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On the mechanism and kinetics of the transport processes in systems with intensive interphase mass transfer. 2. Stability

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Abstract

This research suggests a linear analysis of the stability of non-stationary absorption of concentrated gases in an immobile liquid, where a basic flow is induced as a result of a natural convection and a non-linear mass transfer. A specter of disturbances that lead to a stable dissipative structure with a high mass transfer coefficient has been found. The disturbance amplitude is determined by experimental data for the mass transfer rate in absorption of pure CO_2 in a stagnant water column. It has been shown that conditions for the occurrence of the Marangoni effect do not exist. The theoretical results have a good agreement with the experimental data.

Keywords: Heat and mass transfer; Non-stationary absorption; Non-linear stability

1. Introduction

In the first part of this research, it was shown [1] that in cases of absorption of pure gases in a cylindrical liquid column, a secondary flow is induced as a result of a natural convection and a non-linear mass transfer. Under these conditions, the Marangoni effect is negligible and for the velocity, temperature and concentration the following expressions were obtained:

$$v_z = \varepsilon\left[-\frac{g}{2\nu}z^2 + \left(\frac{1}{2} - \sqrt{\frac{t_0}{\pi t}}\right)\sqrt{\frac{g}{\nu}\sqrt{\frac{D}{t_0}}}z + \sqrt{\frac{D}{\pi t}}\right],$$

$$v_r = \varepsilon\left[-\frac{g}{2\nu}z - \left(\frac{1}{4} - \frac{1}{2}\sqrt{\frac{t_0}{\pi t}}\right)\sqrt{\frac{g}{\nu}\sqrt{\frac{D}{t_0}}}\right]r,$$

$$v_\varphi \equiv 0, \quad p \equiv 0, \quad c^* = \mathrm{erfc}\frac{z}{2\sqrt{Dt}}, \quad \theta \equiv \theta_0,$$
$$\varepsilon = \frac{c^*}{\rho_0}, \quad \nu = \frac{\mu}{\rho_0}. \qquad (1)$$

These results differ significantly from the Benard problem [2,3], where under certain conditions a mechanical equilibrium ($v_z = v_r = v_\varphi = 0$) is possible. The reason for this difference is the non-linear mass transfer, i.e. the large mass flux induces a secondary flow on the phase boundary:

$$z = 0, \quad v_z = \sqrt{\frac{D}{\pi t}} \qquad (2)$$

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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

and in this way, violates the necessary condition for a mechanical equilibrium [4–6].

The process, described by the expressions (1), as may be expected, analogous to the Benard problem, is unstable regarding small disturbances, which makes possible the usage of the linear analysis.

$$\left(1 + \frac{c}{\rho_0}\right) \times \left((4).\frac{\partial v_z'}{\partial t} + v_z'\frac{\partial v_z}{\partial z} + v_z\frac{\partial v_z'}{\partial z} + v_r\frac{\partial v_z'}{\partial r} = -\frac{1}{\rho_0}\frac{\partial p'}{\partial z} + \nu\left(\frac{\partial^2 v_z'}{\partial z^2} + \frac{1}{r}\frac{\partial v_z'}{\partial r} + \frac{\partial^2 v_z'}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2 v_z}{\partial \varphi^2}\right) + \frac{g}{\rho_0}c', (4)(4)\right)$$

2. Linear stability analysis

A process, represented as a superposition of the basic process (1) and small disturbances in the velocity (v_z', v_r', v_φ'), pressure (p'), concentration (c') and temperature (θ') will be considered:

$$v_z + v_z', \quad v_r + v_r', \quad v_\varphi + v_\varphi', \quad p + p', \quad c + c', \quad \theta + \theta'. \tag{3}$$

This new process should satisfy (as well as the basic one) the Oberbeck–Boussinesq equations [1]. The introduction of Eqs. (1) and (3) in these equations leads to a system of equations concerning v_z', v_r', v_φ', p', c' and θ', that will be analyzed in a linearized form with regard to these small disturbances:

$$\left(1 + \frac{c}{\rho_0}\right)\left(\frac{\partial v_r'}{\partial t} + v_z'\frac{\partial v_r}{\partial z} + v_z\frac{\partial v_r'}{\partial z} + v_r'\frac{\partial v_r}{\partial r} + v_r\frac{\partial v_r'}{\partial r}\right) = -\frac{1}{\rho_0}\frac{\partial p'}{\partial r} + \nu\left(\frac{\partial^2 v_r'}{\partial z^2} + \frac{1}{r}\frac{\partial v_r'}{\partial r} + \frac{\partial^2 v_r'}{\partial r^2} - \frac{v_r'}{r^2} + \frac{1}{r^2}\frac{\partial^2 v_r'}{\partial \varphi^2} - \frac{2}{r^2}\frac{\partial v_\varphi'}{\partial \varphi}\right), \tag{5}$$

$$\left(1 + \frac{c}{\rho_0}\right)\left(\frac{\partial v_\varphi'}{\partial t} + v_z\frac{\partial v_\varphi'}{\partial z} + v_r\frac{\partial v_\varphi'}{\partial r} + \frac{1}{r}v_r v_\varphi'\right) = -\frac{1}{\rho_0 r}\frac{\partial p'}{\partial \varphi} + \nu\left(\frac{\partial^2 v_\varphi'}{\partial z^2} + \frac{1}{r}\frac{\partial v_\varphi'}{\partial r} + \frac{\partial^2 v_\varphi'}{\partial r^2} - \frac{v_\varphi'}{r^2} + \frac{1}{r^2}\frac{\partial^2 v_\varphi'}{\partial \varphi^2} + \frac{2}{r^2}\frac{\partial v_r'}{\partial \varphi}\right), \tag{6}$$

$$\frac{\partial c'}{\partial t} + (\rho_0 + c)\left(\frac{\partial v_z'}{\partial z} + \frac{\partial v_r'}{\partial r} + \frac{v_r'}{r} + \frac{1}{r}\frac{\partial v_\varphi'}{\partial \varphi}\right) + v_z'\frac{\partial c}{\partial z} + v_z\frac{\partial c'}{\partial z} + v_r\frac{\partial c'}{\partial z} = 0, \tag{7}$$

$$\frac{\partial \theta'}{\partial t} + v_z\frac{\partial \theta'}{\partial z} + v_r\frac{\partial \theta'}{\partial r} = 0, \tag{8}$$

$$\frac{\partial c'}{\partial t} + v_z'\frac{\partial c}{\partial z} + v_z\frac{\partial c'}{\partial z} + v_r\frac{\partial c'}{\partial r} = D\left(\frac{\partial^2 c'}{\partial z^2} + \frac{1}{r}\frac{\partial c'}{\partial r} + \frac{\partial^2 c'}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2 c'}{\partial \varphi^2}\right), \tag{9}$$

$$\left(1 + \frac{c}{\rho_0}\right)\left(\frac{\partial \theta'}{\partial t} + v_z\frac{\partial \theta'}{\partial z} + v_r\frac{\partial \theta'}{\partial r}\right) = a\left(\frac{\partial \theta'}{\partial z^2} + \frac{1}{r}\frac{\partial \theta'}{\partial r} + \frac{\partial^2 \theta'}{\partial r^2} + \frac{1}{r^2}\frac{\partial \theta'}{\partial \varphi^2}\right); \tag{10}$$

$$t = 0, \quad v_z' = v_r' = v_\varphi' = c' = \theta' = 0; \tag{11}$$

$$z = 0, \quad v_z' = -\frac{D}{\rho_0}\frac{\partial c'}{\partial z}, \quad \mu\left(\frac{\partial v_r'}{\partial z} + \frac{\partial v_z'}{\partial r}\right) = \frac{\partial \sigma}{\partial \theta}\frac{\partial \theta'}{\partial r},$$

$$\mu\left(\frac{\partial v_\varphi'}{\partial z} + \frac{1}{r}\frac{\partial v_z'}{\partial \varphi}\right) = \frac{1}{r}\frac{\partial \sigma}{\partial \theta}\frac{\partial \theta'}{\partial \varphi},$$

$$c' = 0, \quad \lambda\frac{\partial \theta'}{\partial z} = qD\frac{\partial c'}{\partial z}; \tag{12}$$

$$z \to \infty, \quad v_z' = v_r' = v_\varphi' = c' = \theta' = 0; \tag{13}$$

$$r = 0, \quad v_z', v_r', v_\varphi', c', p', \theta' = \text{finite}; \tag{14}$$

$$r = r_0, \quad v_z' = v_r' = v_\varphi' = 0, \quad \frac{\partial c'}{\partial r} = \frac{\partial \theta'}{\partial r} = 0. \tag{15}$$

Eqs. (7) and (8) are obtained from the equation of continuity [1], using the condition $\beta << 1$. The boundary conditions for the pressure are not used, because they will be eliminated in Eqs. (4) and (5). The boundary conditions regarding coordinate φ are not included, because they will be discussed in disturbances, periodical regarding φ.

The system of equations (4)–(15) has partial solutions ("normal" disturbances), that depend exponentially on time:

$$v_z' = \bar{v}_z(t, z, r, \varphi)\exp(-\omega t),$$

$$p' = \bar{p}(t, z, r, \varphi)\exp(-\omega t),$$

$$v_r' = \bar{v}_r(t, z, r, \varphi)\exp(-\omega t),$$

$$c' = \bar{c}(t, z, r, \varphi)\exp(-\omega t),$$

$$v_\varphi' = \bar{v}_\varphi(t, z, r, \varphi)\exp(-\omega t),$$

$$\theta' = \bar{\theta}(t, z, r, \varphi)\exp(-\omega t), \tag{16}$$

where the pre-exponentials also depend on time, because the basic process (1) is non-stationary. The disturbances, presented in this way, decrease or increase with time, depending on the value of ω, and for

$$\omega = 0 \tag{17}$$

the disturbances are "neutral", i.e. a process that do not attenuate and do not intensify with time. The mathematical description of this process is obtained from Eqs. (4)–(15) after the introduction of Eqs. (16) and (17):

$$\left(1 + \frac{c}{\rho_0}\right)\left(\frac{\partial \bar{v}_z}{\partial t} + \bar{v}_z\frac{\partial v_z}{\partial z} + v_z\frac{\partial \bar{v}_z}{\partial z} + v_r\frac{\partial \bar{v}_z}{\partial r}\right) = -\frac{1}{\rho_0}\frac{\partial \bar{p}}{\partial z} + \nu\left(\frac{\partial^2 \bar{v}_z}{\partial z^2} + \frac{1}{r}\frac{\partial \bar{v}_z}{\partial r} + \frac{\partial^2 \bar{v}_z}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2 \bar{v}_z}{\partial \varphi^2}\right) + \frac{g}{\rho_0}\bar{c},$$

$$\left(1 + \frac{c}{\rho_0}\right)\left(\frac{\partial \bar{v}_r}{\partial t} + \bar{v}_z\frac{\partial v_r}{\partial z} + v_z\frac{\partial \bar{v}_r}{\partial z} + \bar{v}_r\frac{\partial v_r}{\partial r} + v_r\frac{\partial \bar{v}_r}{\partial r}\right) = -\frac{1}{\rho_0}\frac{\partial \bar{p}}{\partial r} + \nu\left(\frac{\partial^2 \bar{v}_r}{\partial z^2} + \frac{1}{r}\frac{\partial \bar{v}_r}{\partial r} + \frac{\partial^2 \bar{v}_r}{\partial r^2} - \frac{\bar{v}_r}{r^2} + \frac{1}{r^2}\frac{\partial^2 \bar{v}_r}{\partial \varphi^2} - \frac{2}{r^2}\frac{\partial \bar{v}_\varphi}{\partial \varphi}\right), \tag{19}$$

$$\left(1+\frac{c}{\rho_0}\right)\left(\frac{\partial \bar{v}_\varphi}{\partial t}+v_z\frac{\partial \bar{v}_\varphi}{\partial z}+v_r\frac{\partial \bar{v}_\varphi}{\partial r}+\frac{1}{r}v_r\bar{v}_\varphi\right)$$
$$=-\frac{1}{\rho_0 r}\frac{\partial \bar{p}}{\partial \varphi}+\nu\left(\frac{\partial^2 \bar{v}_\varphi}{\partial z^2}+\frac{1}{r}\frac{\partial \bar{v}_\varphi}{\partial r}+\frac{\partial^2 \bar{v}_\varphi}{\partial r^2}-\frac{\bar{v}_\varphi}{r^2}+\frac{1}{r^2}\frac{\partial^2 \bar{v}_\varphi}{\partial \varphi^2}+\frac{2}{r^2}\frac{\partial \bar{v}_r}{\partial \varphi}\right), \tag{20}$$

$$\frac{\partial \bar{c}}{\partial t}+(\rho_0+c)\left(\frac{\partial \bar{v}_z}{\partial z}+\frac{\partial \bar{v}_r}{\partial r}+\frac{\bar{v}_r}{r}+\frac{1}{r}\frac{\partial \bar{v}_\varphi}{\partial \varphi}\right)+\bar{v}_z\frac{\partial c}{\partial z}+v_z\frac{\partial \bar{c}}{\partial z}+v_r\frac{\partial \bar{c}}{\partial z}=0, \tag{21}$$

$$\frac{\partial \bar{\theta}}{\partial t}+v_z\frac{\partial \bar{\theta}}{\partial z}+v_r\frac{\partial \bar{\theta}}{\partial r}=0, \tag{22}$$

$$\frac{\partial \bar{c}}{\partial t}+\bar{v}_z\frac{\partial c}{\partial z}+v_z\frac{\partial \bar{c}}{\partial z}+v_r\frac{\partial \bar{c}}{\partial r}=D\left(\frac{\partial^2 \bar{c}}{\partial z^2}+\frac{1}{r}\frac{\partial \bar{c}}{\partial r}+\frac{\partial^2 \bar{c}}{\partial r^2}+\frac{1}{r^2}\frac{\partial^2 \bar{c}}{\partial \varphi^2}\right), \tag{23}$$

$$\left(1+\frac{c}{\rho_0}\right)\left(\frac{\partial \bar{\theta}}{\partial t}+v_z\frac{\partial \bar{\theta}}{\partial z}+v_r\frac{\partial \bar{\theta}}{\partial r}\right)=a\left(\frac{\partial^2 \bar{\theta}}{\partial z^2}+\frac{1}{r}\frac{\partial \bar{\theta}}{\partial r}+\frac{\partial^2 \bar{\theta}}{\partial r^2}+\frac{1}{r^2}\frac{\partial^2 \bar{\theta}}{\partial \varphi^2}\right), \tag{24}$$

$$z=0,\quad \bar{v}_z=-\frac{D}{\rho_0}\frac{\partial \bar{c}}{\partial z},\quad \mu\left(\frac{\partial \bar{v}_r}{\partial z}+\frac{\partial \bar{v}_z}{\partial r}\right)=\frac{\partial \sigma}{\partial \theta}\frac{\partial \bar{\theta}}{\partial r},\quad \mu\left(\frac{\partial \bar{v}_\varphi}{\partial z}+\frac{1}{r}\frac{\partial \bar{v}_z}{\partial \varphi}\right)=\frac{1}{r}\frac{\partial \sigma}{\partial \theta}\frac{\partial \bar{\theta}}{\partial \varphi},\quad \bar{c}=0,\quad \lambda\frac{\partial \bar{\theta}}{\partial z}=qD\frac{\partial \bar{c}}{\partial z}; \tag{25}$$

$$z\rightarrow\infty,\quad \bar{v}_z=\bar{v}_r=\bar{v}_\varphi=\bar{c}=\bar{\theta}=0; \tag{26}$$

$$r=0,\quad \bar{v}_z,\bar{v}_r,\bar{v}_\varphi,\bar{p},\bar{c},\bar{\theta}=\text{finite};$$

$$r=r_0,\quad \bar{v}_z=\bar{v}_r=\bar{v}_\varphi=0,\quad \frac{\partial \bar{c}}{\partial r}=\frac{\partial \bar{\theta}}{\partial r}=0. \tag{27}$$

The problem (Eqs. (18)–(27)) obviously has partial solutions, for which the velocity, concentration and temperature depend on φ harmonically, i.e. in Eqs. (18)–(27), the following specter of neutral disturbances may be introduced:

$$\bar{v}_z=\sum_{n=0}^{\infty}v_n(t,z,r)\cos(n\varphi),\quad \bar{v}_r=\bar{v}_\varphi=0,\quad \bar{p}=\sum_{n=0}^{\infty}p_n(t,z,r)\cos(n\varphi),\quad \bar{c}=\sum_{n=0}^{\infty}c_n(t,z,r)\cos(n\varphi),\quad \bar{\theta}=\sum_{n=0}^{\infty}\theta_n(t,z,r)\cos(n\varphi) \tag{28}$$

Introducing Eq. (28) into Eqs. (18)–(27) leads to the following eigenvalues problem:

$$(1+\varepsilon)\left(\frac{\partial v_n}{\partial t}+v_n\frac{\partial v_z}{\partial z}+v_z\frac{\partial v_n}{\partial z}+v_r\frac{\partial v_n}{\partial r}\right)=-\frac{1}{\rho_0}\frac{\partial p_n}{\partial z}+\nu\left(\frac{\partial^2 v_n}{\partial z^2}+\frac{1}{r}\frac{\partial v_n}{\partial r}+\frac{\partial^2 v_n}{\partial r^2}-\frac{n^2}{r^2}v_n\right)+\frac{g}{\rho_0}c_n, \tag{29}$$

$$(1+\varepsilon)\frac{\partial v_r}{\partial z}v_n=-\frac{1}{\rho_0}\frac{\partial p_n}{\partial r}, \tag{30}$$

$$\frac{\partial p_n}{\partial \varphi}=0, \tag{31}$$

$$\frac{\partial c_n}{\partial t}+\rho_0(1+\varepsilon)\frac{\partial v_n}{\partial z}+v_n\frac{\partial c}{\partial z}+v_z\frac{\partial c_n}{\partial z}+v_r\frac{\partial c_n}{\partial z}=0, \tag{32}$$

$$\frac{\partial \theta_n}{\partial t}+v_z\frac{\partial \theta_n}{\partial z}+v_r\frac{\partial \theta_n}{\partial r}=0, \tag{33}$$

$$\frac{\partial c_n}{\partial t}+v_n\frac{\partial c}{\partial z}+v_z\frac{\partial c_n}{\partial z}+v_r\frac{\partial c_n}{\partial r}=D\left(\frac{\partial^2 c_n}{\partial z^2}+\frac{1}{r}\frac{\partial c_n}{\partial r}+\frac{\partial^2 c_n}{\partial r^2}-\frac{n^2}{r^2}c_n\right), \tag{34}$$

$$(1+\varepsilon)\left(\frac{\partial \theta_n}{\partial t}+v_z\frac{\partial \theta_n}{\partial z}+v_r\frac{\partial \theta_r}{\partial r}\right)=a\left(\frac{\partial^2 \theta_n}{\partial z^2}+\frac{1}{r}\frac{\partial \theta_n}{\partial r}+\frac{\partial^2 \theta_n}{\partial r^2}-\frac{n^2}{r^2}\theta_n\right), \tag{35}$$

$$z=0,\quad v_n=-\frac{D}{\rho_0}\frac{\partial c_n}{\partial z},\quad \theta_n=c_n=0,\quad \lambda\frac{\partial \theta_n}{\partial z}=qD\frac{\partial c_n}{\partial z}, \tag{36}$$

$$z \to \infty, \quad v_n = c_n = \theta_n = 0; \tag{37}$$

$$r = 0, \quad v_n, c_n, \theta_n = \text{finite}; \tag{38}$$

$$r = r_0, \quad v_n = 0, \quad \frac{\partial c_n}{\partial r} = \frac{\partial \theta_n}{\partial r} = 0; \quad n = 0, 1, 2, \ldots, \infty. \tag{39}$$

In Eqs. (29)–(35), $c = c^*$ is accepted, because the thickness of the layer, in which the velocity changes, is much less than the one for the concentration.

The pressure in Eq. (29) may be eliminated, if Eq. (30) is integrated with respect to r and then differentiated with respect to z:

$$(1+\varepsilon)\int \frac{\partial v_r}{\partial z}\frac{\partial v_n}{\partial z}\,\mathrm{d}r = -\frac{1}{\rho_0}\frac{\partial p_n}{\partial z}, \quad n = 0, 1, 2, \ldots, \infty. \tag{40}$$

Introducing Eqs. (40), (32) and (33) into Eqs. (29), (34) and (35) leads to the final form of the equations for determination of the "neutral" disturbances in velocity, concentration and temperature:

$$(1+\varepsilon)\left(\frac{\partial v_n}{\partial t} + v_n\frac{\partial v_z}{\partial z} + v_z\frac{\partial v_n}{\partial z} + v_r\frac{\partial v_n}{\partial r}\right) = (1+\varepsilon)\int \frac{\partial v_r}{\partial z}\frac{\partial v_n}{\partial z}\,\mathrm{d}r + \nu\left(\frac{\partial^2 v_n}{\partial z^2} + \frac{1}{r}\frac{\partial v_n}{\partial r} + \frac{\partial^2 v_n}{\partial r^2} - \frac{n^2}{r^2}v_n\right) + \frac{g}{\rho_0}c_n, \tag{41}$$

$$(1+\varepsilon)\frac{\partial v_n}{\partial z} = \frac{D}{\rho_0}\left(\frac{\partial^2 c_n}{\partial z^2} + \frac{\partial^2 c_n}{\partial r^2} + \frac{1}{r}\frac{\partial c_n}{\partial r} - \frac{n^2}{r^2}c_n\right), \tag{42}$$

$$\frac{\partial^2 \theta_n}{\partial z^2} + \frac{\partial^2 \theta_n}{\partial r^2} + \frac{1}{r}\frac{\partial \theta_n}{\partial r} - \frac{n^2}{r^2}\theta_n = 0, \quad n = 0, 1, 2, \ldots, \infty. \tag{43}$$

with boundary conditions:

$$z = 0, \quad v_n = -\frac{D}{\rho_0}\frac{\partial c_n}{\partial z}, \quad c_n = 0, \quad \frac{\partial \theta_n}{\partial z} = \frac{qD}{\lambda}\frac{\partial c_n}{\partial z};$$

$$z \to \infty, \quad v_n = c_n = \theta_n = 0;$$

$$r = 0, \quad v_n, c_n, \theta_n = \text{finite};$$

$$r = r_0, \quad v_n = 0, \quad \frac{\partial c_n}{\partial r} = \frac{\partial \theta_n}{\partial r} = 0; \quad n = 0, 1, 2, \ldots, \infty. \tag{44}$$

3. Analytical solution

The problem (Eqs. (41)–(44)) will be solved by the introduction of dimensionless variables and a partial separation of the variables:

$$t = t_0 T, \quad z = lZ, \quad r = r_0 R, \quad v_n = u_0\left[V_n(Z,T) - Bf_n(R)\right],$$

$$c_n = c^*\left[C_n(Z,T) + Zf_n(R)\right], \quad \theta_n = \frac{qDc^*}{\lambda\theta_0}f_n(R), \quad B = \frac{D\varepsilon}{u_0 l}, \quad n = 0, 1, 2, \ldots, \infty, \tag{45}$$

where the dependence of the disturbances on the coordinates is supposed to be analogous to the basic process (1) for small values of z.

The introduction of Eq. (45) into Eqs. (41)–(44) leads to:

$$(1+\varepsilon)\left\{\frac{u_0}{\varepsilon t_0 g}\frac{\partial V_n}{\partial T} + \frac{u_0^2}{\varepsilon l g}\left[(V_n - Bf_n)\frac{\partial V_z}{\partial Z} + V_z\frac{\partial V_n}{\partial Z} - BV_r f_n'\right]\right\} = (1+\varepsilon)\frac{u_0^2 r_0^2}{\varepsilon l^3 g}\int \frac{\partial V_r}{\partial Z}\frac{\partial V_n}{\partial Z}\,\mathrm{d}R + \frac{\nu u_0}{\varepsilon l^2 g}\frac{\partial^2 V_n}{\partial Z^2} - \frac{\nu u_0}{\varepsilon r_0^2 g}V_n\frac{n^2}{R^2} + C_n + Zf_n, \tag{46}$$

$$f_n'' + \frac{1}{R}f_n' - \frac{n^2}{R^2}f_n = 0, \tag{47}$$

$$(1+\varepsilon)\frac{u_0 l}{\varepsilon D}\frac{\partial V_n}{\partial Z} = \frac{\partial^2 C_n}{\partial Z^2} - \frac{l^2}{r^2}\frac{n^2}{R^2}C_n; \quad n = 0, 1, 2, \ldots, \infty; \tag{48}$$

with boundary conditions:

$$Z = 0, \quad V_n = -B\frac{\partial C_n}{\partial Z}, \quad C_n = 0; \tag{49}$$

$$R = 0, \quad f_n = \text{finite}; \tag{50}$$

$$R=1,\quad f_n'=0;\quad n=0,1,2,\ldots,\infty, \tag{51}$$

where

$$\frac{u_0}{\varepsilon g t_0}\sim 10^{-9},\quad \frac{u_0^2}{\varepsilon g t_0}\sim 10^{-7},\quad \frac{u_0^2 r_0^2}{\varepsilon g l^3}\sim 10^{3},$$

$$\frac{\nu u_0}{\varepsilon g l^2}\sim 1,\quad \frac{\nu u_0}{\varepsilon g r_0^2}\sim 10^{-9},\quad \frac{u_0 l}{\varepsilon D}\sim 10^{-8},\quad \varepsilon\sim 10^{-1},$$

$$u_0=\varepsilon\sqrt{\frac{D}{t_0}}\sim 10^{-7}\ \text{m/s},\quad l=\sqrt{\frac{\nu}{g}\sqrt{\frac{D}{t_0}}}\sim 10^{-7}\ \text{m}. \tag{52}$$

The solution of the Oiler equation (47) is obtained through Grin functions [7], looking for the eigenvalues and eigenfunctions for $n = 0, 1, 2,\ldots, \infty$:

$$f_0=\text{const},$$

$$f_n=\frac{\xi^n+\xi^{-n}}{2n}R^n,\quad R<\xi,$$

$$f_n=\frac{\xi^n}{2n}(R^n+R^{-n}),\quad R<\xi,$$

$$f_n=\frac{\xi^{2n}}{2n}+\frac{1}{2n},\quad R=\xi,\quad 0<\xi<1, n=1,2,\ldots,\infty, \tag{53}$$

where ξ is a parameter that cannot be determined in the approximations of the linear theory.

Keeping in mind the order of the dimensionless variables in Eq. (52), from Eqs. (46) and (48), the following is directly obtained:

$$\frac{\partial^2 C_n}{\partial Z^2}=0;\quad Z=0,\quad C_n=0;$$

$$C_n=\gamma_n Z; \tag{54}$$

$$\frac{\partial V_n}{\partial Z}=0;\quad Z=0,\quad V_n=-B\frac{\partial C_n}{\partial Z};$$

$$V_n=-B\gamma_n;\quad n=0,1,2,\ldots,\infty, \tag{55}$$

where the eigenvalue $\lambda_n<0$ cannot be determined in the approximations of the linear stability analysis.

4. Results and discussion

The obtained solutions (53)–(55) allow defining the final expressions for velocity, concentration and temperature:

$$v_z=\frac{c^*}{\rho_0}\left\{-\frac{g}{2\nu}z^2+\left(\frac{1}{2}-\sqrt{\frac{t_0}{\pi t}}\right)\sqrt{\frac{g}{\nu}\sqrt{\frac{D}{t_0}}}z+\sqrt{\frac{D}{\pi t}}+\sqrt{\frac{gD}{\nu}\sqrt{Dt_0}}\left[-\bar{\gamma}+\sum_{n=1}^{\infty}(\gamma_n+f_n)\cos n\varphi\right]\right\}, \tag{56}$$

$$c=c^*\left\{\operatorname{erfc}\frac{z}{2\sqrt{DT}}+z\sqrt{\frac{g}{\nu}\sqrt{\frac{t_0}{D}}}\left[-\bar{\gamma}+\sum_{N=1}^{\infty}(\gamma_n+f_n)\cos n\varphi\right]\right\},$$

$$\theta=\frac{qc^*}{\lambda}\sqrt{\frac{gD}{\nu}\sqrt{Dt_0}}z\left[f_0+\sum_{n=1}^{\infty}f_n\left(\frac{r}{r_0}\right)\cos n\varphi\right],$$

$$\bar{\gamma}=-(\gamma_0+f_0). \tag{58}$$

From Eq. (57), it is possible to determine the local (at a given moment) mass flow:

$$i=-\frac{D\rho^*}{\rho_0}\left(\frac{\partial c}{\partial z}\right)_{z=0}=\frac{\rho^* c^*}{\rho_0}\left\{\frac{1}{\sqrt{\pi Dt}}+\sqrt{\frac{g}{\nu}\sqrt{\frac{t_0}{D}}}\left[\bar{\gamma}+\sum_{n=1}^{\infty}(\gamma_n+f_n)\cos n\varphi\right]\right\},$$

$$\rho^*=\rho_0+c^*,\quad f_n=f_n\left(\frac{r}{r_0}\right),\quad n=1,2,\ldots,\infty. \tag{59}$$

The amount of absorbed substance through the cross-section πr^2 is determined directly from Eq. (59), integrating with respect to φ in the range $[0, 2\pi]$, and keeping in mind that the integrals of the harmonic functions are equal to zero:

$$I=\pi r_0^2 c^*\frac{\rho^*}{\rho_0}\left(\frac{1}{\sqrt{\pi Dt}}+\gamma\right),\qquad \gamma=\bar{\gamma}\sqrt{\frac{g}{\nu}\sqrt{\frac{t_0}{D}}}. \tag{60}$$

From Eq. (60), the absorption rate (J), the Sherwood number (Sh) and the mass of the absorbed substance (Q) for a period of time t_0 through a unity surface are directly obtained:

$$J=kc^*=\frac{1}{\pi r_0^2 t_0}\int_0^{t_0} I\,\mathrm{d}t, \tag{61}$$

$$Sh = \frac{kt_0}{D} = 2c^* \frac{\rho^*}{\rho_0}\left(\sqrt{\frac{D}{\pi t_0}} + \gamma\right), \tag{62}$$

$$Q = 2c^* \frac{\rho^*}{\rho_0}\left(\sqrt{\frac{Dt_0}{\pi}} + \gamma t_0\right), \tag{63}$$

where k is the mass transfer coefficient of the non-stationary absorption.

In this way, the obtained Eqs. (61)–(63) allow the determination of the absorption rate with an accuracy defined by the parameter γ, whose value cannot be determined in the approximations of the linear stability analysis. The parameter γ may be determined by introducting of an additional physical condition, or from the experimental data.

The study of non-stationary absorption of pure CO_2 in H_2O [8,9] offers experimental data for the dependence of Q on $\sqrt{t_0}$. They were used for the determination of γ in Eq. (63) by means of the least square method. The value of γ was calculated $\gamma = 4.04$. In Fig. 1, Eq. (63) for $\gamma = 4.04$ is shown, and the dots are experimental data from Refs. [8,9].

From Eqs. (62) and (63), it is clear that the increasing of the absorption rate is a result of the stability loss of the main process (1). As a result, the small disturbances may increase until reaching a new stable periodical process, i.e. they are a self-organizing dissipative structure (Eqs. (56)–(58)). This means that the disturbances in Eqs. (4)–(10) are not very small, and therefore, the linear analysis of stability may not be correct, i.e. the obtained results (56)–(58).

The correctness of the used linear analysis of stability of the process (1) may be determined, if a check of the satisfaction of its approximations is carried out. For example, the used Eq. (4) is valid in the cases when:

$$v'_z \frac{\partial v'_z}{\partial z} \ll v_z \frac{\partial v_z}{\partial z}, \quad v'_r \frac{\partial v'_z}{\partial r} \ll v_r \frac{\partial v_z}{\partial r},$$
$$v'_\varphi \frac{\partial v_z}{\partial \varphi} \ll v_\varphi \frac{\partial v_z}{\partial \varphi}. \tag{64}$$

The obtained results for the disturbances (Eqs. (45) and (52)–(55)) show

$$v'_z \frac{\partial v'_z}{\partial z} = v'_r \frac{\partial v'_z}{\partial r} = v'_\varphi \frac{\partial v'_z}{\partial \varphi} = 0. \tag{65}$$

Analogously, the correctness of the elimination of the remaining square terms in Eqs. (5)–(10) may be shown. The terms:

$$v'_z \frac{\partial c'}{\partial z}, \ v'_z \frac{\partial \theta'}{\partial z} \tag{66}$$

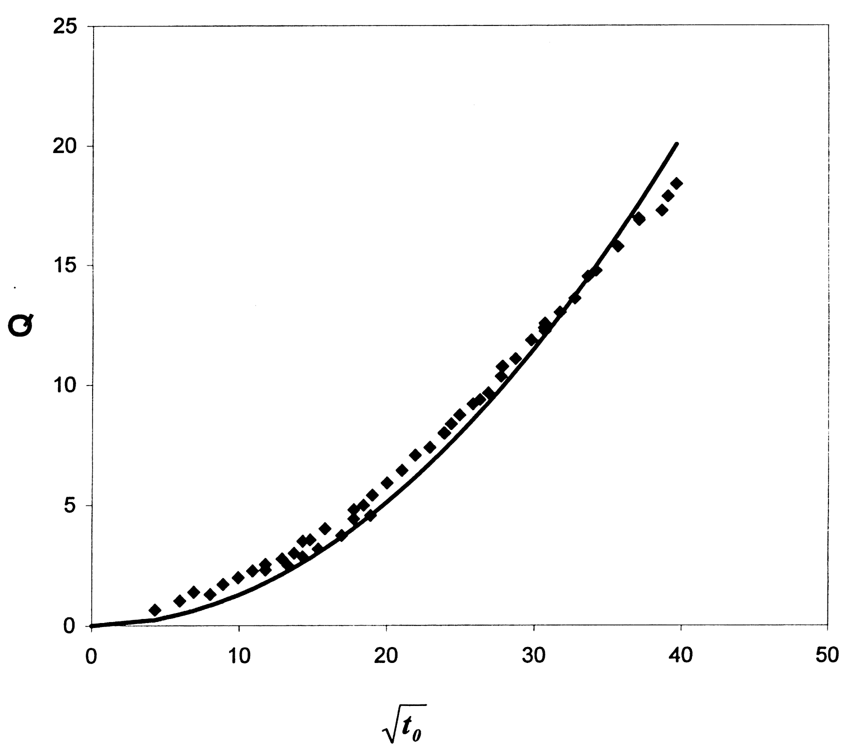

Fig. 1. Comparison between theoretical (Eq. (63)) and experimental (points) results.

are exceptions in Eqs. (9) and (10), but they will also appear in Eqs. (7) and (8) and will be eliminated in the next transformations in obtaining Eqs. (42) and (43).

The analysis of Eqs. (64)–(66) shows that the obtained results (56)–(63) are correct and valid not only for very small disturbances, but also they satisfy the non-linear form of the system of equations (4)–(15).

In Ref. [8], an attempt is made to explain the difference in the experimental data for a non-stationary absorption of pure CO_2 in H_2O in the linear theory of mass transfer and the Marangoni effect. There, it is correctly shown that $(\theta^* - \theta_0) \approx 0.02°C$ (θ^* — temperature of the phase boundary), but it is assumed unreasonably that the fluctuations of θ^* are enough for the stability loss as a result of a surface tension gradient. The usage of the experimental data for the determination of the characteristic velocity of the flow $u_0 = 1.12 \times 10^{-6}$ m/s shows that it is very close to the characteristic velocity in the cases when it is a result of the non-linear mass transfer [1]:

$$u_0 = \frac{c^*}{\rho_0}\sqrt{\frac{D}{t_0}} = 0.876 \times 10^{-6}\ \mathrm{m/s}, \quad t_0 = 10\ \mathrm{s}. \qquad (67)$$

The solution of the Benard problem, taking into account the surface tension gradient [5,10–12], show that the Marangoni effect may occur in layers with thickness not greater than several millimeters. This fact additionally shows that in the case of a non-stationary absorption at large concentration gradients, occurrence of the Marangoni effect cannot be expected.

5. Conclusions

The theoretical analysis of the mechanism and the kinetics of the transport processes in systems with intensive mass transfer shows that in the cases of a gas absorption at large concentration gradients and a chemical reaction in the liquid phase, the mass transfer rate is significantly higher than the one supposed by the linear theory of mass transfer. In the absence of surface active agents and availability of a temperature field, caused by the thermal effect of the chemical reaction, the surface tension gradient is not enough for the occurrence of the Marangoni effect. In the case of a non-stationary absorption of a gas in a stagnant liquid, a flow is induced as a result of a natural convection and a non-linear mass transfer (a density gradient in the volume and a large mass flux through the phase boundary). This problem differs significantly from the Benard problem, as the large concentration gradient at the interphase induces a secondary flow, oriented normally to this surface, and in this way do not allow the existence of a mechanical equilibrium (diffusion in an immobile liquid). In this way, the discussed basic process (movement, diffusion and heat transfer) is unstable regarding disturbances, that may not be small. As a result, the process becomes unstable and is transformed into a periodically stable process, i.e. a self-organizing dissipative structure (velocity, concentration and temperature field), in which the mass transfer rate is significantly higher. The obtained theoretical results are in a good agreement with the experimental data.

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