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On the mechanism and kinetics of the transport processes in systems with intensive interphase mass transfer.
1. Heat and mass transfer

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Abstract

A theoretical analysis of the mechanism and the kinetics of non-stationary absorption is proposed in an immobile liquid at big concentration gradients, when the mass transfer may be a result of a natural convection, non-linear mass transfer and the Marangoni effect. It is shown that the Marangoni effect is negligible under these conditions and the flow rate is limited by the non-linear mass transfer. The rate of the mass transfer is determined. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Mechanism; Kinetics; Heat and mass transfer; Non-linear

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1. Introduction

Experimental studies of systems with intensive mass transfer show, in many cases, serious deviations from the linear theory of mass transfer, which indicates independence of the velocity field from the fields of concentration and temperature. These effects are usually considered as Marangoni effects [1–3] and are explained with the occurrence of tangential secondary flow on the phase boundary, caused by the surface tension gradient as a result of surface gradients of concentration or (and) temperature on the mass transfer surface.

Theoretical studies of systems with intensive interphase mass transfer as a result of big concentration gradients showed [4–8] that these gradients induce normal secondary flows on the phase boundary. On this basis, the non-linear theory of mass transfer [9,10] was built, that also explains the satisfactory deviations of experimental results from the linear theory of mass transfer.

The above mentioned results illustrate the possibility for the simultaneous or independent existence of two mechanisms of heat mass transfer in systems with intensive mass transfer. This makes it necessary to define the conditions for occurrence of the effects of Marangoni and the non-linear mass transfer, which will make possible the creation of adequate models of the chemical engineering processes, under conditions of intensive interphase mass transfer between two phases.

The linear analysis of the hydrodynamic stability in systems with intensive interphase mass transfer showed [11–14] that the normal and the tangential components of the velocity on the phase boundary influences the hydrodynamic stability of flows in the boundary layer, and the influence of the normal component is significantly greater. This suggests that

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Nomenclature

c	concentration
c^*	equilibrium concentration
D	diffusivity
g	earth gravity
i	mass flow
J	absorption rate
k	mass transfer coefficient
l	depth of velocity change
p	pressure
q	thermal effect of the chemical reaction
Q	quantity of the absorbed substance
r	radial coordinate
r_0	radius of the liquid column
t	time coordinate
t_0	time for process performance
v_z	axial velocity component
v_r	radial velocity component
v_φ	angle velocity component
z	axial coordinate
Sh	Sherwood number

Greek symbols

β	coefficient of thermal expansion
θ	temperature
θ_0	initial temperature
λ	heat conductivity
μ	viscosity
π	$= 3.14$
ρ	density
ρ_0	solvent density
σ	surface tension
φ	angle coordinate

a considerable difference is possible in the intensity of the effects of Marangoni and the non-linear mass transfer.

The comparative analysis of these two effects was made in the cases of mass transfer between two phases (gas–liquid and liquid–liquid) [15,16], when substance from the first phase goes to the second phase and reacts chemically with it. The big concentration gradients of the transferred substance create a normal secondary flow on the phase boundary. On the other hand, the thermal effect of the chemical reaction creates a gradient of the surface tension as a result of the temperature non-homogeneity at the phase interface, i.e. tangential secondary flow on the phase boundary.

The obtained theoretical results showed [15,16] that the Marangoni effect is negligible than the effect of the non-linear mass transfer, i.e. the kinetics of mass transfer and the hydrodynamic stability do not depend on the surface tension gradient, caused by the temperature non-homogeneity at the phase interface as a result of the thermal effect of the chemical reaction. It should be noted, however, that the parameter, representing the Marangoni effect, increases with the decrease of the characteristic velocity in the second phase. The obtained results [16], when this phase is immovable, showed that under these conditions, the Marangoni effect is also considerably smaller.

The above mentioned investigations showed that the occurrence of the Marangoni effect may be expected in the limit case of mass transfer between two immovable phases in the absorption of pure gases in an immovable liquid. Under these conditions, it is possible for three processes to take place: natural convection, non-linear mass transfer and Marangoni effect.

Actually, these three effects may have a dual influence on the mechanism and kinetics of heat mass transfer in systems with intensive interphase mass transfer. The first influence is relatively weak and is a result of the secondary flows, that change the velocity field. However, this may lead to changes in the hydrodynamic stability and, therefore, to the creation of self-organizing dissipative structures, having the form of stable periodic flows, that have a very strong influence on the mechanics and the kinetics of mass transfer. These two types of influences will be discussed consequently in the two parts of this paper.

2. Mathematical model

Let us consider a vertical tube with a radius r_0, in which an immovable liquid (H_2O) contacts an immovable gas (CO_2, SO_2, NH_3). The gas is absorbed in the liquid, and the process is accompanied by a thermal effect. As a result, several effects in the liquid may occur, having the form of secondary flows due to the big concentration gradients on the phase boundary (non-linear mass transfer), the density gradient in volume (natural convection) and the surface tension gradient (Marangoni effect).

The mathematical description of this process will be done under the approximation of Oberbeck–Bousinesq equations [17–19], where the influence of the density gradient [20,21], the concentration gradient [9,10] and the surface tension gradient [22–24] will be considered. In this way, in cylindrical coordinates, the problem has the form:

$$\rho\left(\frac{\partial v_z}{\partial t}+v_z\frac{\partial v_z}{\partial z}+v_r\frac{\partial v_z}{\partial r}+\frac{v_\varphi}{r}\frac{\partial v_z}{\partial \varphi}\right)$$
$$=-\frac{\partial p}{\partial z}+\mu\left(\frac{\partial^2 v_z}{\partial z^2}+\frac{1}{r}\frac{\partial v_z}{\partial r}+\frac{\partial^2 v_z}{\partial r^2}+\frac{1}{r^2}\frac{\partial^2 v_z}{\partial \varphi^2}\right)$$
$$+g(\rho-\rho_0), \tag{1}$$

$$\rho\left(\frac{\partial v_r}{\partial t}+v_z\frac{\partial v_r}{\partial z}+v_r\frac{\partial v_r}{\partial r}+\frac{v_\varphi}{r}\frac{\partial v_r}{\partial \varphi}-\frac{v_\varphi^2}{r}\right)$$
$$=-\frac{\partial p}{\partial r}+\mu\left(\frac{\partial^2 v_r}{\partial z^2}+\frac{1}{r}\frac{\partial v_r}{\partial r}+\frac{\partial^2 v_r}{\partial r^2}-\frac{v_r}{r^2}+\frac{1}{r^2}\frac{\partial^2 v_r}{\partial \varphi^2}\right.$$
$$\left.-\frac{2}{r^2}\frac{\partial v_\varphi}{\partial \varphi}\right), \tag{2}$$

$$\rho\left(\frac{\partial v_\varphi}{\partial t}+v_z\frac{\partial v_\varphi}{\partial z}+v_r\frac{\partial v_\varphi}{\partial r}+\frac{v_\varphi}{r}\frac{\partial v_\varphi}{\partial \varphi}+\frac{v_r v_\varphi}{r}\right)$$
$$=-\frac{1}{r}\frac{\partial p}{\partial \varphi}+\mu\left(\frac{\partial^2 v_\varphi}{\partial z^2}+\frac{1}{r}\frac{\partial v_\varphi}{\partial r}+\frac{\partial^2 v_\varphi}{\partial r^2}-\frac{v_\varphi}{r^2}\right.$$
$$\left.+\frac{1}{r^2}\frac{\partial^2 v_\varphi}{\partial \varphi^2}+\frac{2}{r^2}\frac{\partial v_r}{\partial \varphi}\right), \tag{3}$$

$$\frac{\partial \rho}{\partial t}+\frac{\partial(\rho v_z)}{\partial z}+\frac{\partial(\rho v_r)}{\partial r}+\frac{\rho v_r}{r}+\frac{1}{r}\frac{\partial(\rho v_\varphi)}{\partial \varphi}=0, \tag{4}$$

$$\frac{\partial c}{\partial t}+v_z\frac{\partial c}{\partial z}+v_r\frac{\partial c}{\partial r}+\frac{v_\varphi}{r}\frac{\partial c}{\partial \varphi}$$
$$=D\left(\frac{\partial^2 c}{\partial z^2}+\frac{1}{r}\frac{\partial c}{\partial r}+\frac{\partial^2 c}{\partial r^2}+\frac{1}{r^2}\frac{\partial^2 c}{\partial \varphi^2}\right), \tag{5}$$

$$\rho c_p\left(\frac{\partial \theta}{\partial t}+v_z\frac{\partial \theta}{\partial z}+v_r\frac{\partial \theta}{\partial r}+\frac{v_\varphi}{r}\frac{\partial \theta}{\partial r}\right)$$
$$=\lambda\left(\frac{\partial^2 \theta}{\partial z^2}+\frac{1}{r}\frac{\partial \theta}{\partial r}+\frac{\partial^2 \theta}{\partial r^2}+\frac{1}{r^2}\frac{\partial^2 \theta}{\partial \varphi^2}\right), \tag{6}$$

$$\rho=\rho_0\left[1+\frac{c}{\rho_0}-\beta(\theta-\theta_0)\right]; \tag{7}$$

with the corresponding initial and boundary conditions:

$$t=0,\quad v_z=v_r=v_\varphi=c=0,\quad \theta=\theta_0; \tag{8}$$

$$\begin{aligned}&z=0,\quad v_z=-\frac{D}{\rho_0}\frac{\partial c}{\partial z},\\ &\mu\left(\frac{\partial v_r}{\partial z}+\frac{\partial v_z}{\partial r}\right)=\frac{\partial \sigma}{\partial r}=\frac{\partial \sigma}{\partial \theta}\frac{\partial \theta}{\partial r},\mu\left(\frac{\partial v_\varphi}{\partial z}+\frac{1}{r}\frac{\partial v_z}{\partial \varphi}\right)\\ &=\frac{1}{r}\frac{\partial \sigma}{\partial \varphi}=\frac{1}{r}\frac{\partial \sigma}{\partial \theta}\frac{\partial \theta}{\partial \varphi},\quad c=c^*,\\ &\lambda\frac{\partial \theta}{\partial z}=qD\frac{\partial c}{\partial z};\end{aligned} \tag{9}$$

$$z\to\infty,\quad v_z=v_r=v_\varphi=c=0,\quad \theta=\theta_0; \tag{10}$$

$$r=0,\quad v_z, v_r, v_\varphi, c, \theta=\text{finite}; \tag{11}$$

$$r=r_0,\quad v_z=v_r=v_\varphi=0,\quad \frac{\partial c}{\partial r}=\frac{\partial \theta}{\partial r}=0. \tag{12}$$

We will assume that along the angle φ processes are periodical with a period 2π.

Eq. (1) refers to the natural convection by means of the Archimedian force $g(\rho-\rho_0)$. Eq. (9) takes into consideration the large concentration gradients through the connection between the velocity v_z and the concentration gradient $\partial c/\partial z$ and the surface tension gradient (σ) by means of its components on r and φ and their connection with the tangential components of the tension tensor at the surface $z=0$. Eq. (12) gives the conditions at the solid surface of the tube.

3. Dimensionless variables

The problem Eqs. (1)–(12) may be presented in a dimensionless form if the known scales of the physical independent and dependent variables are used. These characteristic scales should be selected in such a way that the values of the dimensionless variables and parameters are not greater in order, than unity.

The characteristic scales may be set in advance and for the discussed example they are of the following order for the time, radial coordinate, concentration and temperature:

$$\begin{aligned}&t_0\sim 10^2\ \text{s},\quad r_0\sim 10^{-2}\ \text{m},\quad c^*\sim(1\text{–}100)\ \text{kg/m}^3\\ &\text{(for different gases)},\quad \theta_0\sim 10\ {}^\circ\text{C}.\end{aligned} \tag{13}$$

The characteristic scales will be used in all cases when the character scales are not known in advance, and will be determined as a result of the quality analysis of the model Eqs. (1)–(12). If we mark the characteristic scale of the velocity along the z axis by u_0, then the scales of the other components of velocity are determined in a way that the equation of continuity (4) is satisfied in dimensionless variables, and for a characteristic scale of pressure, the dynamic pressure $\rho_0 u_0^2$ is used.

The difference in the orders of μ, D and λ shows that the basic change in the velocity, concentration and temperature will be reached at a different depth of the water column. These characteristic depths for the velocity (l), concentration (δ) and temperature (h) will be determined by the quality analysis of Eqs. (1)–(6).

Using the above mentioned considerations, the following dimensionless variables are obtained:

$$
\begin{aligned}
&t = t_0 T, \quad z = lZ_1 = \delta Z_2 = hZ_3, \quad r = r_0 R, \quad \varphi = 2\pi\Phi,\\
&\quad p = \rho_0 u_0^2 P,\\
&v_z(t, z, r, \varphi) = u_0 V_z(T, Z_1, R, \Phi) = u_0 \tilde{V}_z(T, Z_2, R, \Phi)\\
&\qquad = u_0 \tilde{\tilde{V}}_z(T, Z_3, R, \Phi),\\
&v_r(t, z, r, \varphi) = \frac{u_0 r_0}{l} V_r(T, Z_1, R, \Phi)\\
&\qquad = \frac{u_0 r_0}{l} \tilde{V}_r(T, Z_2, R, \Phi)\\
&\qquad = \frac{u_0 r_0}{l} \tilde{\tilde{V}}_r(T, Z_3, R, \Phi),\\
&v_\varphi(t, z, r, \varphi) = 2\pi \frac{u_0 r_0}{l} V_\varphi(T, Z_1, R, \Phi)\\
&\qquad = 2\pi \frac{u_0 r_0}{l} \tilde{V}_\varphi(T, Z_2, R, \Phi)\\
&\qquad = 2\pi \frac{u_0 r_0}{l} \tilde{\tilde{V}}_\varphi(T, Z_3, R, \Phi),\\
&c(t, z, r, \varphi) = c^* C(T, Z_1, R, \Phi) = c^* \tilde{C}(T, Z_2, R, \Phi)\\
&\qquad = c^* \tilde{\tilde{C}}(T, Z_1, R, \Phi),\\
&\theta(t, z, r, \varphi) = \theta_0 \Theta(T, Z_1, R, \Phi)\\
&\qquad = \theta_0 \tilde{\Theta}(T, Z_2, R, \Phi)\\
&\qquad = \theta_0 \tilde{\tilde{\Theta}}(T, Z_3, R, \Phi). \qquad (14)
\end{aligned}
$$

The introduction of Eq. (14) into Eqs. (1)–(12) converts the problem into a dimensionless form, where the dimension parameters are grouped in such a way that the dimensionless parameters are obtained in the order of unity, lower than unity (10^{-1}) and much lower than unity ($\leq 10^{-2}$):

$$
\begin{aligned}
&\left[1 + \frac{c^*}{\rho_0} C - \beta\theta_0(\Theta - 1)\right]\\
&\quad \left[\frac{u_0\rho_0}{g t_0 c^*}\frac{\partial V_z}{\partial T} + \frac{u_0^2\rho_0}{glc^*}\left(V_z \frac{\partial V_z}{\partial Z_1} + V_r \frac{\partial V_z}{\partial R} + \frac{V_\varphi}{R}\frac{\partial V_z}{\partial \Phi}\right)\right]\\
&\quad = -\frac{u_0^2\rho_0}{glc^*}\frac{\partial P}{\partial Z_1} + \frac{\mu u_0}{gl^2c^*}\left[\frac{\partial^2 V_z}{\partial Z_1^2} + \frac{l^2}{r_0^2}\left(\frac{1}{R}\frac{\partial V_z}{\partial R}\right.\right.\\
&\quad \left.\left. + \frac{\partial^2 V_z}{\partial R^2} + \frac{1}{4\pi^2}\frac{1}{R^2}\frac{\partial^2 V_z}{\partial \Phi^2}\right)\right] + C - \frac{\rho_0\beta\theta_0}{c^*}(\Theta - 1), \quad (15)
\end{aligned}
$$

$$
\begin{aligned}
&\left[1 + \frac{c^*}{\rho_0} C - \beta\theta_0(\Theta - 1)\right]\left[\frac{u_0\rho_0}{g t_0 c^*}\frac{\partial V_r}{\partial T} + \frac{u_0^2\rho_0}{glc^*}\right.\\
&\quad \left.\times \left(V_z \frac{\partial V_r}{\partial Z_1} + V_r \frac{\partial V_r}{\partial R} + \frac{v_\varphi}{R}\frac{\partial V_r}{\partial \Phi} - 4\pi^2 \frac{V_\varphi^2}{R}\right)\right]\\
&\quad = -\frac{l^2}{r_0^2}\frac{u_0^2\rho_0}{glc^*}\frac{\partial P}{\partial R} + \frac{\mu u_0}{gl^2c^*}\left[\frac{\partial^2 V_r}{\partial Z_1^2} + \frac{l^2}{r_0^2}\left(\frac{1}{R}\frac{\partial V_r}{\partial R}\right.\right.\\
&\quad \left.\left. + \frac{\partial^2 V_r}{\partial R^2} - \frac{V_r}{R^2} + \frac{1}{4\pi^2}\frac{\partial^2 V_r}{\partial \Phi^2} - \frac{2}{R}\frac{\partial V_\varphi}{\partial \Phi}\right)\right], \qquad (16)
\end{aligned}
$$

$$
\begin{aligned}
&\left[1 + \frac{c^*}{\rho_0} C - \beta\theta_0(\Theta - 1)\right]\left[\frac{u_0\rho_0}{g t_0 c^*}\frac{\partial V_\varphi}{\partial T} + \frac{u_0^2\rho_0}{glc^*}\right.\\
&\quad \left.\times \left(V_z \frac{\partial V_\varphi}{\partial Z_1} + V_r \frac{\partial V_\varphi}{\partial R} + \frac{V_\varphi}{R}\frac{\partial V_\varphi}{\partial \Phi} + \frac{V_r V_\varphi}{R}\right)\right]\\
&\quad = -\frac{l^2}{r_0^2}\frac{u_0^2\rho_0}{glc^*}\frac{1}{R}\frac{\partial P}{\partial \Phi} + \frac{\mu u_0}{gl^2c^*}\\
&\quad \times \left[\frac{\partial^2 V_\varphi}{\partial Z_1^2} + \frac{l^2}{r_0^2}\left(\frac{1}{R}\frac{\partial V_\varphi}{\partial R} + \frac{\partial^2 V_\varphi}{\partial R^2}\right.\right.\\
&\quad \left.\left. - \frac{V_\varphi}{R^2} + \frac{1}{4\pi^2}\frac{1}{R^2}\frac{\partial^2 V_\varphi}{\partial \Phi^2} + \frac{1}{2\pi^2}\frac{1}{R^2}\frac{\partial V_r}{\partial \Phi}\right)\right], \qquad (17)
\end{aligned}
$$

$$
\begin{aligned}
&\frac{lc^*}{\rho_0 u_0 t_0}\frac{\partial C}{\partial T} - \frac{\beta\theta_0 l}{t_0 u_0}\frac{\partial \Theta}{\partial T} + \left(\frac{\partial V_z}{\partial Z_1} + \frac{V_r}{R} + \frac{\partial V_r}{\partial R}\right.\\
&\quad \left. + \frac{1}{R}\frac{\partial V_\varphi}{\partial \Phi}\right)\left[1 + \frac{c^*}{\rho_0} C - \beta\theta_0(\Theta - 1)\right]\\
&\quad + V_z\left(\frac{c^*}{\rho_0}\frac{\partial C}{\partial Z_1} - \beta\theta_0\frac{\partial \Theta}{\partial Z_1}\right) + V_r\left(\frac{c^*}{\rho_0}\frac{\partial C}{\partial R}\right.\\
&\quad \left. - \beta\theta_0\frac{\partial \Theta}{\partial R}\right) + \frac{V_\varphi}{R}\left(\frac{c^*}{\rho_0}\frac{\partial C}{\partial \Phi} - \beta\theta_0\frac{\partial \Theta}{\partial \Phi}\right)\\
&\quad = 0, \qquad (18)
\end{aligned}
$$

$$\frac{\partial \tilde{C}}{\partial T}+\frac{u_0 t_0}{\delta}\left(\tilde{V}_z\frac{\partial \tilde{C}}{\partial Z_2}+\tilde{V}_r\frac{\partial \tilde{C}}{\partial R}+\frac{\tilde{V}_r}{R}\frac{\partial \tilde{C}}{\partial \Phi}\right)$$

$$=\frac{Dt_0}{\delta^2}\left[\frac{\partial^2 \tilde{C}}{\partial Z_2^2}+\frac{\delta^2}{r_0^2}\left(\frac{1}{R}\frac{\partial \tilde{C}}{\partial R}+\frac{\partial^2 \tilde{C}}{\partial R^2}\right.\right.$$

$$\left.\left.+\frac{1}{4\pi^2}\frac{1}{R^2}\frac{\partial^2 \tilde{C}}{\partial \Phi^2}\right)\right], \tag{19}$$

$$\left[1+\frac{c^*}{\rho_0}\tilde{\tilde{C}}-\beta\theta_0\left(\tilde{\tilde{\Theta}}-1\right)\right]\left[\frac{\partial \tilde{\tilde{\Theta}}}{\partial T}+\frac{u_0 t_0}{h}\left(\tilde{\tilde{V}}_z\frac{\partial \tilde{\tilde{\Theta}}}{\partial Z_3}\right.\right.$$

$$\left.\left.+\tilde{\tilde{V}}_r\frac{\partial \tilde{\tilde{\Theta}}}{\partial R}+\frac{\tilde{\tilde{V}}_\varphi}{R}\frac{\partial \tilde{\tilde{\Theta}}}{\partial \Phi}\right)\right]$$

$$=\frac{at_0}{h^2}\left[\frac{\partial^2 \tilde{\tilde{\Theta}}}{\partial Z_3^2}+\frac{h^2}{r_0^2}\left(\frac{1}{R}\frac{\partial \tilde{\tilde{\Theta}}}{\partial R}+\frac{\partial^2 \tilde{\tilde{\Theta}}}{\partial R^2}\right.\right.$$

$$\left.\left.+\frac{1}{4\pi^2}\frac{1}{R^2}\frac{\partial^2 \tilde{\tilde{\Theta}}}{\partial \Phi^2}\right)\right]; \tag{20}$$

$$T=0, \quad V_z=V_r=V_\varphi=\tilde{C}=0, \quad \tilde{\tilde{\Theta}}=1; \tag{21}$$

$$Z_1=Z_2=Z_3=0, \quad V_z=-\frac{Dc^*}{u_0\rho_0\delta}\frac{\partial \tilde{C}}{\partial Z_2},$$

$$\frac{\partial V_r}{\partial Z_1}+\frac{l^2}{r_0^2}\frac{\partial V_z}{\partial R}=\frac{\partial \sigma}{\partial \theta}\frac{\theta_0}{\mu u_0}\frac{l^2}{r_0^2}\frac{\partial \tilde{\tilde{\Theta}}}{\partial R},$$

$$\frac{\partial V_\varphi}{\partial Z_1}+\frac{l^2}{4\pi^2 r_0^2}\frac{1}{R}\frac{\partial V_z}{\partial \Phi}=\frac{\partial \sigma}{\partial \theta}\frac{\theta_0}{\mu u_0}\frac{l^2}{4\pi^2 r_0^2}\frac{1}{R}\frac{\partial \tilde{\tilde{\Theta}}}{\partial \Phi},$$

$$\tilde{C}=1, \quad \frac{\partial \tilde{\tilde{\Theta}}}{\partial Z_3}=\frac{qDhc^*}{\delta\lambda\theta_0}\left(1+\frac{c^*}{\rho_0}\right)\frac{\partial \tilde{C}}{\partial Z_2}; \tag{22}$$

$$Z_1=Z_2=Z_3\rightarrow\infty, \quad V_z=V_r=V_\varphi=\tilde{C}=0, \quad \tilde{\tilde{\Theta}}=1; \tag{23}$$

$$R=0, \quad V_z, V_r, V_\varphi, \tilde{P}, \tilde{C}, \tilde{\Theta}-\text{finite}; \tag{24}$$

$$R=1, \quad V_z=V_r=V_\varphi=0, \quad \frac{\partial \tilde{C}}{\partial R}=\frac{\partial \tilde{\tilde{\Theta}}}{\partial R}=0. \tag{25}$$

Along the Φ coordinate, the functions are periodical, with a period 1.

4. Qualitative analysis

The qualitative analysis of the model Eqs. (15)–(25) begins with the determination of the characteristic scales. The discussed process is a result of the absorption of the gas and its thermal effect, i.e. the field of concentration and temperature is determined by the diffusion and the heat transfer. From here, it directly follows that the parameters in front of the Laplacians in Eqs. (19) and (20) should be of the order of unity;

$$\frac{Dt_0}{\delta^2}=1, \quad \frac{at_0}{h^2}=1, \tag{26}$$

which makes, possible to determine the characteristic linear scales of δ and h:

$$\delta=\sqrt{Dt_0}\sim 10^{-4}\ \text{m}, \quad h=\sqrt{at_0}\sim 10^{-3}\ \text{m}. \tag{27}$$

As a result of the diffusion and the heat transfer, conditions for a natural convection arise, whose influence on the velocity field appears when the parameter in front of the Laplacians in Eqs. (15)–(17) is of the order of unity (viscose flow):

$$\frac{\mu u_0}{gl^2c^*}=1. \tag{28}$$

From Eq. (28), it is obvious that it is not necessary to determine the characteristic velocity of the flow, which depends on the limitation process. Natural convection can not limit the velocity, because at diffusion and heat transfer in a stagnant liquid [17–19] there is a mechanical equilibrium ($u_0=0$) and the natural convection is a result of the loss of stability.

The large concentration gradients induce a secondary flow, whose characteristic velocity may be determined, if the parameter of the non-linear mass transfer in Eq. (22) is of the order of unity:

$$\frac{Dc^*}{v_0\rho_0\delta}=1. \tag{29}$$

In this way, the characteristic scales l and u_0 are obtained directly from Eqs. (28) and (29):

$$u_0=\frac{c^*}{\rho_0}\sqrt{\frac{D}{t_0}}\sim 10^{-7}\ \text{m/s}, \qquad l=\sqrt{\frac{\mu}{\rho_0 g}\sqrt{\frac{D}{t_0}}}\sim 10^{-7}\ \text{m}. \tag{30}$$

The attempt to define the characteristic velocity from the Marangoni effect, i.e. from the condition

$$\frac{\partial\sigma}{\partial\theta}\frac{\theta_0}{\mu u_0}\frac{l^2}{r_0^2}=1 \tag{31}$$

is not successful, because there is no value of u_0 that can satisfy, at the same time, Eqs. (28) and (31). The cases when the characteristic radius is very small, are exceptions:

$$r_0=\sqrt{\frac{\partial\sigma}{\partial\theta}\frac{\theta_0}{\rho_0\varepsilon g}}\sim 10^{-3}\ \mathrm{m}. \tag{32}$$

The characteristic scales in Eqs. (27) and (30), determined in this way, allow the determination of the order of the parameters in Eqs. (15)–(22):

$$\begin{gathered}\varepsilon=\frac{c^*}{\rho_0}\sim 10^{-1},\quad \frac{u_0\rho_0}{gt_0c^*}\sim 10^{-9},\quad \frac{u_0^2\rho_0}{glc^*}\sim 10^{-7},\quad \frac{l^2}{r_0^2}\sim 10^{-10},\\ \frac{lc^*}{\rho_0u_0t_0}\sim 10^{-3},\quad \frac{u_0t_0}{\delta}=\varepsilon\sim 10^{-1},\quad \frac{\delta^2}{r_0^2}\sim 10^{-4},\quad \frac{h^2}{r_0^2}\sim 10^{-2},\\ \frac{u_0t_0}{h}\sim 10^{-2},\quad \frac{\partial\sigma}{\partial\theta}\frac{\theta_0}{\mu u_0}\frac{l^2}{r_0^2}\sim 10^{-3},\quad \alpha=\frac{qDh\rho_0}{\delta\lambda\theta_0}\sim 1,\\ \beta\theta_0\sim 10^{-3},\quad \frac{\partial\sigma}{\partial\theta}\sim 10^{-5}\ \mathrm{kg/m^2\ ^\circ C},\quad \frac{\rho_0\beta\theta_0}{c^*}\sim 10^{-2},\quad \frac{\beta\theta_0 l\rho_0}{t_0\mu}\sim 10^{-5}.\end{gathered} \tag{33}$$

The dimensionless parameters in the model (Eqs. (15)–(25)), determined in this way, are not greater in order than unity, which is a necessary condition for the authenticity of the result from the qualitative analysis.

From Eq. (33), evidently, the parameter of the Marangoni effect (31) is of the order of 10^{-3} and does not influence the velocity, concentration and temperature field. Analogous results are achieved [22–24] in the analysis of the simultaneous influence of the natural convection and the Marangoni effect in the cases of a fixed thickness of the water column, greater than 10^{-3} m. This result shows that under conditions of an intensive mass transfer, the natural convection and the nonlinear mass transfer lead to a flow, whose characteristic velocity is of two orders greater than the velocity, at which the Marangoni effect may occur.

Another significant result of Eq. (33) is that $\beta\theta_0 << (c^*/\rho_0) < 1$, i.e. the temperature change does not influence the density ρ, and further we will assume $\beta=0$.

The different effects in the complex process take place when their corresponding parameters are $> 10^{-2}$, i.e. the problem ((15)–(25)) may be expressed as a zero-order approximation regarding the parameters of order lower than 10^{-2} (and smaller). In this way, from Eqs. (15)–(25) and (33), it follows that:

$$\frac{\partial^2 V_z}{\partial Z_1^2}+C=0, \tag{34}$$

$$\frac{\partial^2 V_r}{\partial Z_1^2}=0, \tag{35}$$

$$\frac{\partial^2 V_\varphi}{\partial Z_1^2}=0, \tag{36}$$

$$\begin{aligned}&(1+\varepsilon C)\left(\frac{\partial V_z}{\partial Z_1}+\frac{V_r}{R}+\frac{\partial V_r}{\partial R}+\frac{1}{R}\frac{\partial V_\varphi}{\partial \Phi}\right)\\&\quad+\varepsilon\left(V_z\frac{\partial C}{\partial Z_1}+V_r\frac{\partial C}{\partial R}+\frac{1}{R}V_\varphi\frac{\partial C}{\partial \varphi}\right)=0,\end{aligned}$$

$$\frac{\partial\tilde{C}}{\partial T}+\varepsilon\left(\tilde{V}_z\frac{\partial\tilde{C}}{\partial Z_2}+\tilde{V}_r\frac{\partial\tilde{C}}{\partial R}+\frac{\tilde{V}_\varphi}{R}\frac{\partial\tilde{C}}{\partial\Phi}\right)=\frac{\partial^2\tilde{C}}{\partial Z_2^2}, \tag{38}$$

$$\left(1+\varepsilon\tilde{\tilde{C}}\right)\frac{\partial\tilde{\tilde{\Theta}}}{\partial T}=\frac{\partial^2\tilde{\tilde{\Theta}}}{\partial Z_3^2}; \tag{39}$$

$$T=0,\quad \tilde{C}=0,\quad \tilde{\tilde{\Theta}}=1; \tag{40}$$

$$Z_1=Z_2=Z_3=0,\quad V_z=-\frac{\partial\tilde{C}}{\partial Z_2},\quad \frac{\partial V_r}{\partial Z_1}=0,\quad \frac{\partial V_\varphi}{\partial Z_1}=0,$$

$$\tilde{C}=1,\quad \frac{\partial\tilde{\tilde{\Theta}}}{\partial Z_3}=\varepsilon\alpha_1(1+\varepsilon)\frac{\partial\tilde{C}}{\partial Z_2}; \tag{41}$$

$$Z_1=Z_2=Z_3\to\infty,\quad V_z=V_r=V_\varphi=\tilde{C}=0,\quad \tilde{\tilde{\Theta}}=1; \tag{42}$$

$$R=0,\quad V_r=0; \tag{43}$$

In the above mentioned system, Eq. (35) is superfluous, because in these approximations the pressure is eliminated ($P \equiv 0$). For the definition of V_r, Eq. (37) is used, and the obtained solution satisfies Eq. (35).

5. Asymptotic solution

The solution of Eqs. (34)–(43) depends on two parameters (α, ε), where ε is a small parameter and the solutions may be expressed in an expansion of ε in the form:

$$V_z = V_z^{(0)} + \varepsilon V_z^{(1)} + \ldots, \quad V_r = V_r^{(0)} + \varepsilon V_r^{(1)} + \ldots,$$

$$V_\varphi = V_\varphi^{(0)} + \varepsilon V_\varphi^{(1)} + \ldots,$$

$$\tilde{C} = \tilde{C}^{(0)} + \varepsilon \tilde{C}^{(1)} + \ldots, \quad \tilde{\tilde{\Theta}} = \tilde{\tilde{\Theta}}^{(0)} + \varepsilon \tilde{\tilde{\Theta}}^{(1)} + \ldots. \qquad (44)$$

The introduction of Eq. (44) into Eqs. (34)–(43) makes it possible to find the zero-order approximations ($\varepsilon = 0$):

$$\frac{\partial^2 V_z^{(0)}}{\partial Z_1^2} + C^{(0)} = 0;$$

$$Z_1 = 0, \quad V_z^{(0)} = -\left(\frac{\partial \tilde{C}^{(0)}}{\partial Z_2}\right)_{Z_2=0}; \qquad (45)$$

$$Z_1 \rightarrow \infty, \quad V_z^{(0)} = 0.$$

$$\frac{\partial^2 V_\varphi^{(0)}}{\partial Z_1^2} = 0;$$

$$Z_1 = 0, \quad \frac{\partial V^{(0)\varphi}}{\partial Z_1} = 0; \qquad Z_1 \rightarrow \infty, \quad V_\varphi^{(0)} = 0. \qquad (46)$$

$$\frac{\partial V_r^{(0)}}{\partial R} + \frac{V_r^{(0)}}{R} = -\frac{\partial V_z^{(0)}}{\partial Z_1} - \frac{1}{R}\frac{\partial V_\varphi^{(0)}}{\partial \Phi};$$

$$R = 0, \quad V_r^{(0)} = 0 \quad \text{(finite)}. \qquad (47)$$

$$\frac{\partial \tilde{C}^{(0)}}{\partial T} = \frac{\partial^2 \tilde{C}^{(0)}}{\partial Z_2^2};$$

$$T = 0, \quad \tilde{C}^{(0)} = 0; \qquad Z_2 = 0, \quad \tilde{C}^{(0)} = 1; \qquad (48)$$

$$Z_2 \rightarrow \infty, \quad \tilde{C}^{(0)} = 0.$$

$$\frac{\partial \tilde{\tilde{\Theta}}^{(0)}}{\partial T} = \frac{\partial^2 \tilde{\tilde{\Theta}}^{(0)}}{\partial Z_3^2};$$

$$T = 0, \quad \tilde{\tilde{\Theta}} = 1; \qquad Z_3 = 0, \quad \frac{\partial \tilde{\tilde{\Theta}}^{(0)}}{\partial Z_3} = 0; \qquad (49)$$

$$Z_3 \rightarrow \infty, \quad \tilde{\tilde{\Theta}}^{(0)} = 1.$$

The solutions of Eqs. (46), (48) and (49) are obtained directly.

$$V_\varphi^{(0)} = 0, \quad \tilde{C}^{(0)} = \operatorname{erfc}\frac{Z_2}{2\sqrt{T}}, \quad \tilde{\tilde{\theta}}^{(0)} \equiv 1. \qquad (50)$$

From Eqs. (14) and (50), it is clear that:

$$C^{(0)} = \operatorname{erfc}\left(\frac{l}{\delta}\frac{Z_1}{2\sqrt{T}}\right) \approx 1, \quad \alpha_0 = \frac{l}{\delta} \sim 10^{-3}. \qquad (51)$$

The introduction of Eq. (51) into Eq. (45) allows the determination of $V_z^{(0)}$, replacing the infinity condition with $V_z(1) = 0$:

$$V_z^{(0)} = -\frac{1}{2}Z_1^2 + \left(\frac{1}{2} - \frac{1}{\sqrt{\pi T}}\right)Z_1 + \frac{1}{\sqrt{\pi T}}. \qquad (52)$$

Replacing Eqs. (50) and (52) into Eq. (47) leads to:

$$V_r^{(0)} = \left[\frac{1}{2}Z_1 + \frac{1}{2\sqrt{\pi T}} - \frac{1}{4}\right]R. \qquad (53)$$

The problem for determination of the first approximation of the concentration $\tilde{C}^{(1)}$ is of the type:

$$\frac{\partial \tilde{C}^{(1)}}{\partial T} = \frac{\partial^2 \tilde{C}^{(1)}}{\partial Z_2^2} - \tilde{V}_z^{(0)}\frac{\partial \tilde{C}^{(0)}}{\partial Z_2};$$

$$T = 0, \quad \tilde{C}^{(1)} = 0; \qquad Z_2 = 0, \quad \tilde{C}^{(1)} = 0; \qquad (54)$$

$$Z_2 \rightarrow \infty, \quad \tilde{C}^{(1)} = 0,$$

where

$$\tilde{V}_z^{(0)}(Z_2, T) = V_z^{(0)}(Z_1, T), \quad Z_1 = \frac{1}{\alpha_0}Z_2. \qquad (55)$$

From Eq. (55), it directly follows that the volume source in Eq. (54):

$$\tilde{V}_z^{(0)}\frac{\partial \tilde{C}^{(0)}}{\partial Z_2} \neq 0 \quad \text{for } 0 \leq Z_2 < \alpha_0 \sim 10^{-3}, \qquad (56)$$

i.e. it influences the mass transfer practically on the interface ($Z_2 = 0$) and may be replaced by a surface flow:

$$S = \int_0^{\alpha} \tilde{V}_z^0 \frac{\partial \tilde{C}^{(0)}}{\partial Z_2}\, \mathrm{d}Z_2. \tag{57}$$

Thus, the problem (54) takes the form:

$$\frac{\partial \tilde{C}^{(1)}}{\partial T} = \frac{\partial^2 \tilde{C}^{(1)}}{\partial Z_2^2};$$

$$T = 0, \quad \tilde{C}^{(1)} = 0; \qquad Z_2 = 0, \quad \frac{\partial \tilde{C}^{(1)}}{\partial Z_2} = -S; \qquad Z_2 \to \infty, \quad \tilde{C}^{(1)} = 0. \tag{58}$$

$$S = -\sqrt{\frac{T}{\pi}} \frac{\alpha_0\, \mathrm{e}^{-\left(\alpha^2/4T\right)} - \sqrt{\pi}\mathrm{erf}\left[\alpha/\left(2\sqrt{T}\right)\right]}{\alpha_0^2} - \left(\sqrt{\frac{T}{\pi}} - \frac{2}{\pi}\right) \frac{\mathrm{e}^{-\left(\alpha^2/4\mathrm{T}\right)} - 1}{\alpha_0} - \frac{1}{\sqrt{\pi T}} \mathrm{erf} \frac{\alpha_0}{2T} \tag{59}$$

From Eq. (59), it is clear that for small values of α_0 ($\alpha_0 \sim 10^{-3}$), $S \approx 0$, therefore

$$\tilde{C}^{(1)} \equiv 0 \tag{60}$$

It is not difficult to show that

$$V_z^{(1)} \equiv 0, \quad V_r^{(1)} \equiv 0, \quad V_\varphi^{(1)} \equiv 0, \quad \tilde{\tilde{\theta}}^{(1)} \equiv 0. \tag{61}$$

6. Mass transfer kinetics

The average absorption rate J (per unit mass interface) for a time interval t_0 may be expressed by means of the mass transfer coefficient k. It may be determined from the average mass flux I

$$J = kc^* = \frac{1}{t_0} \int_0^{t_0} I\, \mathrm{d}t, \quad I = -\frac{D\rho^*}{\rho_0} \left(\frac{\partial c}{\partial z}\right)_{z=0}, \quad \rho^* = \rho_0 + c^*. \tag{62}$$

Thus, Eq. (62) may be used to obtain the Sherwood number for a non-stationary diffusion:

$$Sh = \frac{kt_0}{D} = -(1+\varepsilon)\sqrt{\frac{t_0}{D}} \int_0^1 \left(\frac{\partial \tilde{C}}{\partial Z_2}\right)_{Z_2=0} \mathrm{d}T, \tag{63}$$

for example

$$Sh = 2\sqrt{\frac{t_0}{\pi D}}. \tag{64}$$

The amount of the gas absorbed (Q kg/m^2) for the time interval t_0 s is:

$$Q = \int_0^{t_0} I\, \mathrm{d}t = 2c^* \sqrt{\frac{Dt_0}{\pi}}. \tag{65}$$

7. Conclusions

The results reported (Eqs. (50), (52) and (53)) show that the temperature is practically a constant value and does not influence the field of velocity and concentration. They differ from the solution of the Benard problem [17–22], where $V_z = V_r = V_\varphi = 0$, because the effect of the non-linear mass transfer do not allow the existence of a mechanical equilibrium, where the liquid may stay immobile.

The experimental results from the absorption of CO_2 in an immobile layer of water [25] show that the rate of the absorption is significantly greater than the one that can be determined from Eqs. (62)–(65). This fact indicates that the non-stationary process that is described by Eqs. (50), (52) and (53) (analogous to the Benard problem) is unstable, regarding small periodical disturbances. Their increment may lead to new periodical flows with a constant amplitude, which will evidently change the mechanism and the kinetics of heat mass transfer. For this aim, the linear analysis of stability will be used in the second part of this work.

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