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# Non-linear mass transfer and Marangoni effect in gas–liquid systems

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**Abstract**—The comparative analysis of the influence of the effect of non-linear mass transfer and the Marangoni effect on the mass transfer kinetics and the hydrodynamic stability are done. Co-current gas and liquid flow in the laminar boundary layer along the flat phase surface is considered. One of the components of gas is absorbed by the liquid and reacts with a liquid component. The chemical reaction rate is of first-order. The heat effect from the chemical reaction creates a temperature gradient, i.e. the mass transfer together with a heat transfer can be observed. The data for heat and mass transfer coefficients are obtained. The critical Reynolds numbers, corresponding wave velocities, and wave numbers are obtained.

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## INTRODUCTION

Intensification of mass transfer in the industrial gas–liquid systems is obtained very often by the creation of large concentration gradients. It can be reached in a number of cases as a result of a chemical reaction of the transferred substance in the liquid phase. The heat effect of the chemical reactions creates significantly high temperature gradients. The temperature and concentration gradients created can considerably affect the mass transfer kinetics in gas–liquid systems. Hence, the experimentally defined mass transfer coefficients are significantly different from the ones predicted by the linear theory of mass transfer.

It has been shown in a number of papers [1–7], that the temperature, and the concentration gradients directly tangentially to the interface, can create a interfacial tension gradient. As a result of this a secondary flow is induced. The rate of the induced flow is directed tangentially to the interface. It leads to a change in the velocity distribution in the boundary layer and therefore, to a change in the mass transfer kinetics and hydrodynamic stability of the flow. These effects are considered to be the Marangoni effect and used as an explanation of all experimental deviations from the linear theory of the mass transfer, where the hydrodynamic of the flow does not depend on the mass transfer.

The investigations of gas–liquid systems with intensive interphase mass transfer as a result of large concentration gradients show [8–24] that under these conditions the secondary flow is induced normally directed to the surface. It leads to ‘injection’ or ‘suction’ of a substance in the boundary layer, therefore, to a change in the velocity distribution in the layer and the mass transfer kinetics and hydrodynamic stability of the flow. This effect of non-linear mass transfer

can explain a number of experimental deviations from the linear theory of mass transfer [21], which have been explained with the Marangoni effect.

The two above-mentioned effects (the Marangoni effect and the effect of non-linear mass transfer) can manifest themselves separately, as well as in a combined effect. That is why their influence on the mass transfer kinetics and the hydrodynamic stability should be compared.

## MATHEMATICAL MODEL

Co-current gas and liquid flow in the laminar boundary layer along the flat phase surface will be considered. One of the components of gas is absorbed by the liquid and reacts with a liquid component. The chemical reaction rate is of the first-order. The heat effect from the chemical reaction creates a temperature gradient, i.e. the mass transfer, together with a heat transfer, can be observed. Under these conditions the mathematical model takes the following form:

$$u_j \frac{\partial u_j}{\partial x} + v_j \frac{\partial u_j}{\partial y} = v_j \frac{\partial^2 u_j}{\partial y^2} - \frac{\partial u_j}{\partial x} + \frac{\partial v_j}{\partial y} = 0$$

$$u_j \frac{\partial c_j}{\partial x} + v_j \frac{\partial c_j}{\partial y} = D_j \frac{\partial^2 c_j}{\partial y^2} - (j-1)kc_j$$

$$u_j \frac{\partial t_j}{\partial x} + v_j \frac{\partial t_j}{\partial y} = a_j \frac{\partial^2 t_j}{\partial y^2} + (j-1) \frac{q}{\rho_j c_{pj}} kc_j;$$

$$j = 1 \text{—gas, } i = 2 \text{—liquid.} \quad (1)$$

The influence of the temperature on the chemical reaction rate is not considered in equation (1) because it does not have a considerable effect on the comparative analysis of these two effects, which are the subject of the present investigation.

## NOMENCLATURE

$A$	dimensionless wavenumber	$\beta_r$	the circle frequency
$a$	thermal diffusivity [ $\text{m}^2 \text{s}^{-1}$ ]	$\beta_i$	increment factor
$C$	dimensionless phase velocity	$\beta/\alpha$	phase velocity
$c$	concentration [ $\text{kg mol m}^{-3}$ ]	$\pi$	3.14
$c_p$	specific heat [ $\text{J kg}^{-1} \text{deg}^{-1}$ ]	$\lambda$	heat-conductivity coefficient [ $\text{J.s m}^{-2}$ ], wavelength [m]
$D$	diffusivity [ $\text{m}^2 \text{s}^{-1}$ ]	$\mu$	dynamic viscosity [ $\text{N (m.s. deg)}^{-1}$ ]
$i$	imaginary unit	$\rho$	density [ $\text{kg m}^{-3}$ ]
$k$	chemical reaction rate [ $\text{m s}^{-1}$ ]	$\sigma$	interfacial tension [ $\text{N m}^{-1}$ ]
$k_c$	mass transfer coefficient [ $\text{m s}^{-1}$ ]	$\chi$	Henry constant.
$k_t$	heat transfer coefficient [ $\text{m s}^{-1}$ ]		
$M$	molecule mass [ $\text{kg kg}^{-1} \text{mol}^{-1}$ ]		
$q$	heat effect of the chemical reaction [ $\text{J kg}^{-1} \text{mol}^{-1}$ ]		
$t$	temperature [deg], time		
$u$	velocity in $x$ -direction [ $\text{m s}^{-1}$ ]		
$v$	velocity $y$ -direction [ $\text{m s}^{-1}$ ]		
$x$	coordinate [m]		
$y$	coordinate [m].		
Greek symbols			
$\alpha$	wave number [ $\text{m}^{-1}$ ]		
		Indices	
		0	for a boundary value
		1	for gas
		2	for liquid
		*	for interface
		$r$	for the real part of a complex number
		$i$	for the imaginary part of a complex number.

The boundary conditions of equation (1) determine the potential gas and liquid flows far from the phase boundary. Thermodynamic equilibrium and the continuity of velocity and the flux of momentum, mass and heat fluxes can be detected on the phase boundary. It has been shown in ref. [18] that in the gas-liquid systems the effect of non-linear mass transfer is located in the gas phase. Taking into account these considerations, the boundary conditions take the following form:

$$\begin{aligned}
 x=0 \quad u_j &= u_{j0} \quad c_1 = c_{10} \quad c_2 = 0 \quad t_j = t_0 \\
 y \rightarrow \infty \quad u_1 &= u_{10} \quad c_1 = c_{10} \quad t_1 = t_0 \\
 y \rightarrow -\infty \quad u_2 &= u_{20} \quad c_2 = 0 \quad t_2 = t_0 \\
 y=0 \quad u_1 &= u_2 \quad \mu_1 \frac{\partial u_1}{\partial y} = \mu_2 \frac{\partial u_2}{\partial y} - \frac{\partial \sigma}{\partial x} \\
 v_1 &= -\frac{MD_1}{\rho_1^*} \frac{\partial c_1}{\partial y} \quad v_2 = 0 \\
 c_1 &= \chi c_2 \quad D_1 \frac{\rho_1^*}{\rho_1^*} \frac{\partial c_1}{\partial y} = D_2 \frac{\partial c_2}{\partial y} \quad (\rho_1^* = \rho_1^* + Mc_1^*) \\
 t_1 &= t_2 \quad \lambda_1 \frac{\partial t_1}{\partial y} + \rho_1 c_{p1} v_1 t_1 = \lambda_2 \frac{\partial t_2}{\partial y} \quad j = 1, 2. \quad (2)
 \end{aligned}$$

At a high enough value of  $c_0$ , one can observe a large concentration gradient normally directed to the interface  $(\partial c_1 / \partial y)_{y=0}$ , which induces a secondary flow with the rate  $v_1$ . The tangential concentration and temperature gradients on the phase boundary create the interfacial tension gradient:

$$\frac{\partial \sigma}{\partial x} = \frac{\partial \sigma}{\partial c_2} \frac{\partial c_2}{\partial x} + \frac{\partial \sigma}{\partial t_2} \frac{\partial t_2}{\partial x} \quad (3)$$

which induces a tangential secondary flow, whose rate is proportional to  $\partial \sigma / \partial x$ . Further, we will examine the substance which are not surface active, i.e.  $\partial \sigma / \partial c_2 \approx 0$ .

## HEAT AND MASS TRANSFER KINETICS

The mass transfer rate ( $J_c$ ) and the heat transfer rate ( $J_t$ ) can be determined from the local mass ( $I_c$ ) and heat ( $I_t$ ) fluxes after taking the mean of these fluxes along a length ( $l$ ) of the interface:

$$\begin{aligned}
 J_c &= k_c c_0 = \frac{1}{l} \int_0^l I_c dx \\
 I_c &= \frac{MD_1 \rho_1^*}{\rho_1^*} \left( \frac{\partial c_1}{\partial y} \right)_{y=0} \\
 J_t &= k_t t_0 = \frac{1}{l} \int_0^l I_t dx \\
 I_t &= -\lambda_1 \left( \frac{\partial t_1}{\partial y} \right)_{y=0} + \rho_1 c_{p1} (v_1 t_1)_{y=0} \quad (4)
 \end{aligned}$$

where  $c_1$  and  $t_1$  are determined after solving the problems (1)–(2). In order to do this the following dimensionless variables will be introduced:

$$x = lX \quad y = (-1)^{j+1} \delta_j Y_j \quad \delta_j = \sqrt{\frac{v_j l}{u_{j0}}}$$

$$\begin{aligned}
 u_j &= u_{j0} U_j(X, Y_j) \\
 v_j &= (-1)^{j+1} u_{j0} \frac{\delta_j}{l} V_j(X, Y_j) \\
 c_j &= (-\chi)^{1-j} c_0 C_j(X, Y_j) \\
 t_j &= t_0 + (-1)^{j+1} t_0 T_j(X, Y_j) \quad j = 1, 2. \quad (5)
 \end{aligned}$$

Introducing equation (5) into equations (1) and (2) leads to the following equations:

$$\begin{aligned}
 U_j \frac{\partial U_j}{\partial X} + V_j \frac{\partial U_j}{\partial Y_j} &= \frac{\partial^2 U_j}{\partial Y_j^2}, \quad \frac{\partial U_j}{\partial X} + \frac{\partial V_j}{\partial Y_j} = 0 \\
 U_j \frac{\partial C_j}{\partial X} + V_j \frac{\partial C_j}{\partial Y_j} &= \frac{1}{Sc_j} \frac{\partial^2 C_j}{\partial Y_j^2} - (j-1) Da C_j \\
 U_j \frac{\partial T_j}{\partial X} + V_j \frac{\partial T_j}{\partial Y_j} &= \frac{1}{Pr_j} \frac{\partial^2 T_j}{\partial Y_j^2} + (j-1) Q Da C_j \quad j = 1, 2
 \end{aligned} \quad (6)$$

where

$$\begin{aligned}
 Da &= \frac{kl}{u_{20}} \quad Q = \frac{qc_0}{\chi \rho_2 c_{p2} t_0} \quad Sc_j = \frac{v_j}{D_j} \\
 Pr_j &= \frac{v_j}{a_j} \quad j = 1, 2. \quad (7)
 \end{aligned}$$

The boundary conditions of equations (6) have the following form:

$$\begin{aligned}
 X=0 \quad U_j &= 1 \quad C_1 = 1 \quad C_2 = 0 \quad T_j = 0 \quad j = 1, 2 \\
 Y_1 \rightarrow \infty \quad U_1 &= 1 \quad C_1 = 1 \quad T_1 = 0 \\
 Y_2 \rightarrow \infty \quad U_2 &= 1 \quad C_2 = 0 \quad T_2 = 0 \\
 Y_1 = Y_2 = 0 \quad U_1 &= \theta_1 U_2 \quad \theta_2 \frac{\partial U_1}{\partial Y_1} = -\frac{\partial U_2}{\partial Y_2} + \theta_4 \frac{\partial T_2}{\partial X} \\
 V_1 &= -\theta_3 \frac{\partial C_1}{\partial Y_1} \quad V_2 = 0 \quad C_1 + C_2 = 0 \quad T_1 + T_2 = 0 \\
 \theta_5 \frac{\partial C_1}{\partial Y_1} &= \frac{\partial C_2}{\partial Y_2} \quad \theta_6 \frac{\partial T_1}{\partial Y_1} = \frac{\partial T_2}{\partial Y_2}. \quad (8)
 \end{aligned}$$

The effect of convective transfer in equation (8) is omitted as a small of higher-order, while parameters  $\theta$  have the following form:

$$\begin{aligned}
 \theta_1 &= \frac{u_{20}}{u_{10}} \quad \theta_2 = \frac{\mu_1}{\mu_2} \sqrt{\frac{v_2}{v_1}} \left( \frac{u_{20}}{u_{10}} \right)^{3/2} \\
 \theta_4 &= \frac{\partial \sigma}{\partial t_2} \frac{t_0}{u_{20} u_2} \sqrt{\frac{v_2}{u_{20} l}} \quad \theta_3 = \frac{Mc_0}{\rho_{10}^* Sc_1} \quad (\theta_4 < 0) \\
 \theta_5 &= \chi \frac{D_1}{D_2} \frac{\rho_{10}^*}{\rho_{10}^*} \sqrt{\frac{u_{10} v_2}{u_{20} v_1}} \quad \theta_6 = \frac{\lambda_1}{\lambda_2} \sqrt{\frac{u_{10} v_2}{u_{20} v_1}}. \quad (9)
 \end{aligned}$$

From equations (4) and (5) we can obtain directly

the expressions for the Sherwood and Nusselt numbers:

$$\begin{aligned}
 Sh &= \frac{k_c l}{D_1} = M \sqrt{Re_1} \int_0^1 (1 + \theta_3 Sc_1 C_1^*) \left( \frac{\partial C_1}{\partial Y_1} \right)_{Y_1=0} dX \\
 Nu &= \frac{k_1 l}{\lambda_1} = -Re_1 \left[ \int_0^1 \left( \frac{\partial T_1}{\partial Y_1} \right)_{Y_1=0} dX \right. \\
 &\quad \left. + \theta_3 Pr_1 \int_0^1 (1 + T_1^*) \left( \frac{\partial C_1}{\partial Y_1} \right)_{Y_1=0} dX \right] \\
 C_1^* &= C_1(X, 0), \quad T_1^* = T_1(X, 0) \\
 Re_1 &= \frac{u_{10} l}{v_1} \quad Pr_1 = \frac{u_{10} l}{D_1}. \quad (10)
 \end{aligned}$$

**NUMERICAL METHOD**

The problem (6) with the appropriate set of boundary conditions can be solved conveniently using the following algorithm:

$$\begin{aligned}
 U_1^{(k)} \frac{\partial U_1^{(k)}}{\partial X} + V_1^{(k)} \frac{\partial U_1^{(k)}}{\partial Y_1} &= \frac{\partial^2 U_1^{(k)}}{\partial Y_1^2} \quad \frac{\partial U_1^{(k)}}{\partial X} + \frac{\partial V_1^{(k)}}{\partial Y_1} = 0 \\
 X=0 \quad U_1^{(k)} &= 1 \\
 Y_1=0 \quad U_1^{(k)} &= \theta_1 U_2^{(k-1)} \quad V_1^{(k)} = -\theta_3 \frac{\partial C_1^{(k-1)}}{\partial Y_1} \\
 Y_1 \rightarrow \infty \quad (Y_1 \geq Y_{1\infty}) \quad U_1^{(k)} &= 1 \\
 0 \leq X \leq 1 \quad 0 \leq Y_1 \leq Y_{1\infty} \quad \theta_1 &= 0.1 \quad Y_{1\infty} = 6 \\
 \text{(at the first iteration } \theta_1 &= \theta_3 = 0). \quad (11) \\
 U_2^{(k)} \frac{\partial U_2^{(k)}}{\partial X} + V_2^{(k)} \frac{\partial U_2^{(k)}}{\partial Y_2} &= \frac{\partial^2 U_2^{(k)}}{\partial Y_2^2} \quad \frac{\partial U_2^{(k)}}{\partial X} + \frac{\partial V_2^{(k)}}{\partial Y_2} = 0 \\
 X=0 \quad U_2^{(k)} &= 1 \\
 Y_2=0 \quad \frac{\partial U_2^{(k)}}{\partial Y_2} &= -\theta_2 \left( \frac{\partial U_1^{(k)}}{\partial Y_1} \right)_{Y_1=0} \\
 &\quad + \theta_4 \left( \frac{\partial T_2^{(k-1)}}{\partial X} \right)_{Y_2=0} \quad V_2^{(k)} = 0 \\
 Y_2 \rightarrow \infty \quad (Y_2 \geq Y_{2\infty}) \quad U_2^{(k)} &= 1 \\
 0 \leq X \leq 1 \quad 0 \leq Y_2 \leq Y_{2\infty} \quad \theta_2 &= 0.145 \quad Y_{2\infty} = 6 \\
 \text{(at the first iteration } \theta_4 &= 0). \quad (12) \\
 U_1^{(k)} \frac{\partial C_1^{(k)}}{\partial X} + V_1 \frac{\partial C_1^{(k)}}{\partial Y_1} &= \frac{1}{Sc_1} \frac{\partial C_1^{(k)}}{\partial Y_1^2} \\
 X=0 \quad C_1^{(k)} &= 1 \\
 Y_1=0 \quad C_1^{(k)} &= -C_2^{(k-1)}(X, 0) \\
 Y_1 \rightarrow \infty \quad (Y_1 \geq \bar{Y}_1) \quad C_1^{(k)} &= 1 \\
 0 \leq X \leq 1 \quad 0 \leq Y_1 \leq \bar{Y}_1 \quad Sc_1 &= 0.735 \quad \bar{Y}_1 = 7 \\
 \text{(at the first iteration } C_2^{(k)}(X, 0) &= 0). \quad (13)
 \end{aligned}$$

$$U_2^{(k)} \frac{\partial C_2^{(k)}}{\partial X} + V_2^{(k)} \frac{\partial C_2^{(k)}}{\partial Y_2} = \frac{1}{Sc_2} \frac{\partial^2 C_2^{(k)}}{\partial Y_2^2} - Da C_2^{(k)}$$

$$X = 0 \quad C_2^{(k)} = 0$$

$$Y_2 = 0 \quad \frac{\partial C_2^{(k)}}{\partial Y_2} = \theta_5 \left( \frac{\partial C_1^{(k)}}{\partial Y_1} \right)_{Y_1=0}$$

$$Y_2 \rightarrow \infty (Y_2 \geq \bar{Y}_2) \quad C_2^{(k)} = 0$$

$$0 \leq X \leq 1 \quad 0 \leq Y_2 \leq \bar{Y}_2$$

$$Sc_2 = 564 \quad \theta_5 = 18.3 \quad \bar{Y}_2 = 0.26 \quad Da = 10.$$

(14)

$$U_1^{(k)} \frac{\partial T_1^{(k)}}{\partial X} + V_1 \frac{\partial T_1^{(k)}}{\partial Y_1} = \frac{1}{Pr_1} \frac{\partial^2 T_1^{(k)}}{\partial Y_1^2}$$

$$X = 0 \quad T_1^{(k)} = 0$$

$$Y_1 = 0 \quad T_1^{(k)} = T_2^{(k-1)}(X, 0)$$

$$Y_1 \rightarrow \infty (\bar{Y}_1 \geq Y_1) \quad T_1^{(k)} = 0$$

$$0 \leq X \leq 1 \quad 0 \leq Y_1 \leq \bar{Y}_1 \quad Pr_1 = 0.666 \quad \bar{Y}_1 = 7.4$$

(at the first iteration  $T_2^{(k)}(X, 0) = 0$ ). (15)

$$U_2^{(k)} \frac{\partial T_2^{(k)}}{\partial X} + V_2^{(k)} \frac{\partial T_2^{(k)}}{\partial Y_2} = \frac{1}{Pr_2} \frac{\partial^2 T_2^{(k)}}{\partial Y_2^2} + QDa C_2^{(k)}$$

$$X = 0 \quad T_2^{(k)} = 0$$

$$Y_2 = 0 \quad \frac{\partial T_2^{(k)}}{\partial Y_2} = \theta_6 \left( \frac{\partial T_1^{(k)}}{\partial Y_1} \right)_{Y_1=0}$$

$$Y_2 \rightarrow \infty (Y_2 \geq \bar{Y}_2) \quad T_2^{(k)} = 0$$

$$Pr_2 = 6.54 \quad \theta_6 = 0.034 \quad \bar{Y}_2 = 2.4 \quad QDa = 8.6.$$

(16)

Certain values of the parameters in equations (11)–(16), as well as those to the end of the research, are calculated for the process of absorption of NH<sub>3</sub> in water or water solutions of strong acids.

The solution of equations (11)–(16) allows the determination of

$$J_1 = \int_0^1 \left( \frac{\partial C_1}{\partial Y_1} \right)_{Y_1=0} dX$$

$$J_2 = \int_0^1 C_1(X, 0) \left( \frac{\partial C_1}{\partial Y_1} \right)_{Y_1=0} dX$$

$$J_3 = \int_0^1 \left( \frac{\partial T_1}{\partial Y_1} \right)_{Y_1=0} dX$$

$$J_4 = \int_0^1 T_1(X, 0) \left( \frac{\partial C_1}{\partial Y_1} \right)_{Y_1=0} dX. \quad (17)$$

The introduction of equation (17) into equation (10) allows the determination of the Sherwood and Nusselt numbers:

$$Sh = M \sqrt{Re_1} (J_1 + \theta_3 Sc_1 J_2)$$

$$Nu = -\sqrt{Re_1} [J_3 + \theta_3 Pr_1 (J_1 + J_4)]. \quad (18)$$

### NUMERICAL RESULTS

The results obtained by solution of problems (11)–(16) are shown in Table 1. The comparison of values of  $J_k$  ( $k = 1, \dots, 4$ ) shows that the rate of mass and heat transfer depends sufficiently on concentration gradient ( $\theta_3$ ) and in the cases of absorption ( $\theta_3 = 0.2$ ) and desorption ( $\theta_3 = -0.2$ ) the mass and heat transfer coefficients are different with about 10% from the linear theory predictions ( $\theta_3 = 0$ ). The influence of interfacial tension gradient is insufficient under real conditions ( $0 < \theta_4 < 1$ ). The increase of this parameter does not affect the heat and mass transfer kinetics.

### LINEAR STABILITY ANALYSIS

In a great number of papers [1–7, 25] it has been shown that the tangential flows (as a result of interfacial tension gradients) have a considerable effect on the hydrodynamic stability upon the interface and the flow in the boundary layer. The induction of normal flows (due to large concentration gradients) have an effect of ‘injection’ or ‘suction’ of fluid in the boundary layer, which also changes the hydrodynamic stability in the boundary layer [18, 26–29]. It has been shown

Table 1. Values of average mass and heat fluxes ( $Da = 10$ ,  $\theta_1 = 0.1$ ,  $\theta_2 = 0.145$ ,  $\theta_5 = 18.3$ ,  $\theta_6 = 0.034$ )

No.	$\theta_3$	$\theta_4$	$J_1$	$J_2$	$J_3$	$J_4$
1.	0	0	0.5671	0.09721	-0.01855	0.01337
2.	0.2	0	0.6129	0.11155	-0.02143	0.01554
3.	-0.2	0	0.5274	0.08542	-0.01623	0.01162
4.	0	$10^{-4}$	0.5671	0.09721	-0.01855	0.01338
5.	0	$10^{-3}$	0.5671	0.09721	-0.01855	0.01337
6.	0	$10^{-2}$	0.5670	0.09718	-0.01857	0.01339
7.	0	$10^{-1}$	0.5658	0.09696	-0.01879	0.01364
8.	0	1	0.5658	0.09696	-0.01879	0.01364

in ref. [28] that changes in the normal component of the velocity on the interface influence hydrodynamic stability stronger than changes in the tangential component.

The results obtained, solving equations (11)–(16), give the opportunity to define the influence of the non-linear mass transfer and the Marangoni effect on the hydrodynamic stability of the flow in the boundary layer.

The linear analysis of hydrodynamic stability of the flows in the laminar boundary layers will be considered in the approximations of almost parallel flows. Flow with the velocity components  $u(x, y)$  and  $v(x, y)$  substituted with periodic disturbance with infinitesimal amplitude:

$$\bar{u} = G'(y) \exp i(\alpha x - \beta t) \quad \bar{v} = -i\alpha G(y) \exp i(\alpha x - \beta t) \tag{19}$$

where

$$\alpha = \frac{2\pi}{\lambda} \quad \beta = \beta_r + i\beta_i \quad \frac{\beta}{\alpha} = c_r - ic_i. \tag{20}$$

It can be seen directly from equations (19) and (20) that the disturbance amplitude will grow when  $\beta_i > 0$  and damps when  $\beta_i < 0$ .

It has been demonstrated in ref. [26] that the amplitude of the periodic disturbance  $G(y)$  satisfies the equation of Orr–Sommerfeld type:

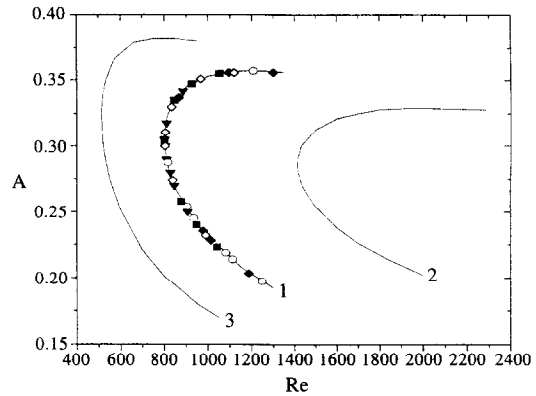
$$\begin{aligned} & \left(u - \frac{\beta}{\alpha}\right)(G'' - \alpha^2 G) - \frac{\partial^2 u}{\partial y^2} G \\ &= -\frac{i v}{\alpha} (G''' - 2\alpha^2 G'' + \alpha^4 G) \\ & \quad + \frac{i}{\alpha} \left[ v G''' - \left(\frac{\partial^2 v}{\partial y^2} - \alpha^2 v\right) G' \right] \\ & y = 0 \quad G = 0 \quad G' = 0 \\ & y \rightarrow \infty \quad G = 0 \quad G' = 0. \end{aligned} \tag{21}$$

The analysis of the flow stability can be done directly if dimensionless variables are introduced into equation (21):

$$\begin{aligned} & (\bar{U}_j - C_j)(\gamma_j'' - A_j^2 \gamma_j) - \frac{\partial^2 \bar{U}_j}{\partial Y_j^2} \gamma_j \\ &= -\frac{i}{A_j Re_j} (\gamma_j''' - 2A_j^2 \gamma_j'' + A_j^4 \gamma_j) \\ & \quad + \frac{i}{A_j Re_j} \left( \bar{V}_j \gamma_j''' - \frac{\partial^2 \bar{V}_j}{\partial Y_j^2} \gamma_j' - A_j^2 \bar{V}_j \gamma_j' \right) \quad j = 1, 2 \end{aligned} \tag{22}$$

where

$$C_j = \frac{\beta_j}{\alpha_j u_{j0}} \quad A_j = \alpha_j \delta_j \quad Re_j = \frac{u_{j0} \delta_j}{\nu_j} = \sqrt{\frac{u_{j0} l}{\nu_j}}$$



- $\theta_4 = 0, \quad \theta_3 = 0 \quad (1);$
  - $\theta_4 = 0, \quad \theta_3 = 0.2 \quad (2);$
  - $\theta_4 = 0, \quad \theta_3 = -0.2 \quad (3);$
  - $\theta_4 = 10^{-4}, \quad \theta_3 = 0 \quad (\heartsuit);$
  - $\theta_4 = 10^{-3}, \quad \theta_3 = 0.2 \quad (\diamond);$
  - $\theta_4 = -10^{-2}, \quad \theta_3 = 0.2 \quad (\blacklozenge);$
  - $\theta_4 = -10^{-1}, \quad \theta_3 = 0 \quad (\circ);$
  - $\theta_4 = -1, \quad \theta_3 = 0 \quad (\blacksquare)$
- Da = 10,  $\theta_1 = 0.1, \theta_2 = 0.145, \theta_5 = 18.3, \theta_6 = 0.034$

Fig. 1. The neutral curves of stability ( $Re_{cr} A_0$ ) for flows of gases in the laminar boundary layer ( $Da = 10, \theta_1 = 0.1, \theta_2 = 0.145, \theta_5 = 18.3, \theta_6 = 0.034$ ).

$$\begin{aligned} \bar{U}_j &= U_j(1, Y) \quad \bar{V}_j = V_j(1, Y_j) \quad \frac{\partial^2 \bar{U}_j}{\partial Y_j^2} = \left(\frac{\partial^2 U_j}{\partial Y_j^2}\right)_{x=1} \\ \frac{\partial^2 \bar{V}_j}{\partial Y_j^2} &= \left(\frac{\partial^2 V_j}{\partial Y_j^2}\right)_{x=1} \quad \gamma_j(Y_j) = G(y) \quad j = 1, 2. \end{aligned} \tag{23}$$

**CRITICAL REYNOLDS NUMBERS**

The solution of equation (22) has been found as it was done in refs [26–29], as a result the neutral curves of stability have been obtained (Fig. 1). The critical Reynolds numbers  $Re_{cr}$ , corresponding wave velocities  $C_r$ , and wave numbers  $A$  are obtained.  $C_{rmin}$  and  $A_{min}$  are also obtained from these results. We denote  $C_{rmin}$  and  $A_{min}$  the minimal values for wave velocities and wave number at which the flow is stable at any Reynolds number  $Re$ , respectively. They are shown in Table 2 for different values of the parameters

Table 2. Values of the critical Reynolds numbers  $Re_{cr}$ , corresponding wave velocities  $C_r$ , wave numbers  $A$  and  $C_{rmin}$ ,  $A_{min}$  ( $Da = 10, \theta_1 = 0.1, \theta_2 = 0.145, \theta_5 = 18.3, \theta_6 = 0.034$ )

No.	$\theta_3$	$\theta_4$	$Re_{cr}$	$A_{max}$	$C_{rmin}$
1.	0	0	800	0.357	0.4503
2.	0.2	0	1411	0.329	0.4187
3.	-0.2	0	512	0.382	0.4763
4.	0	$10^{-4}$	800	0.357	0.4503
5.	0	$10^{-3}$	800	0.357	0.4503
6.	0	$10^{-2}$	800	0.357	0.4503
7.	0	$10^{-1}$	799	0.356	0.4505
8.	0	1	799	0.356	0.4505

$\theta_3$ ,  $\theta_4$ , taking into account the intensity of the secondary flows, as a result of concentration gradients and tangential temperature gradients.

## RESULTS AND DISCUSSION

The numerical analysis of the influence of the effect on non-linear mass transfer and the Marangoni effect on the mass transfer kinetics and the hydrodynamic stability in gas-liquid systems leads to some basic conclusions:

- (1) In the cases of absorption, the increase in intensity of the mass transfer directed from the volume of the gas phase toward the phase boundary ( $\theta_3 > 0$ ) leads to an increase of the mass transfer rate ( $J_1$ ) and an increase of the critical Reynolds numbers ( $Re_{cr}$ ), i.e. stabilize the flow.
- (2) In the cases of desorption the increase in intensity of the mass transfer directed from the phase boundary toward the volume of the gas phase ( $\theta_3 < 0$ ) leads to a decrease of the mass transfer rate ( $J_1$ ) and a decrease of the critical Reynolds numbers ( $Re_{cr}$ ), i.e. destabilize the flow.
- (3) The rise of the temperature gradient along the phase boundary length ( $\theta_4$ ) leads to a decrease of the mass transfer rate ( $J_1$ ) and a decrease of the critical Reynolds numbers ( $Re_{cr}$ ), i.e. destabilize the flow. This Marangoni effect, however, is insufficient in gas-liquid systems with movable phase boundary.
- (4) The flow in the liquid phase is globally stable.

## REFERENCES

1. Hennenberg, M., Bisch, P. M., Vignes-Adler, M. and Sanfeld, A., Interfacial instability and longitudinal waves in liquid-liquid systems. *Lecture Note in Physics*, no. 105. Springer, Berlin, 1979, pp. 229-259.
2. Linde, H., Schwartz, P. and Wilke, H., Dissipative structures and nonlinear kinetics of the Marangoni-instability. *Lecture Note in Physics*, no. 105, 1979, pp. 75-120.
3. Sanfeld, A., Steinchen, A., Hennenberg, M., Bisch, P. M., Van Lamswerde-Galle, D. and Dall-Vedove, W., Mechanical and electrical constraints and hydrodynamic interfacial instability. *Lecture Note in Physics*, no. 105, 1979, pp. 168-204.
4. Savistowski, H., Interfacial convection. *Ber. Bunsenges Phys. Chem.*, 1981, **85**, 905-909.
5. Sorensen, T. S. and Hennenberg, M., Instability of a spherical drop with surface chemical reaction and transfer of surfactants. *Lecture Note in Physics*, no. 105, 1979, pp. 276-315.
6. Scriven, L. E. and Sterling, C. V., The Marangoni effects. *Nature (London)*, 1960, **127**, (4733), 186-188.
7. Velarde, J. and Castillo, L., Transport and reactive phenomena leading to interfacial instability. *Convective Transport and Instability Phenomena*, ed. J. Zierp and H. Oertel. Braun Verlag, 1981, pp. 235-264.
8. Boyadjiev, Chr., Non-linear mass transfer in falling films. *International Journal of Heat and Mass Transfer*, 1982, **25**, 535-540.
9. Boyadjiev, Chr., Influence of same non-linear effects on the mass transfer kinetics in falling liquid films. *International Journal of Heat and Mass Transfer*, 1984, **27**, 1277-1280.
10. Boyadjiev, Chr., Thermocapillary effects in falling liquid films. I. General theory. *Hungarian Journal of Industrial Chemistry*, 1988, **16**, 195-201.
11. Boyadjiev, Chr., Thermocapillary effects in falling liquid films. II. Fast chemical reactions. *Hungarian Journal of Industrial Chemistry*, 1988, **16**, 203-210.
12. Boyadjiev, Chr. and Vulchanov, N., Non-linear mass transfer in boundary layers—1. Asymptotic theory. *International Journal of Heat and Mass Transfer*, 1988, **31**, 795-800.
13. Vulchanov, N., Boyadjiev, Chr., Non-linear mass transfer in boundary layers—2. Numerical investigation. *International Journal of Heat and Mass Transfer*, 1988, **31**, 801-805.
14. Boyadjiev, Chr., Non-linear mass transfer between gas and falling liquid film flow. 1. Numerical analysis. *Inzheverno Fizicheskii Journal*, 1990, **59**, 92-98 (in Russian).
15. Boyadjiev, Chr. and Toshev, E., Non-linear mass transfer between gas and falling liquid film flow. 2. Asymptotic analysis. *Inzheverno Fizicheskii Journal*, 1990, **59**, (2), 277-286.
16. Boyadjiev, Chr., Non-linear mass transfer between gas and falling liquid film flow. 3. Multicomponent mass transfer. *Inzheverno Fizicheskii Journal*, 1990, **59**, 593-602 (in Russian).
17. Boyadjiev, Chr. and Vulchanov, N., Influence of the interphase mass transfer on the rate of mass transfer—1. The system 'solid-fluid (gas)'. *International Journal of Heat and Mass Transfer*, 1990, **33**, 2039-2044.
18. Vulchanov, N. and Boyadjiev, Chr., Influence of the interphase mass transfer on the rate of mass transfer—2. The system 'gas-liquid'. *International Journal of Heat and Mass Transfer*, 1990, **33**, 2045-2049.
19. Boyadjiev, Chr., Asymptotic theory of non-linear mass transfer in systems with intensive interphase mass transfer. *Inzheverno Fizicheskii Journal*, 1991, **60**, 845-862.
20. Boyadjiev, Chr., On the kinetics of the intensive interphase mass transfer. *Russian Journal of Engineering Thermophysics*, 1992, **2**, 289-297.
21. Boyadjiev, Chr., The theory of non-linear mass transfer in systems with intensive interphase mass transfer. *Bulgarian Chemical Communications*, 1993, **26**, 33-57.
22. Sapundzhiev, Ts. and Boyadjiev, Chr., Non-linear mass transfer in liquid-liquid systems. *Russian Journal of Engineering Thermophysics*, 1993, **3**, 185-198.
23. Toshev, E. and Boyadjiev, Chr., Numerical simulation of a non-linear mass transfer process in a channel. *Hungarian Journal of Industrial Chemistry*, 1994, **22**, 81-85.
24. Krylov, V. S., Problems in the theory of mass transfer phenomena in systems with intensive interphase mass transfer. *Uspehi himii*, 1980, **49**, 118-146 (in Russian).
25. Buevich, J. A., On the theory of interfacial convection. *Inzheverno Fizicheskii Journal*, 1985, **49**, 230-238.
26. Boyadjiev, Chr., Halatchev, I. and Tchavdarov, B., The linear stability in systems with intensive interphase mass transfer. Part 1. Gas(liquid)-solid. *International Journal of Heat and Mass Transfer*, 1996, **39**, 2571-2580.
27. Boyadjiev, Chr. and Halatchev, I., The linear stability in systems with intensive interphase mass transfer. Part 2. Gas-liquid. *International Journal of Heat and Mass Transfer*, 1996, **39**, 2581-2585.
28. Halatchev, I. and Boyadjiev, Chr., The linear stability in systems with intensive interphase mass transfer. Part 3. Liquid-liquid. *International Journal of Heat and Mass Transfer*, 1996, **39**, 2587-2592.
29. Boyadjiev, Chr. and Halatchev, I., The linear stability in systems with intensive interphase mass transfer. Part 4. Gas-liquid film flow. *International Journal of Heat and Mass Transfer*, 1996, **39**, 2593-2597.