}^{-1/2}c = 0. \tag{4.2}$$

Here, the indices α and β for the variable τ are omitted, and case α corresponds to substitution of the value $\tau = \tau_\alpha$ from Eqs. (2.6) into (1.6), (4.2), while the case β corresponds to substituting the value $\tau = \tau_\beta$ from Eq. (2.8).

We seek the solution of the problem (1.6) and (4.2) in the form

$$c(\tau, \zeta, \omega) = 1 - \frac{1}{\sqrt{\pi}} \int\limits_0^\tau \Psi(\lambda, \omega)(\tau - \lambda)^{-1/2} \exp\left\{-\frac{\zeta^2}{4(\tau - \lambda)}\right\} d\lambda. \tag{4.3}$$

Here, c is the solution of Eq. (1.6) and satisfies the initial and first boundary condition (4.2) for any bounded kernel Ψ, for which the limiting conditions are satisfied [12]:

$$\lim_{\zeta\to 0} c = 1 - \frac{1}{\sqrt{\pi}} \int\limits_0^\tau \Psi(\lambda, \omega)(\tau - \lambda)^{-1/2}\, d\lambda, \quad \lim_{\zeta\to 0} \frac{\partial c}{\partial\zeta} = \Psi(\tau, \omega). \tag{4.4}$$

Substituting expression (4.3) into the last boundary condition (4.2), taking into account the properties (4.4) and the relation $\sqrt{\mathrm{Pe}}\Psi f = kC$, $C = c(\tau, 0, \omega)$, we arrive at the following integral equation for the surface concentration

$$C = 1 - \frac{k}{\sqrt{\pi\,\mathrm{Pe}}} \int\limits_0^\tau \frac{C d\lambda}{f(\lambda, \omega)\sqrt{\tau - \lambda}}, \tag{4.5}$$

which generalizes the results in [13] to the nonstationary case.

For example, in the case of a stationary Stokes flow around a drop (3.1), the equation for the surface concentration (4.5) with sudden switching on of the reaction (case β) takes the form

$$C = 1 - \frac{k}{\sqrt{\pi\,\mathrm{Pe}}} \int\limits_{\tau_\alpha(S(\omega))}^{\tau_\alpha} \frac{C d\lambda}{f(\lambda)\sqrt{\tau_\alpha - \lambda}} \qquad (f(\tau) \equiv f(\mu(\tau))), \tag{4.6}$$

where the functions τ_α, f, S, and ω are defined in (3.3).

It is evident that for $t \to +\infty$ Eq. (4.6) goes over into the stationary equation [13], and in this case, the following time dependence of the surface concentration occurs in the forward critical point:

$$C = \left\{1 + \frac{k}{\sqrt{2\pi\,\mathrm{Pe}}}\left[\pi - B\left(e^{-2t}, \frac{1}{2}, \frac{1}{2}\right)\right]\right\}^{-1}.$$

Here B(x, p, q) is the incomplete β function.

We note that the problem with arbitrary kinetics for the surface reaction kF(c) can be viewed in a similar manner. In this case, on the right side of the equation for the surface concentration (4.5), F(C) will replace C in the integrand.

5. Nonstationary Diffusion toward the Surface of a Film. Periodic Regimes. Let us now examine convective diffusion toward the surface of a reacting film, flowing down a vertical wall in a periodic regime (or toward an oscillating surface of an infinite fluid at rest). Under these conditions, the hydrodynamic model of motion of the film often leads to the following expression for the velocity components in Eq. (1.1) [3, 4] (ν is the wave vector; $\varkappa\nu$ is the frequency):

$$\Omega(t,\ x) = U + b\cos[\nu(x - \varkappa t)],\ g \equiv 1\ (x = \eta). \tag{5.1}$$

Here, it will be shown that the results in Secs. 1 and 2 can be used to analyze (some of) the periodic solutions of Eqs. (1.1), (5.1) under the condition of complete absorption of the reagent on the surface of the film and constant concentration far from it

$$\xi = 0,\ c = 0,\ \xi \to \infty,\ c \to 1 \tag{5.2}$$

Another condition for periodicity of c with respect to t must be added to the boundary conditions (5.2)

$$c(t) = c(t + 2\pi(\varkappa\nu)^{-1}) \tag{5.3}$$

and some normalizing condition must also be added [see below (5.6)].

A similar problem with the boundary condition c = 1 at x = 0 [instead of (5.3)] was examined in [3, 4].

For simplicity, we will present the intermediate results only for the case

$$\nu = \varkappa = 1,\ U = 2,\ |b| < 1,$$

and we will write the final expression for arbitrary $\varkappa$, b, ν, and U.

The variables ω and f are determined from Eqs. (2.3) and (2.4), which, taking into account (4.1), lead to (z = x − t)

$$f = 1 + b\cos z,\ \omega = x - z - \frac{2}{\sqrt{1-b^2}}E(z, b, 1), \tag{5.4}$$

$$E(z, b, 1) = \begin{cases} \gamma(z, b, 1) & \text{for } 0 \leqslant z \leqslant \pi, \\ \gamma(\pi, b, 1) + \gamma(z - \pi, b, 1) & \text{for } \pi \leqslant z \leqslant 2\pi, \end{cases}$$

$$\gamma(z, b, \delta) = \operatorname{arctg}\left(\sqrt{\left|\frac{\delta - b}{\delta + b}\right|}\operatorname{tg}\frac{z}{2}\right).$$

Taking into account (5.4), the general expression for the variable τ (1.4) can be written in the form [it is easiest to obtain it directly from the equation for τ (1.3)]

$$\tau = z + b\sin z + A(\omega)\ (z = x - t). \tag{5.5}$$

In order that the variable τ be periodic with respect to t, the condition $\tau(t) = \tau(t + 2\pi)$ must be satisfied, which leads to the following equation for determining τ:

$$A(\omega) = A(\omega - 2\pi - \langle f^{-1}\rangle 2\pi) + 2\pi\cdot\langle f\rangle, \tag{5.6}$$

$$\langle h\rangle = \frac{1}{T_0}\int\limits_0^{T_0} h\,dt,\quad \langle f\rangle = 1,\quad \langle f^{-1}\rangle = \frac{1}{\sqrt{1-b^2}},$$

where h is any periodic function with period T_0; $\langle h\rangle$ is the average value of h over the period.

We seek the solution of (5.6) in the form

$$A(\omega) = p\omega + l \qquad (p,\ l = \text{const}), \tag{5.7}$$

from where we obtain $p = \langle f\rangle(1 + \langle f^{-1}\rangle)^{-1}$, while the coefficient l can be chosen arbitrarily and must be determined from the normalization condition.

Similarly, for arbitrary magnitudes of the parameters $\varkappa$, b, ν, and U entering into (5.1), we have the following expression for the new variables (1.2)-(1.5) ($|\varkappa - U| > |b|$):

$$f = \Omega(\nu z) - \varkappa,\quad \tau = \frac{b}{\nu}\sin\nu z + \frac{U - \varkappa}{\varkappa + \sqrt{(U-\varkappa)^2 - b^2}} \tag{5.8}$$

$$\times\{\sqrt{(U-\varkappa)^2 - b^2}\,x + \varkappa z - 2\varkappa\nu^{-1}E(\nu z, b, U - \varkappa)\} \qquad (z = x - \varkappa t).$$

Here, τ is written out to within an additive constant, and the expression for ω is omitted (since it will not enter into the final expression), while the function E is defined in (5.4).

In the variables (1.2)-(1.5) and (5.8), Eq. (1.1) reduces to (1.6) with the boundary conditions

$$\zeta = 0,\ c = 0,\ \zeta \to \infty,\ c \to 1. \tag{5.9}$$

The periodic solutions of the problem are

$$c = \operatorname{erf}\left(\frac{\sqrt{\mathrm{Pe}}\,\xi\,|f(z)|}{2\sqrt{\tau(z,x)+\tau_0}}\right), \quad \tau_0 = \mathrm{const}\left(\tau_0 > \tau\left(\frac{\pi}{2}, 0\right)\right). \tag{5.10}$$

In order to determine the magnitude of τ_0, it is necessary to give an additional normalization-type condition. For example, for chemical reactors (mass exchangers) with finite length L, it may be assumed that the average flow rate of the reagent Q (which is determined by the difference between the mass of the reagent at the inlet and outlet of the reactor) is known. Calculating with the help of (5.10) for arbitrary τ_0 the total inflow of the reagent to the surface of the film over a period and equating to the flow rate Q, we obtain an algebraic (transcendental) equation for determining τ_0:

$$\left\langle \frac{1}{2}\int_0^L \frac{\sqrt{\mathrm{Pe}}\, f(z)\, dx}{\sqrt{\tau(z,x)+\tau_0}} \right\rangle = Q. \tag{5.11}$$

For sufficiently large x, we obtain from expression (5.10) an asymptotic equation for the local diffusion flow on the surface of the film (in the case (5.4))

$$j(b) = \left(\frac{\partial c}{\partial \xi}\right)_{\xi=0} = \sqrt{\frac{\mathrm{Pe}}{\pi}}\left(\frac{1+\langle f^{-1}\rangle}{\langle f\rangle}\right)^{1/2} f(z)\, x^{-1/2} \qquad (x \to \infty). \tag{5.12}$$

From this expression, it is evident that the local diffusion flow (its asymptotic behavior) decreases inversely proportional to the square root of the distance from the inlet to the reactor with a coefficient of proportionality that depends on the average values of f and f^{-1} over a period of the oscillations.

For a nonoscillating film (b = 0), the local diffusion flow will be determined by the expression j(0) (5.12). Forming the ratio, we obtain (for $x \to \infty$)

$$\frac{\langle j(b)\rangle}{j(0)} = \frac{1}{\sqrt{2}}\left(1 + \frac{1}{\sqrt{1-b^2}}\right)^{1/2} > 1. \tag{5.13}$$

It is evident from here that oscillations can greatly increase the intensity of the mass transfer process to the surface of the film.

6. Case of Discontinuous Solutions. Equation (1.6) (or (1.1)) admits partial solutions c = F(ω) that depend only on ω (F is an arbitrary function).

If initially such a solution becomes discontinuous when passing through some characteristic, e.g., for t = 0 the conditions

$$\eta < 0,\ c = c^-,\ \eta > 0,\ c = c^+\ (\omega(0,0) = 0,\ \operatorname{sign}\omega(0,\eta) = \operatorname{sign}\eta)$$

are satisfied, then the evolution of this solution (in the entire space without boundary conditions) will also be determined by a discontinuous function $c = c^-$ with $\omega(t, \eta) < 0$ and $c = c^+$ for $\omega(t, \eta) > 0$. This indicates that in boundary layer problems involving nonstationary convective diffusion, described by Eq. (1.1), a situation with a discontinuity in the concentration can arise (solution of the shock-wave type). Such solutions are a result of the hyperbolic nature of the boundary-layer equation (1.1) with respect to the variables t and η.

In order to illustrate a discontinuity of this kind, we shall examine the problem of nonstationary convective diffusion to the surface of a sphere, around which there is a stationary flow of a perfect incompressible fluid with velocity U_∞ at infinity We assume that on the part of the sphere near the point of inflow, there is a lacquered inclusion, i.e., in the region $0 \leqslant \theta \leqslant \pi - \theta_0$, $0 < \theta_0 < \pi$ there is a total absorption of matter; initially, the concentration in the flow is constant and equal to unity, while for $\theta = \pi - \theta_0$ (at the inlet to the boundary layer), a constant concentration equal to ρ = const is maintained.

Choosing $^3/_2 U_\infty$ as a characteristic velocity scale, and the radius of the sphere as the characteristic length scale, we find that the concentration distribution (in the region $0 \leqslant \theta \leqslant \pi - \theta_0$) in this case is described by Eqs. (1.1, (3.1) with the following initial and boundary conditions:

$$t = 0,\ c = 1,\ \xi = 0,\ c = 0,\ \mu = \mu_0,\ c = \rho\ (\mu_0 = -\cos\theta_0 > -1). \tag{6.1}$$

The characteristic of Eq. (1.1), satisfying the condition $\omega_*(0, \mu_0) = 0$ (this condition was chosen for convenience), has the form

$$\omega_* = \omega_*(t, \mu, \mu_0) = \omega(t, \mu) - \omega(0, \mu_0), \tag{6.2}$$

where the function $\omega(t, \mu)$ is defined in (3.3).

For $t = 0$, the characteristic $\omega_* = 0$ separates regions with different values of the concentration: $c = \rho$ for $\omega < 0$ and $c = 1$ for $\omega > 0$, while the point of discontinuity moves with a variable velocity [which is determined by the right side of (1.5)] and is described by the equation

$$\mu_* = \mu_*(t, \mu_0) = [(1 + \mu_0)e^t - (1 - \mu_0)][(1 + \mu_0)e^t + (1 - \mu_0)]^{-1}. \tag{6.3}$$

In this case, in the region $\mu_0 < \mu < \mu_*$, the concentration distribution is described by Eq. (1.6) (case α) with the boundary conditions

$$\zeta = 0, \quad c = 0, \quad \tau_{\alpha*} = \tau_\alpha(\mu) - \tau_\alpha(\mu_0) = 0, \quad c = \rho\,(\omega_* < 0), \tag{6.4}$$

while in the region $\mu_* < \mu < 1$ by Eq. (1.6) (case β) with the boundary conditions

$$\zeta = 0, \quad c = 0, \quad \tau_\beta = 0, \quad c = 1 \qquad (\omega_* > 0). \tag{6.5}$$

Here, the variables ζ, τ_α, and τ_β are defined by relations (3.3).

The solution of Eq. (1.6) for boundary conditions (6.4) is given by Eq. (3.5) with $q = \rho$ and τ_β replaced by $\tau_{\alpha*}$, while the solution of the problem (1.6) and (6.5) is given by expression (3.5) with $q = 1$. For this reason, the total solution of the boundary layer problem of diffusion in the entire region $\mu_0 \leqslant \mu \leqslant 1$ has the form (Θ is the unit Heaviside function)

$$c = \rho\Theta(-\omega_*)\,\mathrm{erf}\left(\frac{\sqrt{\mathrm{Pe}}\,(r-1)(1-\mu^2)}{4\sqrt{\tau_\alpha(\mu) - \tau_\alpha(\mu_0)}}\right) + \Theta(\omega_*)\,\mathrm{erf}\left(\frac{\sqrt{\mathrm{Pe}}\,(r-1)(1-\mu^2)}{4\sqrt{\tau_\alpha(\mu) - \tau_\alpha(S(\omega))}}\right), \tag{6.6}$$

where the function $S(\omega)$ is defined in (3.3).

It is evident from this equation that the concentration c with the transition through the characteristic $\omega = 0$ ($\mu = \mu_*(t)$) is discontinuous; in particular, for $\rho = 0$ the concentration in the region $\omega_* < 0$ equals zero, while for $\omega_* > 0$, it is given by the second term in (6.6) and differs from zero.

It should be noted that a solution of the type (6.6) for the conditions (2.1) and $g \equiv 1$ in the case of initial and boundary conditions $c(t = 0) = c(x = 0) = c_\infty$ was obtained in [7], but the most important property of this solution, namely, its discontinuity at $\omega_* = 0$, was not noted therein.

Equation (6.6) shows that there exists a region $\omega_* > 0$ in which the boundary conditions have no effect at the entrance to the boundary layer with $\mu = \mu_0$. This indicates that the velocity of propagation of the perturbations, determined by Eq. (1.5), is finite and also that there exists a region of influence $\omega_* < 0$ of the boundary condition with $\mu = \mu_0$. A similar situation also occurs in the more general case (see Sec. 7) and, in particular, is typical for fluid films (since there is no singularity there $\Omega(\eta^-) \neq 0$ at the entrance to the diffusion boundary layer).

It is clear that in reality there cannot be such a discontinuity, while in the vicinity of a moving discontinuity front there exists a narrow region (of thickness $O(\mathrm{Pe}^{-1/2})$) with high gradients, in which the concentration varies smoothly and rapidly. In this region, molecular diffusion in the tangential direction toward the surface of the sphere becomes important, and the equation of the boundary layer (1.1) is no longer applicable. For this reason, in order to analyze the concentration distribution near the front, it is not necessary to examine the complete equation of convective diffusion.

Let us investigate the limiting behavior of solution (6.6) for $\theta_0 \to 0$ ($\mu_0 \to -1$). Taking into account the property $\lim\limits_{\mu_0 \to -1} \omega_*(t, \mu, \mu_0) = +\infty\,(\mu > -1)$ and passing to the limit with $\mu_0 \to -1$ in (6.6), we find that the concentration distribution in this case is continuous and is described only by the second term in (6.6) [or Eq. (3.5) with $q \equiv 1$], and coincides with [2, 6]. This means that for $\theta_0 = 0$, the concentration distribution in the flow is (completely) determined only by the initial condition (6.5) [i.e., it is impossible to satisfy the initial and boundary condition (6.4) and (6.5) simultaneously]. In addition, passing in the expression obtained to the limit with $\mu \to -1$ [i.e., in (3.5) with $q \equiv 1$], we find that the concentration distribution in the nonstationary case differs from the stationary case by a factor $(1 - e^{-2t})^{-1/2}$ in the integrand in the probability integral; and for $t > 0$ and $r < \infty$ $c(t, r, \pi) < 1$.

7. Case of Arbitrary Initial and Boundary Conditions. In the general case, the initial and boundary conditions for Eq. (1.1) have the form ($\eta = 0$)

$$t = 0, \quad c = c_\beta^0(\eta, \xi); \tag{7.1}$$

$$\eta = 0, \quad c = c_\alpha^0(t, \xi); \tag{7.2}$$

$$\xi = 0, \quad c = 0. \tag{7.3}$$

Here, the boundary condition on the reacting surface is taken in the form (7.3) for simplicity.

In what follows, we assume that for $0 \leqslant \eta < \infty$, $\Omega(t, \eta) > 0$, and $g > 0$ (1.1) (including the boundary $\eta = 0$, i.e., $\Omega(t, 0) > 0$), so that the Jacobian J in the entire region $0 \leqslant \eta < \infty$ differs from zero and the transformation (1.2)-(1.5) is not singular.

Arguing as in Sec. 6, in the general case, we find that the region of influence of the boundary condition (7.2) is given by the inequality

$$\omega(t, \eta) \leqslant 0 \ (\omega(0, 0) = 0, \ \eta > 0, \ \omega(0, \eta) > 0),$$

where ω is the particular solution of the first equation (1.4), while the velocity of the front (discontinuity) is determined by Eq. (1.5). The boundary condition (7.2) does not affect the solution of (1.1), (7.1)-(7.3) in the region $\omega > 0$, while in the region $\omega < 0$ the solution does not depend on the initial condition (7.1) and is determined only by the boundary condition (7.2).

In the region $\omega < 0$, we will transform to variables (1.2)-(1.5), (2.6) ω, ζ, τ_α, while in the region $\omega > 0$ to the variables ω, ζ, τ_β (2.8). In each of these regions, the concentration distribution will be described by Eq. (1.6) with the corresponding initial condition

$$\tau_{\alpha,\beta} = 0, \quad c = c_{\alpha,\beta}^0(\zeta, \omega), \tag{7.4}$$

where α corresponds to $\omega < 0$, while β corresponds to $\omega > 0$; correspondingly, expressions are obtained for $c_{\alpha,\beta}$ from the initial and boundary conditions (7.1) and (7.2) by transforming to the new variables using Eqs. (1.2)-(1.5), (2.6), and (2.8).

The solution of the problem (1.6) and (7.4) has the form ($\gamma = \alpha, \beta$)

$$c = \Theta(-\omega) c_\alpha(\omega, \ \zeta, \ \tau_\alpha) + \Theta(\omega) c_\beta(\omega, \ \zeta, \ \tau_\beta), \tag{7.5}$$

$$c_\gamma = \frac{1}{2\sqrt{\pi\tau_\gamma}} \int_0^\infty \left\{ \exp\left[-\frac{(\zeta - \zeta^*)^2}{4\tau_\gamma} \right] - \exp\left[-\frac{(\zeta + \zeta^*)^2}{4\tau_\gamma} \right] \right\} c_\gamma^0(\omega, \zeta^*, \tau_\gamma)\, d\zeta^*.$$

In the vicinity of the front $\omega = 0$, the tangential derivatives of the concentration are large and the equation of the diffusion boundary layer (1.1) is no longer applicable, and for this reason, here it is necessary to examine the complete equation of convective diffusion. In this case, the problem for the concentration distribution in the vicinity of the front can be formulated with the help of the method of joined asymptotic expansions [14, 15].

Introducing in the vicinity of the discontinuity $\eta = \eta^*(t)$ ($\omega = 0$) stretched coordinates

$$t, \ Y = \sqrt{\mathrm{Pe}}\,\xi, \ X = \sqrt{\mathrm{Pe}}\,\omega(t, \eta), \tag{7.6}$$

and substituting them into the complete equation of convective diffusion and separating out the leading terms in the expansion with Pe→∞ (it is assumed that $Y = O(1)$, $X = O(1)$), we obtain the following equation for the concentration c* in the vicinity of the front $\eta = \eta^*(t)$ ($\omega = 0$):

$$\frac{\partial c^*}{\partial t} - e(t)\, Y \frac{\partial c^*}{\partial Y} = \frac{\partial^2 c^*}{\partial Y^2} + s^2(t) \frac{\partial^2 c^*}{\partial X^2}, \tag{7.7}$$

$$e(t) = \left[\frac{1}{\sqrt{g}} \frac{\partial \Omega}{\partial \eta} \right]_{t, \eta = \eta^*(t)}, \quad s(t) = \left[\frac{\partial \omega}{\partial \eta} \right]_{t, \eta = \eta^*(t)}.$$

Equation (7.7) must be supplemented by the conditions for joining for $|X| \to \infty$ with solutions of (7.5), as well as the initial and boundary conditions (7.1) and (7.3)

$$
\begin{gathered}
X \to -\infty, \quad c^* \to c_\alpha(0, \zeta, \tau^*_\alpha(t)), \quad X \to +\infty, \quad c^* \to c_\beta(0, \zeta, \tau^*_\beta(t)), \\
Y = 0, \quad c^* = 0, \quad t = 0, \quad c^* = \Theta(-X) c^0_\alpha(0, Y) + \Theta(X) c^0_\beta(0, Y), \\
\tau^*_\alpha(t) \equiv \tau_\alpha(t, \eta^*(t)), \quad \tau^*_\beta(t) \equiv \tau_\beta(t, \eta^*(t)).
\end{gathered}
\tag{7.8}
$$

Equation (7.7) with the initial and boundary conditions (7.8) gives the concentration distribution in the vicinity of the point of discontinuity.

In spite of the fact that Eq. (7.5) incorrectly describes the concentration distribution in the vicinity of the front, it gives (asymptotically) the correct result in the region $|\omega| > O(\mathrm{Pe}^{-1/2})$, $\mathrm{Pe} \to \infty$ and determines the leading term in the expansion (with respect to the Peclet number) for the total diffusion inflow of matter to the reacting surface.

In the general case, $g^{-1/2}\Omega = O(|\eta - \eta^-|^\varepsilon)$ for $\eta \to \eta^-$ and it can be shown that for $0 \leqslant \varepsilon < 1$ the solution of the problem (1.1) and (7.1)-(7.3) is given by Eqs. (7.5), while for $\varepsilon \geqslant 1$, the solution of Eqs. (1.1) and (7.3) is determined only by the initial condition (7.1) and does not depend on the boundary condition (7.2) (instead of which, it is necessarily to give the mild condition that the derivative is bounded $|(\partial c/\partial \eta)_{\eta=\eta^-}| < \infty$) and is given by expression c_β (7.5) (the case with $\varepsilon = 1$ was examined in Sec. 6).

In conclusion, we note that the transformation (1.2)-(1.5) permits solving more complicated problems involving multicomponent isothermal reactions, occurring on reacting surfaces (for high Peclet numbers) and described by systems of equations of the type (1.1).

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