EFFECT OF MASS EXCHANGE AND HETEROGENOUS CHEMICAL REACTION ON STABILITY OF LIQUID FILM

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Stability is analyzed of a laminar liquid film during a heterogeneous chemical reaction. The dispersion equation is obtained and stability regions are found for longwave, as well as shortwave, perturbations.

§1. Mass-transfer processes on the interface surface may exert a considerable effect on stability characteristics of this surface; in particular, they may result in a specific surface instability – the so-called interface turbulence [1] whose mechanism is closely related to the rate of mass transfer; this result has been verified by a number of experiments [2-6].

The above-mentioned effect is of considerable interest in practice in view of the increase of artificially produced mass-transfer processes in a number of chemical reactors (for example, in thin-layer reactors). The mass exchange is generally accompanied by homogeneous or heterogenous chemical reactions which take place either in the liquid film or in the surrounding (usually gaseous) phase.

In its full formulation the investigation of stability of this kind of system with regard to small perturbations is very complex and mathematically involved. However, to obtain preliminary qualitative results a somewhat idealized scheme of surface instability is considered below (the existence of thin hydrodynamic and diffusion boundary layers is assumed close to the surface, the chemical reactions being heterogeneous and of the first order). The problem investigated in this article is as follows: to find the regions (depending on the wavelength of the perturbations) of stability of a laminar film by solving the dispersion equation taking into account the Marangoni effect [1].

§2. Let us consider a thin liquid film whose surface separates it from the gas phase. A laminar flow of the film takes place ($\mathrm{Re} \leq 20\text{-}30$, $\mathrm{Pr} \gg 1$) down a vertical plate in the gravitation field with a gas flow in contact with the surface. It is assumed that the gas motion takes place with a sufficiently slow rate so as to maintain the laminar state of the liquid flow.

For such a system the mass exchange is limited by the transfer processes in the liquid, since their rate is much lower than the corresponding rates in a gas; this enables one to consider the mass transfer only in the liquid phase. On the film surface a monomolecular chemical reaction $A \rightarrow B$, takes place for which a number of assumptions is made: the reaction is irreversible; the product of reaction B is chemically passive; the reagent A is chemically passive in the film; the kinetics of the process is mixed, that is, the rate of the chemical reaction is comparable with the speed of transporting the reacting matter.

The equations of motion for the liquid, as well as the equation of convective diffusion in a thin film, can be considerably simplified, since the approximations can be used for hydrodynamic and for diffusive boundary layers [7].

In our system the analysis of mass transfer consists in solving a linearized stability problem with respect to two-dimensional infinitely small perturbations of velocity and of concentration which are expanded into a Fourier series along the film with an amplitude depending on the cross section coordinate.

§3. The motion of the liquid film is governed by the nonstationary Navier–Stokes equation in the boundary-layer approximation in the (x, y) coordinate plane; x is measured along the film plane in the direction of

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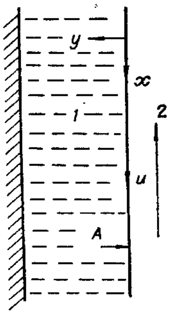

Fig. 1

the original unperturbed laminar flow and y is normal to the plane towards the depth of the liquid (Fig. 1, where 1 denotes the liquid film and 2, the gas flow). To analyze the hydrodynamic stability of the film, the velocity components are represented in the form

$$u_x = u_x^{(0)} + u_x^{(1)},\ u_y = u_y^{(0)} + u_y^{(1)},$$

where $u_x^{(0)}$, $u_y^{(0)}$ are the solutions of the stationary equation and $u_x^{(1)}$, $u_y^{(1)}$ are small perturbations. It follows from the general theory of convective diffusion in fluids [7] that for high Prandtl numbers the thickness of the diffusion boundary layer is many times smaller than that of the hydrodynamic boundary layer; the latter enables one to set $u_x^{(0)}$ identically equal to the velocity u of the liquid flow on the film surface. If we proceed now to the flow function,

$$u_x^{(1)} = \partial\psi/\partial y,\ u_y^{(1)} = -\partial\psi/\partial x$$

so that the continuity equation becomes an identity and bearing in mind that $u_x^{(0)} = u$, $u_y^{(0)} = 0$, then the Navier–Stokes equation is reduced to the Helmholtz type equation,

$$(\partial/\partial t + u\partial/\partial x)\Delta\psi = \nu\Delta^2\psi, \tag{3.1}$$

where ν is the kinematic viscosity. A solution of Eq. (3.1) is sought in the form

$$\psi = \Psi(y)\exp\,[i(kx + \omega t)]$$

with amplitude

$$\Psi(y) = A\exp\,(\lambda y),$$

where ω and k are the frequency of oscillations and the wave number of the perturbations, respectively; A is a numerical multiplier. Equation (3.1) then yields for λ the relation

$$(\lambda^2 - k^2)[\lambda^2 - k^2 - i(\omega + u\,k)\nu^{-1}] = 0,$$

and, hence, together with the boundary conditions,

$$u_x^{(1)} \to 0,\ u_y^{(1)} \to 0\ (y \to \infty)$$

it follows that

$$\lambda_1 = k,\ \lambda_2 \equiv \lambda = -[k^2 + i(\omega + uk)/\nu]\,\nu^{1/2}.$$

If one regards the film surface as flat,

$$u_y^{(1)} = 0\ \ (y = 0),$$

one obtains a solution of Eq. (3.1) uniquely determined up to a constant,

$$\Psi = A[\exp\,(-ky) - \exp\,(-\lambda y)\,]\exp\,[i(kx + \omega t)]. \tag{3.2}$$

§4. Mass transfer in a liquid film is governed by the convective-diffusion equation in the boundary-layer approximation. The stationary concentration of the reagent A satisfies the equation

$$u\partial c_a^{(0)}/\partial x = D\partial^2 c_a^{(0)}/\partial y^2, \tag{4.1}$$

where $c_a^{(0)}$ denotes the stationary concentration; D is the diffusion coefficient. Another variable is now introduced, namely,

$$\eta = (u/4D)y^2x^{-1},$$

which results in replacing Eq. (4.1) by an ordinary differential equation of the second order,

$$\eta d^2 c_a^{(0)}/d\eta^2 + (\eta + 1/2)\, dc_a^{(0)}/d\eta = 0. \tag{4.2}$$

The boundary condition on the film surface can be specified by the mixed kinetics of the chemical reaction, that is,

$$D\partial c_a^{(0)}/\partial y = -qc_a^{(0)} \ (y = 0), \tag{4.3}$$

where q is the constant rate of chemical reaction. Considering that the change in concentration occurs in thin liquid layers, the conditions far from the film surface are naturally considered, therefore they are specified at an infinitely large distance from it, i.e.,

$$c_a^{(0)} = c_0 \ (y \to \infty). \tag{4.4}$$

Integrating Eq. (4.2) and using the boundary conditions (4.3) and (4.4), one obtains the sought distribution of the stationary concentration in which the explicit dependence on x has been replaced by the parametric dependence on the linear dimension L,

$$c_a^{(0)} = -\frac{c_0 (uD/\pi L)^{1/2}}{q\,[1 - (uD/\pi L)^{1/2}/q]} + \frac{c_0 \operatorname{erf}[(u/4DL)^{1/2} y]}{[1 - (uD/\pi L)^{1/2}/q]},$$

and from the above one obtains in the case of $q \gg (uD/\pi L)^{1/2}$ the relation

$$c_a^{(0)} = c_0 \operatorname{erf}[(uy^2/4DL)^{1/2}]. \tag{4.5}$$

We now proceed to the solving of the nonstationary equation of convective diffusion for the concentration of the substance A written in the form

$$c_a = c_a^{(0)} + c_a^{(1)},$$

where

$$c_a^{(1)} = G_a(y) \exp[i(kx + \omega t)].$$

The nonstationary diffusion equation in its linear approximation with the obvious estimate

$$\partial c_a^{(0)}/\partial x \ll \partial c_a^{(0)}/\partial y$$

taken into account is transformed into

$$D\partial^2 c_a^{(1)}/\partial y^2 - u\partial c_a^{(1)}/\partial x - \partial c_a^{(1)}/\partial t = -(\partial\psi/\partial x)(\partial c_a^{(0)}/\partial y), \tag{4.6}$$

where the expressions for the stationary concentration $c_a^{(0)}$ and the stream function ψ are given by the distributions (3.2) and (4.5). The system of equations (3.2), (4.5), and (4.6) is now completed by the boundary condition

$$c_a^{(1)} = 0 \ (y \to \infty). \tag{4.7}$$

On the film surface the continuity condition for the tangential component of the stress tensor must also be satisfied, that is, the equality of the viscous stress and the surface force per unit of film surface,

$$\mu\left[\partial u_x^{(1)}/\partial y + \partial u_y^{(1)}/\partial x\right] = \left(d\sigma/dc_a^{(1)}\right)\left(\partial c_a^{(1)}/\partial x\right), \tag{4.8}$$

where μ is the dynamic viscosity coefficient; σ is the surface-tension coefficient. By virtue of the known kinetics of a chemical reaction one has

$$D\partial c_a^{(1)}/\partial y = -qc_a^{(1)} \ (y = 0). \tag{4.9}$$

Equation (4.6) is reduced to the ordinary inhomogeneous differential equation for the perturbation amplitude $G_a(y)$:

$$d^2G_a/dy^2 + \alpha G_a = f(y),$$

where

$$\alpha = -(i/D)(uk + \omega);$$

$$f(y) = -(2ik/\pi^{1/2} D)A\,[\exp(-ky) - \exp(-\lambda y)]\,c_0\,(u/4DL)^{1/2} \exp(-uy^2/4DL),$$

and hence by using also the boundary condition (4.7) one finds

$$G_a(y) = [B + A_1 I_2(y)] \exp(-i\alpha^{1/2} y) + A_1 [I_1(\infty) - I_1(y)] \exp(i\alpha^{1/2} y). \tag{4.10}$$

where

$$A_1 = ik(c_0/D)(u/\pi DL)^{1/2}A;$$

$$I_1(y) = \frac{1}{2i}\int\limits_{\tau=0}^{y}(e^{-k\tau} - e^{-\lambda\tau})\exp[-u\tau^2/4DL - i\alpha^{1/2}\tau]\,d\tau;\quad I_2(y) = \frac{1}{2i}\int\limits_{\tau=0}^{y}(e^{-k\tau} - e^{-\lambda\tau})\exp[-u\tau^2/4DL + i\alpha^{1/2}\tau]\,d\tau;$$

By substituting (4.10) in (4.8) and (4.9), one obtains a system of two algebraic equations for the constants A and B with a vanishing determinant,

$$i^{1/2}D^{1/2}(\omega + uk)^{3/2} + q(\omega + uk) + 2c_0\delta(\nu/\mu)(u/\pi DL)^{1/2}k^2 I_1(\infty) = 0, \tag{4.11}$$

where

$$\delta = d\sigma/dc_a^{(1)}.$$

The above condition represents the sought dispersion equation which can be separated into two real equations:

$$D^{1/2}W_2 + q(\Omega_1 + uk) + c_0\delta(\nu/\mu)(u/\pi DL)^{1/2}k^2\,\mathrm{Im}\,I = 0; \tag{4.12}$$
$$D^{1/2}W_1 - q\Omega_2 + c_0\delta(\nu/\mu)(u/\pi DL)^{1/2}k^2\,\mathrm{Re}\,I = 0,$$

where Ω_1, Ω_2 are the real and imaginary parts of ω, $I = 2iI_1(\infty)$, respectively;

$$W_{1,2} = \frac{1}{\sqrt{2}}\{\mp\Omega_2[\Omega_2^2 - 3(\Omega_1 + uk)^2] + [\Omega_2^2[\Omega_2^2 - 3(\Omega_1 + uk)^2]^2 + (\Omega_1 + uk)^2[3\Omega_2^2 - (\Omega_1 + uk)^2]^2]^{1/2}\}^{1/2}$$

§5. We now proceed to the solving of the obtained dispersion equation. It is noticed that by reducing $I_1(\infty)$ to an integral of the Poisson type, one is able to find its exact analytic form though the bulkiness of the latter makes it very difficult to solve analytically the dispersion equation itself. Only asymptotic values of the integral $I_1(\infty)$ are therefore used. First of all, stationary perturbations are found which spread in the state of neutral stability, that is, for $\omega = 0$ (the perturbations neither grow nor are attenuated in the course of time). If in the case of small wave numbers ($k \ll L^{-1}$) one estimates the integral by the steepest-descent method [8], then one obtains the principal term of its asymptotic expression, namely,

$$I_1(\infty) = [(i - 2)/2](\pi DL/u)^{1/2}[2(D/\nu)^{1/2} - (D/\nu)]Lk.$$

One then finds from (4.11) the value of the sought wave number,

$$k_n = (1/\sqrt{3})(q\mu u)^{1/2}[c_0\delta D^{1/2}(2\nu^{1/2} - D^{1/2})]^{-1/2}\overline{L}_n^{1/2},$$

where

$$L_n = (27/4)\mu u^3 D^{3/2}[q^3 c_0\delta(2\nu^{1/2} - D^{1/2})]^{-1}. \tag{5.1}$$

The relation (5.1) is a condition imposed on the parameters so that neutral stability takes place for longwave perturbations. In the case of high wave numbers ($k \gg u/D$, $k \gg L^{-1}$), to estimate $I_1(\infty)$ one neglects terms of higher orders of smallness in the index of the exponential in the expression under the integral sign, thus obtaining

$$I_1(\infty) = u/2k(2\nu k - iu).$$

One now obtains from the dispersion equation the shortwave perturbations spreading in the neutral stability state,

$$k_n = \{(1/\sqrt{2})(D^{1/2}u^{3/2}/q\nu) \pm [Du^3/2q^2\nu^2 - 2c_0\delta(u/\pi DL_n)^{1/2}(\mu q)^{-1} - 2u/\nu]^{1/2}\}^2.$$

The value L_n, that is, the condition which has to be imposed on the parameters, can also be obtained from Eqs. (4.12).

By considering now the nonstationary perturbations ($\omega \neq 0$), one can find the trivial solution of the dispersion equation,

$$\Omega_1 = -uk,\ \Omega_2 = 0. \tag{5.2}$$

Consequently, perturbations whose real frequency satisfies the relation (5.2) spread in the state of oscillatory stability. An estimate of the integral by the method of steepest descent for $k \ll L^{-1} + \Omega_1/u$ given by

$$I_1(\infty) = [(i - 2)/2](\pi DL/u)^{1/2}[2(D/\nu)^{1/2} - (D/\nu)](k + \Omega_1/u)L$$

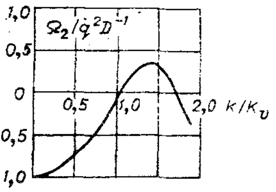

Fig. 2

enables one to find the other value of the real frequency of perturbations whose stability is of oscillatory character,

$$\Omega_1 = 2c_0\delta (L/\mu u)^2 (2\nu^{1/2} - D^{1/2}) k_v^4 - uk_v,$$

where

$$k_v = (1/\sqrt{3})\ (q\mu u)^{1/2}\ [c_0\delta L D^{1/2}(2\nu^{1/2} - D^{1/2})]^{-1/2}.$$

A similar estimate can also be obtained in the general case of complex frequency for longwave perturbations ($k \ll L^{-1} + |\omega|/u$).

In the latter case the dispersion relation is given by

$$\Omega_2 = -3c_0^2\delta^2 (L/\mu u)^2 (2\nu^{1/2} - D^{1/2})^2 k^4 + 4qc_0\delta (L/\mu u) D^{-1/2} (2\nu^{1/2} - D^{1/2}) k^2 - q^2/D.$$

This function is shown in Fig. 2. The domain $\Omega_2 < 0$ corresponds to the unstable state and $\Omega_2 > 0$, to the stable one. For high wave numbers ($k \gg u/D$) the integral is estimated by means of the expression

$$I_1(\infty) = -(1/4)(\omega + uk)\nu^{-1}k^{-3},$$

and the dispersion equation then implies that

$$\Omega_2 = 0.$$

Consequently, perturbations whose stability is not oscillatory in character do not exist in the shortwave domain under consideration.

§6. The quantitative results obtained in the preceding section show the periodic character of stability for the system under investigation, that is, the alternating pattern of the stability domains with variation in the wavelength of the perturbations. The rate of growth for the perturbations then depends on the physical parameters of the systems as follows: a) a strong dependence of the surface tension on the concentration of the dissolved matter contributes to a rapid intensification of the perturbations; b) the increase of the Prandtl numbers, which indicate that convective mass transfer prevails over molecular, also increases the rate of growth of the perturbations; c) the growth rate of the hydrodynamic flux delays this process; d) the higher rates of chemical reaction are associated with the rapid growth of instability in the domain of longwave perturbations.

To be able to describe the experimental results one has to consider not only heterogenous chemical reactions, but also homogenous reactions in the liquid cover; the interface boundary should not be considered as fixed in space, that is, hydrodynamic perturbations of the film surface should be taken into account. As regards the experimental results [4, 5] it is important to establish the effect of film thickness on the stabilization of mass transfer in a given chemical reactor.

Continuity of development of originally stationary motions in a liquid film is certainly of interest. The linear analysis of stability of the system under consideration indicates a smooth state [9] of the original perturbations.

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