THEORY OF CONVECTIVE DIFFUSION IN THIN LIQUID FILMS

V. S. Krylov, Kh. Boyadzhiev, and V. G. Levich *

UDC 66.015

The present paper deals with an improvement of the existing methods for calculating mass transfer through a liquid-gas boundary surface under the conditions of waveless film flow. The first attempt at solving the problem of gas absorption by a laminarly flowing liquid film was undertaken in studies by V. V. Vyazovov [1]. In particular, a solution was presented for the limiting case of infinitely large Peclet numbers, where the nonuniformity of the velocity profile in the film does not affect the rate of mass transfer. A solution was derived also for the limiting case of infinitely small Peclet numbers. The latter solution has the following trivial meaning: in the absence of convective motion the concentration profile is a linear function of the distance to the film surface, and the corresponding Nusselt number is constant. The awkward formulas in the form of slowly converging series [1, 2] derived for arbitrary Peclet numbers, are incorrect for the reasons discussed below. However, a completely correct solution (in which the actual hydraulic flow regime is taken into account) can be derived by starting from the condition that the following parameter is small:

$$\varepsilon = (2\nu D / g\delta^3)^{1/2}, \tag{1}$$

where ν denotes the kinematic viscosity of the liquid, D the diffusion coefficient of the substance absorbed by the liquid, g the acceleration of free fall, δ the film thickness. If $\varepsilon \ll 1$, the main change in concentration of the absorbed gas takes place in a thin liquid layer adjacent to the film surface, i.e., in the so-called diffusion boundary layer [3]. In the zero approximation with respect to parameter ε, the film as a whole is assumed to move at a velocity equal to that of the surface [4]. Since the actual velocity is maximum near the surface of the freely flowing film (and lower in the deeper layers), the zero approximation with respect to parameter ε yields the highest possible value (under the considered regime of waveless flow) of the average diffusive flow [3, 4].

$$\overline{\mathrm{Nu}} = (4\delta / \pi l \varepsilon^2)^{1/2} = (2g\delta^4 / \pi l \nu D)^{1/2}, \tag{2}$$

where l denotes the length of the film. To improve formula (2), it is necessary to calculate the next approximation with respect to parameter ε. However, the original equation of convective diffusion is such that utilization of the usual perturbation theory in the derivation of higher approximations gives rise to irregularities which cause the corresponding integral corrections to the diffusive flow to diverge. Here, the situation is the same as in the case of mass transfer from single drops [5]. For this reason we found it convenient to improve the zero approximation by applying the modified perturbation theory, which, in the literature, is known as the Poincaré-Lighthill-Go method [6], in the theoretical calculation of the diffusion boundary layer. Below, this method will be applied to convective diffusion in laminar liquid films.

We shall choose such a coordinate system that the x-axis is parallel to the direction in which the liquid moves, and the y-axis perpendicular to the solid wall; the positions of the solid wall and the free film surface are denoted by y = 0 and y = δ, respectively. The equation of convective diffusion then reads [1]:

$$\frac{g}{2\nu}(2\delta y - y^2)\frac{\partial c}{\partial x} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right). \tag{3}$$

If absorption takes place in an initially pure liquid, the following boundary conditions may be applied:

$$c(0, y) = 0, \quad c(x, 0) = 0, \quad c(x, \delta) = c_0 = \mathrm{const.} \tag{4}$$

*Corresponding Member of the Academy of Sciences of the USSR.

Institute of Electrochemistry, Academy of Sciences of the USSR. Translated from Doklady Akademii Nauk SSSR, Vol. 175, No. 1, pp. 156-159, July, 1967. Original article submitted January 12, 1967.

If the dimensionless variables of the theory of the diffusion boundary

$$X = x / l, \quad \rho = (1 - y / \delta) / \varepsilon \tag{5}$$

are used, Eq. (3) and boundary conditions (4) transform into

$$\frac{\delta}{l}(1 - \varepsilon^2\rho^2)\frac{\partial c}{\partial X} - \frac{\partial^2 c}{\partial \rho^2} = \frac{\varepsilon^2\delta^2}{l^2}\frac{\partial^2 c}{\partial X^2} \tag{6}$$

$$c(0, \rho) = 0, \quad c(X, \infty) = 0, \quad c(X, 0) = c_0. \tag{7}$$

Equation (6) contains two small parameters: $\alpha = \delta/l$ and $\beta = \varepsilon^2\delta/l$. Since the relationship $\beta \ll \alpha$ holds at large values of the Peclet number ($Pe = g\delta^3/2\nu D \gg 1$), we may search for a solution in the form of a power series of β:

$$c = c^{(0)} + \beta c^{(1)} + \beta^2 c^{(2)} + \dots \tag{8}$$

The coefficients $c^{(0)}$, $c^{(1)}$, etc., will be functions of parameter α. Since in papers [1, 2] the term $(\varepsilon^2\delta^2/l^2)\,\partial^2 c/\partial X^2$ was left out, the solutions derived in these papers are formally correct up to the first-order terms of α and β. However, at large Peclet numbers, for which the solution may be represented by series expansion (8), the approximation is actually correct up to zero-order terms of ε. In fact, the equation solved in [1, 2] reads as follows after transformation to the dimensionless variables (5):

$$(\alpha - \beta\rho^2)\,\partial c / \partial X = \partial^2 c / \partial \rho^2.$$

The term proportional to β (see Eq. (6)) is lacking on the right-hand side in the above equation, and to find the correct solution it is necessary to strike out the term $-\beta\rho^2\,\partial c/\partial X$ on the left. This yields formula (2), which corresponds to the limiting case of infinitely large Peclet numbers. If, however, the Peclet number is of the order of unity ($\varepsilon \sim 1$), Eq. (3), transformed to dimensionless coordinates, reads

$$\alpha(2Y - Y^2)\,\partial c / \partial X = \varepsilon^2(\partial^2 c / \partial Y^2 + \alpha^2 \partial^2 c / \partial X^2).$$

The term proportional to α^2 is neglected in the solution used in papers [1, 2]. However, from the angle of the perturbation theory this approximation is incorrect, since the retained terms contain parameters of different orders of magnitude (the term on the left $\sim\alpha \ll 1$, and the term on the right $\sim\varepsilon^2 \sim 1$).

If Eq. (6) is solved by applying the usual perturbation theory to parameter β, the first nonzero correction to the local diffusive flow through the film surface reads

$$\frac{3\varepsilon D c_0}{4\sqrt{\pi}\delta}\left[(\alpha/X)^{3/2} - {}^2/_3(\alpha/X)^{-1/2}\right],$$

which results in a divergent correction to the average diffusive flow through the entire film surface. Even stronger divergences will arise in the next approximations. In order that the correction to the local diffusive flow which is proportional to the first power of parameter ε will not show this hazardous irregularity at $X \to 0$, it is necessary to carry out a further transformation of the coordinates

$$\rho = z, \quad X = \alpha\tau + \beta f(\tau, z), \tag{9}$$

where $f(\tau, z)$ denotes a function whose actual shape is to be found from the requirement that the correction to the concentration distribution proportional to ε^2 must at $X = 0$ have an irregularity not larger than the irregularity of the main term (term independent of ε).

Changing over in Eq. (6) from the variables X, ρ to the variables τ, z and utilizing expansion (8), we find the well-known zero approximation [1, 3].

$$c^{(0)}(\tau, z) = c_0\,\mathrm{erfc}(z / 2\sqrt{\tau}). \tag{10}$$

Function $c^{(1)}(\tau, z)$ must satisfy the equation

$$\frac{\partial c^{(1)}}{\partial \tau} - \frac{\partial^2 c^{(1)}}{\partial z^2} = \frac{c_0 z}{2\sqrt{\pi\tau^3}}e^{-z^2/4\tau}\left\{z^2 + \frac{\partial f}{\partial \tau} - \frac{\partial^2 f}{\partial z^2} + \frac{\partial f}{\partial z}\left(\frac{z}{\tau} - \frac{2}{z}\right) - \frac{3}{2\tau} + \frac{z^2}{4\tau^2}\right\} \tag{11}$$

with the boundary conditions

$$c^{(1)}(\tau, \infty) = -c_0(4\pi\tau^3)^{-1/2}\lim_{z\to\infty}\left[z f(\tau, z)\, e^{-z^2/4\tau}\right] \quad (\tau > 0); \tag{12a}$$

$$c^{(1)}(\tau, 0) = -c_0 (4\pi\tau^3)^{-1/2} \lim_{z\to 0} [z f(\tau, z)] \qquad (\tau > 0); \tag{12b}$$

$$c^{(1)}(0, z) = 0 \qquad (z > 0). \tag{12c}$$

The terms $-3/2\tau$ and $z^2/4\tau^2$ in braces on the right in Eq. (11) are responsible for the strongest irregularity (of the type $X^{-3/2}$) in the expression for the local flow at $X \to 0$. Consequently, $f(\tau, z)$ must be so chosen that the equation for $c^{(1)}(\tau, z)$ will not contain the terms mentioned. We, therefore, require that function $f(\tau, z)$ must satisfy the equation

$$\frac{\partial f}{\partial \tau} + \frac{\partial f}{\partial z}\left(\frac{z}{\tau} - \frac{2}{z}\right) - \frac{\partial^2 f}{\partial z^2} = \frac{3}{2\tau}\left(1 - \frac{z^2}{6\tau}\right). \tag{13}$$

As follows from physical considerations, function f must ensure that the right-hand sides of boundary conditions (12a) and (12b) are finite. There exists one further physical condition that imposes a restriction on function f. This condition consists in that the expression for the local diffusive flow ($j(X)$) must be finite for arbitrary X. From formulas (9) and (10) and the definition of $j(X)$ it follows that to an accuracy of first-order terms of ε inclusively

$$j(X) = D\left(\frac{\partial c}{\partial y}\right)_{y=\delta} = \frac{Dc_0}{\delta\varepsilon}\sqrt{\frac{\alpha}{\pi X}}\left\{1 - \frac{\varepsilon^2}{c_0}\sqrt{\frac{\pi X}{\alpha}}\left[\frac{\partial c^{(1)}}{\partial z}(X, 0) - \frac{c_0}{2}\sqrt{\frac{\alpha^3}{\pi X^3}}\lim_{z\to 0}\left(z\frac{\partial f(X, z)}{\partial z}\right)\right]\right\}. \tag{14}$$

The condition that $j(X)$ must be finite at $X > 0$ implies that

$$\left|\lim_{z\to 0}\left(z\frac{\partial f(X, z)}{\partial z}\right)\right| < \infty. \tag{15}$$

From Eq. (13) it follows that $f(\tau, z) = \psi(\zeta)$, where $\zeta = z/\sqrt{\tau}$. For $\psi(\zeta)$ we find the ordinary differential equation

$$\frac{d^2\psi}{d\zeta^2} + \left(\frac{2}{\zeta} - \frac{\zeta}{2}\right)\frac{d\psi}{d\zeta} = \frac{\zeta^2}{4} - \frac{3}{2}, \tag{16}$$

the general solution of which reads

$$\psi(\zeta) = -\frac{\zeta^2}{4} + \frac{A_1}{\zeta}e^{\zeta^2/4}\left\{1 + \sum_{k=0}^{\infty}\frac{(-1)^{k+1}\zeta^{2k+2}}{2^{k+1}(k+1)!!}\right\} + A_2, \tag{17}$$

where A_1 and A_2 are arbitrary constants. From condition (15) it unambiguously follows that $A_1 = 0$. Since the constant A_2 does not occur in Eq. (11), nor in boundary conditions (12), it may be set equal to zero. We thus find the following solution for $c^{(1)}(\tau, z)$:

$$c^{(1)}(\tau, z) = \frac{c_0 z}{2}\sqrt{\frac{\tau}{\pi}}\, e^{-z^2/4\tau}\left(1 + \frac{z^2}{3\tau}\right). \tag{18}$$

Substituting this solution in (14), we get

$$j(X) = \frac{Dc_0}{\delta\varepsilon}\sqrt{\frac{\alpha}{\pi X}}\left(1 - \frac{\beta X}{2\alpha^2}\right). \tag{19}$$

The dimensionless flow (Nusselt number), averaged over the entire length l of the film, equals

$$\overline{\mathrm{Nu}} = \frac{\delta}{Dc_0}\int_0^1 j(X)\,dX = \left(\frac{4\delta}{\pi l \varepsilon^2}\right)^{1/2} - \left(\frac{l\varepsilon^2}{9\pi\delta}\right)^{1/2}. \tag{20}$$

The correction to formula (2), which is due to the nonuniformity of the velocity profile in the film, is thus found to be directly proportional to the small parameter ε (i.e., inversely proportional to the square root of the Peclet number). However, the coefficient before this parameter in the correction, being of the same order of magnitude as the square root of the ratio between the length and the thickness of the film, may be very large, so that the derived correction may become of size in some cases. An estimate shows that at the Peclet number Pe $\sim 10^4$ and the ratio $l/\vartheta \sim 10^4$ this correction amounts to 20%.

The method of the modified perturbation theory may be used in finding the corrections to the flow that are proportional to higher powers of ε (ε^3, ε^5 etc.). However, then, instead of transformation (9), other transformations must be introduced, since the function $f(\tau, z)$ used in the present paper does not eliminate divergences of an order higher than the first. For example, if a transformation (9) with the function $f(\tau, z) = -z^2/4\tau$ is applied to the equation for $c^{(2)}(\tau, z)$, the correction to the flow has a singularity of the order $X^{-5/2}$ in the point $X = 0$. Therefore, to find function $c^{(2)}(\tau, z)$, the coordinates must be transformed as follows:

$$\rho = z, \quad X = \alpha\tau + \beta f(\tau, z) + \beta^2 f_1(\tau, z),$$

where function $f_1(\tau, z)$ must be so chosen that the correction $c^{(2)}(\tau, z)$ has no dangerous singularities.

LITERATURE CITED

1. V. V. Vyazovov, ZhTF, 10, No. 18, 1519 (1940); Zhurnal Khim. Prom., 17, No. 12, 14 (1940).
2. M. E. Pozin, ZhPKh, 20, 205 (1947).
3. V. G. Levich, Physicochemical Hydrodynamics [in Russian], Moscow (1959).
4. V.G. Levich, ZhFKh, 22, 721 (1948).
5. V. P. Vorotilin, V. S. Krylov, and V. G. Levich, PMM, 29, No. 2, 343 (1965).
6. Tsyan' Syuésén', Collection: Problems of Mechanics [Russian translation], IL (1959), Vol. 2.