

## TWO-PHASE FILM ADSORPTION COMPLICATED BY AN IRREVERSIBLE FIRST-ORDER CHEMICAL REACTION IN THE LIQUID PHASE IN A UNIDIRECTIONAL FLOW REGIME

V. N. Babak and T. B. Babak

UDC 541.44+546.3

*We developed a general procedure for calculating two-phase film chemisorption with a first-order chemical reaction in the liquid phase in a plane irrigated channel. We obtained numerical solutions for the case of practical interest of a fast reaction in which the acceleration factor can attain a considerable value. Sufficient conditions for the applicability of this absorption regime were found.*

A theoretical investigation of two-phase chemisorption in a plane-parallel channel constituting a component of regular irrigated packings was carried out in [1]. For a number of limiting cases analytical solutions were obtained that made it possible to find the general laws governing absorption. The present work is a continuation of those investigations. We suggest a practically convenient procedure for calculating two-phase chemisorption in the presence of an irreversible first-order chemical reaction for arbitrary values of the governing parameters. A film of a liquid absorbent (of thickness  $h$ ) falls down the walls of a rectangular channel (of width  $2R$ ) under gravity in contact with a cocurrent gas containing a soluble component A that in the liquid phase enters into an irreversible first-order chemical reaction with the formation of a product C:  $A \Rightarrow C$ . In dimensionless coordinates the problem is formulated as [1]

$$U_g \frac{\partial C_g}{\partial x'} = \frac{\partial^2 C_g}{\partial y_g^2}, \quad U_{liq} \frac{\partial C_{liq}}{\partial x'} = \frac{\partial^2 C_{liq}}{\partial y_{liq}^2} - a^2 C_{liq}, \quad U_{liq} \frac{\partial C}{\partial x'} = \frac{\partial^2 C}{\partial y_{liq}^2} + a^2 C_{liq}, \quad (1)$$

$$\left( \frac{\partial C_{liq}}{\partial y_{liq}} \right)_s = \left( -\frac{1}{\epsilon \beta^2} \right) \left( \frac{\partial C_g}{\partial y_g} \right)_s, \quad C_{gs} = C_{liqs}, \quad \left( \frac{\partial C}{\partial y_{liq}} \right)_s = 0 \quad \text{at} \quad y_g = y_{liq} = 1, \quad (2)$$

$$\left( \frac{\partial C_g}{\partial y_g} \right)_s = 0 \quad \text{at} \quad y_g = 0; \quad \frac{\partial C_{liq}}{\partial y_{liq}} = \frac{\partial C}{\partial y} = 0 \quad \text{at} \quad y_{liq} = 0,$$

$$C_g = 1, \quad C_{liq} = C = 0 \quad \text{at} \quad x' = x'' = 0, \quad (3)$$

The  $x$ - $y$  coordinate system was such that  $y = 0$  at the center of the rectangular channel;  $y = R - h$  and  $y = R$  on the falling liquid film surface and on one of the walls, respectively; the equality  $x = 0$  holds at the entrance of the gas into the apparatus. The dimensionless coordinates  $y_g$ ,  $y_{liq}$ ,  $x'$ , and  $x''$  and the functions  $C_g$ ,  $C_{liq}$ , and  $C$  are associated with the corresponding dimensional quantities  $x$ ,  $y$ ,  $C_g$ ,  $C_{liq}$ ,  $C$  in the following manner

$$y = (R - h) y_g, \quad y = R - h y_{liq}, \quad x = (h Pe_{liq}) x' = (R Pe_g) x'',$$

---

Institute of New Chemical Problems, Russian Academy of Sciences, Chernogolovka, Russia. Translated from *Inzhenerno-Fizicheski Zhurnal*, Vol. 70, No. 2, pp. 187-194, March-April, 1997. Original article submitted December 2, 1994.

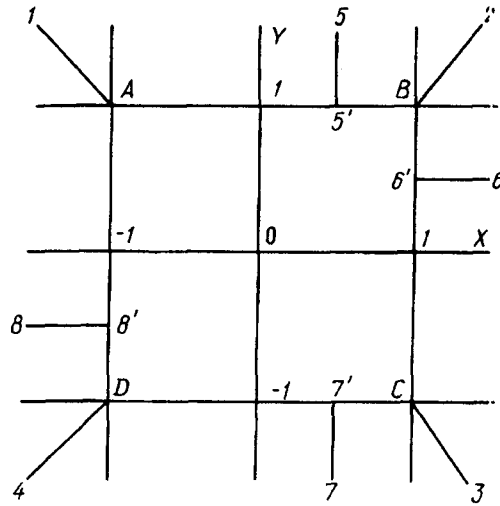


Fig. 1. Hydrodynamic plane  $X-Y$ .

$$C_g' = C_0 C_g(x', y_g), \quad C_{liq}' = k C_0 C_{liq}(x', y_{liq}), \quad C' = k C_0 C(x', y_{liq}),$$

where  $k$  is the distribution coefficient;  $C_0$  is the constant gas concentration at the inlet to the channel;  $Pe_g = R\bar{U}_g/D_g$ ,  $Pe_{liq} = h\bar{U}_{liq}/D_{liq}$  are the Peclet numbers;  $D$  is the diffusion coefficient;  $U$  is the dimensionless velocity in phase; the subscripts liq and g relate to the liquid and gas, respectively. As we can see, the distributions of concentrations  $C_g(x', y_g)$ ,  $C_{liq}(x', y_{liq})$ , and  $C(x', y_{liq})$  depend generally on three dimensionless parameters:  $\varepsilon$ ,  $\beta$ , and  $a$ . The first two of these are hydrodynamic parameters ( $\varepsilon = kh\bar{U}_{liq}/RU_g$ ,  $\beta^2 = RPe_g/hPe_{liq}$ ); they depend on the velocities of contacting phases. The third parameter  $a^2 = kh^2/D_{liq}$  will be called the chemisorption parameter; it contains the chemical reaction constant  $k$  as a multiplier. In [1] it was shown that for the solution to be easily represented, it is convenient to select  $\varepsilon$  and  $\varepsilon\beta$  as independent hydrodynamic variables and consider this solution in the plane of the variables  $X-Y$  ( $X = \log \varepsilon$ ,  $Y = -\log \varepsilon\beta$ ), which was introduced earlier for investigating a two-phase problem of absorption [2]. This plane is shown in Fig. 1. Generally, the chemisorption parameter at any point must take all admissible values  $0 < a^2 < \infty$ .

**Main Regularities in the Solution of Eqs. (1)-(3) [1].** The chemical reaction begins to exert its influence on mass transfer at distances from the gas apparatus entrance  $x' \sim 1/a^2$ . At rather small values of  $x'$ ,  $x' \ll 1/a^2$ , there is a regime of two-phase physical absorption ( $I = I_{abs}$ ). If  $x' \gg 1/a^2$ , the absorption of A occurs in the fast-reaction regime. In the latter case the substance A entering through the interface is mainly consumed in forming the product C [3, 4]; here the distribution of concentration of the substance A in the liquid phase can be obtained analytically:

$$C_{liq} \Rightarrow C_{gs}(x) \operatorname{ch}(ay_{liq})/\operatorname{ch}(a). \quad (4)$$

In the fast-reaction regime there is no need to solve general problem (1)-(3), since the dimensionless diffusion flux can be found from a simplified single-phase statement:

$$U_g \frac{\partial C_g}{\partial x''} = \frac{\partial^2 C_g}{\partial y_g^2}, \quad (5)$$

$$\left( \frac{\partial C_g}{\partial y} \right)_s = -P_g C_{rs} \text{ at } y_g = 1; \quad C_g = 1 \text{ at } x'' = 0,$$

$P_g = \varepsilon\beta^2 a \operatorname{th}(a)$  is a dimensionless parameter. Problem (5) is a one-parameter problem; it depends only on  $P_g$ . Its solution for large and small values of  $P_g$  was obtained analytically [1]:

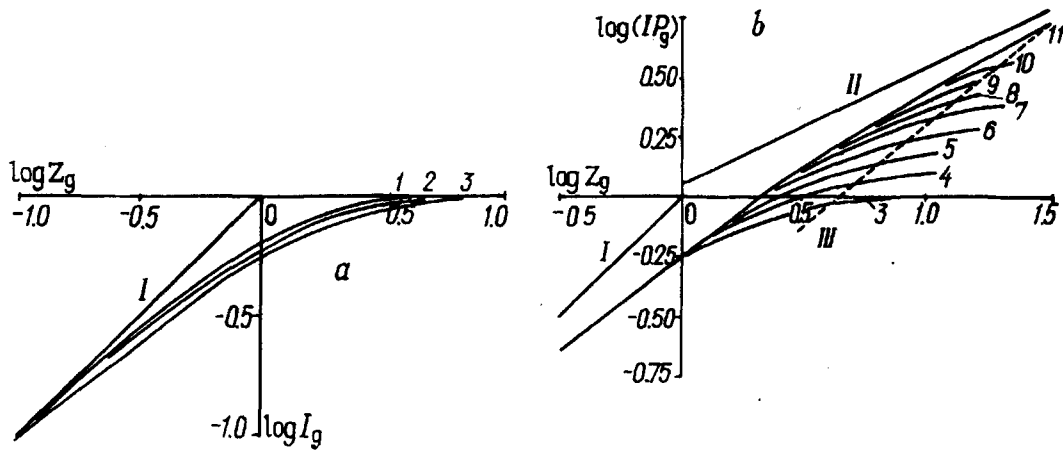


Fig. 2. Numerical calculation of  $\varphi_g(Z_g)$  for  $\log P_g \leq 0$  (a) and  $\log P_g \geq 0$  (b): 1)  $\log P_g \leq -0.8$ ; 2)  $-0.4$ ; 3) 0; 4) 0.1; 5) 0.2; 6) 0.3; 7) 0.4; 8) 0.5; 9) 0.6; 10) 0.7; 11)  $\leq 0.8$ ; I, II, asymptotic  $Z, 2\sqrt{Z/\pi}$  dependences, respectively; III,  $I \Rightarrow I_g(x'')$  transition.

$$I_{g\infty} = \frac{1}{P_g} \left\{ \frac{2}{\sqrt{\pi}} \sqrt{P_g^2 x''} - (1 - \exp(-P_g^2 x'')) (1 - \operatorname{erf}(\sqrt{P_g^2 x''})) \right\} \quad (P_g \gg 1), \quad (6)$$

$$I_{g0} \approx 1 - \exp(-P_g x'') \quad (P_g \ll 1), \quad (7)$$

where  $\operatorname{erf}(x)$  is the error function. A characteristic property of solution (5) is a monotonic change in the surface concentration  $C_{gs}(x')$  from unity to zero over a certain region  $x'_0$ . The order of the magnitude of this region for  $P_g \leq 1$  is  $x'_0 \sim 1/P_g > 1$  (7); when  $P_g > 1$ ,  $x'_0 \sim 1/P_g < 1$  (6). At the distances from the entrance  $x'' \gg x'_0$  the resistance to chemisorption is completely controlled by the gas phase, and, consequently, the diffusion flux is determined by an analytical dependence obtained by solving the equation of transfer only in the gas phase at the zero boundary condition  $C_s = 0$  [5]:

$$I_g \approx I_\infty = 1 - \sum_{n=0}^{\infty} \frac{2}{\pi^2 (n + 1/2)^2} \exp[-\pi^2 (n + 1/2)^2 x'']. \quad (8)$$

This is the so-called regime of maximum absorption.

**Numerical Solution for the Fast Chemical Reaction Regime.** This solution was obtained by the conventional elimination method [2]. For the results of calculations to be presented in a practically convenient form, we will determine the longitudinal coordinate  $Z_g$  as a function of  $P_g$  as follows (see Eqs. (6) and (7)):

$$Z_g \equiv \begin{cases} P_g x'', & \text{if } P_g \leq 1, \\ P_g^2 x'', & \text{if } P_g > 1. \end{cases} \quad (9)$$

Simultaneously, we introduce the dimensionless goal function  $\varphi_g(Z_g)$ , using which and knowing  $Z_g$ , we can easily find the dimensionless diffusion flux  $I_g$  and, conversely, determine  $Z_g$  from the prescribed value of  $I_g$ . Generally, the goal function is proportional to  $I_g$  and coincides with the latter when  $P_g \leq 1$ :

$$\varphi_g \equiv \begin{cases} I_g(Z_g), & \text{when } P_g \leq 1, \\ P_g I_g(Z_g), & \text{when } P_g > 1. \end{cases} \quad (10)$$

Calculations of the function  $\varphi_g(Z_g)$  separately for  $P_g \leq 1$  and  $P_g > 1$  are presented in Fig. 2. As we can see, the influence of this parameter on  $I_g$  is not very great when  $\log P_g \leq 0$ : the maximum difference from the

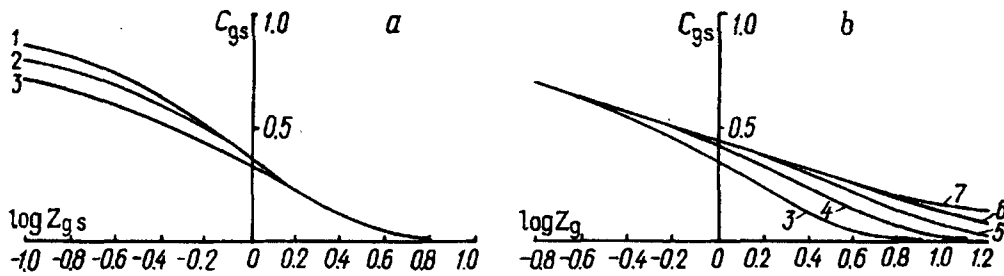


Fig. 3. Numerical calculation of the surface concentration  $C_{gs}(Z_g)$  for  $\log P_g \leq 0$  (a) and  $\log P_g \geq 0$  (b): 1)  $\log P_g \leq -0.8$ ; 2)  $-0.4$ ; 3) 0; 4) 0.2; 5) 0.4; 6) 0.6; 7)  $\geq 0.8$ .

limiting analytical dependence (7) (curve 1, Fig. 2a) does not exceed 20%. At small enough values of  $Z_g$  (in practice,  $\log Z_g \leq -0.8$ )  $I_g(Z_g) \rightarrow Z_g$ , whereas at large values of  $Z_g$  ( $\log Z_g \geq 0.6$ )  $I_g \rightarrow 1$ . In the region with  $\log P_g > 0$ , the influence of  $\log P_g$  on the goal function is usually more pronounced (Fig. 2b). We can easily see that the family of one-parameter curves  $\varphi_g(P_g Z_g)$  (the parameter  $P_g$ ) has analytical dependence (6) as an enveloping function (curve 11, Fig. 2b). The asymptotic values of this envelope at small and large values of  $Z_g$  are equal to  $Z_g$  and  $2\sqrt{Z_g/\pi}$ , respectively (curves I and II, Fig. 2b). At any fixed value of  $\log Z_g \geq 0$  it is sufficient to perform numerical calculations of  $\varphi_g(Z_g)$  only over a limited interval  $\log Z_{g \min} \leq \log Z_g \leq \log Z_{g \max}$ . Beyond its limits, in the region of  $\log Z_g \leq \log Z_{g \min}$ , the goal function  $\varphi_1 \approx P_g I_{g\infty}(Z_g)$ . When  $\log Z_g \geq \log Z_{g \max}$  (see Eq. (8)),  $I_g \rightarrow I_{\infty}(x')$ . In the latter case  $C_{gs} \rightarrow 0$ . A calculation of  $C_{gs}$  is presented in Fig. 3. As we can see,  $\log P_g < 0$  should be practically constant (see corresponding solutions for  $I_g$ , Fig. 2a). However, when  $\log P_g > 0$ , the value of  $\log Z_{g \max}$  increases sharply with an increase in this parameter. When comparing  $\varphi_g(Z_g)$  with the limiting function  $P_g I_{\infty}(x')$ , the dependence of  $\log Z_{g \max}$  on  $\log P_g$  was found parametrically (the dashed straight line in Fig. 2b). In the region located to the right of this straight line the approximate equalities  $I_g \approx I_{\infty}(x')$  are satisfied with an error not exceeding 5%. With an increase in  $\log P_g$ , the width of the interval  $[\log Z_{g \min}, \log Z_{g \max}]$  decreases sharply. At  $\log P_g = 0$  its maximum value is 0.7 (curve 3, Fig. 2b) and its minimum is zero (curve 11,  $\log P_g = 0.8$ ). At rather large values of  $\log P_g \geq 0.8$  the goal functions  $\varphi_g(Z_g)$  deviate from envelope (6) (curve 11, Fig. 2b) in the region of  $\log Z_g > 1.5$ , and, consequently, there is no need for numerical calculations at such large values of  $P_g$ , since at the accuracy adopted (5%) the transition  $\varphi_g \Rightarrow P_g I_{g\infty}(Z_g)$  occurs at  $\log Z_g = 1.5$  (see Fig. 2b). Together with the analytical dependence  $I_{\infty}(x')$  (8) the graphs depicted in Fig. 2 allow us to obtain a solution of problem (5) at any values of the chemisorption parameter  $P_g$ , and, consequently, a solution of general problem (1)-(3) at distances from the entrance at which these two solutions coincide. However, one can generally evaluate this distance only by solving numerically problem (1)-(3) over the starting length of chemisorption  $x' \sim 1/a^2$ .

**Solution of Problem (1)-(3) Over the Starting Length.** In this region the dimensionless longitudinal coordinate  $Z$  should be introduced in the following manner [3]:

$$Z = a^2 x' = A^2 x'' \quad (A = a\beta). \quad (11)$$

The calculation results will be presented as the chemical reaction acceleration factor  $\Phi$ :

$$\Phi(X, Y, a^2, Z) \equiv \frac{I(X, Y, a^2, Z)}{I_{\text{abs}}(X, Y, Z)}.$$

For this purpose, along with  $I$  we calculate the corresponding dimensionless flux  $I_{\text{abs}}$  for two-phase physical absorption (the solution of problem (1)-(3) at  $a = 0$ ), which was investigated numerically in [2]. It was proved that it was sufficient to tabulate  $I_{\text{abs}}$  in a limited region of the  $X$ - $Y$  plane (Fig. 1), in the so-called absorption square  $ABCD$  ( $-1 < X < 1$ ,  $-1 < Y < 1$ ). Outside the confines of this square  $I_{\text{abs}}$  coincides with corresponding relations for the points located on its boundary. For example,  $I_{\text{abs}}$  for point No. 1 (the  $X \leq -1$ ,  $Y \geq 1$  region) coincides with the solution at point A (Fig. 1), 2  $\Rightarrow$  B ( $X \geq 1$ ,  $Y \geq 1$ ), 3  $\Rightarrow$  C ( $X \geq 1$ ,  $Y \leq -1$ ), 4  $\Rightarrow$  D ( $X \leq -1$ ,  $Y \leq -1$ ). Similarly, the solution for point No. 5 from the  $Y \geq 1$  region coincides with the corresponding solution at point 5',

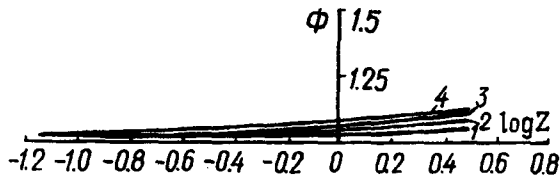


Fig. 4. Calculation of the acceleration factor at point C of the absorption square ( $X = 1, Y = -1$ ): 1)  $\log \kappa \leq -0.8$ ; 2)  $-0.4$ ; 3)  $0.4$ ; 4)  $\geq 0.8$ .

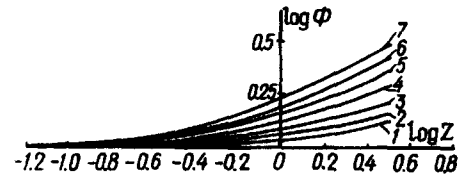


Fig. 5. Calculation of the acceleration factor at point A of the absorption square ( $X = -1, Y = 1$ ): 1)  $\log \kappa \geq 1.2$ ; 2)  $0.8$ ; 3)  $0.4$ ; 4)  $0$ ; 5)  $-0.4$ ; 6)  $\leq -1.2$ .

$6 \Rightarrow 6' (X \geq 1), 7 \Rightarrow 7' (Y \leq -1), 8 \Rightarrow 8' (X \leq -1)$ . Evidently, it is also sufficient to tabulate  $\Phi(Z)$  only within the absorption square  $ABCD$ , since an increase in the rate of mass transfer in the presence of a chemical reaction depends only on the concentration distribution in the course of physical absorption. Taking into account the fact that  $\Phi(Z) \Rightarrow 1$  when  $Z \Rightarrow 0$ , we will represent  $\Phi(Z)$  at any point of the hydrodynamic plane in the form of parametric curves, where the chemisorption parameter should generally cover all values from 0 to  $\infty$ . Typical calculations for two points of the hydrodynamic plane C and A belonging to the boundary of the absorption square  $ABCD$  are presented in Figs. 4 and 5. As the chemisorption parameter in these figures we selected the following values:  $1.21 a^2$  for point C and  $121 a^2$  for A. The meaning of the coefficients at  $a^2$  will be explained in what follows. It is known that in the first case (point C) the resistance to transfer in two-phase physical absorption is virtually concentrated in the gas phase ( $C_{\text{abs}} = 0$ ). In this case, the acceleration factor  $\Phi(Z)$  differs insignificantly from unity (see Fig. 4). In the second case (point A)  $C_{\text{abs}} \approx 1$ , the resistance is concentrated in the liquid phase; consequently,  $\Phi(Z)$  may differ appreciably from unity: its maximum value over the interval  $\log Z < 0.5$  is equal to 3 (see Fig. 5). As seen from Figs. 4 and 5, the factor  $\Phi(Z)$  is bounded from above and below by two limiting dependences. As will be shown in what follows, they both have a definite physical meaning. We will consider this problem in more detail.

Earlier [2], to investigate two-phase absorption, the notion of an active region of mass exchange  $L_{\text{abs}}$  was introduced (in the coordinates  $x'$  and  $x''$ ,  $L'_{\text{abs}}$  and  $L''_{\text{abs}}$ ) as the length over which  $I_{\text{abs}} \approx \varepsilon/(1 + \varepsilon)$ . In order of magnitude, in the left and right halves of the hydrodynamic plane the following expressions were derived for  $L_{\text{abs}}$ :

$$L''_{\text{abs}} \approx \left(1 + \frac{1}{\varepsilon\beta}\right)^2, \text{ if } X \geq 0, \quad L'_{\text{abs}} \approx (1 + \varepsilon\beta)^2, \text{ if } X < 0. \quad (12)$$

Moreover, in chemically reacting systems it is customary to introduce the notion of  $L_{\text{chem}}$  ( $L'_{\text{chem}}, L''_{\text{chem}}$ ) as the characteristic length of the reactor beginning from which the chemical interaction in it becomes appreciable [3, 4]. As applied to the considered first-order chemical reaction in order of magnitude [1]:

$$L'_{\text{chem}} \approx 1/a^2, \quad L''_{\text{chem}} \approx 1/A^2. \quad (13)$$

It is believed that chemical interaction is weak if  $L_{\text{abs}} \ll L_{\text{chem}}$  and strong if  $L_{\text{chem}} \ll L_{\text{abs}}$  [3, 4]. In both variants the solution of problem (1)-(3) is very much simplified.

**Weak Chemical Interaction.** In this case, chemical reaction begins to manifest itself at distances from the entrance at which in the case of physical absorption there is volumetric equilibrium in the system:  $C_{\text{abs}}^g \approx C_{\text{abs}}^{\text{liq}} \approx 1/(1 + \varepsilon)$  [2]. It is assumed that further the equilibrium is not violated; it is possible to integrate transfer equation (1) with respect to the transverse coordinate  $y_g, y_{\text{liq}}$  in both phases and obtain an ordinary differential equation of first order for the concentration  $C_g(x)$ :

$$\frac{dC_g}{dx''} = -A^2 \left(\frac{\varepsilon}{1 + \varepsilon}\right) C_g \quad (x'' \gg L''_{\text{abs}}). \quad (14)$$

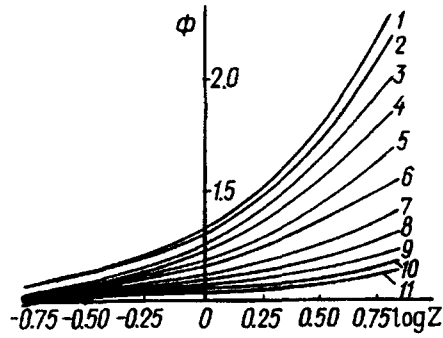


Fig. 6. Calculation of the acceleration factor  $\Phi_\infty$  in the case of strong chemical interaction: 1)  $Y \leq -1$ ; 2)  $-0.75$ ; 3)  $-0.5$ ; 4)  $-0.25$ ; 5)  $0$ ; 6)  $0.25$ ; 7)  $0.5$ ; 8)  $0.75$ ; 9)  $Y \geq 1$ ; 10)  $\geq 1.25$ ; 11) relation (20).

Its solution with obvious boundary conditions  $C_g \Rightarrow 1/(1 + \epsilon)$  for  $x^*A^2 \Rightarrow 0$  has the form

$$I \equiv 1 - \bar{C}_g \approx \frac{\epsilon}{1 + \epsilon} + \frac{1 - \exp(-\epsilon Z/(1 + \epsilon))}{1 + \epsilon},$$

where  $Z = x^*A^2$  is the dimensionless length of the apparatus.

The corresponding acceleration factor, designated as  $\Phi_0$ , is

$$\Phi_0(Z) \approx \frac{I}{\epsilon/(1 + \epsilon)} = 1 + \frac{1}{\epsilon} \left[ 1 - \exp\left(-\frac{\epsilon Z}{1 + \epsilon}\right) \right]. \quad (15)$$

The function  $\Phi_0(Z)$  depends only on one hydrodynamic parameter  $\epsilon$  (or  $X$ ). When  $\epsilon \gg 1$ ,  $\Phi_0(Z) \Rightarrow 1$ . Then the gas phase is depleted completely due to physical absorption over the interval  $x^* \sim L_{\text{abs}}^*$ , and the chemical reaction, whose influence begins to manifest itself in the region with  $x^* \sim 1/A^2$ , does not exert any effect on the process. As  $\epsilon$  is decreased, the factor  $\Phi_0(Z)$  is increased, but over any finite interval of length  $Z$  the values of this function are limited:

$$\Phi_0 = 1 + Z \quad (\epsilon \Rightarrow 0, Z \ll 1/\epsilon). \quad (16)$$

**Strong Chemical Interaction.** In this case at distances from the gas entrance at which the influence of the reaction becomes pronounced, there are diffusion boundary layers at the interface in both phases. Introducing dimensionless variables for the transverse coordinates in both phases  $y_{gn}$ ,  $y_{liqn}$  by the formulas

$$y_{gn} = A(1 - y_g), \quad y_{liqn} = a(1 - y_n),$$

we transform problem (1)-(3):

$$\frac{\partial C_g}{\partial Z} = \frac{\partial^2 C_g}{\partial y_{gn}^2}, \quad \frac{\partial C_{liq}}{\partial Z} = \frac{\partial^2 C_{liq}}{\partial y_{liqn}^2} - C_{liq}, \quad (17)$$

$$\left( \frac{\partial C_g}{\partial y_{gn}} \right)_s = -\epsilon\beta \left( \frac{\partial C_{liq}}{\partial y_{liqn}} \right)_s \quad \text{at } y_{gn} = y_{liqn} = 0;$$

$$C_g = 1 \quad (y_{gn} \Rightarrow \infty); \quad C_{liq} = 0 \quad (y_{liqn} \Rightarrow \infty); \quad (18)$$

$$C_g = 1, \quad C_{liq} = 0 \quad \text{at } Z = 0.$$

The solution of (17)-(18) depends on one hydrodynamic parameter  $\epsilon\beta$  (or  $Y$ ). The corresponding functions  $\Phi(Z)$  (which will be designated as  $\Phi_\infty(Z)$ ) also depend only on  $Y$ :

$$\Phi_{\infty}(Y, Z) \equiv \frac{1 - \bar{C}_g}{I_{\text{abs}}} = \frac{\int_0^{\infty} (1 - C_g) dy_{gn}}{\frac{2}{\sqrt{\pi}} \frac{\varepsilon\beta}{1 + \varepsilon\beta} \sqrt{Z}} \quad (19)$$

Here, we used an analytical dependence for  $I_{\text{abs}}$  over the starting length of absorption ( $x \ll L_{\text{abs}}$ ) [2]. Numerical calculations of the parametric curves  $\Phi_{\infty}(Z)$  (the parameter  $Y$ ) for a number of discrete values of  $Y$  are presented in Fig. 6. As is seen, an effect of this parameter on the solution is observed only within a limited interval  $-1 \leq Y \leq 1$ ; moreover, as  $\varepsilon\beta$  is increased, the acceleration factor is decreased. Beyond this interval  $\Phi_{\infty}(Z)$  is virtually independent of  $Y$ . The explanation of this is as follows. It is known that when  $Y \leq -1$  the resistance to mass transfer at the considered distances from the entrance ( $x \ll L_{\text{abs}}$ ) in physical absorption is governed by the gas phase ( $C_{\text{gs}} \ll 1$ ,  $I_{\text{abs}} \approx I_{\infty}(x'')$ , (8)) [2]. The presence of an irreversible chemical reaction can lead only to a decrease in the surface concentration of substance A, which has virtually no effect on the limiting diffusion flux  $I_{\infty}$ ; therefore,  $\Phi_{\infty} \approx 1$  (curve 11). In the other limiting case at small enough values of  $\varepsilon\beta$  (in practice,  $Y \geq 1$ ) at the considered distances from the entrance the resistance to chemisorption is concentrated in the liquid phase ( $C_{\text{gs}} \approx 1$ ), and the film can be assumed to have an infinite thickness. This is the regime of short-term contact of phases. For this case Danckwerts [5] obtained an analytical formula for the flux of substance A through the phase interface. Using this formula and taking into account the fact that at the considered distances  $\bar{C}_{\text{abs}} = 2\sqrt{x'/\pi}$ , the acceleration factor  $\Phi_{\infty}$  can be represented in the following form

$$\Phi_{\infty} \approx \frac{\text{erf}(\sqrt{Z})(Z + 1/2) + \sqrt{Z/\pi} \exp(-Z)}{2\sqrt{Z/\pi}} \quad (20)$$

Curve 1 (Fig. 5) virtually coincides with Eq. (20).

The aforementioned results for weak and strong chemical interactions allow us to approach the problem of selection of the chemisorption parameter for the two-phase problem of chemisorption (1)-(3). It will be shown in what follows that the use of  $a^2$  as this parameter is not always possible, as it might seem when considering problem (1)-(3) formally. In [3], the ratio between the characteristic lengths of absorption and chemical reaction was used to investigate single-phase chemisorption. This ratio, which will be denoted by  $\kappa$ , was adopted in the present work as the chemisorption parameter for the two-phase problem. Using Eqs. (12) and (13) for the right ( $X > 0$ ) and left ( $X < 0$ ) halves of the hydrodynamic plane, it is possible to obtain an explicit expression for  $\kappa$ :

$$\kappa \equiv \frac{L_{\text{abs}}}{L_{\text{chem}}} = \begin{cases} \left(1 + \frac{1}{\varepsilon\beta}\right)^2 A^2 & \text{when } X \geq 0, \\ (1 + \varepsilon\beta)^2 a^2 & \text{when } X < 0. \end{cases} \quad (21)$$

As follows from the two limiting cases considered above,  $\Phi \Rightarrow \Phi_0$  when  $\kappa \Rightarrow 0$ , and  $\Phi \Rightarrow \Phi_{\infty}$  when  $\kappa \Rightarrow \infty$ . The parameter  $\kappa$  is proportional to  $a^2$ , but it differs from the latter advantageously, because it was obtained on the basis of physical considerations and, consequently, it is expected that the boundaries of the interval  $[\kappa_{\text{min}}, \kappa_{\text{max}}]$  within which the reaction exerts its influence on  $\Phi$  will depend little on hydrodynamic variables (see the corresponding solution for points A and C, Figs. 4 and 5). Numerical investigations carried out inside the absorption square showed that for the majority of practical calculations it was possible to assume that  $\log \kappa_{\text{min}} \approx -1$ ,  $\log \kappa_{\text{max}} \approx 1$ . Beyond the interval  $-1 \leq \log \kappa \leq 1$  the difference between  $\Phi$  and the corresponding dependences  $\Phi_0$  and  $\Phi_{\infty}$  over the region with  $\log Z \leq 0.5$  usually does not exceed 5%. We note that the values of  $\kappa$  in Figs. 4 and 5 are specific cases of Eq. (21).

The results obtained allow us to ascertain why the quantity  $a^2$  could not generally be used as the chemisorption parameter. In fact, since at any point of the hydrodynamic plane the interval of the effect of  $\log \kappa$  is  $[-1, 1]$ , then, for example, in the left half of the plane  $X < 0$  (see Eq. (21)) the corresponding interval for  $\log a^2$  is  $-1 - (1 + \varepsilon\beta)^2 \leq \log a^2 \leq 1 - (1 + \varepsilon\beta)^2$ . The width of the latter interval, just as for  $\log \kappa$ , is equal to 2, but

the values of  $\log a^2$  from this interval in the region of the hydrodynamic plane lying below the horizontal straight line  $CD$  (Fig. 1) can be very small ( $\log a^2 \Rightarrow -\infty$ , if  $Y \Rightarrow -\infty$ ), and, consequently, calculations of  $\Phi(Z)$  are difficult. We could observe an analogous situation on the right half of the  $X-Y$  plane ( $X > 0$ ) for points located above the horizontal line  $AB$  if we selected  $\log A^2$  as the chemisorption parameter. In this case  $-1 - (1 + 1/\varepsilon\beta)^2 \leq \log A^2 \leq 1 - (1 + 1/\varepsilon\beta)^2$  and, consequently, when  $Y \Rightarrow \infty$ ,  $\log A^2 \Rightarrow -\infty$ .

We will clear up a question about the minimum size of the region  $Z$  over which it is necessary to calculate the acceleration factor  $\Phi(Z)$ . Obviously, the magnitude of this region should be limited, since it is known that the dimensionless diffusion flux  $I \Rightarrow I_g(Z)$  when  $Z \gg 1$  [2]. Its specific dimensions can be found only by numerical calculations of both fluxes ( $I, I_g$ ) at the same values of  $Z$ . The boundary values  $Z_b$  at which it is possible to assume that  $I \simeq I_g$  depend generally on the required accuracy with which the latter equality is satisfied, as well as on the magnitude and distribution of the concentration  $C_s^{\text{abs}}$ . As an example, Figs. 4 and 5 present calculations of  $\Phi(Z)$  at two extreme points of the absorption square  $C$  and  $A$ . As is known, in the first case the resistance to mass transfer in absorption is virtually concentrated in the gas phase ( $C_s^{\text{abs}} \simeq 0.1$ ) [3]. The difference between  $I$  and  $I_\infty(x'')$ , Eq. (8), is small and the transition  $I \Rightarrow I_g$  (if we confine ourselves to 10% accuracy) occurs at  $\log Z \simeq -0.6$ . In the second case the resistance in absorption is virtually concentrated in the liquid phase ( $C_s^{\text{abs}} \simeq 0.9$ ) [3], and the difference between  $I$  and  $I_\infty$  is generally large, and, as calculations show, the transition  $I \Rightarrow I_g$  occurs at  $\log Z \simeq 0.5$ . The surface concentration  $C_s^{\text{abs}}$  is a complex function of length, but at any point of the hydrodynamic plane this concentration satisfies the inequality  $0 \leq C_s^{\text{abs}} \leq 1$  [3]. The latter means that a sufficient condition for applicability of fast chemical reaction (5), irrespective of  $X, Y$ , and  $\kappa$ , is satisfaction of the inequality  $\log Z \geq 0.5$ . In this case, the error does not exceed 10% anywhere.

On the basis of the aforementioned investigations we may conclude that considerable acceleration of mass transfer due to a first-order chemical reaction in the liquid phase can generally be attained only at large enough values of the dimensionless length of the mass exchange apparatus  $Z$ . Over the limited region  $\log Z \leq 0.5$  in which the maximum value of the acceleration factor  $\Phi_{\text{max}} = \max [\Phi_0(Z), \Phi_\infty(Z)]$ , the inequality  $\Phi \leq 4$  is satisfied at any values of the physicochemical parameters ( $X, Y, \kappa$ ) (see Fig. 5, as well as analytical formulas (15) and (16)). The use of the solutions of chemisorbents instead of water at such small acceleration factors is hardly advisable (the well-known difficulties of preparing solutions, corrosion of equipment, etc.). All this means that even though the solution at  $\log Z \leq 0.5$  is of a certain theoretical interest (mainly for laboratory investigations), only the regime of a fast chemical reaction is of practical value. In this case the procedure for calculation of the dimensionless diffusion flux consists in the following:

1. The dimensionless coordinate  $Z$  is calculated, and realization of the inequality  $\log Z \geq 0.5$  is checked.
2. If  $\log Z \leq 0.5$ , the chemisorption parameter  $P_g$  and the dimensionless length  $Z_g$ , Eq. (9), are calculated.
3. If  $\log P_g$  lies beyond the interval  $[-1, 1]$ , the dimensionless diffusion flux  $I_g(Z_g)$  is determined from analytical formulas (6) or (7), otherwise, using the graphs of Fig. 2, the goal function  $\varphi_g(Z_g)$  and then the corresponding diffusion flux from Eq. (10) are determined.

## NOTATION

$C'_g, C'_{\text{liq}}, C'$ , concentrations of substance A in gas and liquid and of reaction product C, mole/liter;  $C_0$ , constant concentration of substance A at the entrance, mole/liter;  $C_g = C'/C_0, C_{\text{liq}} = C'_{\text{liq}}/kC_0, C = C'/kC_0$ , dimensionless concentrations;  $\bar{C}_g = \int_0^1 U_g C_g dy_g$ , mean dimensionless concentration of A in gas;  $D$ , diffusion coefficient,  $\text{m}^2/\text{sec}$ ;  $h, R$ , film thickness and channel half-width, m;  $I = (1 - \bar{C}_g)$ , dimensionless diffusion flux of substance A;  $k$ , direct reaction rate constant, liter/mole · sec;  $K$ , the Henry coefficient;  $x, y$ , rectangular system of coordinates, m;  $x' = x/hPe_{\text{liq}}, x'' = x/RPe_g$ , dimensionless coordinates in the longitudinal direction;  $y_g = y/R, y_{\text{liq}} = (R - y)/h$ , dimensionless transverse coordinates;  $U$ , dimensionless velocity of phase;  $\bar{U}$ , mean velocity of phase, m/sec;  $Pe_g = R\bar{U}_g/D_g, Pe_{\text{liq}} = h\bar{U}_{\text{liq}}/D_{\text{liq}}; a^2 = k h^2/D_{\text{liq}}; A^2 = a^2\beta^2; \varepsilon = h\bar{U}_{\text{liq}}k/R\bar{U}_g; \beta^2 = RPe_g/hPe_{\text{liq}}; X = \log(\varepsilon); Y = -\log(\varepsilon\beta)$ ,



dimensionless parameters; Subscripts and superscripts: liq, liquid; g, gas; abs, physical absorption; n, new coordinates.

## REFERENCES

1. V. N. Babak, L. P. Kholpanov, V. A. Malyusov, and N. M. Zhavoronkov, *Teor. Osnovy Khim. Tekhnol.*, **11**, No. 1, 28-37 (1977).
2. V. N. Babak, T. B. Babak, L. P. Kholpanov, V. A. Malyusov, and N. M. Zhavoronkov, *Teor. Osnovy Khim. Tekhnol.*, **12**, No. 1, 3-12 (1978).
3. G. Astarita, *Mass Transfer with Chemical Reaction* [Russian translation], Leningrad (1971).
4. P. V. Dancwerts, *Gas-Liquid Reactions* [Russian translation], Moscow (1973).
5. P. V. Dancwerts, *Trans. Faraday Soc.*, **46**, 300-307 (1950).