REVIEWS

ASYMPTOTIC THEORY OF NONLINEAR MASS TRANSFER IN

SYSTEMS WITH INTENSE MASS EXCHANGE

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Introduction. Nonlinear effects in mass transfer processes are a consequence of the existence of very high concentration gradients. Each of them affects differently the rate of mass transfer, but all of their actions are mutually related. Nevertheless, for theoretical investigation of nonlinear mass transfer it is necessary to classify the basic effects.

A primary nonlinear effect can occur when the dependence of the mass flux on the concentration gradient is nonlinear. This nonlinearity is usually accounted for by the concentration dependence of the diffusion coefficient.

Another nonlinear effect, manifested even at concentration gradients which are not too high, is related to the concentration dependence of viscosity, diffusion, and other coefficients. This effect must be accounted for in a number of cases [1], but its effect on process rates cannot change the kinetics of mass transfer qualitatively.

From the theoretical and practical points of view the interest in the nonlinear effect is due to generation of secondary flow resulting from intense mass exchange [2, 3].

Mass transfer through an interphase boundary is always associated with momentum transfer. In cases of intense mass exchange, however, this transfer is commensurate with momentum transfer of the fundamental flow. Thus, intense mass exchange induces secondary flow at the phase separation surface. The rate of these flows is normal with respect to the interphase surface.

The rate of induced flow resulting from intense mass exchange $v_n$ can be determined [4] from the mass flux through the phase separation surface:

$$v_n = -\frac{MD}{\rho_0^*}\frac{\partial c}{\partial n},$$                                            (1)

where M, D, and c are the molecular mass, diffusion coefficient, and transferred material coefficient, $\rho_0^*$ is the specific mass of the medium at the phase separation surface where mass transfer occurs, and $\partial/\partial n$ is the normal derivative to the interphase surface.

The new velocity component $v_n$ (within the linear theory of mass transfer $v_n = 0$) affects substantially the hydrodynamics of the fundamental flow. Thus, the velocity vector v depends on the concentration distribution, and the left hand side of the convective diffusion equation

$$\mathbf{v}\,\mathrm{grad}\,c = \mathrm{div}\,(D\,\mathrm{grad}\,c)$$

is nonlinear.

The induced velocity at the phase separation boundary $v_n$ is the reason for convective transport, i.e., the mass flux through the phase boundary has diffusion and convective components:

$$I = -MD\frac{\partial c}{\partial n} + Mc^*v_n = -\frac{MD\rho^*}{\rho_0^*}\frac{\partial c}{\partial n},$$               (2)

where $\rho^* = \rho_0^* + Mc^*$, and $c^*$ is the transferred material concentration at the phase boundary.

It is seen from (2) that the nonlinear effect, as a result of induced velocity $v_n$, has a dual manifestion [5].

The first part of the nonlinear effect is the new component of convective transport. It is accounted for by the expression

$$\frac{\rho^*}{\rho_0^*} = 1 + \frac{Mc^*}{\rho_0^*},$$

when $Mc^*/\rho_0^* > 10^{-2}$, i.e., this part of the nonlinear effect is manifested as a function of the material concentration at the phase boundary, and in a number of cases can be assumed to be unimportant [1].

The second part of the nonlinear effect is associated with the effect of induced velocity $v_n$ at the laminar boundary layer [5], leading to a variation in the concentration distribution in the diffusion boundary layer at the solid surface [6, 7], as well as to a moving gas—fluid phase surface [8, 9].

The nonlinear effect due to the large concentration gradient of the given material affects similarly the multicomponent mass transfer when the concentration gradients of other materials are not large.

The change in the hydrodynamic boundary layer [5] as a result of nonlinear mass transfer affects similarly the rate of heat and mass transfer [10].

In gas—fluid systems with a moving phase boundary these effects are differently manifested [8] in the gas and fluid phases in the case of single-component and multicomponent mass exchange. Similar results are also obtained [11-13] when the fluid flows as a thin film over a smooth vertical surface.

All these topics are the subject of the present review. It is shown below that the direction of intense mass exchange affects heat and mass transfer.

Nonlinear Mass Transfer. The kinetics of nonlinear mass transfer is considered on the example of longitudinal flow of a semi-infinite film within the boundary layer approximation [7, 8]. The mathematical description of the hydrodynamics and of the mass transfer is

$$u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = \nu\frac{\partial^2 u}{\partial y^2}, \quad \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0,$$

$$u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} = D\frac{\partial^2 c}{\partial y^2}, \quad x = 0, \; u = u_0, \; c = c_0, \tag{3}$$

$$y = 0, \; u = 0, \; v = -\frac{MD}{\rho_0^*}\frac{\partial c}{\partial y}, \; c = c^*, \; y \to \infty, \; u = u_0, \; c = c_0,$$

where one assumes longitudinal film flow by a potential flow with velocity $u_0$ and transported material concentration $c_0$. The concentration $c^*$ at the solid surface is always constant as a result of quickly established thermodynamic equilibrium, and the normal velocity component is determined by expression (1) as a result of intense mass exchange.

The rate of mass transfer for a surface of length $\ell$ is determined from (3) by averaging the local mass flux:

$$J = Mk(c^* - c_0) = \frac{1}{l}\int_0^l I\,dx, \tag{4}$$

where k is the mass transfer coefficient, while I is found from (2):

$$I = -\frac{MD\rho^*}{\rho_0^*}\left(\frac{\partial c}{\partial y}\right)_{y=0}.$$

To solve (3) it is necessary to introduce the self-similar variables:

$$u = 0{,}5u_0\varepsilon\Phi', \quad v = 0{,}5\left(\frac{u_0\nu}{x}\right)^{0,5}(\eta\Phi' - \Phi),$$

$$c = c_0 + (c^* - c_0)\Psi, \quad y = \eta\left(\frac{u_0}{4Dx}\right)^{-0,5}, \tag{5}$$

where $\varepsilon = Sc^{0,5}$, $Sc = \nu/D$, $\Phi = \Phi(\eta)$, $\Psi = \Psi(\eta)$.

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In the new variables the problem (3) acquires the form:

$$\Phi''' + \varepsilon^{-1}\Phi\Phi'' = 0, \quad \Psi'' + \varepsilon\Phi\Psi' = 0,$$

$$\Phi(0) = \theta\Psi'(0), \quad \Phi'(0) = 0, \quad \Phi'(\infty) = \frac{2}{\varepsilon}, \tag{6}$$

$$\Psi(0) = 1, \quad \Psi(\infty) = 0,$$

where

$$\theta = \frac{M(c^* - c_0)}{\varepsilon\rho_0^*} \tag{7}$$

is a parameter taking into account the effect of nonlinear mass transfer. Within the linear theory of boundary layer diffusion $\theta = 0$.

In the new variables it follows from (4) that

$$\text{Sh} = \frac{kl}{D} = -\frac{\rho^*}{\rho_0^*}\text{Pe}^{0,5}\Psi'(0), \quad \text{Pe} = \frac{u_0 l}{D}. \tag{8}$$

It is seen from (8) that the kinetics of mass transfer is determined from the dimensionless diffusion flux $\Psi'(0)$, which can be obtained by solving problem (6). It can be found in [7] by a perturbation method following the representation of $\Phi$ and $\Psi$ in the form of a power series in the small parameter $\theta$:

$$\Phi = \Phi_0 + \theta\Phi_1 + \theta^2\Phi_2 + \dots, \quad \Psi = \Psi_0 + \theta\Psi_1 + \theta^2\Psi_2 + \dots \tag{9}$$

Thus, for $\Psi'(0)$ one can write;

$$\Psi'(0) = -\frac{2}{\varepsilon\varphi_0} + \theta\frac{2\varphi_3}{\varphi_0^3} + \theta^2\left(-\frac{4\varepsilon\varphi_3^2}{\varphi_0^5} + \frac{\varepsilon\varphi_{33}}{\varphi_0^4} + \frac{4\overline{\varphi}_{33}}{\varepsilon\varphi_0^4}\right), \tag{10}$$

where

$$\varphi_0 = \begin{cases} 3{,}01\,\text{Sc}^{-0,35} & \text{— for gases,} \\ 3{,}12\,\text{Sc}^{-0,34} & \text{— for fluids,} \end{cases}$$

$$\varphi_3 = \begin{cases} 6{,}56\,\text{Sc}^{-0,80} & \text{— for gases} \\ 5{,}08\,\text{Sc}^{-0,67} & \text{— for fluids,} \end{cases}$$

$$\varphi_{33} = \begin{cases} 24{,}0\,\text{Sc}^{-1,3} & \text{— for gases,} \\ 12{,}2\,\text{Sc}^{-1,0} & \text{— for fluids,} \end{cases}$$

$$\overline{\varphi}_{33} = \begin{cases} 0{,}326\,\text{Sc}^{-1,6} & \text{— for gases,} \\ 0{,}035\,\text{Sc}^{-1,1} & \text{— for fluids.} \end{cases}$$

To verify the accuracy of the asymptotic theory problem (6) was solved numerically [8], and the results obtained $\Psi_N'(0)$ are compared with the results of the asymptotic theory $\Psi'(0)$ in Table 1. It is immediately seen that the direction of intense mass exchange affects substantially the kinetics of mass transfer, which cannot be foreseen within the approximate linear theories ($\theta = 0$). When the mass exchange is directed from the bulk to the phase boundary ($\theta < 0$), an increase in the concentration gradient leads to an increase in the diffusion mass transfer. If the mass exchange is directed from the phase boundary to the bulk ($\theta > 0$), an increase in the concentration gradient leads to a decrease in the diffusion mass transfer.

Analysis of Eqs. (6)-(8) shows that intense mass exchange affects the kinetics of mass transfer by changing the hydrodynamics of the flow. As a consequence, similar variations can be expected in the kinetics of mass transfer of other components for which the concentration gradients are not very large.

Multicomponent Mass Transfer. The theory of diffusion in multicomponent systems [14, 15] shows that the independent diffusion approximation can be used both when the component concentrations are low, and when the diffusion coefficients of the separate components are close to each other. This makes it possible to consider, along with transfer of a component with a large concentration gradient, transfer of the other n components for which the concentration gradient $c_i$ ($i = 1, \dots, n$) is not large. Thus, the system of equations (3) must be augmented:

TABLE 1. Comparison of Asymptotic Theory
Results with Numerical Experiments

| $\theta$ | $\varepsilon=1$ | | $\varepsilon=10$ | |
|---|---|---|---|---|
| | $-\Psi'_N(0)$ | $-\Psi'(0)$ | $-\Psi'_N(0)$ | $-\Psi'(0)$ |
| 0,00 | 0,664 | 0,664 | 0,314 | 0,305 |
| +0,05 | 0,641 | 0,641 | 0,248 | 0,250 |
| —0,05 | 0,689 | 0,689 | 0,459 | 0,415 |
| +0,10 | 0,620 | 0,620 | 0,207 | 0,250 |
| —0,10 | 0,716 | 0,716 | — | 0,581 |
| +0,20 | 0,581 | 0,584 | 0,160 | 0,418 |
| —0,20 | 0,779 | 0,776 | — | 1,080 |
| +0,30 | 0,548c | 0,555 | — | 0,808 |
| —0,30 | 0,855 | 0,843 | — | 1,800 |

$$u \frac{\partial c_i}{\partial x} + v \frac{\partial c_i}{\partial y} = D_i \frac{\partial^2 c_i}{\partial y^2} \; ; \; x = 0, \; c_i = c_{0i};$$

$$y = 0, \; c_i = c_i^*; \; y \to \infty, \; c_i = c_{0i}, \; i = 1, \ldots, n. \tag{11}$$

In the dimensionless variables (5) Eqs. (6) must be supplemented by

$$\Psi_i'' + \bar{\varepsilon_i} \Phi \Psi_i' = 0, \; \Psi_i(0) = 1, \; \Psi_i(\infty) = 0, \; i = 1, \ldots, n, \tag{12}$$

where

$$\bar{\varepsilon_i} = \varepsilon \alpha_i; \; \alpha_i = \left( \frac{\varepsilon_i}{\varepsilon} \right)^2; \; \varepsilon_i = Sc_i^{0,5};$$

$$Sc_i = \frac{\nu}{D_i}; \quad \Psi_i = \Psi_i(\eta) = \frac{c_i - c_{0i}}{c_i^* - c_{0i}}, \; i = 1, \ldots, n. \tag{13}$$

The rate of multicomponent mass transfer in the gas (fluid) at the boundary with a solid surface of length $\ell$ is determined by the mean value of the mass flux

$$J_i = M_i k_i (c_i^* - c_{0i}) = \frac{1}{l} \int_0^l I_i dx, \; i = 1, \ldots, n, \tag{14}$$

containing the convective component due to induced flow at the phase boundary:

$$I_i = - M_i D_i \left( \frac{\partial c_i}{\partial y} \right)_{y=0} + M_i (c_i v)_{y=0} =$$

$$= - M_i D_i \left[ \left( \frac{\partial c_i}{\partial y} \right)_{y=0} + \frac{M_i \alpha_i}{\rho_0^*} \left( c_i \frac{\partial c}{\partial y} \right)_{y=0} \right], \; i = 1, \ldots, n. \tag{15}$$

An expression for the Sherwood number is obtained directly from (5), (13)-(15):

$$Sh_i = \frac{k_i l}{D_i} = Pe^{0,5} \left[ \Psi_i'(0) + \theta \bar{\varepsilon_i} \frac{c_i^*}{c_i^* - c_{0i}} \Psi'(0) \right], \; i = 1, \ldots, n,$$

where $\Psi'(0)$ is calculated by (10), and to determine $\Psi_i'(0)$ it is necessary to solve the system of equations (6) and (12). This solution was obtained [12] by an asymptotic method while using for $\Psi_i$ ($i = 1, \ldots, n$) expansions similar to (9). Thus, one can write down for $\Psi_i'(0)$

$$\Psi_i'(0) = - \frac{2}{\varepsilon \varphi_{0i}} + \theta \frac{2 \bar{\varepsilon_i} \varphi_{3i}}{\varepsilon \varphi_0 \varphi_{0i}^2} - \theta^2 \left[ \frac{2 \bar{\varepsilon_i} \varphi_{3i}}{\varphi_0^2 \varphi_{0i}^2} \left( \frac{\varphi_3}{\varphi_0} + \frac{\bar{\varepsilon_i} \varphi_{3i}}{\varepsilon \varphi_{0i}} \right) - \right.$$

$$\left. - \frac{\bar{\varepsilon_i}^2 \varphi_{33i}}{\varepsilon \varphi_0^2 \varphi_{0i}^2} - \frac{\bar{\varepsilon_i} \bar{\varphi}_{33i}}{\varepsilon^2 \varphi_0^2 \varphi_{0i}^2} \right], \; i = 1, \ldots, n,$$

where

$$\varphi_{0i} = \varphi_0(Sc_i); \; \varphi_{3i} = \varphi_3(Sc_i);$$

$$\varphi_{33i} = \varphi_{33}(Sc_i); \; \bar{\varphi}_{33i} = \bar{\varphi}_{33}(Sc_i), \; i = 1, \ldots, n.$$

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The accuracy verification of the asymptotic theory of multicomponent mass transfer (under conditions of intense mass exchange of one of the components) was carried out by numerical solution of the problem (6) and (12). The comparison of the results of numerical experiments $\Psi'_{iN}(0)$ with results of the asymptotic theory $\Psi'_i(0)$ is shown in Tables 2 and 3. It is immediately seen that intense mass exchange of a single component from the bulk to the solid surface ($\theta < 0$) increases diffusional mass transfer for all components. These effects differ due to the difference in diffusion coefficient values for $Sc_i = Sc$, $\Psi'_i(0) = \Psi'(0)$, $i = 1,\ldots,n$. In cases of intense mass exchange direction from the solid surface to the bulk ($\theta > 0$), multicomponent mass transfer decreases. These effects are independent of the direction variable of mass exchange for components with small concentration gradients, and can be used to control the kinetics of multicomponent mass transfer.

Analysis of Eqs. (3) and (11) shows that similar effects can also be observed in situations of heat transfer.

Heat Transfer. The effect of nonlinear mass transfer on the kinetics of heat transfer is considered by us without taking into account thermal diffusion and diffusional thermal conductivity [15]. Within the boundary layer approximation Eqs. (3) must be supplemented by:

$$u\frac{\partial t}{\partial x} + v\frac{\partial t}{\partial y} = a\frac{\partial^2 t}{\partial y^2}\; ; \; x = 0,\; t = t_0;$$

$$y = 0,\; t = t^*;\; y \to \infty,\; t = t_0, \tag{16}$$

where $t_0$ and $t^*$ are the temperatures in the bulk and at the solid surface, respectively, and a is the coefficient of temperature conductivity.

The rate of heat transfer for a surface of length $\ell$ is determined by the mean value of the local thermal flux

$$J_t = k_t(t^* - t_0) = \frac{1}{l}\int_0^l I_t dx, \tag{17}$$

where the local thermal flux $I_t$ also has a convective component:

$$I_t = -\lambda\left(\frac{\partial t}{\partial y}\right)_{y=0} + \rho_0^* c_p (vt)_{y=0}, \tag{18}$$

and $\lambda$ and $c_p$ are the thermal conductivity and heat capacity of the medium.

Equations (16) can be written in the self-similar variables (5):

$$T'' + \bar{\varepsilon_t}\Phi T' = 0,\; T(0) = 1,\; T(\infty) = 0, \tag{19}$$

where

$$T = T(\eta) = \frac{t - t_0}{t^* - t_0}\; ; \; \bar{\varepsilon_t} = \varepsilon\alpha_t;\quad \alpha_t\frac{D}{a} = Le^{-1}. \tag{20}$$

To determine the kinetics of heat transfer it is required to find the Nusselt number while using (17), (18), and (20):

TABLE 2. Comparison of the Asymptotic Theory with Numerical Experiments

| $\varepsilon = 1$ | $\alpha_i = 2$ | $\bar{\varepsilon_i} = 2$ |
|---|---|---|
| $\theta$ | $-\Psi'_{iN}(0)$ | $-\Psi'_i(0)$ |
| 0,0 | 0,845 | 0,847 |
| +0,1 | 0,762 | 0,765 |
| —0,1 | 0,943 | 0,945 |
| +0,2 | 0,689 | 0,700 |
| —0,2 | 1,060 | 1,061 |
| +0,3 | 0,633 | 0,652 |
| —0,3 | 1,212 | 1,190 |

TABLE 3. Comparison of the Asymptotic Theory with Numerical Experiments

| $\varepsilon = 20$ | $\alpha_i = 0,5$ | $\bar{\varepsilon_i} = 10$ |
|---|---|---|
| $\theta$ | $-\Psi'_{iN}(0)$ | $-\Psi'_i(0)$ |
| 0,00 | 0,198 | 0,194 |
| +0,03 | 0,167 | 0,169 |
| —0,03 | 0,275 | 0,250 |
| +0,05 | 0,154 | 0,170 |
| +0,10 | 0,132 | 0,234 |

$$\mathrm{Nu} = \frac{k_t l}{\lambda} = -\mathrm{Pe}^{0,5}\left[T'(0) + \theta\bar{\varepsilon}_t\,\frac{t^*}{t^* - t_0}\,\Psi'(0)\right],$$

where the dimensionless thermal flux $T'(0)$ is determined by solving the system of equations (6) and (19), which was obtained by the asymptotic method of [14]:

$$T'(0) = -\frac{2}{\varepsilon\varphi_{0t}} + \theta\,\frac{2\alpha_t\varphi_{3t}}{\varphi_0\varphi_{0t}^2} - \theta^2\left[\frac{2\bar{\varepsilon}_t\varphi_{3t}}{\varphi_0^2\varphi_{0t}^2}\left(\frac{\varphi_3}{\varphi_0} + \frac{\alpha_t\varphi_{3t}}{\varphi_{0t}}\right) - \frac{\alpha_t\bar{\varepsilon}_t\varphi_{33t}}{\varphi_0^2\varphi_{0t}^2} - \frac{\alpha_t\bar{\varphi}_{33t}}{\varepsilon\varphi_0^2\varphi_{0t}^2}\right];$$

$$\varphi_{0t} = \varphi_0\left(\varepsilon\cdot\bar{\varepsilon}_t\right),\quad \varphi_{3t} = \varphi_3\left(\varepsilon\cdot\bar{\varepsilon}_t\right),\quad \varphi_{33t} = \varphi_{33}\left(\varepsilon\cdot\bar{\varepsilon}_t\right),\quad \bar{\varphi}_{33t} = \bar{\varphi}_{33}\left(\varepsilon\cdot\bar{\varepsilon}_t\right).$$

The accuracy verification of the asymptotic theory of heat transfer under conditions of intense mass exchange was carried out numerically [10]. It is seen from Table 4 that nonlinear mass transfer can increase or decrease heat transfer as a function of direction of intense mass exchange. This effect is the complete analog to those observed in the cases of nonlinear and multicomponent mass transfer under condition of intense mass exchange.

When nonlinear mass transfer is directed to the solid surface ($\theta < 0$), heat transfer increases with an increasing concentration gradient. Under conditions of intense mass transfer from the solid surface to the gas ($\theta > 0$) heat transfer decreases with increasing concentration gradient.

The effect of the direction of intense mass exchange on the heat transfer coefficient and on nonlinear mass transfer can be used to control the rate of the heat transfer process in gas—solid systems.

Nonlinear mass transfer in fluids does not affect heat transfer due to the large values of the Lewis number ($\alpha_t \sim 10^{-2}$), since the thickness of the diffusion boundary layer (where nonlinear mass transfer occurs) is much smaller than the thickness of the temperature boundary layer.

Mass Exchange in Gas—Fluid Systems. The kinetics of nonlinear mass exchange in gas—fluid systems is considered within the diffusion boundary layer approximation for the cases of uniflow gas and fluid motions with planar phase boundaries. If the gas and fluid are denoted as the first and second phases, problem (3) acquires the form

$$u_j\frac{\partial u_j}{\partial x} + v_j\frac{\partial u_j}{\partial y} = \nu_j\frac{\partial^2 u_j}{\partial y^2},\quad \frac{\partial u_j}{\partial x} + \frac{\partial v_j}{\partial y} = 0,$$

$$u_j\frac{\partial c_j}{\partial x} + v_j\frac{\partial c_j}{\partial y} = D_j\frac{\partial^2 c_j}{\partial y^2},\quad j = 1,\ 2, \tag{21}$$

with boundary conditions taking into account the continuity of velocities and momentum and mass fluxes at the phase boundary:

$$x = 0,\quad u_j = u_{j0},\quad c_j = c_{j0},\quad j = 1,\ 2;\quad y = 0,\quad u_1 = u_2,$$

$$\mu_1\frac{\partial u_1}{\partial y} = \mu_2\frac{\partial u_2}{\partial y},\quad c_1 = \chi c_2,\quad \frac{D_1\rho_1^*}{\rho_{10}^*}\frac{\partial c_1}{\partial y} = \frac{D_2\rho_2^*}{\rho_{20}^*}\frac{\partial c_2}{\partial y},$$

$$v_j = -\frac{MD_j}{\rho_{j0}}\frac{\partial c_j}{\partial y},\quad j = 1,\ 2;\quad y \to \infty,\quad u_1 = u_{10}, \tag{22}$$

$$c_1 = c_{10};\quad y \to -\infty,\quad u_2 = u_{20},\quad c_2 = c_{20}.$$

The rate of mass exchange for a surface of length $\ell$ is determined by averaging the local mass flux:

$$J = MK_1\left(c_{10} - \chi c_{20}\right) = \frac{1}{l}\int_0^l I_1 dx = MK_2\left(\frac{c_{10}}{\chi} - c_{20}\right) = \frac{1}{l}\int_0^l I_2 dx, \tag{23}$$

where $K_j$ ($j = 1,\ 2$) are the mass exchange coefficients, and the local mass fluxes are determined from (3):

$$I_j = -\frac{MD_j\rho_j^*}{\rho_{j0}^*}\left(\frac{\partial c_j}{\partial y}\right)_{y=0},\quad j = 1,\ 2. \tag{24}$$

| TABLE 4. Comparison of the Asymptotic Theory with Numerical Experiments | | | | TABLE 5. Comparison of the Asymptotic Theory with Numerical Experiments | | |
|---|---|---|---|---|---|---|

**TABLE 4. Comparison of the Asymptotic Theory with Numerical Experiments**

| $\varepsilon=1$ | $\alpha=2$ | $\overline{\varepsilon}_j=2$ | $\varepsilon_j=2^{0,5}$ |
|---|---|---|---|
| $\theta$ | $-T'_N(0)$ | $-T'(0)$ | |
| 0,0 | 0,864 | 0,847 | |
| +0,1 | 0,762 | 0,765 | |
| −0,1 | 0,943 | 0,945 | |
| +0,2 | 0,690 | 0,700 | |
| −0,2 | 1,063 | 1,059 | |
| +0,3 | 0,633 | 0,652 | |
| −0,3 | 1,212 | 1,190 | |

**TABLE 5. Comparison of the Asymptotic Theory with Numerical Experiments**

| $\varepsilon_3=1$ | $\theta_1=0,1$ | $\theta_2=0,152$ |
|---|---|---|
| $\theta_3$ | $-\Psi'_{1N}(0)$ | $-\Psi'_1(0)$ |
| 0,0 | 0,730 | 0,738 |
| −0,1 | 0,682 | 0,689 |
| +0,1 | 0,785 | 0,787 |
| −0,2 | 0,641 | 0,642 |
| +0,2 | 0,851 | 0,837 |
| −0,3 | 0,605 | 0,595 |
| +0,3 | 0,932 | 0,888 |

The Sherwood number can be determined directly from (23) and (24):

$$Sh_j = \frac{K_j l}{D_j} = -\frac{\rho_j^*}{\rho_{j0}^*}\frac{\chi^{j-1}}{c_{10}-\chi c_{20}}\int_0^l \left(\frac{\partial c_j}{\partial y}\right)_{y=0} dx, \quad j=1,\ 2. \tag{25}$$

The solution of problem (21) and (22) can be found by introducing the self-similar variables:

$$u_j = 0,5 j u_{j0}\varepsilon_j\Phi_j', \quad v_j = (-1)^{j-1}0,5 j\left(\frac{u_{j0}v_j}{x}\right)^{0,5}(\zeta_j\Phi_j' - \Phi_j),$$

$$c_j = c_{j0} - (-\chi)^{1-j}(c_{10}-\chi c_{20})\Psi_j, \quad \Phi_j = \Phi_j(\zeta_j), \quad \Psi_j = \Psi_j(\zeta_j), \tag{26}$$

$$\zeta_j = (-1)^{j-1} y\left(\frac{u_{j0}}{4D_j x}\right)^{0,5}, \quad \zeta_j = Sc_j^{0,5}, \quad Sc_j = \frac{v_j}{D_j}, \quad j=1,\ 2.$$

As a result we obtain:

$$\Phi_j'' + j\varepsilon_j^{-1}\Phi_j\Phi_j'' = 0, \quad \Psi_j'' + j\varepsilon_j\Phi_j\Psi_j' = 0,$$

$$\Phi_j(0) = (-1)^j \theta_{j+2}\Psi_j'(0), \quad \Phi_j'(\infty) = \frac{2}{j\varepsilon_j}, \quad \Psi_j(\infty) = 0, \quad j=1,\ 2;$$

$$\Phi_1'(0) = 2\theta_1\frac{\varepsilon_2}{\varepsilon_1}\Phi_2'(0), \quad \Phi_2''(0) = -0,5\theta_2\left(\frac{\varepsilon_1}{\varepsilon_2}\right)^2\Phi_1''(0), \tag{27}$$

$$\Psi_2'(0) = -\frac{\chi}{\varepsilon_0}\Psi_1'(0), \quad \Psi_1(0)+\Psi_2(0)=1,$$

where

$$\theta_1 = \frac{u_{20}}{u_{10}}; \quad \theta_2 = \frac{\mu_1}{\mu_2}\left(\frac{v_2}{v_1}\right)^{0,5}\left(\frac{u_{10}}{u_{20}}\right)^{1,5}; \quad \theta_3 = \frac{M(c_{10}-\chi c_{20})}{\varepsilon_1\rho_{10}^*};$$

$$\theta_4 = \frac{M(c_{10}-\chi c_{20})}{2\varepsilon_2\chi\rho_{20}^*}; \quad \varepsilon_0 = \frac{\rho_{10}^*\rho_2^*}{\rho_{20}^*\rho_1^*}\left(\frac{D_2 u_{20}}{D_1 u_{10}}\right)^{0,5}.$$

In the new variables we find from (25) for the Sherwood number

$$Sh_j = \frac{\rho_j^*}{\rho_{j0}^*}Pe_j^{0,5}\Psi_j'(0), \quad Pe_j = \frac{u_{j0}l}{D_j}, \quad 1,\ 2. \tag{28}$$

For quantitative determination of the kinetics of nonlinear mass exchange one must determine $\Psi_j'(0)$ (j = 1, 2) in (28), i.e., solve the system of equations (27). The solution was obtained by a perturbation method following the representation of the functions sought in the form of expansions in powers of the small parameters $\theta_k \ll 1$ (k = 1,..., 4). Accurately up to the first approximation we have [8]

$$\Psi_1'(0) = -\frac{2}{\varepsilon_1\varphi_{10}}\frac{1}{1+a_0} - \frac{2\theta_1}{\alpha\varepsilon_1\varphi_{10}^2}\frac{1}{(1+a_0)^2} -$$

$$- \frac{8\theta_2 \alpha \varepsilon_2 \bar{\varphi}_2}{\varepsilon_1 \varphi_{10}} \frac{a_0}{(1+a_0)^2} - \frac{2\theta_3 \varphi_{13}}{\varphi_{10}^3} \frac{1}{(1+a_0)^2} + \frac{8\theta_4 \varepsilon_2}{\pi \varepsilon_1 \varphi_{10}} \frac{a_0^2}{(1+a_0)^3} ,$$

$$\Psi_2'(0) = - \frac{\mathsf{\Gamma 2}}{\sqrt{\pi}} \frac{a_0}{1+a_0} - \frac{2\theta_1}{\sqrt{\pi} \alpha \varphi_{10}} \frac{a_0}{(1+a_0)^2} - \tag{29}$$

$$- \frac{8\theta_2 \alpha \varepsilon_2 \bar{\varphi}_2}{\sqrt{\pi}} \frac{a_0^2}{(1+a_0)^2} - \frac{2\theta_3 \varepsilon_1 \varphi_{13}}{\sqrt{\pi} \varphi_{10}^2} \frac{a_0}{(1+a_0)^2} + \frac{8\theta_4 \varepsilon_2}{\pi^{3/2}} \frac{a_0^3}{(1+a_0)_3} .$$

When the rate of interphase mass exchange is limited by diffusion resistance in the gas, $\chi/\varepsilon_0 \to 0$, i.e., $a_0 \to 0$, one can write for the Sherwood number:

$$Sh_1 = \frac{\rho_1^*}{\rho_{10}^*} Pe_1^{0,5} \left( \frac{2}{\varepsilon_1 \varphi_{10}} + \frac{2\theta_1}{\alpha \varepsilon_1 \varphi_{10}^2} + \frac{2\theta_3 \varphi_{13}}{\varphi_{10}^3} \right) . \tag{30}$$

When the process is limited by the fluid phase resistance, $\chi/\varepsilon_0 \to \infty$, $a_0 \to \infty$, i.e.,

$$Sh_2 = \frac{\rho_2^*}{\rho_{20}^*} Pe_2^{0,5} \left( \frac{2}{\sqrt{\pi}} + \frac{8\theta_2 \alpha \varepsilon_2 \varphi_2}{\sqrt{\pi}} - \frac{8\theta_4 \varepsilon_2}{\pi^{3/2}} \right) . \tag{31}$$

Comparison of nonlinear effect in a gases and a fluid [9] shows that the ratio of parameters $\theta_3$ and $\theta_4$ is:

$$\frac{\theta_3}{\theta_4} = \frac{2\varepsilon_2 \rho_{20}^* \chi}{\varepsilon_1 \rho_{10}^*} \gg 1.$$

It acquires a minimum value in cases of well dissolved gases, when $\theta_3$ is larger than $\theta_4$ by two orders of magnitude, i.e., for the numerical calculations one can always take $\theta_4 = 0$.

Analysis of the results obtained (29)-(31) shows that the nonlinear effects are substantial when nonlinear mass exchange is limited by mass transfer in the gas phase ($\chi/\varepsilon_0 = 0$). For commensurate diffusion resistances ($\chi/\varepsilon_0 \sim 1$) the nonlinear effects are substantially smaller, and their manifestation in the fluid phase is a result of the hydrodynamic effect of the gas phase. These effects are totally absent when the process is limited by mass transfer in the fluid phase.

The effect of direction of mass exchange on diffusion mass transfer in gas—fluid systems is similar to that observed in gas(fluid)—solid systems, i.e., diffusion mass transfer with absorption is larger than diffusion mass transfer with desorption.

Numerical analysis [15] shows that the deviations of diffusion flux values in the cases of absorption and desorption from the diffusion flux values for $\theta_3 = 0$ are nonsymmetric if the concentration gradients are identical in absolute value and only their directions are opposite. This "contradiction" of the asymptotic theory (30) (where the deviations are symmetric) is explained by the absence of quadratic terms (proportional to $\theta_3^2$). Obviously, the asymptotic theory requires a refinement taking into account all quadratic terms. When nonlinear mass exchange is limited by mass transfer of the gas phase, problem (27) acquires the form

$$\Phi_1''' + \varepsilon_1^{-1} \Phi_1 \Phi_1'' = 0, \quad \Phi_2''' + 2\varepsilon \Phi_2^{-1} \Phi_2 \Phi_2'' = 0, \quad \Psi_1'' + \varepsilon_1 \Phi_1 \Psi_1' = 0;$$

$$\Phi_1(0) = -\theta_3 \Psi_1'(0), \quad \Phi_2(0) = 0, \quad \Phi_1'(\infty) = \frac{2}{\varepsilon_1}, \quad \Phi_2'(\infty) = \frac{1}{\varepsilon_2} ,$$

$$\tag{32}$$

$$\Phi_1'(0) = 2\theta_1 \frac{\varepsilon_2}{\varepsilon_1} \Phi_2'(0), \quad \Phi_2''(0) = -0,5\theta_2 \left( \frac{\varepsilon_1}{\varepsilon_2} \right)^2 \Phi_1''(0),$$

$$\Psi_1(0) = 1, \quad \Psi_1(\infty) = 0.$$

The solution of problem (32) with account of all quadratic terms makes it possible to determine $\Psi_1'(0)$:

$$- \Psi_1'(0) = \frac{2}{\varepsilon_1 \varphi_{10}} + \theta_1 \frac{2}{\alpha \varepsilon_1 \varphi_{10}^2} + \theta_3 \frac{1 \varphi_{13}}{\varphi_{10}^3} + \theta_1^2 \left( - \frac{\varepsilon_1^3 \varphi_{11}}{4\alpha^2 \varphi_{10}^2} + \frac{\varepsilon_1 \varphi_{12}}{\varphi_{10}^2} + \frac{2}{\alpha^2 \varepsilon_1 \varphi_{10}^3} \right) +$$

$$\tag{33}$$

$$+ \theta_3^2 \left( \frac{2\varepsilon_1 \varphi_{13}^2}{\varphi_{10}^5} - \frac{\varepsilon_1 \varphi_{133}}{\varphi_{10}^4} - \frac{4\varphi_{133}}{\varepsilon_1 \varphi_{10}^4} \right) + \theta_1 \theta_3 \left( \frac{\varepsilon_1 \varphi_{13}}{\alpha \varphi_{10}^4} - \frac{2\varphi_{113}}{\alpha \varphi_{10}^3} - \frac{2\bar{\varphi}_{113}}{\alpha \varphi_{10}^3} + \frac{4\varphi_{13}}{\alpha \varphi_{10}^4} \right) .$$

A number of functions of the Sherwood number appear in expressions (29)-(31) and (33):

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$$\varphi_{10} = \varphi_0\,(\mathrm{Sc}_1), \quad \varphi_{13} = \varphi_3\,(\mathrm{Sc}_1), \quad \overline{\varphi}_2 = \frac{1}{8}\sqrt{\frac{\pi}{\mathrm{Sc}_2}}, \quad a_0 = \frac{\chi\,\sqrt{\pi}}{\varepsilon_0\varepsilon_1\varphi_{10}},$$

$$\varphi_{11} = \varphi_1\,(\mathrm{Sc}_1) = 3{,}01\,\mathrm{Sc}_1^{-1,608}, \quad \varphi_{12} = \varphi_2\,(\mathrm{Sc}_1) = 3{,}05\,\mathrm{Sc}_1^{-1,285},$$

$$\varphi_{133} = \varphi_{33}\,(\mathrm{Sc}_1), \quad \overline{\varphi}_{133} = \overline{\varphi}_{33}\,(\mathrm{Sc}_1), \quad \varphi_{113} = \varphi_{13}\,(\mathrm{Sc}_1) = \mathrm{Sc}_1^{-1,3},$$

$$\overline{\varphi}_{113} = \overline{\varphi}_{13}\,(\mathrm{Sc}_1) = 4{,}18\,\mathrm{Sc}_1^{-0,46}.$$

Relationship (33) is the basic result of the asymptotic theory of nonlinear mass exchange in gas—fluid systems, and is in good agreement (Table 5) with the results of numerical solution $\Psi'_{1N}(0)$ of problem (32). The theoretical result (33) primarily shows that the direction of intense mass exchange in gas—fluid systems affects its kinetics. This effect is hydrodynamic, justifying the expectation of a similar effect in cases of multicomponent mass exchange as well.

Multicomponent Mass Exchange in Gas—Fluid Systems. The kinetics of multicomponent mass exchange in gas—fluid systems is of practical interest when the mass exchange of one of the components is intense and is limited by mass transfer of this component in the gas phase.

Consider n components, for which mass exchange does not affect the hydrodynamic flow. For low concentrations $c_{ij}$ (i = 1,..., n; j = 1, 2) of diffusing materials and not substantially different diffusion coefficients $D_{ij}$ (i = 1,..., n; j = 1, 2) the theory of multicomponent mass exchange can be treated within the independent diffusion approximation [14, 15]. For this purpose it is necessary to substitute $c_2 \equiv c_{20}$ into (21) and (22) and sumpplement the transport equations for components with low concentration gadients:

$$u_j\,\frac{\partial c_{ij}}{\partial x} + v_j\,\frac{\partial c_{ij}}{\partial y} = D_{ij}\,\frac{\partial^2 c_{ij}}{\partial y^2}; \quad x = 0, \quad c_{ij} = c_{ij0};$$

$$y = 0, \quad c_{i1} = \chi_i c_{i2}, \quad -D_{i1}\frac{\partial c_{i1}}{\partial y} + c_{i1}v_1 = -D_{i2}\,\frac{\partial c_{i2}}{\partial y};$$

$$y \to \infty, \quad c_{i1} = c_{i10}; \quad y \to -\infty, \quad c_{i2} = c_{i20}.$$

In dimensionless variables, (26) and (32) must be supplemented:

$$\Psi''_{ij} + j\varepsilon_j\alpha_{ij}\Phi_j\Psi'_{ij} = 0, \quad \Psi_{i1}(0) + \Psi_{i2}(0) = 1,$$

$$\Psi'_{i1}(0) = \frac{\varepsilon_{i0}}{\chi_i}\,\Psi'_{i2}(0) + \varepsilon_1\theta_3\alpha_{i1}\left[\Psi_{i1}(0) - \frac{c_{i10}}{c_{i10} - \chi_i c_{i20}}\right]\Psi'_1(0), \tag{34}$$

$$\Psi_{ij}(\infty) = 0, \quad i = 1, \ldots, n; \quad j = 1, 2,$$

where

$$\Psi_{ij} = \Psi_{ij}(\zeta_j) = -(-\chi_i)^{j-1}\,\frac{c_{ij} - c_{ij0}}{c_{i10} - \chi_i c_{i20}};$$

$$\varepsilon_{i0} = \frac{D_{i2}}{D_{i1}}\left(\frac{u_{20}D_1}{u_{10}D_2}\right)^{0,5}; \quad \alpha_{ij} = \frac{D_j}{D_{ij}},$$

and $\chi_i$ (i = 1,..., n) is the Henry number for the separate components.

The solution of problem (34) was found by a perturbation method with account of the fact that the functions $\Phi_j$ (j = 1, 2) depend only on the three small parameters $\theta_k$ (k = 1, 2, 3).

The equations for the rates of multicomponent mass exchange are

$$J_{ij} = M_i K_{ij}\chi_i^{1-j}(c_{i10} - \chi_i c_{i20}) = -\frac{1}{l}\int_0^l I_{ij}\,dx,$$

$$I_{ij} = -M_i D_{ij}\left(\frac{\partial c_{ij}}{\partial y}\right)_{y=0}(2-j)M_i(v_j c_{ij})_{y=0},$$

$$\mathrm{Sh}_{ij} = \frac{K_{ij}l}{D_{ij}} = -\mathrm{Pe}_j^{0,5}\Big\{\Psi'_{ij}(0) + \tag{35}$$

$$+ (2-j)\varepsilon_j\theta_3\alpha_{ij}\Psi'_j(0)\left[\frac{c_{ij0}}{c_{i10} - \chi_i c_{i20}} - \Psi_{ij}(0)\right]\Big\}, \quad i = 1, \ldots, n; \quad j = 1, 2.$$

From (35) one obtains an expression for the Sherwood number:

$$\text{Sh}_{i1} = -\text{Pe}_1^{0,5}\left\{\Psi'_{i1}(0) + \theta_3\varepsilon_{i1}\Psi'_1(0)\left[\frac{c_{i10}}{c_{i10} - \chi c_{i20}} - \Psi_{i1}(0)\right]\right\}, \tag{36}$$

$$\text{Sh}_{i2} = -\text{Pe}_2^{0,5}\Psi'_{i2}(0), \quad i = 1, \ldots, n,$$

where for $\Psi'_1(0)$ and for $\Psi_{i1}(0)$ one must use the zeroth approximations:

$$\Phi_1^{(0)'}(0) = -\frac{2}{\varepsilon_1\varphi_{10}}, \quad \Psi_{i1}(0) = \frac{1}{1 + a_i}, \quad i = 1, \ldots, n,$$

while $\Psi'_{i1}(0)$ and $\Psi'_{i2}(0)$ are obtained by solving problem (34):

$$-\Psi'_{i1}(0) = \frac{2}{\varepsilon_1\varphi_{10i}}\frac{1}{1 + a_i} + \frac{2\theta_1}{\alpha\varepsilon_1\varphi_{10i}^2}\frac{1}{(1 + a_i)^2} +$$

$$+ \frac{8\theta_2\alpha\varepsilon_{i2}\overline{\varphi}_{i2}}{\varepsilon_1\varphi_{10i}\sqrt{\alpha_{i2}}}\frac{a_i}{(1 + a_i)^2} + \theta_3\left[\frac{2\alpha_{i1}\varphi_{13i}}{\varphi_{10}\varphi_{10i}^2}\frac{1}{(1 + a_i)^2} + \frac{\varepsilon_{i1}a_i}{\varphi_{10}(1 + a_i)}\left(\frac{2}{1 + a_i} - \frac{c_{i10}}{c_{i10} - \chi_i c_{i20}}\right)\right]; \tag{37}$$

$$-\Psi'_{i2}(0)\frac{2\sqrt{\alpha_{i2}}}{\sqrt{\pi}}\frac{a_i}{1 + a_i} + \frac{2\theta_1\sqrt{\alpha_{i2}}}{\sqrt{\pi}\,\alpha\varphi_{10i}}\frac{a_i}{(1 + a_i)^2} + \frac{8\theta_2\alpha\varepsilon_{i2}\overline{\varphi}_{i2}}{\sqrt{\pi}}\frac{a_i^2}{(1 + a_i)^2} + \theta_3\left[\frac{2\sqrt{\alpha_{i2}}\,\varepsilon_{i1}\varphi_{13i}}{\sqrt{\pi}\,\varphi_{10}\varphi_{10i}}\frac{a_i}{(1 + a_i)^2} - \right.$$

$$\left. - \frac{\sqrt{\alpha_{i2}}\,\varepsilon_i\varepsilon_{i1}\varphi_{10i}}{\sqrt{\pi}}\frac{a_i}{1 + a_i}\left(\frac{1}{1 + a_i} - \frac{c_{i10}}{c_{i10} - \chi_i c_{i20}}\right)\right], \quad i = 1, \ldots, n.$$

Functions of the Schmidt number appear in (37):

$$\varphi_{10i} = \varphi_0(\overline{\varepsilon}_{i1}^2), \quad \varphi_{13i} = \varphi_3(\overline{\varepsilon}_{i1}^2), \quad \overline{\varphi}_{i2} = \frac{\sqrt{\pi}}{8\varepsilon_2\sqrt{\alpha_{i2}}},$$

$$a_i = \frac{\sqrt{\pi}\,\chi_i}{\varphi_{10i}\varepsilon_1\varepsilon_{i0}\sqrt{\alpha_{i2}}}, \quad \overline{\varepsilon}_{ij} = \sqrt{\varepsilon_j\varepsilon_{ij}}, \quad \varepsilon_{ij} = \varepsilon_j\alpha_{ij}, \quad i = 1, \ldots, n; \; j = 1, 2.$$

When mass exchange is limited by mass transfer in the gas phase, $\chi_i/\varepsilon_{i0} \to 0$, one can substitute in (37) $a_i = 0$, $i = 1,\ldots,n$, and expression (36) for $\text{Sh}_{i1}$ acquires the form:

$$\text{Sh}_{i1} = \text{Pe}_1^{0,5}\left(\frac{2}{\varepsilon_1\varphi_{10i}} + \frac{2\theta_1}{\alpha\varepsilon_1\varphi_{10i}^2} + \frac{2\theta_3\alpha_{i1}\varphi_{13i}}{\varphi_{10}\varphi_{10i}^2}\right), \quad i = 1, \ldots, n. \tag{38}$$

If mass exchange is limited by mass transfer in the fluid phase, $\chi_i/\varepsilon_{i0} \to \infty$, one can substitute in (37) $a_i^{-1} = 0$, $i = 1,\ldots,n$, and expression (36) for $\text{Sh}_{i2}$ acquires the form:

$$\text{Sh}_{i2} = \text{Pe}_2^{0,5}\left(\frac{2\sqrt{\alpha_{i2}}}{\sqrt{\pi}} + \frac{8\theta_2\alpha\varepsilon_{i2}\overline{\varphi}_{i2}}{\sqrt{\pi}}\right), \quad i = 1, \ldots, n. \tag{39}$$

When the diffusion resistances of both phases are commensurate ($\chi_i/\varepsilon_{i0} \sim 1$), it follows from (37) that an increase in the large concentration gradient ($\theta_3$) leads to an increase in diffusion mass transfer in the gas phase and to a decrease in the diffusion mass transfer in the fluid phase.

It is seen from (39) that when multicomponent mass exchange is limited by mass transfer in the fluid phase the nonlinear effect in the gas does not affect the rate of the process.

<u>Mass Exchange in Gas—Discharging Film Systems of Fluid—Solid Surface</u>. The theoretical results obtained so far show that nonlinear effect are of practical importance in gas—fluid systems, when intense mass exchange is limited by mass transfer in the gas phase. Under these condition nonlinear mass exchange between the gas and the discharging fluid film is described by the equations of motion in the fluid and the gas, and by the equation of convective diffusion in the gas.

At the film surface one must match the tangential components of the velocity, the stress tensor, and the mass flux in the fluid and in the gas. The normal velocity component of the fluid vanishes (the "nonflow" condition of the fluid film), while the normal velocity

component of the gas is equal to the induced flow velocity as a result of intense mass exchange.

Starting from the considerations above, it was shown in [11] that by using the dimensionless variables

$$X = \frac{x}{l}, \quad Y = \frac{y}{h_0}, \quad \tilde{Y} = \frac{y-h}{\tilde{\delta}}, \quad H(X) = \frac{h}{h_0}, \quad U(X,\ Y) = \frac{u}{u_0}, \quad V(X,\ Y) = \frac{v}{\varepsilon_0 u_0},$$

$$\tilde{U}(X,\ \tilde{Y}) = \frac{\tilde{u}}{\tilde{u}_0}, \quad \tilde{V}(X,\ \tilde{Y}) = \frac{\tilde{v}}{\tilde{\varepsilon}\tilde{u}_0}, \tag{40}$$

$$\tilde{C} = \frac{\tilde{c}-\chi c_0}{\tilde{c}_0-\chi c_0}, \quad \varepsilon_0 = \frac{h_0}{l}, \quad u_0 = \frac{g h_0^2}{3 v}, \quad \tilde{\varepsilon}_0 = \frac{\tilde{\delta}}{l}, \quad \tilde{\delta} = \left(\frac{\tilde{D}l}{\tilde{u}_0}\right)^{0,5},$$

within the zeroth approximation in the small parameters $\varepsilon_0$ and $\theta_0$, $\theta_3$ one obtains the four mutually related problems:

$$\frac{\partial^2 U}{\partial Y^2} = -3, \quad \frac{\partial U}{\partial X} + \frac{\partial V}{\partial Y} = 0; \quad Y = 0, \quad U = 0, \quad V = 0;$$

$$Y = H, \frac{\partial U}{\partial Y} = \theta_2 \left(\frac{\partial \tilde{U}}{\partial \tilde{Y}}\right)^{\tilde{Y}=0}; \tag{41}$$

$$X \to L_\infty, \quad \frac{\partial U}{\partial X} \to 0;$$

$$H'U(X,\ H) = V(X,\ H); \quad X \to L_\infty, \quad H \to 1; \tag{42}$$

$$\tilde{U}\frac{\partial \tilde{U}}{\partial X} + \tilde{V}\frac{\partial U}{\partial \tilde{Y}} = \tilde{S}c \frac{\partial^2 \tilde{U}}{\partial \tilde{Y}^2} + \delta_0 H' \tilde{U}\frac{\partial \tilde{U}}{\partial \tilde{Y}};$$

$$\frac{\partial \tilde{U}}{\partial X} + \frac{\partial \tilde{Y}}{\partial \tilde{Y}} = \delta_0 H'\frac{\partial \tilde{U}}{\partial \tilde{Y}}; \quad X = 0, \quad \tilde{U} = 1;$$

$$\tag{43}$$

$$\tilde{Y} = 0, \quad \tilde{U} = \theta_1 U(X,\ H), \quad V = -\theta_3 \frac{\partial \tilde{C}}{\partial \tilde{Y}} + \delta_0 H' \tilde{U};$$

$$\tilde{Y} \to \infty, \quad U = 1;$$

$$\tilde{U}\frac{\partial \tilde{C}}{\partial X} + \tilde{V}\frac{\partial \tilde{C}}{\partial \tilde{Y}} = \frac{\partial^2 \tilde{C}}{\partial \tilde{Y}^2} + \delta_0 H' \tilde{U}\frac{\partial \tilde{C}}{\partial \tilde{Y}};$$

$$\tag{44}$$

$$X = 0, \quad \tilde{C} = 1; \quad \tilde{Y} = 0, \quad \tilde{C} = 0; \quad \tilde{Y} \to \infty, \quad \tilde{C} = 1,$$

$$L_\infty = \frac{l_\infty}{l}; \quad \delta_0 = \frac{h_0}{\tilde{\delta}}; \quad \tilde{S}c = \frac{\tilde{V}}{\tilde{D}}; \quad \theta_0 = \frac{\tilde{\rho}^* \sqrt{\tilde{u}_0 \tilde{D}l}}{h_0 u_0 \rho_0^*};$$

$$\tag{45}$$

$$\theta_1 = \frac{u_0}{\tilde{u}_0}; \quad \theta_2 = \frac{\tilde{\mu}\delta_0}{\mu\theta_1}; \quad \theta_3 = \frac{M}{\tilde{\rho}_0^*}(\tilde{c}_0 - \chi c_0.)$$

In expressions (40) and (45) x and y are the longitudinal and transverse coordinates, u, v and $\tilde{u}$, $\tilde{v}$ are the velocity components in the film and in the gas, h is the film thickness, $\tilde{c}$ is the concentration of the absorbing material in the gas, $\tilde{u}_0$ is the velocity of the potential flow in the gas, $h_0$ is the film thickness in the Nusselt theory, and $\mu$, $\tilde{\mu}$ and $v$, $\tilde{v}$ are the dynamic and kinematic viscosity coefficients of the fluid and of the gas.

The problems (41) and (42) can be solved accurately within an arbitrary function, which can be determined following solution of the problem (43), (44):

$$U = -\frac{3}{2}Y^2 + \left[3H + \theta_2 \left(\frac{\partial \tilde{U}}{\partial \tilde{Y}}\right)_{\tilde{Y}=0}\right]Y, \tag{46}$$

$$V = -\frac{1}{2}\left[3H' + \theta_2 \frac{d}{dX}\left(\frac{\partial \tilde{U}}{\partial \tilde{Y}}\right)_{\tilde{Y}=0}\right]Y^2;$$

$$H^3 = 1 - \frac{1}{2}\theta_2\left(\frac{\partial \tilde{U}}{\partial \tilde{Y}}\right)_{\tilde{Y}=0}H^2. \tag{47}$$

In (46) $\theta_2$ is a small parameter, i.e., U in the zeroth approximation in $\theta_2$ can be substituted into (46). This makes it possible to solve (43) within the zeroth approximation in $\theta_2$. For this purpose one must substitute into (43) U(X, H) within the zeroth approximation in the small parameter $\theta_2$, i.e.,

$$U(X, H) = \frac{3}{2}, \tag{48}$$

which is obtained from (46) and (47) by substituting $\theta_2 = 0$.

The velocity and concentration distributions in the gas can be found from (43) and (44) for the self-similar variables:

$$\tilde{U} = 0{,}5\tilde{\varepsilon}\Phi', \quad \tilde{V} = 0{,}5\tilde{\varepsilon}\frac{1}{\sqrt{X}}\left(\eta\Phi' - \Phi\right), \quad \tilde{C} = 1 - \Psi,$$

$$\Phi = \Phi(\eta), \quad \Psi = \Psi(\eta), \quad \eta = \frac{\tilde{Y}}{2\sqrt{X}}, \quad \tilde{\varepsilon} = \tilde{Sc}^{0,5}.$$

Thus, from (43) and (44) one obtains directly:

$$\Phi''' + \tilde{\varepsilon}^{-1}\Phi\Phi'' = 0, \quad \Psi'' + \tilde{\varepsilon}\Phi\Psi' = 0,$$

$$\Phi(0) = -\Theta_3\tilde{\varepsilon}^{-1}\Psi'(0), \quad \Phi'(0) = 3\Theta_1\tilde{\varepsilon}^{-1}, \quad \Phi'(\infty) = 2\tilde{\varepsilon}^{-1}, \tag{49}$$

$$\Psi(0) = 1, \quad \Psi(\infty) = 0.$$

The rate of mass transfer is determined by the Sherwood number, which can be obtained similarly to (28). In the new variables this expression acquire the form

$$\tilde{Sh} = \frac{\tilde{\rho}^*}{\tilde{\rho}_0^*}\tilde{Pe}^{0,5}\Psi'(0), \quad \tilde{Pe} = \frac{\tilde{u}_0 l}{\tilde{D}},$$

where $\Psi'(0)$ is the solution of problem (49). For practically interesting cases the parameters $\theta_1$ and $\theta_3$ in (39) are small, which makes it possible to use a perturbation method [12], as was done to obtain (33):

$$-\Psi'(0) = \frac{2}{\tilde{\varepsilon}\varphi_0} + \frac{3\theta_1}{\alpha\tilde{\varepsilon}\varphi_0^2} + \frac{2\Theta_3\varphi_3}{\tilde{\varepsilon}\varphi_0^3} + \theta_1^2\left(\frac{9\tilde{\varepsilon}\varphi_2}{4\varphi_0^2} + \right.$$

$$+ \frac{9}{2\alpha^2\tilde{\varepsilon}\varphi_0^3} - \frac{9\tilde{\varepsilon}^3\varphi_1}{16\alpha^2\varphi_0^2}\right) + \theta_3^2\left(\frac{4\varphi_3^2}{\tilde{\varepsilon}\varphi_0^5} - \frac{\varphi_{33}}{\tilde{\varepsilon}\varphi_0^4} - \frac{4\overline{\varphi}^{33}}{\tilde{\varepsilon}^3\varphi_0^4}\right) + \theta_1\theta_3\left(\frac{9\varphi_3}{\alpha\tilde{\varepsilon}\varphi_0^4} - \frac{3\varphi_{13}}{\alpha\tilde{\varepsilon}\varphi_0^3} - \frac{3\overline{\varphi}_{13}}{\alpha\tilde{\varepsilon}\varphi_0^3}\right). \tag{50}$$

Thus, one can also obtain the final expressions for the film velocity and thickness:

$$U = -\frac{3}{2}Y^2 + \left[3H + \frac{\alpha\theta_2}{\tilde{\varepsilon}\sqrt{X}}\right]Y,$$

$$V = -\frac{1}{2}\left[3H' - \frac{\alpha\theta_2}{2\tilde{\varepsilon}X\sqrt{X}}\right]Y^2, \tag{51}$$

where H is determined from:

$$H = 1 - \frac{\alpha\theta_2}{6\tilde{\varepsilon}\sqrt{X}}. \tag{52}$$

Several functions of the Schmidt number appear in (50): $\varphi_0 = \varphi_0(\tilde{Sc})$, $\varphi_1 = \varphi_1(\tilde{Sc})$, $\varphi_2 = \varphi_2(\tilde{Sc})$, $\varphi_3 = \varphi_3(\tilde{Sc})$, $\varphi_{33} = \varphi_{33}(\tilde{Sc})$, $\overline{\varphi}_{33} = \overline{\varphi}_{33}(\tilde{Sc})$, $\varphi_{13} = \varphi_{13}(\tilde{Sc})$, $\overline{\varphi}_{13} = \overline{\varphi}_{13}(\tilde{Sc})$.

The accuracy of the asymptotic theory results was established [11] by numerical solution of the problem (49).

A difference in the mass transfer rates in absorption and desorption processes of well dissolved gases was observed experimentally by a number of authors [16-19]. This has been always explained by the Marangoni effect, i.e., by the hydrodynamic effect resulting from induced secondary flow, whose velocity is tangential to the interphase surface. This flow is generated by the surface tension gradient resulting from the nonuniform temperature distribution and (or) concentration at the interphase surface.

A theory has been suggested in the present paper, explaining these experimental results by using the nonlinear effects generated as a result of induced secondary flows, whose velocity is normal to the phase boundary. The secondary flows are induced by the large mass fluxes.

Explanation of the mass transfer mechanism in cases of intense mass exchange requires experimental data on absorption and desorption and comparative analysis of these data by means of the theories of nonlinear mass transfer and the Marangoni effect. In this context it is also interesting to determine the effect of normal secondary flows (as a result of intense mass exchange) on hydrodynamic flow stability at the interphase surface.

Multicomponent Mass Exchange between Gas and a Fluid Film. A number of experimental studies are available in the literature [18, 20, 21], where as a result of parallel mass exchange in gas—fluid and fluid—fluid systems mass transfer of a single component leads to a change in mass transfer of another component. In these cases one usually observes an increase in the rate of mass transfer, which has been explained by the Marangoni effect, as it cannot be explained by means of linear mass transfer theory.

This effect has been treated [13] as multicomponent mass exchange when the concentration gradient of one of the components in the gas phase affects the flow hydrodynamics, i.e., as a nonlinear effect.

Let $\tilde{c}_i$ and $c_i$ ($i = 1,\ldots, n$) be, respectively, the component concentrations in the gas and in the fluid, whose mass transfer does not affect the flow hydrodynamics. The distribution of these concentrations is determined from

$$\tilde{c}_i = \chi_i c_{0i} + (\tilde{c}_{0i} - \chi_i c_{Ci})\,\tilde{C}_i,$$

$$c_i = c_{0i} + (\tilde{c}_{0i}/\chi_i - c_{Ci})\,C_i, \quad i = 1, \ldots, n, \tag{53}$$

where $\tilde{c}_{0i}$ and $c_{0i}$ are the initial concentrations of absorbing (desorbing) material in the gas and in the fluid.

It was shown in [13] that when mass exchange is limited by mass transfer in the gas phase, the concentration distribution can be obtained from the expressions $\tilde{C}_i = 1 - \Psi_i(\eta)$, $i = 1,\ldots, n$, where $\Psi_i$ are found by solving the problem

$$\Psi_i'' + \bar{a}_i \Phi \Psi_i' = 0, \quad \Psi_i(0) = 1, \quad \Psi_i(\infty) = 0, \quad i = 1, \ldots, n. \tag{54}$$

In (54) $\bar{a}_i = \varepsilon_i^2/\tilde{\varepsilon}$, while $\Phi(\eta)$ takes into account nonlinear mass transfer in the gas phase and is the solution of Eq. (49). The solution of problem (54) was found in [13] by an asymptotic method, while for $\Psi_i'(0)$ one obtains an expression similar to (50):

$$-\Psi_i'(0) = \frac{2}{\tilde{\varepsilon}\varphi_{0i}} + \theta_1 \frac{3}{\alpha\tilde{\varepsilon}\varphi_{0i}^2} + \theta_3 \frac{2\bar{a}_i\varphi_{3i}}{\tilde{\varepsilon}^2\varphi_c\varphi_{0i}^2} + \theta_1^2\left(\frac{9\bar{a}_i\varphi_{2i}}{4\varphi_{0i}^2} + \frac{9}{2\alpha^2\tilde{\varepsilon}\varphi_{0i}^3} - \frac{9\bar{a}_i^2\tilde{\varepsilon}\varphi_{1i}}{16\alpha^2\varphi_{0i}^2}\right) +$$

$$+ \theta_3^2\left(\frac{2\bar{a}_i\varphi_3\varphi_{3i}}{\tilde{\varepsilon}^2\varphi_0^3\varphi_{0i}^2} + \frac{2\bar{a}_i^2\varphi_{3i}^2}{\tilde{\varepsilon}^3\varphi_0^2\varphi_{0i}^3} - \frac{\bar{a}_i^2\varphi_{33i}}{\tilde{\varepsilon}^3\varphi_0^2\varphi_{0i}^2} - \frac{4\bar{a}_i\bar{\varphi}_{33i}}{\tilde{\varepsilon}^4\varphi_0^2\varphi_{0i}^2}\right) + \tag{55}$$

$$+ \theta_1\theta_3 \frac{3\bar{a}_i}{\alpha\tilde{\varepsilon}^2\varphi_0\varphi_{0i}^2}\left[\varphi_{3i}\left(1 + \frac{\varphi_{0i}}{\varphi_0}\right) + \varphi_{13i}\bar{\varphi}_{13i}\right], \quad i = 1, \ldots, n,$$

where

$$\varphi_{0i} = \varphi_0(\tilde{Sc}_i), \quad \varphi_{1i} = \varphi_1(\tilde{Sc}_i), \quad \varphi_{2i} = \varphi_2(\tilde{Sc}_i), \quad \varphi_{3i} = \varphi_3(\tilde{Sc}_i),$$

$$\varphi_{33i} = \varphi_{33}(\tilde{Sc}_i), \quad \bar{\varphi}_{33i} = \bar{\varphi}_{33}(\tilde{Sc}_i), \quad \varphi_{13i} = \varphi_{13}(\tilde{Sc}_i),$$

$$\bar{\varphi}_{13i} = \bar{\varphi}_{13}(Sc_i), \quad i = 1, \ldots, n.$$

Comparison of $\Psi_i'(0)$ from (55) with $\Psi'(0)$ from (50) shows that they differ little due to the nonsubstantial difference between the quantities $\tilde{\varepsilon}_i$ and $\tilde{\varepsilon}$. It hence follows that in

cases of multicomponent mass transfer, when mass transfer of one of the components is nonlinear due to the large concentration gradient, the mass transfer coefficients for all components have similar values.

Expression (55) makes it possible to calculate [13] the Sherwood number when mass exchange is limited by mass transfer in the gas:

$$\tilde{Sh}_i = \frac{\tilde{K}_i l}{\tilde{D}_i} = \tilde{Pe}_i^{0,5} \Psi_i'(0).$$

It was shown in [13] that when mass exchange is limited by mass transfer in the film, one can write for the concentration distributions:

$$Fo_i = \frac{D_i l}{u_0 h_0^2}, \quad Y_i = \frac{H - Y}{\sqrt{Fo_i}}, \quad i = 1, \ldots, n. \tag{56}$$

where U, V, and H are determined from (51) and (52), $C_i$ are determined from (53), and Fo and $Y_i$ are:

$$U\frac{\partial C_i}{\partial X} + \frac{H'U - V}{\sqrt{Fo_i}} \frac{\partial C_i}{\partial Y_i} = \frac{\partial^2 C_i}{\partial Y_i^2}; \quad X = 0, \quad C_i = 0;$$

$$Y_i = 0, \quad C_i = 1; \quad Y_i = \infty, \quad C_i = 0, \quad i = 1, \ldots, n,$$

Denoting $\theta_{1i} = Fo_i$, $i = 1,\ldots, n$, within the first approximation in the small parameters $\theta_{1i}$ and $\theta_2$ ($i = 1,\ldots, n$) Eq. (56) acquires the form

$$\left[\frac{3}{2}(1 - \theta_{1i}Y_i^2) + \theta_2 \frac{\alpha}{2\tilde{\varepsilon}\sqrt{\bar{X}}}\right]\frac{\partial C_i}{\partial X} + \theta_2 \frac{\alpha Y_i}{4\tilde{\varepsilon}X\sqrt{\bar{X}}} \frac{\partial C_i}{\partial Y_i} = \frac{\partial^2 C_i}{\partial Y_i^2}, \quad i = 1, \ldots, n.$$

The concentration distribution can be found in the form

$$C_i = C_{0i} + \theta_{1i}C_{1i} + \theta_2 C_{2i} + \ldots, \quad i = 1, \ldots, n.$$

Thus [13], within the zeroth approximation one obtains directly

$$C_{0i} = \operatorname{erfc}\xi_i, \quad \xi_i = \left(\frac{3Y_i^2}{8X}\right)^{0,5}, \quad i = 1, \ldots, n, \tag{57}$$

and in the first approximation (by means of the Green's function):

$$C_{1i} = \frac{1}{\sqrt{6\pi}}\left(Y_i\sqrt{\bar{X}} + \frac{Y_i^3}{2\sqrt{\bar{X}}}\right)\exp\left(-\frac{3Y_i^2}{8X}\right), \quad C_{2i} \equiv 0, \quad i = 1, \ldots, n. \tag{58}$$

From (57) and (58) one can also determine the Sherwood number, when multicomponent mass exchange is limited by mass transfer in the fluid:

$$Sh_i = \frac{K_i l}{D_i} = Pe_i^{0,5}\int_0^1 \left(\frac{\partial C_i}{\partial Y_i}\right)_{Y_i=0} dX =$$

$$= -\left(\frac{6Pe_i}{\pi}\right)^{0,5}\left(1 - \frac{Fo_i}{9}\right). \tag{59}$$

It is seen from (59) that within the zeroth approximation in the small parameter $\theta_0\theta_3$ nonlinear mass transfer in the gas phase does not affect multicomponent mass transfer in a fluid film. It has been shown in [13] that for very large concentration gradients one must also take into account the first approximation in the small parameter $\theta_0\theta_3$.

The basic conclusions from the asymptotic theory results of nonlinear mass transfer in systems with intense mass exchange can be reduced to the following:

1. Intense mass exchange (as a result of large concentration gradients) induces secondary flows, affecting the coefficients of nonlinear mass transfer, multicomponent mass transfer, and heat transfer.

2. The direction of mass flux during intense mass exchange affects heat and mass transfer.

3. When the mass flux is directed from the bulk of the phase to the interphase surface, an increase in the concentration gradient leads to an increase in diffusion mass transfer, multicomponent mass transfer, and heat transfer.

4. When the mass flux is directed from the interphase surface to the bulk of the phase, an increase in the concentration gradient leads to a decrease in diffusion mass transfer, multicomponent mass transfer, and heat transfer.

5. Induced secondary flows at the phase separation boundary affect the hydrodynamics of a laminar boundary layer during both blowing in and suction, i.e., intense mass exchange can affect the hydrodynamic flow stability at the interphase boundary and can be a cause for generation of turbulence.

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