

On the Marangoni Instability in Gas Absorption

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Abstract. The non-steady-state process of a gas absorption by initially motionless liquid is investigated. Nonlinear analysis of the thermo-capillary instability showed that the transition of the process to unstable convective regime is determined by two sharply different characteristic times. First one is the time of neutral perturbations, when the fluctuations of the concentration of absorbable substance, temperature and the liquid velocity stop decrease and begin to grow together, but their intensity is too small to influence on the absorption rate. The second one is the time much greater than the first, when the perturbations reach sufficient values, and the absorption process turns to the convective regime. The results obtained explain the well-known experimental data on delaying of the transition of the absorption process to the unstable convective regime.

1. Introduction

It is well known that the process of a gas absorption by a liquid goes in diffusion regime only up to some critical time, after which it turns to unstable convective regime, accompanied by a higher rate of mass transfer [1]. The theoretical analysis performed in [2,3] showed that the origin of diffusion-convective instability is the temperature dependence of the surface tension of liquid. Thermo-capillary effect or Marangoni effect is widely used in industry as an opportunity to intensification of chemical processes at the liquid – gas interface [4, 5]. Mathematical modeling of non-steady-state absorption involves the problem of determining the critical time of transition of the process to unstable convective regime and the calculation of mass transfer rate under the conditions of surface convection. One unsolved problem is the following: the experimentally observed critical time of the absorption of carbon dioxide by water exceeds theoretical estimations about 1,000 times [2, 3].

The aim of our work is the studying of the mechanism of the transition of absorption process from the diffusion to unstable convective regime based on the nonlinear analysis of the development of small perturbations.

In Section 2, the problem is formulated and the basic equations are determined. In Section 3, a linear analysis of small perturbations in the absorption process is performed. Preliminary evaluations are obtained. Section 4 presents the results of a nonlinear analysis of the development of small perturbations. In Conclusions, Section 5, the mechanism of the transition of the absorption process from diffusion to unstable convective regime is discussed.

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2. The problem statement. The basic equations

Non-steady-state process of the absorption of a component *A* from a gaseous phase by initially motionless liquid is studied. In the beginning of the process the concentration of component in the liquid phase is equal to zero, the liquid temperature is constant and equal to T_0 . The main resistance to heat and mass transfer is concentrated in the liquid phase. Liquid layer thickness is considered infinite.

In the diffusion regime the concentration *c* of a component *A* is described by the following well-known equation [6]

$$\frac{\partial c^{(0)}}{\partial t} - D \frac{\partial^2 c^{(0)}}{\partial z^2} = 0, \tag{1}$$

Where *D* is molecular diffusivity, *t* is a time; the superscript (0) corresponds to the diffusion regime. The *z* coordinate is directed deep into the liquid by the normal to the liquid surface, the value $z = 0$ corresponds to the gas-liquid interface.

At the interface the concentration of the component *A* take the equilibrium value c_* corresponding to its partial pressure in the gaseous phase [7]. In the liquid depth, the concentration is equal to zero.

The solution of non-steady-state diffusion in a motionless liquid is well known [8]. Let us give an expression for the flux density of absorbable material at the interface

$$j^{(0)} = -D \frac{\partial c^{(0)}}{\partial z} = c_* \left(\frac{D}{\pi t} \right)^{1/2}. \tag{2}$$

The absorption process is accompanied by heat generation, which leads to a change in temperature and the surface tension of liquid. For a small temperature changes the surface tension σ varies linearly

$$\sigma = \sigma_0 - \varepsilon(T - T_0), \tag{3}$$

where ε is negative coefficient of surface tension. Inhomogeneity of the surface tension creates frictional stress that causes liquid motion and may cause convective instability of the process [1,4]. Under the conditions of surface convection the absorption process is described by joint solution of the equations of convective diffusion, thermal conductivity, and the equations of liquid motion.

$$\frac{\partial c}{\partial t} + \mathbf{v} \nabla c - D \Delta c = 0, \tag{4}$$

$$\frac{\partial T}{\partial t} + \mathbf{v} \nabla T - \chi \Delta T = 0, \tag{5}$$

$$\frac{\partial}{\partial t} \text{rot } \mathbf{v} + (\mathbf{v} \nabla) \text{rot } \mathbf{v} - (\text{rot } \mathbf{v} \nabla) - \nu \Delta \text{rot } \mathbf{v} = 0, \tag{6}$$

where χ is thermal conductivity, $\mathbf{v} = (v_x, v_y, v_z)$ is a vector of a liquid velocity, ν is kinematic viscosity, coordinates *x*, *y* are directed parallel to the gas-liquid interface.

Boundary conditions are as follows. At the interface we have

$$c = c_*, \quad D \frac{\partial c}{\partial z} = \Delta H \lambda \frac{\partial T}{\partial z}, \quad v_z = 0, \quad \rho \nu \frac{\partial v_x}{\partial z} = -\frac{\partial \sigma}{\partial x}, \quad \rho \nu \frac{\partial v_y}{\partial z} = -\frac{\partial \sigma}{\partial y} \tag{7}$$

for $z = 0$,

where $\lambda = \rho c_p \chi$ is specific heat conductivity of liquid, ρ is its density, c_p is its specific heat capacity at constant pressure. In the depth of the liquid the conditions are

$$c \rightarrow 0, \quad T \rightarrow T_0, \quad v_x \rightarrow 0, \quad v_y \rightarrow 0, \quad v_z \rightarrow 0 \quad \text{for } z \rightarrow \infty. \tag{8}$$

For further analysis, let us turn to dimensionless variables

$$C = c / c_*, \quad \theta = (T - T_0) / T_*, \quad (\mathbf{V}_x, \mathbf{V}_y, \mathbf{V}_z) = (v_x / v_*, v_y / v_*, v_z / v_*), \tag{9}$$

$$\tau = t / t_*, \quad (X, Y, Z) = (x / z_*, y / z_*, z / z_*),$$

where the characteristic scales of the length z_* , the time t_* , the velocity v_* and the temperature T_* are equal to:

$$z_* = \frac{\lambda \mu}{\varepsilon \Delta H c_*} \left(\frac{\chi}{D} \right)^{1/2}; \quad t_* = \frac{l}{D} \left(\frac{\lambda \mu}{\varepsilon \Delta H c_*} \right)^2; \quad v_* = \frac{z_*}{t_*}; \quad T_* = (D \chi)^{1/2} \frac{\Delta H c_*}{\lambda} \tag{10}$$

$\mu = \rho \lambda$ is dynamic viscosity.

In dimensionless variables, equations (4) - (6) take the form

$$\partial C / \partial \tau + \mathbf{V} \nabla C - Le^{-1} \Delta C = 0, \tag{11}$$

$$\partial \theta / \partial \tau + \mathbf{V} \nabla \theta - \Delta \theta = 0, \tag{12}$$

$$\frac{\partial}{\partial t} \text{rot } \mathbf{V} + (\mathbf{V} \nabla) \text{rot } \mathbf{V} - (\text{rot } \mathbf{V} \nabla) - Pr^{-1} \Delta \text{rot } \mathbf{V} = 0, \tag{13}$$

where $Le = \chi / D$ is the Lewis number, $Pr = \nu / D$ is the Prandtl number.

3. The linear instability analysis

3.1. The linearized equations

Let us represent the values of concentration and temperature as the sum of the unperturbed solutions corresponding to the diffusion in motionless liquid, and sinusoidal varying small perturbations

$$C(\mathbf{R}, \tau) = C^{(0)}(Z, \tau) + c^{(1)}(Z, \tau) \cos KX; \quad \theta(\mathbf{R}, \tau) = \theta^{(0)}(Z, \tau) + \theta^{(1)}(Z, \tau) \cos KX. \tag{14}$$

Superscript (1) corresponds to a small perturbation; \mathbf{R} is the radius vector, K is dimensionless wave number. In the linear approximation only normal to the surface velocity component is significant. It is represented in the form

$$V_z(\mathbf{R}, \tau) = V^{(1)}(Z, \tau) \cos KX. \tag{15}$$

The following equations are valid for undisturbed concentration and temperature

$$\frac{\partial C^{(0)}}{\partial \tau} - Le^{-1} \frac{\partial^2 C^{(0)}}{\partial Z^2} = 0; \quad \frac{\partial \theta^{(0)}}{\partial \tau} - \frac{\partial^2 \theta^{(0)}}{\partial Z^2} = 0. \tag{16}$$

Initial and boundary conditions for (16) are given in the following form

$$C^{(0)} = 1, \quad \sqrt{Le} \frac{\partial T^{(0)}}{\partial Z} = \frac{\partial C^{(0)}}{\partial Z} \quad \text{for } Z = 0; \quad C^{(0)} \rightarrow 0, \quad \theta^{(0)} \rightarrow 0 \quad \text{for } Z \rightarrow \infty; \tag{17}$$

$$C^{(0)} = 0, \quad \theta^{(0)} = 0; \quad \text{for } \tau = 0.$$

Well-known solution of the problem (16), (17) gives the following expressions for the mass flux density $J^{(0)}$ and the heat flux density $Q^{(0)}$

$$J^{(0)} = (Le \cdot \pi \cdot \tau)^{-1/2}, \quad Q^{(0)} = (\pi \cdot \tau)^{-1/2}. \tag{18}$$

The linearized form of small perturbation equations is as follow

$$\left(\frac{\partial}{\partial \tau} - Le^{-1} \left(\frac{\partial^2}{\partial Z^2} + K^2 \right) \right) C^{(1)} = -V^{(1)} \frac{\partial C^{(0)}}{\partial Z}, \tag{19}$$

$$\left(\frac{\partial}{\partial \tau} - \frac{\partial^2}{\partial Z^2} + K^2 \right) \theta^{(1)} = -V^{(1)} \frac{\partial \theta^{(0)}}{\partial Z}, \tag{20}$$

$$\left(\frac{\partial}{\partial \tau} - Pr^{-1} \left(\frac{\partial^2}{\partial Z^2} + K^2 \right) \right) \left(-\frac{\partial^2}{\partial Z^2} + K^2 \right) V^{(1)} = 0. \tag{21}$$

Let us write the boundary conditions for small perturbations. On the liquid – surface interface we have

$$C^{(1)} = 0, \quad \sqrt{Le} \frac{\partial \theta^{(1)}}{\partial Z} = \frac{\partial C^{(1)}}{\partial Z}, \quad V^{(1)} = 0, \quad \frac{\partial^2}{\partial Z^2} V^{(1)} = K^2 \theta^{(1)} \quad \text{for } Z = 0. \tag{22}$$

In the depth of the liquid

$$C^{(1)} \rightarrow 0, \quad \theta^{(1)} \rightarrow 0, \quad V^{(1)} \rightarrow 0, \quad \frac{\partial V^{(1)}}{\partial Z} \rightarrow 0 \quad \text{for } Z \rightarrow \infty. \tag{23}$$

3.2. The neutral perturbations

Critical time of the transition of the process from diffusion to convective regime is determined from the conditions for the existence of neutral perturbations [2,3]. Perturbations are considered neutral if their partial derivatives with respect to time are zero. The time of neutral perturbations for a given wave number $\tau(K)$ may be found by solving the following equation [3]

$$2K\tau[\exp(4K^2\tau)\text{erfc}(2K\sqrt{\tau}) - \frac{1}{\sqrt{Le}}\exp(\frac{4K^2\tau}{Le})\text{erfc}(2K\sqrt{\frac{\tau}{Le}})] = 1. \tag{24}$$

Critical time τ_{cr} is equal to the minimum on the wave numbers of the time of neutral disturbances.

$$\tau_{cr} = \min_K \tau(K) = \tau(K_{cr}), \tag{25}$$

Where K_{cr} is a critical wave number. For an infinite Lewis number the critical time is equal to π [2,3]. The following asymptotic interpolation formulae of the critical time and the critical wave number versus the Lewis number for $Le > 50$ are written down in [9]

$$\tau_{cr} = \pi(1 + 3\pi^{1/3}Le^{-1/3} + 12Le^{-2/3}), \tag{26}$$

$$K_{cr} = (2^{-1}\pi^{-2/3}Le^{1/6} - 0.7Le^{-1/6} + 0.9Le^{-1/2}), \tag{27}$$

For the case of $Le = 79$, which corresponds to the absorption of carbon dioxide by the water, we have $K_{cr} = 0.25$, $\tau_{cr} = 8.57$.

Here are profiles of neutral disturbances of concentration of absorbable substance, temperature and liquid velocity

$$C_n(Z) = B[-2\tau * \exp[\frac{4K^2\tau}{Le} + KZ] * \operatorname{erfc}(\frac{4K\tau + Z * Le}{2\sqrt{Le * \tau}}) + 2\tau * \exp[\frac{4K^2\tau}{Le} - KZ] * \operatorname{erfc}(2k\sqrt{\tau / Le})], \tag{28}$$

$$\theta_n(Z) = B[4\tau * \exp[\frac{4K^2\tau}{Le} - KX] \frac{\operatorname{erfc}(2K\sqrt{\tau / Le})}{\sqrt{Le}} - 2\tau * \exp[4K^2\tau - KX] * \operatorname{erfc}(2K\sqrt{\tau})] \tag{29}$$

$$- 2\tau * \exp[4K^2\tau + KX] * \operatorname{erfc}(\frac{4K\tau + X}{2\sqrt{\tau}})],$$

$$V_n(Z) = BZ * e^{-KZ}. \tag{30}$$

Subscript n corresponds to the neutral disturbance, B is arbitrary constant. Time τ is a function of the wave number K and satisfies (24).

3.3. Analysis of the most rapidly growing perturbations

The transition from diffusion to convective mass transfer regime is determined the fastest growing perturbations. Solutions (28) - (30) at the critical value of the wave number represent the perturbations of concentration, temperature and velocity, which are the first to stop decrease and begin to grow together. Let us investigate the development of these disturbances during the whole process of absorption. Non-stationary perturbations satisfy the equations (19) - (21) with boundary conditions (22) - (23). As additional conditions require their coincidence with neutral perturbations at a critical time

$$C^{(1)}(Z, \tau) = C_n(Z), \quad \theta^{(1)}(Z, \tau) = \theta_n(Z), \quad V^{(1)}(Z, \tau) = V_n(Z) \tag{31}$$

for $\tau = \tau_{cr}$, $K = K_{cr}$

Solution of the transport equations in $\tau < \tau_{cr}$ belongs to the class of ill-posed problems [10]. The additional assumptions are required to solve it. Let us define the initial conditions in the following form

$$C^{(1)}(Z, \tau) = B \sum_{i=0}^p M_{1,i} L_i^0(2KZ) e^{-KZ}, \quad \theta^{(1)}(Z, \tau) = B \sum_{i=0}^p M_{2,i} L_i^0(2KZ) e^{-KZ}, \tag{32}$$

$$V^{(1)}(Z, \tau) = 2BKZ \sum_{i=0}^p M_{3,i} L_i^2(2KZ) e^{-KZ} \quad \text{for } \tau = 0$$

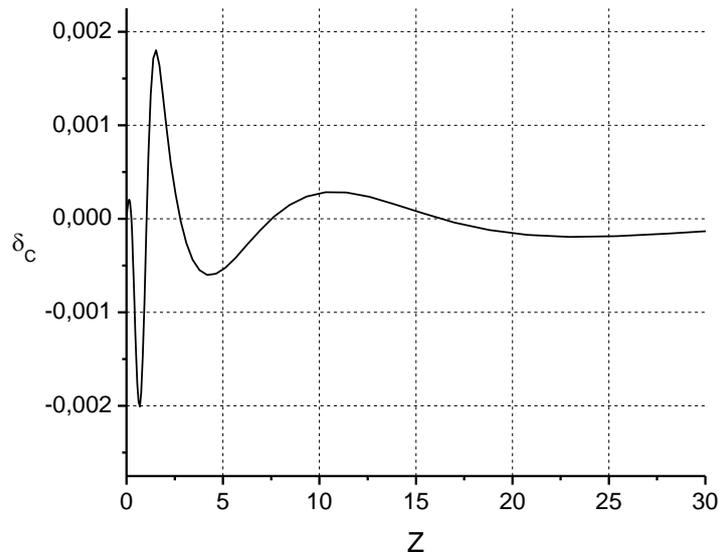


Figure 1. The difference between the numerical solution of non-stationary problem and the neutral perturbation of concentration

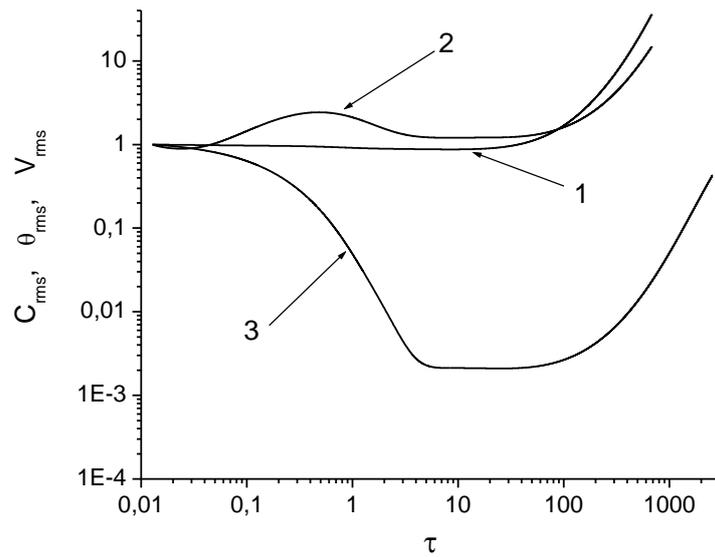


Figure 2. The intensities of disturbances versus time.
 1 – C_{rms} , 2 – θ_{rms} , 3 – V_{rms}

where the constant B is defined in formulae (28) - (30), L_i^β are the Laguerre polynomials, M is a matrix $3 \times (p+1)$ of undetermined coefficients, the latter are found by solving the following equations

$$\begin{aligned}
 \int_0^\infty Z^m C^{(1)}(Z, \tau_{cr}) \exp(-KZ) dZ &= \int_0^\infty Z^m C_n(Z) \exp(-KZ) dZ, \\
 \int_0^\infty Z^m \theta^{(1)}(Z, \tau_{cr}) \exp(-KZ) dZ &= \int_0^\infty Z^m \theta_n(Z) \exp(-KZ) dZ, \\
 \int_0^\infty Z^m V^{(1)}(Z, \tau_{cr}) \exp(-KZ) dZ &= \int_0^\infty Z^m V_n(Z) \exp(-KZ) dZ, \quad m=0,1..p.
 \end{aligned}
 \tag{33}$$

Formulae (33) correspond to the approximate implementation of conditions (31).

Results of computations of the evolution of the fastest growing perturbation are shown in figure 1 and figure 2. Computations were performed using the following parameters: $Le=79$, $Pr=7$, $p=3$. Concordance of the numerical solution of the non-stationary problem with the neutral perturbations at the critical time is shown in figure 1. Their difference being divided by the maximum amplitude of the perturbation

$$\delta_C = [C^{(1)}(Z, \tau_{cr}) - C_n(Z)] / C_{nmax}, \quad C_{nmax} = \max_Z C_n(Z)
 \tag{33}$$

does not exceed 0.2%.

Figure 2 presents the time dependent quadratic means for perturbations of concentration, temperature and velocity normalized to their initial values

$$\begin{aligned}
 C_{rms}(\tau) &= \left[\int_0^\infty (C^{(1)}(Z, \tau))^2 dZ \right]^{1/2} \left[\int_0^\infty (C^{(1)}(Z, 0))^2 dZ \right]^{-1/2}, \\
 \theta_{rms}(\tau) &= \left[\int_0^\infty (\theta^{(1)}(Z, \tau))^2 dZ \right]^{1/2} \left[\int_0^\infty (\theta^{(1)}(Z, 0))^2 dZ \right]^{-1/2}, \\
 V_{rms}(\tau) &= \left[\int_0^\infty (V^{(1)}(Z, \tau))^2 dZ \right]^{1/2} \left[\int_0^\infty (V^{(1)}(Z, 0))^2 dZ \right]^{-1/2}.
 \end{aligned}
 \tag{34}$$

On the time interval $\tau < \tau_{cr}$, ($\tau_{cr} = 8.57$) the intensities of concentration and temperature perturbations are virtually unchanged, but the intensity of the velocity perturbations sharply diminishes, its root mean square decreases by approximately 500 times. The initial intensity restores at the time greater than 3000; that exceeds the critical time more than 300 times. Transition from diffusion to convective mass transfer regime take place when the mass flux, caused by the velocity and concentration, being equal to $\frac{1}{2}V^{(1)}C^{(1)}$, in the main part of the diffusion layer becomes

of the same order as the diffusion flux in a motionless liquid $J^{(0)}$, i.e. when the perturbations of the velocity and the concentration are sufficiently large. The analysis has shown that the most rapidly growing perturbations decrease sharply before starting to rise. Critical time, being defined as the time of neutral perturbations, corresponds to the prominent minimum of the perturbations of velocity and concentration and cannot be regarded as a time of the transition from diffusion to convective regime. Such a transition can only take place much later when the disturbances reach the required intensity. Next, let us consider the mechanism of the transition from diffusion to convective mass transfer on the basis of nonlinear analysis of perturbations.

4. Nonlinear analysis.

The values $C^{(0)}$ and $C^{(1)}$ in formula (14) can be regarded as the zero and the first Fourier components of the concentration. In the linear analysis the zero Fourier component is unperturbed concentration corresponding to diffusion in a motionless liquid. Let us perform nonlinear analysis, taking into account the influence of disturbances on the zero Fourier components of concentration. Let us replace the linearized equation (15) to the following

$$\frac{\partial C^{(0)}}{\partial \tau} - Le^{-1} \frac{\partial^2 C^{(0)}}{\partial Z^2} = -\frac{1}{2} \frac{\partial}{\partial Z} (V^{(1)} C^{(1)}). \tag{35}$$

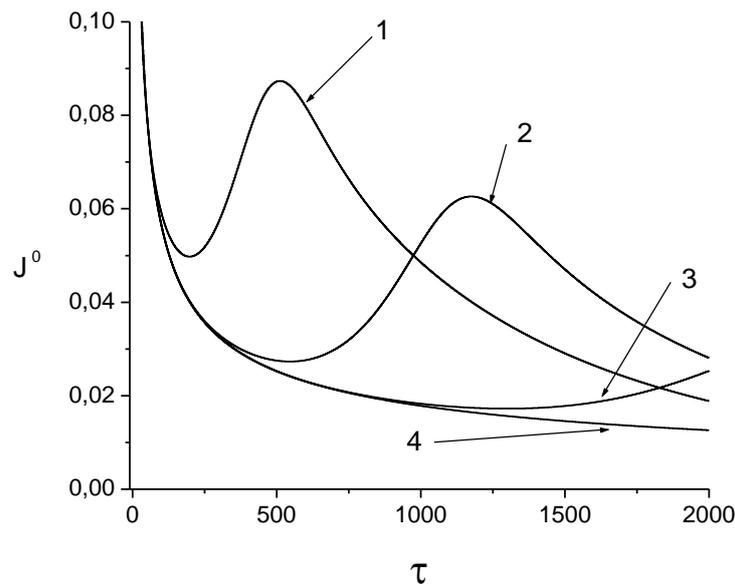


Figure 3. Mass flux density at different initial intensity of concentration disturbances. 1 - $\epsilon=0.1$, 2 - $\epsilon=0.01$, 3 - $\epsilon=0.001$, 4 – flux density in motionless liquid

We calculated the perturbations of concentration, temperature and velocity for the initial conditions (31) and different values of the parameter B, which determines the initial intensity ϵ of concentration perturbations. Their influence on the zero Fourier component of the flux density of absorbed substance

$$J^0(\tau) = -Le^{-1} \frac{\partial}{\partial Z} C^{(0)}(Z, \tau) \quad \text{for } Z = 0 \tag{36}$$

is shown in Figure 3. The time when the flux under the condition of surface convection begins to exceed the flux in motionless liquid is quite clearly visible on the chart for all initial intensities of concentration disturbances. It allows us to conclude the presence of a second critical time when the developed the velocity and concentration disturbances causes the transition from diffusion to convective mass transfer regime.

5. Conclusions

The mechanism of the transition of absorption process from diffusion to unstable convective regime is as follows. Upon reaching the first critical time defined as the time of neutral disturbances, the fluctuations of concentration, temperature and velocity are no longer decrease and begin to grow together. However, their intensity is too small; they cannot influence the interfacial mass transfer rate. It takes time, much greater the first critical for these disturbances to grow and reach the value necessary to change the flux of absorbed substance. At this time, much exceeding the first critical, concentration and velocity perturbations grow much faster than zero Fourier component of the concentration; that creates clearly defined second critical time, when the flux under the conditions of the surface convection begins to exceed the flux to motionless liquid. Executed simulations of the evolution of small perturbations of concentration, velocity and temperature do not allow to accurately calculating the second critical time, however, our analysis shows that this value is much larger than the first critical time.

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