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On the mechanism and kinetics of the transport processes in systems with intensive interphase mass transfer. 3. Comparative analysis of the absorption and desorption rates

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Abstract

A theoretical analysis of non-stationary desorption of a gas from a saturated stagnant liquid solution is done. The rate of the mass transfer is determined. A linear stability analysis where a basic flow is induced as a result of a non-linear mass transfer is applied. The disturbance amplitude is determined by using experimental data for mass transfer rate for CO_2 desorption from saturated H_2O solution in a N_2 gas phase. A comparative analysis between absorption and desorption mass transfer rate shows a good agreement with the experimental data. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Mechanism; Kinetics; Absorption; Desorption; Comparative analysis

1. Introduction

The mass transfer rate of the non-stationary absorption of pure CO_2 in a stagnant cylindrical layer of the water has been investigated in the first two reports [1,2]. It has been demonstrated in [2], that the increased mass transfer rate (compared with this one predicted from the linear theory) is a result of the system stability loss due to a dissipative structure arising [3,5].

The experimental data of different investigators shows that in case of CO_2 desorption in water the results coincide with the prediction of the linear theory. The theoretical analysis of the difference between the absorption and desorption mass transfer rates will be discussed in the present work.

2. Mathematical model

Carbon dioxide desorption from a saturated stagnant water solution to a nitrogen gas phase has been investigated experimentally by several research groups [3–5]. In this case the CO_2 concentration in the gas phase changes from the equilibrium value at the interface to zero in the bulk of the gas. This needs the use of Oberbeck–Boussinesq [1] equations for both phases. As shown in [1] the temperature is practically a constant. Thus the Oberbeck–Boussnesq equation for the gas (1) and the liquid (2) phase are

$$\rho_i\left(\frac{\partial v_z^{(i)}}{\partial t}+v_z^{(i)}\frac{\partial v_z^{(i)}}{\partial z}+v_r^{(i)}\frac{\partial v_z^{(i)}}{\partial r}+\frac{v_\varphi^{(i)}}{r}\frac{\partial v_z^{(i)}}{\partial \varphi}\right)$$
$$=-\frac{\partial p_i}{\partial z}+\mu_i\left(\frac{\partial^2 v_z^{(i)}}{\partial z^2}+\frac{1}{r}\frac{\partial v_z^{(i)}}{\partial r}+\frac{\partial^2 v_z^{(i)}}{\partial r^2}+\frac{1}{r^2}\frac{\partial^2 v_z^{(i)}}{\partial \varphi^2}\right)$$
$$+g(\rho_i-\rho_{0i}),$$

$$\rho_i\left(\frac{\partial v_r^{(i)}}{\partial t}+v_z^{(i)}\frac{\partial v_r^{(i)}}{\partial z}+v_r\frac{\partial v_r^{(i)}}{\partial r}+\frac{v_\varphi}{r}\frac{\partial v_r^{(i)}}{\partial \varphi}-\frac{v_\varphi^{(i)2}}{r}\right)$$
$$=-\frac{\partial p_i}{\partial r}+\mu_i\left(\frac{\partial^2 v_r^{(i)}}{\partial z^2}+\frac{1}{r}\frac{\partial v_r^{(i)}}{\partial r}+\frac{\partial^2 v_r^{(i)}}{\partial r^2}-\frac{v_r^{(i)}}{r^2}\right.$$
$$\left.+\frac{1}{r^2}\frac{\partial^2 v_r^{(i)}}{\partial \varphi^2}-\frac{2}{r^2}\frac{\partial v_\varphi^{(i)}}{\partial \varphi}\right),$$

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$$\rho_i\left(\frac{\partial v_\varphi^{(i)}}{\partial t}+v_z^{(i)}\frac{\partial v_\varphi^{(i)}}{\partial z}+v_r^{(i)}\frac{\partial v_\varphi^{(i)}}{\partial r}+\frac{v_\varphi^{(i)}}{r}\frac{\partial v_\varphi^{(i)}}{\partial \varphi}+\frac{v_r^{(i)}v_\varphi^{(i)}}{r}\right)$$

$$=-\frac{1}{r}\frac{\partial p_i}{\partial\varphi}+\mu_i\left(\frac{\partial^2 v_\varphi^{(i)}}{\partial z^2}+\frac{1}{r}\frac{\partial v_\varphi^{(i)}}{\partial r}+\frac{\partial^2 v_\varphi^{(i)}}{\partial r^2}-\frac{v_\varphi^{(i)}}{r^2}\right.$$

$$\left.+\frac{1}{r^2}\frac{\partial^2 v_\varphi^{(i)}}{\partial\varphi^2}+\frac{2}{r^2}\frac{\partial v_r^{(i)}}{\partial\varphi}\right),$$

$$\frac{\partial\rho_i}{\partial t}+\frac{\partial(\rho_i v_z^{(i)})}{\partial z}+\frac{\partial(\rho_i v_r^{(i)})}{\partial r}+\frac{\rho_i v_r^{(i)}}{r}+\frac{1}{r}\frac{\partial(\rho_i v_\varphi^{(i)})}{\partial\varphi}=0,$$

$$\frac{\partial c_i}{\partial t}+v_z^{(i)}\frac{\partial c_i}{\partial z}+v_r^{(i)}\frac{\partial c_i}{\partial r}+\frac{v_\varphi^{(i)}}{r}\frac{\partial c_i}{\partial\varphi}$$

$$=D_i\left(\frac{\partial^2 c_i}{\partial z^2}+\frac{1}{r}\frac{\partial c_i}{\partial r}+\frac{\partial^2 c_i}{\partial r^2}+\frac{1}{r^2}\frac{\partial^2 c_i}{\partial\varphi^2}\right),$$

$$\rho_i=\rho_{0i}\left(1+\frac{a^{2-i}c_i}{\rho_{0i}}\right),\quad i=1,2, \tag{1}$$

where ρ_{01} is the nitrogen density and ρ_{02} is the density of water.

Under CO_2 diffusion in N_2(20°C), a is determined through the densities of both gases

$$a=\frac{\rho_{CO_2}-\rho_{N_2}}{\rho_{CO_2}}=0.367. \tag{2}$$

Taking into account the interaction between the phases during the desorption process and as follows from [1] the boundary conditions of (1) are:

$$t=0,\quad v_z^{(i)}=v_r^{(i)}=v_\varphi^{(i)}=c_1=0,\quad c_2=c_{20};$$

$$z=0,\quad v_z^{(i)}=-\frac{D_i}{\rho_{0i}}\frac{\partial c_i}{\partial z},\quad v_r^{(1)}=v_r^{(2)},$$

$$v_\varphi^{(1)}=v_\varphi^{(2)},$$

$$\mu_1\left(\frac{\partial v_r^{(1)}}{\partial z}+\frac{\partial v_z^{(1)}}{\partial\varphi}\right)=\mu_2\left(\frac{\partial v_r^{(2)}}{\partial z}+\frac{\partial v_z^{(2)}}{\partial\varphi}\right),$$

$$\mu_1\left(\frac{\partial v_\varphi^{(1)}}{\partial z}+\frac{1}{r}\frac{\partial v_z^{(1)}}{\partial\varphi}\right)=\mu_2\left(\frac{\partial v_\varphi^{(2)}}{\partial z}+\frac{1}{r}\frac{\partial v_z^{(2)}}{\partial\varphi}\right), \tag{3}$$

$$c_1=\chi c_2,\quad \frac{D_1\rho_1^*}{\rho_{01}}\frac{\partial c_1}{\partial z}=\frac{D_2\rho_2^*}{\rho_0^*}\frac{\partial c_2}{\partial z};$$

$$z\to\infty,\quad v_z^{(1)}=v_r^{(1)}=v_\varphi^{(1)}=c_1=0;$$

$$z\to-\infty,\quad v_z^{(2)}=v_r^{(2)}=v_\varphi^{(2)}=c_2=c_0;$$

$$r=0,\quad v_z^{(i)},v_r^{(i)},v_\varphi^{(i)},\quad c_i\text{-finite};$$

$$r=r_0,\quad v_z^{(i)}=v_r^{(i)}=v_\varphi^{(i)}=0,$$

$$\frac{\partial c_i}{\partial r}=0,\quad i=1,2.$$

3. Dimensionless variables

The solution of the problems (1) and (3) requires the use of dimensionless variables for both phases similar to those used in [1]:

$$t=t_0T,\quad z=l_iZ_1^{(i)}=\delta_iZ_2^{(i)},\quad r=r_0R,\quad \varphi=2\pi\Phi,$$

$$p_i=\rho_{0i}u_{0i}^2P^{(i)},$$

$$v_z^{(i)}(t,z,r,\varphi)=u_{0i}V_z^{(i)}(T,Z_1^{(i)},R,\Phi)$$

$$=u_{0i}\tilde{V}_z^{(i)}(T,Z_2^{(i)},R,\Phi),$$

$$v_r^{(i)}(t,z,r,\varphi)=\frac{u_{0i}r_0}{l_i}V_r^{(i)}(T,Z_1^{(i)},R,\Phi)$$

$$=\frac{u_{0i}r_0}{\delta_i}\tilde{V}_r^{(i)}(T,Z_2^{(i)},R,\Phi), \tag{4}$$

$$v_\varphi^{(i)}(t,z,r,\varphi)=2\pi\frac{u_{0i}r_0}{l_i}V_\varphi^{(i)}(T,Z_1^{(i)},R,\Phi)$$

$$=2\pi\frac{u_{0i}r_0}{\delta_i}\tilde{V}_\varphi^{(i)}(T,Z_2^{(i)},R,\Phi),$$

$$c^{(i)}(t,z,r,\varphi)=c_{0i}^*C^{(i)}(T,Z_1^{(i)},R,\Phi)$$

$$=c_{0i}^*\tilde{C}^{(i)}(T,Z_2^{(i)},R,\Phi),\quad i=1,2,$$

where for the following characteristic scales the order is known.

$$t_0\sim10^2\ \text{s},\quad r_0\sim10^{-2}\ \text{m},\quad \chi=1.06,\quad c_0=1.72\ \text{kg/m}^3,$$

$$c_{01}^*=\chi c_0,\quad c_{02}^*=c_0. \tag{5}$$

The substitution of (4) into (1) and (3) converts the problem in a dimensionless form

$$\left[1+\frac{\bar{c}_{0i}^*}{\rho_{0i}}C^{(i)}\right]\left[\frac{u_{0i}\rho_{0i}}{gt_0\bar{c}_{0i}^*}\frac{\partial V_z^{(i)}}{\partial T}+\frac{u_{0i}^2\rho_{0i}}{gl_i\bar{c}_{0i}^*}\right.$$

$$\left.\times\left(V_z^{(i)}\frac{\partial V_z^{(i)}}{\partial Z_1^{(i)}}+V_r^{(i)}\frac{\partial V_z^{(i)}}{\partial R}+\frac{V_\varphi^{(i)}}{R}\frac{\partial V_z^{(i)}}{\partial\Phi}\right)\right]$$

$$=-\frac{u_{0i}^2\rho_{0i}}{gl_i\bar{c}_{0i}^*}\frac{\partial P^{(i)}}{\partial Z_1^{(i)}}+\frac{\mu_iu_{0i}}{gl_i^2\bar{c}_{0i}^*}\left[\frac{\partial^2V_z^{(i)}}{\partial Z_1^{(i)2}}+\frac{l_i^2}{r_0^2}\right.$$

$$\left.\times\left(\frac{1}{R}\frac{\partial V_z^{(i)}}{\partial R}+\frac{\partial^2V_z^{(i)}}{\partial R^2}+\frac{1}{4\pi^2}\frac{1}{R^2}\frac{\partial^2V_z^{(i)}}{\partial\Phi^2}\right)\right]+C^{(i)},$$

$$\left[1+\frac{\bar{c}_{0i}^*}{\rho_{0i}}C^{(i)}\right]\left[\frac{u_{0i}\rho_{i0}}{gt_0\bar{c}_{0i}^*}\frac{\partial V_r^{(i)}}{\partial T}+\frac{u_{0i}^2\rho_{0i}}{gl_i\bar{c}_{0i}^*}\right.$$

$$\left.\times\left(V_z^{(i)}\frac{\partial V_r^{(i)}}{\partial Z_1^{(i)}}+V_r^{(i)}\frac{\partial V_r^{(i)}}{\partial R}+\frac{V_\varphi^{(i)}}{R}\frac{\partial V_r^{(i)}}{\partial\Phi}-4\pi^2\frac{V_\varphi^{(i)2}}{R}\right)\right]$$

$$=-\frac{l_i^2}{r_0^2}\frac{u_{0i}^2\rho_{0i}}{gl_i\bar{c}_{0i}^*}\frac{\partial P^{(i)}}{\partial R}+\frac{\mu_iu_{0i}}{gl_i^2\bar{c}_{0i}^*}\left[\frac{\partial^2V_r^{(i)}}{\partial Z_1^{(i)2}}+\frac{l_i^2}{r_0^2}\right.$$

$$\left.\times\left(\frac{1}{R}\frac{\partial V_r^{(i)}}{\partial R}+\frac{\partial^2V_r^{(i)}}{\partial R^2}-\frac{V_r^{(i)}}{R^2}+\frac{1}{4\pi^2}\frac{\partial^2V_r^{(i)}}{\partial\Phi^2}-\frac{2}{R}\frac{\partial V_\varphi^{(i)}}{\partial\Phi}\right)\right],$$

$$
\begin{aligned}
&\left[1+\frac{\bar{c}^*_{0i}}{\rho_{0i}}C^{(i)}\right]\left[\frac{u_{0i}\rho_{0i}}{gt_0\bar{c}^*_{0i}}\frac{\partial V^{(i)}_{\varphi}}{\partial T}+\frac{u^2_{0i}\rho_{0i}}{gl_i\bar{c}^*_{0i}}\right.\\
&\quad\left.\times\left(V^{(i)}_z\frac{\partial V^{(i)}_{\varphi}}{\partial Z^{(i)}_1}+V^{(i)}_r\frac{\partial V^{(i)}_{\varphi}}{\partial R}+\frac{V^{(i)}_{\varphi}}{R}\frac{\partial V^{(i)}_{\varphi}}{\partial \Phi}+\frac{V^{(i)}_r V^{(i)}_{\varphi}}{R}\right)\right]\\
&\quad=-\frac{l^2_i}{r^2_0}\frac{u^2_{0i}\rho_{0i}}{gl_i\bar{c}^*_{0i}}\frac{1}{R}\frac{\partial P^{(i)}}{\partial \Phi}+\frac{\mu_i u_{0i}}{gl^2_i\bar{c}^*_{0i}}\\
&\quad\times\left[\frac{\partial^2 V^{(i)}_{\varphi}}{\partial Z^{(i)2}_1}+\frac{l^2_i}{r^2_0}\left(\frac{1}{R}\frac{\partial V^{(i)}_{\varphi}}{\partial R}+\frac{\partial^2 V^{(i)}_{\varphi}}{\partial R^2}-\frac{V^{(i)}_{\varphi}}{R^2}\right.\right.\\
&\quad\left.\left.+\frac{1}{4\pi^2}\frac{1}{R^2}\frac{\partial^2 V^{(i)}_{\varphi}}{\partial \Phi^2}+\frac{1}{2\pi^2}\frac{1}{R^2}\frac{\partial V^{(i)}_r}{\partial \Phi}\right)\right],
\end{aligned}
$$

$$
\begin{aligned}
&\frac{l_i c^*_{0i}}{\rho_{0i}u_{0i}t_0}\frac{\partial C^{(i)}}{\partial T}-\left(\frac{\partial V^{(i)}_z}{\partial Z^{(i)}_1}+\frac{V^{(i)}_r}{R}+\frac{\partial V^{(i)}_r}{\partial R}+\frac{1}{R}\frac{\partial V^{(i)}_{\varphi}}{\partial \Phi}\right)\\
&\quad\times\left[1+\frac{\bar{c}^*_{0i}}{\rho_{0i}}C^{(i)}\right]+V^{(i)}_z\frac{\bar{c}^*_{0i}}{\rho_{0i}}\frac{\partial C^{(i)}}{\partial Z^{(i)}_1}+V^{(i)}_r\frac{\bar{c}^*_{0i}}{\rho_{0i}}\frac{\partial C^{(i)}}{\partial R}\\
&\quad+\frac{V^{(i)}_{\varphi}}{R}\frac{\bar{c}^*_{0i}}{\rho_{0i}}\frac{\partial C^{(i)}}{\partial \Phi}=0,
\end{aligned}
$$

$$
\begin{aligned}
&\frac{\partial \tilde{C}^{(i)}}{\partial T}+\frac{u_{0i}t_0}{\delta_i}\left(\tilde{V}^{(i)}_z\frac{\partial \tilde{C}^{(i)}}{\partial Z^{(i)}_2}+\tilde{V}^{(i)}_r\frac{\partial \tilde{C}^{(i)}}{\partial R}+\frac{\tilde{V}^{(i)}_r}{R}\frac{\partial \tilde{C}^{(i)}}{\partial \Phi}\right)\\
&\quad=\frac{D_i t_0}{\delta^2_i}\left[\frac{\partial^2 \tilde{C}^{(i)}}{\partial Z^{(i)2}_2}+\frac{\delta^2_i}{r^2_0}\left(\frac{1}{R}\frac{\partial \tilde{C}^{(i)}}{\partial R}+\frac{\partial^2 \tilde{C}^{(i)}}{\partial R^2}+\frac{1}{4\pi^2}\frac{1}{R^2}\frac{\partial^2 \tilde{C}^{(i)}}{\partial \Phi^2}\right)\right];
\end{aligned}
\tag{6}
$$

$$T=0,\quad V^{(i)}_z=V^{(i)}_r=V^{(i)}_{\varphi}=\tilde{C}^{(1)}=0,\quad \tilde{C}^{(2)}=1;$$

$$Z^{(i)}_1=Z^{(i)}_2=0,\quad V^{(i)}_z=-\frac{D_i c^*_{0i}}{u_{0i}\rho_{0i}\delta_i}\frac{\partial \tilde{C}^{(i)}}{\partial Z^{(i)}_2},$$

$$\frac{\partial V^{(1)}_r}{\partial Z^{(1)}_1}+\frac{l^2_1}{r^2_0}\frac{\partial V^{(1)}_z}{\partial R}=\frac{\mu_2 u_{02} l^2_1}{\mu_1 u_{01} l^2_2}\left(\frac{\partial V^{(2)}_r}{\partial Z^{(2)}_1}+\frac{l^2_2}{r^2_0}\frac{\partial V^2_z}{\partial R}\right),$$

$$\frac{\partial V^{(1)}_{\varphi}}{\partial Z^{(1)}_1}+\frac{l^2_1}{4\pi^2 r^2_0}\frac{1}{R}\frac{\partial V^{(1)}_z}{\partial \Phi}=\frac{\mu_2 u_{02} l^2_1}{\mu_1 u_{01} l^2_2}\left(\frac{\partial V^{(2)}_{\varphi}}{\partial Z^{(2)}_1}+\frac{l^2_2}{r^2_0 4\pi^2}\frac{\partial V^{(2)}_z}{\partial R}\right),$$

$$C^{(1)}=C^{(2)},\quad \frac{\partial C^{(1)}}{\partial Z^{(1)}_1}=\frac{D_2\rho^*_2\rho_{01}\delta_1}{D_1\rho^*_1\rho_{02}\delta_2\chi}\frac{\partial \tilde{C}^{(2)}}{\partial Z^{(2)}_1};$$

$$Z^{(1)}_1\to\infty,\quad V^{(1)}_z=V^{(1)}_r=V^{(1)}_{\varphi}=C^{(1)}=0;$$

$$Z^{(2)}_1\to-\infty,\quad V^{(2)}_z=V^{(2)}_r=V^{(2)}_{\varphi}=0,\quad C^{(2)}=1;$$

$$R=0,\quad V^{(i)}_z, V^{(i)}_r, V^{(i)}_{\varphi},\quad C^{(i)}\text{-finite};$$

$$R=1,\quad V^{(i)}_z=V^{(i)}_r=V^{(i)}_{\varphi}=0,\quad \frac{\partial C^{(i)}}{\partial R}=0,\quad i=1,2,$$

where

$$\bar{c}^*_{0i}=a^{2-i}c^*_{0i},\quad i=1,2.$$

4. Qualitative analysis

The qualitative analysis of (6) may be applied similarly to that employed when the absorption was studied [1]. This allows the evaluation of the characteristic scales for both phases as

$$
\begin{aligned}
&\frac{D_i t_0}{\delta^2_i}=1,\quad \delta_i=\sqrt{D_i t_0},\quad \delta_1\sim 10^{-2}\ \text{m},\quad \delta_2\sim 10^{-4}\ \text{m},\\
&\frac{\mu_i u_{0i}}{gl^2_i\bar{c}^*_{0i}}=1,\quad \frac{D_i c^*_{0i}}{u_{0i}\rho_{0i}\delta_i}=1,\\
&u_{0i}=\frac{c^*_i}{\rho_{0i}}\sqrt{\frac{D_i}{t_0}},\quad u_{0i}\sim 10^{-4}\ \text{m/s},\quad u_{02}\sim 10^{-8}\ \text{m/s},\\
&l_i=\sqrt{\frac{a^{2-i}\mu_i}{\rho_{0i}g}\sqrt{\frac{D_i}{t_0}}},\quad l_1\sim 10^{-5}\ \text{m},\quad l_2\sim 10^{-7}\ \text{m}.
\end{aligned}
\tag{7}
$$

The characteristic scales (7) permit the evaluation of the parameter orders in (6).

$$
\begin{aligned}
&\varepsilon=\frac{c^*_i}{\rho_{0i}}\sim\bar{\varepsilon}_i=\frac{\bar{c}^*_i}{\rho_{0i}}\sim\left[1,10^{-3}\right],\\
&\frac{u_{0i}\rho_{0i}}{gt_0\bar{c}^*_i}\sim\left[10^{-7},10^{-9}\right],\quad \frac{u^2_{0i}}{gl_i\bar{\varepsilon}_i}\sim\left[10^{-3},10^{-7}\right],\\
&\frac{l^2_i}{r^2_0}\sim\left[10^{-6},10^{-10}\right],\quad \frac{\delta^2_i}{r^2_0}\sim\left[1,10^{-4}\right],\\
&\frac{l_i}{t_0 u_{0i}\bar{\varepsilon}_i}\sim\left[10^{-3},10^{-4}\right],\quad \frac{u_{0i}t_0}{\delta_i}=\varepsilon_i\sim\left[1,10^{-3}\right],\\
&b=\frac{\mu_2 u_{02} l^2_1}{\mu_1 u_{01} l^2_2}\sim 1,\quad \frac{D_2\rho^*_2\rho_{01}\delta_1}{D_1\rho^*_1\rho_{02}\delta_2\chi}\sim 10^{-2},
\end{aligned}
\tag{8}
$$

where both values for the gas phase (first) and for the liquid phase (second) are shown in the square brackets.

5. Analytical solution

The order of the latter parameter (10^{-2}) in (8) shows that in the case of CO_2 desorption from a saturated water the process is limited by the mass transfer in the liquid phase, i.e. $C^{(1)}\equiv 0$. That is the way, only the equations for the liquid phase will be considered. For simplicity the superscript (2) will be omitted. Thus, the set (6) gives:

$$\begin{aligned}
&\frac{\partial^2 V_z}{\partial Z_1^2} + C = 0, \quad \frac{\partial^2 V_r}{\partial Z_1^2} = 0, \quad \frac{\partial^2 V_\varphi}{\partial Z_1^2} = 0,\\
&\frac{\partial V_z}{\partial Z_1} + \frac{V_r}{R} + \frac{\partial V_r}{\partial R} + \frac{1}{R}\frac{\partial V_\varphi}{\partial \Phi} = 0,\\
&\frac{\partial \tilde{C}}{\partial T} = \frac{\partial^2 \tilde{C}}{\partial Z_2^2};\\
&T = 0, \quad \tilde{C} = 0;\\
&Z_1 = Z_2 = 0, \quad V_z = -\frac{\partial \tilde{C}}{\partial Z_2}, \quad \frac{\partial V_r}{\partial Z_1} = 0, \quad \frac{\partial V_\varphi}{\partial Z_1} = 0,\\
&\tilde{C} = 0;\\
&Z_1 = Z_2 \to -\infty, \quad V_z = V_r = V_\varphi = 0, \quad \tilde{C} = 1;\\
&R = 0, \quad V_r\text{-finite.}
\end{aligned} \tag{9}$$

The solution for $\tilde{C}$ could be obtained from (9) as follows:

$$\begin{aligned}
&\tilde{C} = -\operatorname{erf}\frac{Z_2}{2\sqrt{T}} \quad (Z_2 \leqslant 0),\\
&\left\langle \tilde{C} = \operatorname{erfc}\frac{Z_2}{2\sqrt{T}} \ (Z_2 \geqslant 0)\right\rangle,\\
&Z_2 = \alpha_0 Z_1, \quad \alpha_0 = \frac{l}{\delta} \sim 10^{-3}.
\end{aligned} \tag{10}$$

Here and up to the end of this paper, the results concerning absorption will be shown in the brackets $\langle\ \rangle$.

The solution of (10) gives:

$$\begin{aligned}
&C = -\operatorname{erf}\left(\alpha_0 \frac{Z_1}{2\sqrt{T}}\right) \approx 0,\\
&\left\langle C = \operatorname{erfc}\left(\alpha \frac{Z_1}{2\sqrt{T}}\right) \approx 1\right\rangle.
\end{aligned} \tag{11}$$

The substitution of (11) into (9) shows that under a gas desorption from a stagnant liquid there are no conditions allowing a natural convection. Thus, for the flow velocity components (induced by the mass transfer in the liquid phase) could be obtained:

$$\begin{aligned}
&\frac{\partial^2 V_z}{\partial Z_1^2} = 0 \quad \left\langle \frac{\partial^2 V_z}{\partial Z_1^2} = 1 \right\rangle; \quad Z_1 = 0,\\
&V_z = -\left(\frac{\partial \tilde{C}}{\partial Z_2}\right)_{Z_2=0}; \quad Z_1 = -1, \quad V_z = 0.\\
&\frac{\partial V_r}{\partial R} + \frac{V_r}{R} = -\frac{\partial V_z}{\partial Z_1} - \frac{1}{R}\frac{\partial V_\varphi}{\partial \Phi}; \quad R = 0, \quad V_r^{(0)}\text{-finite.}\\
&\frac{\partial^2 V_\varphi}{\partial Z_1^2} = 0; \quad Z_1 = 0, \quad \frac{\partial V_\varphi}{\partial Z_1} = 0; \ Z_1 = -1, \ V_\varphi = 0.
\end{aligned} \tag{12}$$

In the above problems, the boundary conditions at $(-\infty)$ are substituted by the conditions at (-1), i.e., at the border of the boundary layer. The solutions of these problems follow immediately:

$$\begin{aligned}
&V_z = \frac{1}{\sqrt{\pi T}}(Z_1 + 1), \quad (Z_1 \leqslant 0),\\
&\left\langle V_z = -\frac{1}{2}Z_1^2 + \left(\frac{1}{2} - \frac{1}{\sqrt{\pi T}}\right)Z_1 + \frac{1}{\sqrt{\pi T}}, \ (Z_1 \geqslant 0)\right\rangle,\\
&V_r = -\frac{1}{2\sqrt{\pi T}}R, \ \left\langle V_r = \left(\frac{1}{2}Z_1 + \frac{1}{2\sqrt{\pi T}} - \frac{1}{4}\right)R\right\rangle,\\
&V_\varphi \equiv 0.
\end{aligned} \tag{13}$$

The result (13) indicates that the larger concentration gradient in the liquid (at the interface) induces the flow in the liquid phase.

6. Mass transfer kinetics

The velocity field (13) and the concentration distribution in the liquid (10) may be expressed as

$$\begin{aligned}
&v_z = \varepsilon_0\sqrt{\frac{D}{\pi t}}\left(\frac{z}{l} + 1\right), \quad v_r = -\frac{\varepsilon_0}{2l}\sqrt{\frac{D}{\pi t}}r, \quad \varepsilon_0 = \frac{c_0}{\rho_0},\\
&v_\varphi \equiv 0, \quad c = -c_0\operatorname{erf}\frac{z}{2\sqrt{Dt}}, \quad l = \sqrt{\frac{\mu}{\rho_0 g}\sqrt{\frac{D}{t_0}}}.
\end{aligned} \tag{14}$$

The mass transfer rate could be obtained in a way already applied in [1]. The relationships for the Sherwood number and for the amount of the desorbed substance are similar to those obtained for the absorption process [1], where in case of desorption $c^* = 0$ and $\rho^* = \rho_0$

$$\begin{aligned}
&Sh = \frac{kl}{D} = \sqrt{\frac{\nu}{\pi g t_0}\sqrt{\frac{1}{Dt_0}}},\\
&Q = -D\int_0^{t_0}\left(\frac{\partial c}{\partial z}\right)_{z=0}\mathrm{d}t = 2c_0\sqrt{\frac{Dt_0}{\pi}}\ \text{kg/m}^2.
\end{aligned} \tag{15}$$

7. Linear stability analysis

By application of small perturbations on the axial velocity, the pressure, the concentration, the temperature and the density in the complete set of equations of Oberbeck–Boussinesq [1,2]

$$\begin{aligned}
&v_z + v_z', \quad p + p', \quad c + c', \quad \theta_0 + \theta', \quad \rho + \rho',\\
&\theta_0 = \text{const}, \quad \rho = \rho_0\left(1 + \frac{c}{\rho_0}\right),\\
&\rho' = \rho_0\left(\frac{c'}{\rho_0} - \beta\theta'\right),
\end{aligned} \tag{16}$$

the desorption process could be studied for a stability.

After linearization according to the small disturbances taking into account (15) the following equations for v_z', p', c' and θ' are obtained:

$$
\begin{aligned}
&\left(1+\frac{c}{\rho_0}\right)\left(\frac{\partial v_z'}{\partial t}+v_z'\frac{\partial v_z}{\partial z}+v_z\frac{\partial v_z'}{\partial z}+v_r\frac{\partial v_z'}{\partial r}\right)=-\frac{1}{\rho_0}\frac{\partial p'}{\partial z}\\
&\qquad+\nu\left(\frac{\partial^2 v_z'}{\partial z^2}+\frac{1}{r}\frac{\partial v_z'}{\partial r}+\frac{\partial^2 v_z'}{\partial r^2}+\frac{1}{r^2}\frac{\partial^2 v_z'}{\partial \varphi^2}\right)+\frac{g}{\rho_0}c',\\
&\frac{\partial p'}{\partial r}=0,\quad \left\langle\left(1+\frac{c}{\rho_0}\right)v_z'\frac{\partial v_r}{\partial z}=-\frac{1}{\rho_0}\frac{\partial p'}{\partial r}\right\rangle,\\
&\frac{\partial p'}{\partial \varphi}=0,
\end{aligned}
\tag{17}
$$

$$
\frac{\partial \rho'}{\partial t}+\rho\frac{\partial v_z'}{\partial z}+v_z'\frac{\partial \rho}{\partial z}+v_z\frac{\partial \rho'}{\partial z}+v_r\frac{\partial \rho'}{\partial r}=0,
\tag{18}
$$

$$
\begin{aligned}
&\frac{\partial c'}{\partial t}+v_z'\frac{\partial c}{\partial z}+v_z\frac{\partial c'}{\partial z}+v_r\frac{\partial c'}{\partial r}\\
&\qquad=D\left(\frac{\partial^2 c'}{\partial z^2}+\frac{1}{r}\frac{\partial c'}{\partial r}+\frac{\partial^2 c'}{\partial r^2}+\frac{1}{r^2}\frac{\partial^2 c'}{\partial \varphi^2}\right),\\
&\left(1+\frac{c}{\rho_0}\right)\left(\frac{\partial \theta'}{\partial t}+v_z\frac{\partial \theta'}{\partial z}+v_r\frac{\partial \theta'}{\partial r}\right)\\
&\qquad=a\left(\frac{\partial^2 \theta'}{\partial z^2}+\frac{1}{r}\frac{\partial \theta'}{\partial r}+\frac{\partial^2 \theta'}{\partial r^2}+\frac{1}{r^2}\frac{\partial^2 \theta'}{\partial \varphi^2}\right);
\end{aligned}
\tag{19}
$$

$$
\begin{aligned}
&t=0,\quad v_z'=c'=\theta'=0;\\
&z=0,\quad v_z'=-\frac{D}{\rho_0}\frac{\partial c'}{\partial z},\quad \frac{\partial v_z'}{\partial r}=\frac{\partial \sigma}{\partial \theta}\frac{\partial \theta'}{\partial r},\\
&\frac{\partial v_z'}{\partial \varphi}=\frac{\partial \sigma}{\partial \theta}\frac{\partial \theta'}{\partial \varphi},\\
&c'=0,\quad \lambda\frac{\partial \theta'}{\partial z}=qD\frac{\partial c'}{\partial z};\\
&z\to-\infty,\quad v_z'=-\frac{D}{\rho_0}\frac{\partial c'}{\partial z},\quad \theta'=0;\\
&r=0,\quad v_z',c',p',\theta'\text{-finite};\\
&r=r_0,\quad v_z'=0,\quad \frac{\partial c'}{\partial r}=\frac{\partial \theta'}{\partial r}=0,
\end{aligned}
\tag{20}
$$

where

$$
\rho=\rho_0+c-\rho_0\beta(\theta-\theta_0).
\tag{21}
$$

The introduction of (21) into (18) leads to two equations for c' and θ', because of $\beta\ll 1$

$$
\begin{aligned}
&\frac{\partial c'}{\partial t}+v_z\frac{\partial c'}{\partial z}+v_z'\frac{\partial c'}{\partial z}+v_r\frac{\partial c'}{\partial r}=-(\rho_0+c)\frac{\partial v_z'}{\partial z},\\
&\frac{\partial \theta'}{\partial t}+v_z\frac{\partial \theta'}{\partial z}+v_r\frac{\partial \theta'}{\partial r}=0.
\end{aligned}
\tag{22}
$$

After that, introducing (22) into (19) the following can be obtained:

$$
\begin{aligned}
&-(\rho_0+c)\frac{\partial v_z'}{\partial z}=D\left(\frac{\partial^2 c'}{\partial z^2}+\frac{1}{r}\frac{\partial c'}{\partial r}+\frac{\partial^2 c'}{\partial r^2}+\frac{1}{r^2}\frac{\partial^2 c'}{\partial \varphi^2}\right),\\
&0=\frac{\partial^2 \theta'}{\partial z^2}+\frac{1}{r}\frac{\partial \theta'}{\partial r}+\frac{\partial^2 \theta'}{\partial r^2}+\frac{1}{r^2}\frac{\partial^2 \theta'}{\partial \varphi^2},
\end{aligned}
\tag{23}
$$

The pressure could be eliminated in (17)

$$
\frac{1}{\rho_0}\frac{\partial p'}{\partial z}=0\quad \left\langle-\frac{1}{\rho_0}\frac{\partial p'}{\partial z}=\int\frac{\partial v_z'}{\partial z}\frac{\partial v_r}{\partial z}\,\mathrm{d}r\right\rangle.
\tag{24}
$$

8. Eigenvalues problem

The perturbations v_z', c' and θ' in (17)–(24) may be expressed through Fourier series of eigenfunction, where ω and n are eigenvalues

$$
\begin{aligned}
&v_z'=\exp(\omega t)\sum_{n=0}^{\infty}v_n(t,z,r)\cos(n\varphi),\\
&c'=\exp(\omega t)\sum_{n=0}^{\infty}c_n(t,z,r)\cos(n\varphi),\\
&\theta'=\exp(\omega t)\sum_{n=0}^{\infty}\theta_n(t,z,r)\cos(n\varphi).
\end{aligned}
\tag{25}
$$

By introduction of (25) into (17)–(24) the set of equations which have stable periodic solutions at $\omega=0$ is obtained

$$
\begin{aligned}
&\frac{\partial v_n}{\partial t}+v_n\frac{\partial v_z}{\partial z}+v_z\frac{\partial v_n}{\partial z}+v_r\frac{\partial v_n}{\partial r}\\
&\qquad=\nu\left(\frac{\partial^2 v_n}{\partial z^2}+\frac{1}{r}\frac{\partial v_n}{\partial r}+\frac{\partial^2 v_n}{\partial r^2}-\frac{n^2}{r^2}v_n\right)\\
&\qquad\quad+\frac{g}{\rho_0}c\left\langle+\int\frac{\partial v_r}{\partial z}\frac{\partial v_n}{\partial z}\,\mathrm{d}r\right\rangle,\\
&-(\rho_0+c)\frac{\partial v_n}{\partial z}=\frac{D}{\rho_0}\left(\frac{\partial^2 c_n}{\partial z^2}+\frac{\partial^2 c_n}{\partial r^2}+\frac{1}{r}\frac{\partial c_n}{\partial r}-\frac{n^2}{r^2}c_n\right),\\
&\left(\frac{\partial^2 \theta_n}{\partial z^2}+\frac{\partial^2 \theta_n}{\partial r^2}+\frac{1}{r}\frac{\partial \theta_n}{\partial r}-\frac{n^2}{r^2}\theta_n\right)=0;\\
&t=0,\quad v_n=c_n=\theta_n=0;\\
&z=0,\quad v_n=-\frac{D}{\rho_0}\frac{\partial c_n}{\partial z},\quad \frac{\partial v_n}{\partial r}=\frac{\partial \sigma}{\partial \theta}\frac{\partial \theta_n}{\partial r},\\
&c_n=0,\quad \lambda\frac{\partial \theta_n}{\partial \theta_z}=qD\frac{\partial c_n}{\partial c_z};\\
&z\to-\infty,\quad v_n=-\frac{D}{\rho_0}\frac{\partial c_n}{\partial z},\quad \theta_n=0;\\
&r=0,\quad v_n=c_n,\quad \theta_n\text{-finite};\\
&r=r_0,\quad v_n=0,\quad \frac{\partial c_n}{\partial r}=\frac{\partial \theta_n}{\partial r}=0;\\
&n=0,1.2,\ldots,\infty.
\end{aligned}
\tag{26}
$$

The first equation in (26) shows that the difference between the absorption and desorption processes is determined by the velocity distribution in the main flow-under desorption $\partial v_r/\partial z=0$.

The solution of (26) could be presented in a similar way in case of absorption

$$\begin{aligned}
&v_n = u_0[V_n(Z,T) - Bf_n(R)],\\
&c_n = c_0[C_n(Z,T) + Zf_n(R)],\\
&\theta_n = \theta_0\theta_n(Z,T), \quad n = 0,1,2,\ldots,\infty,\\
&T = \frac{t}{t_0}, \quad Z = \frac{z}{l}, \quad R = \frac{r}{r_0}, \quad B = \frac{D\varepsilon_0}{u_0 l}.
\end{aligned} \tag{27}$$

By introduction of new variables (27) into (26) the following is obtained:

$$\begin{aligned}
&\frac{l^2}{\nu t_0}\frac{\partial V_n}{\partial T} + \frac{u_0 l}{\nu}\left[(V_n - Bf_n)\frac{\partial V_z}{\partial Z} + V_z\frac{\partial V_n}{\partial Z} - BV_r f_n'\right]\\
&\quad = \frac{\partial^2 V_n}{\partial Z^2} - \frac{l^2}{r_0^2}\frac{n^2}{R^2}V_n + \frac{\varepsilon_0 l^2 g}{\nu u_0}(C_n + Zf_n)\\
&\quad \left\langle + \frac{u_0 l}{\nu}\frac{r_0^2}{l^2}\int\frac{\partial V_r}{\partial Z}\frac{\partial V_n}{\partial Z}\,\mathrm{d}R\right\rangle,\\
&\frac{u_0 l}{\varepsilon_0 D}\frac{\partial V_n}{\partial Z} = \frac{\partial^2 C_n}{\partial Z^2} - \frac{l^2}{r_0^2}\frac{n^2}{R^2}C_n,\\
&\frac{\partial^2\theta_n}{\partial z^2} = 0,\\
&f_n'' + \frac{1}{R}f_n' - \frac{n^2}{R^2}f_n = 0;\\
&Z = 0, \quad V_n = -B\frac{\partial C_n}{\partial Z}, \quad C_n = 0, \quad \theta_n = \frac{qDc^*}{\lambda\theta_0}\frac{\partial C_n}{\partial Z};\\
&Z \to -\infty, \quad V_n = -B\frac{\partial C_n}{\partial Z}; \quad R = 0, \quad f_n\text{-finite};\\
&R = 1, \quad f_n' = 0; \quad n = 0,1,2,\ldots,\infty,
\end{aligned} \tag{28}$$

where the solutions for f_n $(n = 0,1,2,\ldots,\infty)$ are

$$\begin{aligned}
&f_0 = \text{constant},\\
&f_n = \frac{\xi^n + \xi^{-n}}{2n}R^n, \quad R < \xi,\\
&f_n = \frac{\xi^n}{2n}(R^n + R^{-n}), \quad R > \xi,\\
&f_n = \frac{\xi^{2n} + 1}{2n}, \quad R = \xi,\\
&0 < \xi < 1, \quad n = 1,2,\ldots,\infty.
\end{aligned}$$

The order of the dimensionless parameters in (28) is

$$\begin{aligned}
&\frac{l^2}{\nu t_0} \sim 10^{-10}, \quad \frac{u_0 l}{\nu} \sim 10^{-9}, \quad \frac{l^2}{r_0} \sim 10^{-10},\\
&\frac{\varepsilon_0 l^2 g}{\nu u_0} \sim 10^{-2}, \quad \frac{u_0 l}{\varepsilon_0 D} \sim 10^{-3}, \quad \left\langle\frac{u_0 l}{\nu}\frac{r_0^2}{l^2} \sim 10\right\rangle.
\end{aligned} \tag{29}$$

In (28) the small parameters may be assumed zero and the resulting set for the determination of V_n, C_n and θ_n $(n = 0,1,2,\ldots,\infty)$ is

$$\begin{aligned}
&\frac{\partial^2 V_n}{\partial Z^2} = 0 \quad \left\langle\frac{\partial V_n}{\partial Z} = 0\right\rangle, \quad \frac{\partial^2 C_n}{\partial Z^2} = 0, \quad \frac{\partial^2\theta_n}{\partial Z^2} = 0,\\
&Z = 0, \quad V_n = -B\frac{\partial C_n}{\partial Z}, \quad C_n = 0, \quad \frac{\partial\theta_n}{\partial Z} = 0,\\
&Z \to -\infty, \quad V_n = -B\frac{\partial C_n}{\partial Z},\\
&\theta_n = 0, \quad n = 0,1,2,\ldots,\infty.
\end{aligned} \tag{30}$$

The problem (30) has the following solution:

$$\begin{aligned}
&V_n = -B\gamma_n, \quad C_n = \gamma_n Z, \quad \theta_n \equiv 0, \quad \gamma_n \leqslant 0, \quad Z \leqslant 0,\\
&n = 0,1,2,\ldots,\infty,
\end{aligned} \tag{31}$$

where the velocity and the concentration are determined with an accuracy unspecified constant that could not be obtained in the approximation of the linear stability theory. Thus, through the solution of (31) the final expressions for the velocity and the concentration are determined as follows:

$$\begin{aligned}
&v_z = \varepsilon_0\left\{\sqrt{\frac{D}{\pi t}}\left(\frac{z}{l} + 1\right) - \frac{D}{l}\left[\gamma + \sum_{n=1}^{\infty}(\gamma_n + f_n)\cos(n\varphi)\right]\right\},\\
&c = c_0\left\{\operatorname{erf}\frac{z}{2\sqrt{Dt}} - \frac{z}{l}\left[\gamma + \sum_{n=1}^{\infty}(\gamma_n + f_n)\cos(n\varphi)\right]\right\},
\end{aligned} \tag{32}$$

where

$$l = \sqrt{\frac{\nu}{g}\sqrt{\frac{D}{\tau_0}}} \quad \text{and} \quad \gamma = \gamma_0 + f_0. \tag{33}$$

The result developed shows that under desorption of CO_2 from a stagnant saturated water the desorption rate may be expressed by a relationship similar to that obtained for the absorption. So, the process rate can be determined from (15) and (32):

$$\begin{aligned}
&J = kc_0 = \frac{c_0 D}{l}Sh,\\
&Sh = \frac{kl}{D} = 2\sqrt{\frac{\nu}{\pi g t_0}\sqrt{\frac{1}{Dt_0}}} - \gamma,\\
&Q = c_0\left[2\sqrt{\frac{Dt_0}{\pi}} - \gamma\left(\frac{g}{\nu}\right)^{1/2}D^{3/4}t_0^{5/4}\right],
\end{aligned} \tag{34}$$

where Q is a quality of the adsorbed substance through a unit area per time t_0 [s]. The obtained result (34) is valid for the case of absorption when $c_0 = c^*(\varepsilon \ll 1)$.

The eigenvalue γ is determined by the least-squares method applied to the experimental data obtained in [3–5]. In case of absorption $\gamma = -4.204 \times 10^{-4}$, while in case of desorption $\gamma = 3.032 \times 10^{-5}$. This result indicates that desorption process is stable in the contrast of the absorption one. In this case, the mass transfer rate may

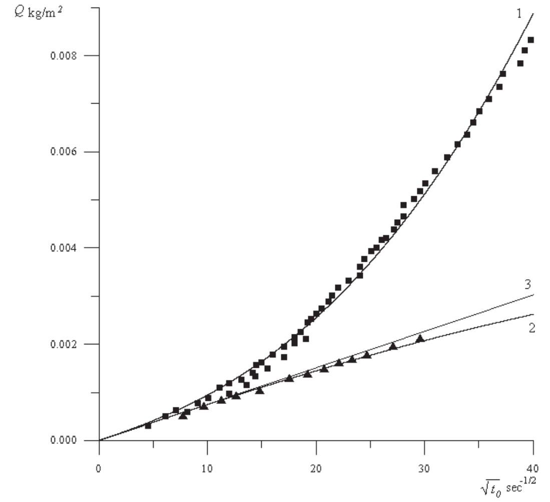

Fig. 1. Comparison of the absorption and desorption rates (5.34) of CO_2 in H_2O: (1) absorption ($\gamma = -4.204 \times 10^{-4}$); (2) desorption ($\gamma = 3.029 \times 10^{-5}$); (3) linear theory ($\gamma = 0$); experimental data: (■) – absorpion, (▲) – desorption.

be determined by (15). Fig. 1 presents the relationship $Q = Q(\sqrt{t_0})$, in (34) for absorption (line 1), desorption (line 2) and according the linear theory of mass transfer, i.e., $\gamma = 0$ (line 3), compared with the experimental data [3–5].

9. Conclusions

The comparative analysis of the both process shows that under desorption of CO_2 from a stagnant saturated water there are no conditions allowing a natural convection. As a result the axial velocity component depends linearly on the axial coordinate while the radial component is independent of the same coordinate. This result is opposite to that obtained under absorption, where the relationship of the axial coordinate is of a power 2. Thus, the axial perturbations of the concentration attenuate and the respective axial perturbations of the velocity attenuate too. The radial perturbations are symmetrical and do not affect the mass transfer rate. The concentration gradient at the interface induces a flow, but its velocity is small and has no effect on the mass transfer rate. This fact, together with the absence of a natural convection in desorption make the induced flow stable with respect to the axial perturbations provoked by the perturbations of the concentration.

Due to the stability of the desorption process and the absence of the non-linear mass transfer effect it follows that the process rate may be determined according the linear theory of the non-stationary mass transfer (15). This result is confirmed by the experimental data [3–5] shown in Fig. 1.

References

[1] Chr. Boyadjiev, On the mechanism and kinetics of the transport processes in systems with intensive interphase mass transfer. 1. Heat and mass transfer, Int. J. Heat Mass Transfer 43 (2000) 2749.

[2] Chr. Boyadjiev, On the mechanism and kinetics of the transport processes in systems with intensive interphase mass transfer. 2. Stability, Int. J. Heat Mass Transfer 43 (2000) 2759.

[3] V.V. Dilman, N.N. Kulov, V.A. Lothov, V.I. Najdenov, On the difference between absorption and desorption rate, Theoret. Fundamentals Chem. Technol. 32 (1998) 377.

[4] R.E. Plevan, J.A. Quinn, The effect of monomolecular films on the rate of gas absorption into a quiescent liquid, AIChEJ 12 (1955) 894.

[5] V.V. Dilman, V.I. Najdeniv, V.V. Olevskii, Marangoni instability in gas absorption, Chem. Industry (Russia) 8 (1992) 465.