TWO-PHASE ABSORPTION COMPLICATED BY A SECOND-ORDER IRREVERSIBLE CHEMICAL REACTION IN A LIQUID PHASE UNDER DIRECT-FLOW CONDITIONS (SOLUTION FOR THE FOURTH QUADRANT OF A HYDRODYNAMIC PLANE)

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In the contex of two-phase film mass transfer, we carry out a theoretical investigation of the chemisorption of a gaseous-mixture component in wetted plane-parallel channels at large chemisorption capacities of an absorber.

The problem of extracting a gaseous-mixture component (in particular, CO_2) by liquid absorbers (for example, by solutions of such amines as monoethanolamine, diethanolamine, etc.), provided this component enters into a second-order chemical reaction, was set up in a general form previously [1]. For the sake of definiteness, a steady-state hydrodynamic section of a vertically wetted channel (of width $2R$) was considered, in which a gas and a thin liquid film (of thickness h) moved in the regime of descending direct flow.

With the degree of solution carbonization $\alpha \leq 0.5$, an irreversible reaction between CO_2 and amine (monoethanolamine) follows the scheme [2, 3]

$$CO_2 + RNH_2 \rightleftharpoons RNHCOO^- + H^+,\tag{1}$$

where $RNHCOO^-$ is the carbamine ion; $R = CH_2-CH_2-OH^-$ is the neutral group.

The problem is treated on the basis of two-phase mass-transfer considerations: an equation of convective diffusion in a gas for CO_2 and corresponding transfer equations for $[CO_2]$ and $[RNH_2]$ in a liquid with volumetric sources $\pm k[CO_2][RNH_2]$ are solved on condition of conjugation of fluxes and concentrations at the phase interface. Taking into account the fact that the following relationship exists between the concentrations of RNH_2 and $RNHCOO^-$ [4, 5]

$$[RNH_2] = N' - 2[RNHCOO^-],\tag{2}$$

in the liquid phase it is possible to consider the diffusion equation either for $[RNH_2]$ or for $[RNHCOO^-]$ with sources of the form $\pm k[CO_2] (N'-2[RNHCOO^-])$, where the minus sign holds for $[RNH_2]$ and the plus sign for $[RNHCOO^-]$. Both these approaches are equivalent; however, for the convenience of further investigation we shall examine the latter.

A system of Cartesian coordinates (x, y) is selected so that the conditions $y = 0$, $y = R-h$, and $y = R$ are satisfied at the channel center, on the film surface, and on one of the walls, respectively, whereas the equality $x = 0$ holds in the inlet section of the channel. In [1], the problem considered is formulated rather generally in a hydrodynamically steady-state section; moreover, the velocity distributions in the phases $U'_g(y)$ and $U'_{liq}(y)$, as well as as the specific values of the coefficients of transverse diffusion D_g and D_{liq}, depend on the regime of motion: laminar or turbulent [2, 3]. An important case in practice is considered, when the input concentration of amine N' is much

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in excess of the concentration in the liquid phase kC_0, which is in equilibrium with the input concentration of the gas C_0. If we introduce the ratio of these concentrations N, then

$$N = \frac{N'}{2kC_0} \gg 1 .$$ (3)

In [6], it was shown that, on satisfaction of condition (3), a change in the concentration of amine becomes noticeable at rather large distances from the inlet section of the channel:

$$(k\,N'x)/\overline{U}_{\text{liq}} \gg 1 ,$$ (4)

where the overbar denotes the average value of the corresponding quantity, in the given case, of the liquid velocity. This means that it is sufficient to investigate absorption, complicated by the second-order chemical reaction, at distances from the inlet that satisfy inequality (4). Otherwise, the interaction between CO_2 and amine can be considered as a chemical reaction of the pseudofirst order, whose solution is known [7]. Let us introduce the dimensionless coordinates and functions according to the following formulas [1]:

$$y = R - hy_g , \quad y = R - hy_{\text{liq}} , \quad x = h\,\text{Pe}_{\text{liq}}\,x' = R\,\text{Pe}_g\,x'' ,$$

$$C_g' = C_0\,C_g\,(x'',y_g) , \quad C_{\text{liq}}' = kC_0\,C_{\text{liq}}\,(x',y_{\text{liq}}) , \quad C' = (N'/2)\,C\,(x',y_{\text{liq}}) .$$

In [7], it was shown that, on satisfaction of conditions (3) and (4), one can neglect the convective terms in the transfer equation for CO_2 and the source term in the corresponding equation for carbamine. Physically, this means that at such lengths the interaction between CO_2 and amine occurs in the so-called regime of fast reaction [2, 3] when the entire carbonic acid, penetrating through the phase interface, transforms to a bound state (of the form [RNHCOO$^-$]). Moreover, in the region of the basic change in [CO_2], the concentration of [RNHCOO$^-$] can be considered constant and equal to its value at the phase interface. In this case, the profile of [CO_2] in the film is expressed by the analytical relation

$$C_{\text{liq}}\,(x',y_{\text{liq}}) = C_{gs}\,(x)\,\frac{\cosh\,[ay_{\text{liq}}\,\sqrt{1 - C_s\,(x)}\,]}{\cosh\,[a\,\sqrt{1 - C_s\,(x)}\,]} ,$$ (5)

where $a^2 = k \cdot N'h^2/D_{\text{liq}}$ is the chemisorption parameter.

Using formula (5), in [1] the two-phase chemisorption problem was reduced to an equivalent two-phase diffusion problem for determining C_g and C with nonlinear conditions at the phase interface. In dimensionless form this problem can be formulated as follows:

$$\frac{\partial C_g}{\partial x_g''} = \frac{\partial^2 C_g}{\partial y_g^2} , \quad \frac{\partial C}{\partial x'} = \frac{\partial^2 C}{\partial y_{\text{liq}}^2} ;$$ (6)

$$\left(\frac{\partial C}{\partial y_{\text{liq}}}\right)_s = P_{\text{liq}}\,\sqrt{1 - C_s\,(x)}\,\frac{\tanh\,(a\,\sqrt{1 - C_s\,(x)})}{\tanh\,(a)}\,C_{gs} ;$$ (7)

$$\left(\frac{\partial C_g}{\partial y_g}\right)_s = -P_g\,\sqrt{1 - C_s\,(x)}\,\frac{\tanh\,(a\,\sqrt{1 - C_s\,(x)})}{\tanh\,(a)}\,C_{gs}$$ (8)

when $y_g = y_{\text{liq}} = 1$;

$$\left(\frac{\partial C_g}{\partial y_g}\right) = 0 , \quad \left(\frac{\partial C}{\partial y_{liq}}\right) = 0 \tag{9}$$

when $y_g = y_{liq} = 0$

$$C_g = 1 , \quad C = 0 \tag{10}$$

when $x' = x'' = 0$. The parameters P_{liq} and P_g are equal to

$$P_{liq} \equiv \frac{a}{N} \tanh{(a)} , \quad P_g \equiv \varepsilon\beta^2 a \tanh{(a)} = (\varepsilon N\beta^2) P_{liq} , \tag{11}$$

$$\varepsilon = \frac{\overline{U}_{liq} hk}{R\overline{U}_r} , \quad \beta^2 = \frac{R \, Pe_g}{h \, Pe_{liq}} .$$

Over the stretch $a^2 x' \gg 1$ (the conditions are equivalent to Eq. (4)), virtually the whole of the dissolved carbonic acid is in a chemically bound state [7]. Consequently, the dimensionless integral equation of material balance coincides in form with the corresponding equation for two-phase physical absorption. With account for the substitution $\varepsilon \Rightarrow \varepsilon N$ and $C_{liq} \Rightarrow C$,

$$I \equiv (1 - \overline{C}_g) = \varepsilon N \overline{C} \equiv \varepsilon \, N \, \Sigma , \tag{12}$$

where

$$\overline{C}_g = \int_0^1 U_g C_g \, dy_g , \quad \Sigma = \int_0^1 U_{liq} C_{liq} dy_{liq} .$$

Physically, the functions $\Sigma(x)$ and $I(x)$ are the dimensionless integral diffusion fluxes from the side of the gas and liquid, while the parameters, ε and εN are the absorption and chemisorption factors, respectively, for extended packing elements [3]. The parameters $\varepsilon\beta$ and $\varepsilon\beta N$ have respectively the same sense for short channels [8]. Formally, the solution of problem (6)-(10) depends on four dimensionless parameters, ε, β, N, and a (or on their independent combinations). We note that a successful choice of one system of independent variables or another is of fundamental importance. This choice frequently makes it possible not only to give a pictorial representation of chemisorption (distributions of concentrations, dependences of dimensionless fluxes on length) in the general case, but also to obtain simple conditions for the implementation of the known absorption regimes: reactions of pseudofirst order, instantaneous and slow chemical reactions, conditions under which resistance to transfer is concentrated in a gas, liquid, etc. [1]. The determination of the conditions for the existence of such limiting regimes is the main objective of the present work. In these cases, the calculation procedure for chemisorbers is simplified greatly, since the functions $I(x)$ are usually described by convenient analytical formulas. Undoubtedly, these formulas depend on the regimes of the motion of phases (velocity distributions); however, the specific form of the dimensionless functions $U_g(y_g)$ and $U_{liq}(y_{liq})$ (since, by definition, all these functions are of the order of unity) cannot apparently affect the realization of the above-mentioned limiting absorption regimes on condition that all the transfer coefficients correspond to the motion regime under consideration. Considering the aforegoing, we carried out a theoretical investigation of the problem for the case $U_g = U_{liq} = 1$ (pistonlike phase motion usually typical for turbulent regimes). This considerably simplifies the mathematical calculations, not distorting the essence of the phenomena.

In [1], to investigate two-phase chemisorption with a second-order irreversible chemical reaction, a rectangular coordinate system of the hydrodynamic variables $X_N - Y_N$ was introduced, where $X_N = \log \varepsilon N$ and $Y_N = -\log (\varepsilon\beta N)$. The term "hydrodynamic" indicates that the corresponding quantities depend on the loads of contacting phases. The hydrodynamic variables for absorption $X = \log \varepsilon$, $Y = -\log \varepsilon\beta$, and X_N and Y_N form the linear relationships $X_N = X + \log N$, $Y_N = Y - \log N$. Graphically this corresponds to the situation where the planes
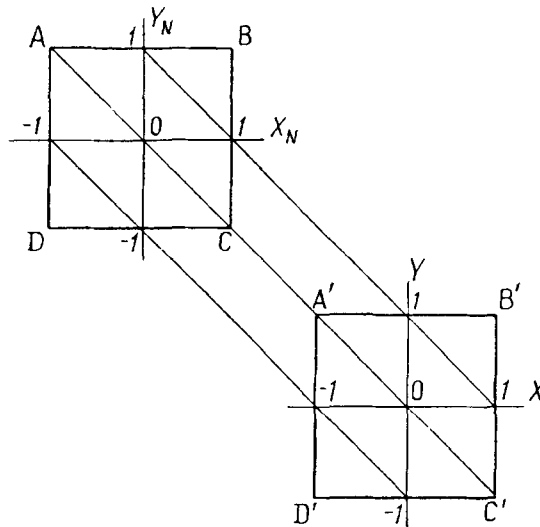
Fig. 1. Hydrodynamic planes X_N-Y_N and $X-Y$.

$(X-Y)$ and (X_N-Y_N) are displaced from each other by an amount $\log N$ (see Fig. 1). The aim of our investigation is to obtain a solution of (6)-(10) at any point of the X_N-Y_N plane. Below, we will show that for this purpose it is sufficient to obtain a solution only at the inner points of the square ABCD (see Fig. 1). It is easy to see that for $N \gg 1$ this square is located in the upper-left corner of the absorption hydrodynamic plane $X-Y$, where the inequalities $X \leq -1$ and $Y \geq 1$ ($\varepsilon \ll 1$, $\varepsilon\beta \ll 1$) are satisfied. It is known that in this region the diffusion resistance for physical absorption is concentrated in the liquid phase, whereas the surface concentration is $C_{gs}^{abs} = 1$ at any x [8]. Formally, when $x \Rightarrow 0$, chemical interaction can be neglected since the process of absorption proceeds due to physical absorption (generally this occurs when $a^2 x' \leq 1$) [4]. We can show that in the case considered ($N \gg 1$) the conditions $C_{gs} = 1$ and $C_s = 0$ are retained even at considerable distances from the inlet ($a^2 x \gg 1$). This means that in this region the regime of a fast chemical reaction is realized with the resistance to chemisorption in the liquid phase, with the dimensionless diffusion fluxes being equal to

$$\Sigma = \int\limits_0^{x'} \frac{\partial C_{liq}}{\partial y_{liq}} dx' = P_{liq} x' , \quad I = P_g x''. \tag{13}$$

In what follows, this region will be called the initial segment of chemisorption.

The investigations showed that the solution of the problem of two-phase chemisorption (6)-(10) is qualitatively different depending on to which of the four quadrants of the hydrodynamic plane (to the first $X_N \geq 0$, $Y_N \geq 0$; second $X_N \leq 0$, $Y_N \geq 0$; third $X_N \leq 0$, $Y_N \leq 0$, or fourth $X_N \geq 0$, $Y_N \leq 0$) the considered point X_N, Y_N belongs. In view of the variety of the regimes observed, it does not appear possible to present in one article the results of investigation for all of the four quadrants. Previously, in [1] the solution for points of the second quadrant, i.e., at small values of the chemisorption capacity ($\varepsilon N \leq 1$, $\varepsilon\beta N \leq 1$), was investigated theoretically. In the present work, we study the opposite case at large chemisorption capacities ($\varepsilon N \geq 1$, $\varepsilon\beta N \geq 1$), i.e., the solution in the fourth quadrant of the hydrodynamic plane X_N-Y_N ($X_N \geq 0$, $Y_N \leq 0$) (see Fig. 1).

As noted above, at any point of the hydrodynamic plane X_N, Y_N the solution should generally depend also on two other dimensionless parameters. Usually, they are selected in such a way that they could contain the chemical reaction constant k as a multiplier. Hereafter, we will call such parameters kinetic. For example, for the points of the second quadrant [1], such parameters were taken to be P_{liq} and a. It was shown that the influence of a on the solution is insignificant, i.e., of no fundamental importance, because it is manifested only through the multiplier $\tanh (a\sqrt{1 - C_s(x)}$ /$\tanh (a)$ in boundary conditions (7), (8) which is always of the order of unity. The qualitative picture of the behavior of the solution (Σ, I, C_{gs}, C_s) is mainly determined by two hydrodynamic parameters X_N, Y_N and by one kinetic parameter P_{liq}. Similarly, as will be shown below, the solution in the fourth

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quadrant depends basically on the position of the point X_N, Y_N on the hydrodynamic plane and, in addition, on the magnitude of the kinetic parameter P_g (Eq. (11)).

As is seen from Fig. 1, in the fourth quadrant the relationship between the characteristic lengths RPe_g and hPe_{liq} can be arbitrary: for the points that lie above the bisectrix AC, the inequality $\beta \leq 1$ is satisfied, while for those that lie below it, the inequality $\beta \geq 1$ holds. Since, in the region considered, $X_N \geq 0$, according to the general theory [1] it is convenient to select the parameter $I(x)$ as a goal function for calculating the length of the packing device.

Before proceeding to the general investigation of problem (6)-(10), we will obtain a formal solution for two important limiting cases: long and short channels.

Solution for Long Channels. Suppose the length of the channel is so large that even over the initial portion of chemisorption ($C_{gs} = 1$, $C_s = 0$) the diffusion layers in the gaseous and liquid phases intergrow completely. From material balance (12) for the surface concentrations we obtain

$$C = C_s = \frac{I}{\varepsilon N}, \quad C_g = C_{gs} = 1 - I. \tag{14}$$

From the general statement of Eqs. (6)-(10) we can show that the function $I(Z)$ can be found from the solution of the ordinary differential equation

$$\frac{dI}{dZ} = \sqrt{\left(1 - \frac{I}{\varepsilon N}\right)} \frac{\tanh\left[a\sqrt{\left(1 - \frac{I}{\varepsilon N}\right)}\right]}{\tanh(a)} [1 - I(Z)], \quad I(0) = 0, \tag{15}$$

where $Z = P_g x''$. Hereafter, we will denote this solution by $I_0(a, X_N, Z)$. The function $I_0(Z)$ is two-parametric; it depends on the determining parameters X_N and a. Equation (15) admits separation of variables and can be solved in an implicit form for I_0 in quadratures. For large values of a ($a \gg 1$) we can obtain an analytical relation [9]:

$$\left(1 - \frac{I_0}{\varepsilon N}\right)^{1/2} = \left(1 - \frac{1}{\varepsilon N}\right)^{1/2} \left\{ \frac{1 + \varepsilon N \left(1 - \left(1 - \frac{1}{\varepsilon N}\right)^{1/2}\right)^2 \exp\left(-\left(1 - \frac{1}{\varepsilon N}\right)^{1/2} Z\right)}{1 - \varepsilon N \left(1 - \left(1 - \frac{1}{\varepsilon N}\right)^{1/2}\right)^2 \exp\left(-\left(1 - \frac{1}{\varepsilon N}\right)^{1/2} Z\right)} \right\}. \tag{16}$$

Similarly, for small values of a, we obtain

$$I_0 = \frac{1 - \exp\left[-\frac{\varepsilon N - 1}{\varepsilon N} Z\right]}{1 - \exp\left[-\frac{\varepsilon N - 1}{\varepsilon N} Z\right] \Big/ \varepsilon N} \quad (a \ll 1). \tag{17}$$

The functions $I_0(Z)$ are monotonic; moreover, approximation (13) ($I_0 = Z$) is satisfied when $Z \ll 1$, and the function $I_0 \Rightarrow 1$ when $Z \gg 1$. It can be shown that the differences between relations (16) and (17) at any values of εN do not exceed 10%, i.e., as expected, the influence of the parameter a on the solution $I_0(a, X_N, Z)$ is insignificant. In this case, the absorption process is said to proceed in the kinetic regime, since the concentration of carbamine in the liquid in the lateral direction does not change.

Solution for Short Channels. In this case, it can be considered that diffusional boundary layers exist in both phases. After the introduction of the variables $y_{g.n}$, y_n, and Z instead of y_g, y_{liq}, and x'' according to the formulas

$$1 - y_g = \frac{1}{P_g} y_{g.n}, \quad 1 - y_{liq} = \frac{\beta}{P_g} y_n, \quad Z = P_g^2 x'' \tag{18}$$

we will transform dimensionless problem (6)-(10) as

$$U_g = \frac{\partial C_g}{\partial Z} = \frac{\partial^2 C_g}{\partial y_{g.n}^2}, \quad U_{liq} \frac{\partial C}{\partial Z} = \frac{\partial^2 C}{\partial y_n^2}, \tag{19}$$

$$\left(\frac{\partial C_g}{\partial y_{g.n}}\right) = - \sqrt{1 - C_s(Z)} \, \frac{\tanh(a\sqrt{1 - C_s(Z)})}{\tanh(a)} C_{gs}, \tag{20}$$

$$\left(\frac{\partial C}{\partial y_n}\right)_s = - \frac{1}{\varepsilon \beta N} \sqrt{1 - C_s(Z)} \, \frac{\tanh(a\sqrt{1 - C_s(Z)})}{\tanh(a)} C_{gs} \tag{21}$$

at $y_{g.n} = y_n = 0$;

$$\left(\frac{\partial C}{\partial y_n}\right)_\infty = \left(\frac{\partial C_g}{\partial y_{g.n}}\right)_\infty = 0 \quad (y_n \Rightarrow \infty, \ y_{g.n} \Rightarrow \infty), \tag{22}$$

$$C_g = 1, \quad C = 0 \tag{23}$$

at $Z = 0$. Formally, problem (19)-(22) is obtained from (6)-(10) when $P_g \Rightarrow \infty$. The equation of material balance in the new variables takes the form

$$I_n \equiv \int_0^\infty U_g (1 - C_g) \, dy_{g.n.} = \varepsilon \beta N \int_0^\infty U_{liq} C dy_n = (\varepsilon \beta N) \Sigma_n, \tag{24}$$

where physically I_n and Σ_n are also dimensionless fluxes in the gas and liquid, respectively.

As is seen, the solution of problem (19)-(23) depends only on two determining parameters, i.e., hydrodynamic Y_N and chemisorption a. Now, we will obtain certain analytical formulas for the initial segment, where the conditions $C_s(Z) \ll 1$ and $C_{gs} \simeq 1$ are satisfied. Taking into account the fact that in short channels diffusional boundary layers exist in the gas and liquid, we will seek the solution of the problem in the form

$$1 - C_g = (x_g'')^{1/2} f_{1/2}(\eta_g) (- P_g)/f_{1/2}'(0) + \dots, \tag{25}$$

$$C \simeq (x')^{1/2} f_{1/2}(\eta_{liq}) (- P_{liq})/f_{1/2}'(0) + \dots, \tag{26}$$

where η_g and η_{liq} are the self-similar variables

$$\eta_g = (1 - y_g)/\sqrt{x''} = y_{g.n.}/\sqrt{Z}, \quad \eta_{liq} = (1 - y_{liq})/\sqrt{x'} = y_n/\sqrt{Z},$$

and the prime denotes differentiation of the function $f(\eta)$ with respect to the variable η.

Substituting expansion (26) into transfer equation (19), for $f_{1/2}(\eta)$, we obtain [1]

$$f_{1/2}(\eta) = \exp\left(-\frac{\eta^2}{4}\right) - \left(\frac{\eta}{2}\right) \int_\eta^\infty \exp\left(-\frac{t^2}{4}\right) dt.$$

Consequently, the surface concentrations C_{gs} and C_s vary over the initial segment in the following way:

$$C_{gs} \simeq 1 - \frac{2\sqrt{Z}}{\sqrt{\pi}}, \quad C_s \simeq \frac{1}{\varepsilon \beta N} \frac{2\sqrt{Z}}{\sqrt{\pi}} \quad (Z \ll 1). \tag{27}$$

As is seen, the function $C_{gs}(Z)$ depends only slightly on the parameters Y_N and a and decreases monotonically. It can be assumed that

$$C_{gs} \Rightarrow 0 \quad \text{for} \quad Z \gg 1, \tag{28}$$

The latter means that in the case of large-length Z the resistance to chemisorption is completely concentrated in the gas. In this case, the distribution of concentrations in the phases is known [4]:

$$C_g \Rightarrow \mathrm{erf}\,(\eta_g), \quad C \Rightarrow \frac{1}{\varepsilon \beta N} \mathrm{erfc}\,(\eta_{\mathrm{liq}}). \tag{29}$$

In particular, at the phase interface

$$C_s \Rightarrow \frac{1}{\varepsilon \beta N} \leq 1. \tag{30}$$

It can be easily shown that the asymptotic functions $I_n(Z)$ for large and small values of Z are equal to

$$I_n \Rightarrow \begin{cases} Z & (Z \ll 1), \\ \dfrac{2}{\sqrt{\pi}} \sqrt{Z} & (Z \gg 1). \end{cases} \tag{31}$$

Formally, statements (15) and (19)-(23) should hold at any point X_N, Y_N irrespective of its position in the fourth quadrant for $P_g \Rightarrow 0$ and $P_g \Rightarrow \infty$, respectively.

Below, by means of theoretical investigations of the solutions of general problem (6)-(10) for different regions of the fourth quadrant, we will obtain more exact conditions for the applicability of the solutions for short and long channels, as well as of other analytical formulas. This will make it possible to visually represent the solution in this quadrant and subsequently to construct a procedure for calculating two-phase chemisorption for arbitrary values of physicochemical, kinetic, and geometric quantities.

Investigation of the Solution for $\beta \leq 1$ *(the Region above the Straight Line AC).* In this region the inequality $R\mathrm{Pe}_g \leq h\mathrm{Pe}_{\mathrm{liq}}$ is satisfied between the characteristic dimensions in the gaseous ($R\mathrm{Pe}_g$) and liquid ($h\mathrm{Pe}_{\mathrm{liq}}$) phases. Consequently, a boundary layer in the gas grows more rapidly than in the liquid. When $P_g \leq \beta^2$, all the conditions for applicability of the kinetic regime (Eqs. (14) and (15)) are satisfied, even over the initial stretch of chemisorption. In particular, the function $I(Z)$ can be obtained analytically (Eqs. (16) and (17)). With a further increase in P_g ($\beta^2 \leq P_g \leq 1$), a diffusional boundary layer is observed over the initial segment of chemisorption in the liquid phase. In this case, for the distribution of the concentration C approximation (26) is valid. Then

$$I \simeq P_g x'' = Z, \quad C_{gs} \simeq 1 - I, \tag{32}$$

$$C_s \simeq \frac{P_{\mathrm{liq}}}{-f_{1/2}'} (x')^{1/2} = \frac{\sqrt{P_g}}{\varepsilon \beta N} \frac{2}{\sqrt{\pi}} \sqrt{Z}, \tag{33}$$

Considering that $I < 1$, we may assume that $I \Rightarrow 1$ and $C_{gs} \Rightarrow 0$ when $Z = P_g x'' \geq 1$. Therefore, from the balance equation we have $\overline{C} \Rightarrow 1/\varepsilon N < 1$. This means that within the region $Z > 1$ the distribution of C_g is determined from formulas (29), while C can be found from the following one-phase problem:

$$\frac{\partial C}{\partial x'} = \frac{\partial^2 C}{2 y_{\text{liq}}^2} , \quad \int_0^1 C \, dy_{\text{liq}} = \frac{1}{\varepsilon N} . \tag{34}$$

Solution (34) for $x' < 1$ exists in the form [1]

$$C = \frac{\exp \left(- \eta_{\text{liq}}^2 / 4\right)}{\varepsilon N \sqrt{\pi} \sqrt{x'}} . \tag{35}$$

In particular, C_s changes as follows:

$$C_s \simeq \frac{\sqrt{P_g}}{\varepsilon \beta N} \frac{1}{\sqrt{\pi}} \frac{1}{\sqrt{Z}} \quad (Z > 1 , \ x' < 1) . \tag{36}$$

Comparing formulas (33) and (36), obtained at small and large values of Z, we conclude that the concentration of carbamine C_s in the region $Z \sim 1$ passes through the maximum of the order of $\sqrt{P_g}/\varepsilon \beta N$, which increases together with the parameter P_g. For $x' > 1$, when boundary layers grow through both phases

$$C_s \Rightarrow \frac{1}{\varepsilon N} < 1 . \tag{37}$$

When $P_g \gg 1$, the diffusional boundary layers are observed over the initial segment of chemisorption in both phases. In this case, the solution for $x'' < 1$ is determined by formulas (25)-(31), where $P_g^2 x'' = Z$. Over the finite segment $1 < Z$, $x'' < 1$ $(1/P_g^2 < x'' < 1)$ the function $C_s(Z)$ is equal to the maximum value $1/\varepsilon \beta N$. For $x'' > 1$, where a boundary layer grows in the gas, approximations (36) and (37) are valid. In this region, the concentration C_s decreases from the maximum value $1/\varepsilon \beta N$ to the minimum value $1/\varepsilon N$ (when $x' > 1$).

The two-phase problem of chemisorption (Eqs. (6)-(10)) is greatly simplified when $\varepsilon N \gg 1$. It can be assumed in this case that the parameter $\beta \Rightarrow 0$. Physically, this means that there always exist diffusional boundary layers in the liquid phase and, consequently, the statement of problem (6)-(10) can be reduced to the following:

$$U_g \frac{\partial C_g}{\partial x''} = \frac{\partial^2 C_g}{\partial y_g^2} , \quad U_{\text{liq}} \frac{\partial C}{\partial x''} = \frac{\partial^2 C}{\partial y_{\text{liq.n}}^2} , \tag{38}$$

$$\left(\frac{\partial C}{\partial y_{\text{liq.n}}}\right) = - \frac{P_g}{\varepsilon \beta N} \sqrt{1 - C_s(x')} \ \frac{\tanh \left(a \sqrt{1 - C_s(x')}\right)}{\tanh (a)} C_{gs} ,$$

$$\left(\frac{\partial C_g}{\partial y_g}\right) = - P_g \sqrt{1 - C_s(x)} \ \frac{\tanh \left(a \sqrt{1 - C_s(x)}\right)}{\tanh (a)} C_{gs} \tag{39}$$

at $y_g = 1$, $y_{\text{liq.n}} = 0$;

$$\left(\frac{\partial C_g}{\partial y_g}\right) = 0 , \quad \left(\frac{\partial C}{\partial y_{\text{liq.n}}}\right) = 0 \tag{40}$$

at $y_g = 0$, $y_{\text{liq.n}} \Rightarrow \infty$, respectively;

$$C_g = 1 , \quad C = 0 \tag{41}$$

at $x_g = 0$, where $y_{\text{liq.n}} = (1 - y_{\text{liq}})/\beta$.

Problem (38)-(41) does not depend on X_N. We will denote the dimensionless diffusion flux I in the case considered by $I_Y(P_g, Y_N, a, Z)$. We can show that approximations (32)-(36) follow from statement (38)-(41) when

$P_g \ll 1$. Since, in the fourth quadrant, $\varepsilon\beta N \geq 1$, it is easy to see that $C_s \ll 1$, and, consequently, from Eqs. (38)-(41) for I_Y we obtain

$$I_Y = 1 - \exp(-Z) \quad (P_g \ll 1).$$ (42)

This formula coincides with Eqs. (16) and (17) for $\varepsilon N \gg 1$.

When $P_g \gg 1$, problem (38)-(41) over the segment x'' is equivalent to problem (19)-(23). For this, it is sufficient to substitute the following variables: $x'' = Z/P_g^2$, $1 - y_g = y_{g.n}/P_g$, $y_{liq.n} = y_n/P_g$. In this case, approximations (25)-(31) are satisfied, while for small and large values of Z approximation (31) is valid. We note that when $Z \gg 1$ ($x'' \gg 1/P_g^2$), the resistance to transfer is concentrated in the gaseous phase ($C_{gs} \Rightarrow 0$); consequently, I_y coincides with the solution of the single-phase diffusion problem with the zero boundary condition $C_{gs} = 0$ [2]:

$$I_\infty = 1 - \sum_{n=0}^{\infty} \frac{2}{\pi^2 (n + 1/2)^2} \exp\left[-\pi^2 (n + 1/2)^2 x''\right].$$ (43)

Generally, the problem of the applicability of a simplified statement (Eqs. (38)-(41)) can be solved only as a result of the numerical calculation of general problem (6)-(10) and its comparison with solution (38)-(41). However, even on the basis of the results obtained above, it is possible to assume that on the hydrodynamic plane in the region located to the right of the vertical straight lines $X_N = \text{const} \gg 1$, the equality $I \simeq I_y$ is satisfied at any values of a and P_g (this occurs practically to the right of the straight line BC ($X_N > 1$)) (see Fig. 1).

Note that for $\beta < 1$ in the region of the hydrodynamic plane located above AC, the surface concentration of carbamine has a complex bell-shaped form, with its maximum value being smaller than $1/\varepsilon\beta N < 1$ irrespective of the quantities a and P_g.

Investigation of the Solution for $\beta > 1$ (the Region below the Straight Line AC). In this region, the inequality $hPe_{liq} < RPe_g$ is satisfied; consequently, the boundary layer grows through the liquid more rapidly than in the gas. With such a relationship between the characteristic lengths, when $P_g < 1$, the limiting regime of absorption (Eqs. (14), (15)) is evidently realized at which $I \simeq I_0(X_N, a, Z)$, where $Z = P_g x''$. Then over the entire segment of chemisorption considered ($0 < I < 1$) the lateral change in the concentration in both phases can be neglected. As the factor P_g ($1 < P_g < \beta$) increases, the kinetic regime of absorption is retained, i.e., formulas (14) remain valid for the liquid phase. However, in the gaseous phase (at least, at the lengths $x'' < 1$) one observes a boundary layer; consequently, approximations (25), (27), and (29) are valid for C_g. Note that in the region $1/P_g^2 < x'' < 1$ formula (24) for I virtually coincides with Eq. (43) (see Eq. (31)). Thus, when $x'' > 1/P_g^2$, for C_s (since $x' > 1$) we obtain an analytical formula:

$$C_s(x') \Rightarrow I_\infty(x'')/\varepsilon N.$$ (44)

And, finally, we will investigate the solution for $P_g > \beta$. In this case, over the segment $x' < 1$ ($x'' < 1/\beta^2$), where the boundary layer exists in both phases, Eqs. (19)-(23) are valid, in particular, solutions (25)-(31). When $x'' > 1/P_g^2$ the surface concentration $C_s(x'')$ approaches the constant value $1/\varepsilon\beta N$ and virtually does not change up to $x' < 1$. This value, however, is not an asymptote for $C_s(x'')$, since subsequently ($x' > 1$), when the absorption regime becomes kinetic, the value of $C_s(x)$ increases by law (44). In this case $C \Rightarrow C_s$.

Thus, in the region located below the straight line AC, the surface concentration C_s always increases and generally is a step-function. Exceptions are the points in the immediate vicinity of AC ($\beta \simeq 1$), where the intermediate ($1/\varepsilon\beta N$) and asymptotic ($1/\varepsilon N$) values virtually coincide. In the latter case, C_s increases monotonically. Its maximum value is equal to $1/\varepsilon N < 1$.

In the region $\beta \gg 1$, the two-phase chemisorption problem (Eqs. (6)-(10)) is simplified if the parameter $\varepsilon\beta N \gg 1$. It can be assumed in this case that $\beta^2 \Rightarrow \infty$ (Fig. 1). This means that $hPe_{liq} \Rightarrow 0$, i.e., at any values of x and P_g chemisorption proceeds in the kinetic regime ($C = C_s$). From the equation of material balance we obtain

$$C = C_s = I/\varepsilon N .$$
(45)

Substituting relation (45) into Eqs. (6)-(10) for the concentration in the gaseous phase, we obtain the following problem:

$$\frac{\partial C_g}{\partial x''} = \frac{\partial^2 C_g}{\partial y_g^2} ,$$
(46)

$$\left(\frac{\partial C_g}{\partial y_g}\right)_s = - P_g \sqrt{1 - I/\varepsilon N} \ \frac{\tanh (a \sqrt{1 - I/\varepsilon N})}{\tanh (a)} C_{gs} ,$$
(47)

$$\left(\frac{\partial C_g}{\partial y_g}\right) = 0 \quad \text{at} \quad y_g = 0 , \quad C_g = 1 \quad \text{at} \quad x'' = 0 .$$

The solution of problem (46), (47) does not depend on Y_N. In this case, we will denote the dimensionless diffusion flux by $I_X(P_g X_N, a, x'')$. We can show that for small $P_g < 1$ the function $I_X \Rightarrow I_0(X_N, a, Z)$, where $Z = P_g x'$. Approximation (14) is satisfied for the concentration in the gas. In the other limiting case $P_g \gg 1$, the equality $I_X = I_0(\infty, a, Z)/P_g$ is satisfied over the segment $x'' \ll 1$. At distances from the entry of the gas into the apparatus $x_g \geq 1/P_g^2$, the last formula goes over continuously into Eq. (43) $(I_X \Rightarrow I_\infty(x_g''))$. Since the value of $\varepsilon\beta N$ is constant on the horizontal straight lines $Y_N = $ const, we may assume that $I \simeq I_X$ in the region of the hydrodynamic plane located below the straight line CD $(Y_N = -1)$ (see Fig. 1).

Now, we shall carry out an analysis of the theoretical solutions obtained above for different regions of the hydrodynamic plane X_N-Y_N. First of all, we shall consider the concentration of CO_2 at the phase interface $C_{gs}(x)$. A characteristic feature of the solution for the problem of chemisorption in the fourth quadrant is the monotonic dependence of C_{gs} on the length. At any point X_N, Y_N the function C_{gs} decreases from unity to zero over a certain segment l_∞'', whose order of magnitude depends on P_g: $l'' \sim 1/P_g$ if $P_g < 1$, and $l'' \sim 1/P_g^2$ if $P_g > 1$. Proceeding from the form of transfer equation (6), it can be concluded that the dimensionless flux $I(x)$ (the basic calculating characteristic of a mass-transfer device) is a monotonically increasing function. The values of this function at small, $x'' \leq l'$, and large, $x'' \geq l''$, values of x'' can be obtained analytically, i.e., from formulas (13) and (43) (these are the regimes of a fast chemical reaction with resistance to transfer in the liquid phase and of an instantaneous chemical reaction, respectively).

As for $C_s(x)$, the shape of this curve depends on the relationship between the characteristic dimensions $h\text{Pe}_{\text{liq}}$ and $R\text{Pe}_g$. When $\beta > 1$ (the region below AC), the function $C_s(x)$ is monotonically increasing; it changes from zero to $1/\varepsilon N < 1$. When $\beta < 1$ (the region above AC), the function $C_s(x)$ is more complex — it is bell-shaped; however, its maximum value does not exceed $1/\varepsilon\beta N < 1$. On the basis of the analytical results obtained above, we may conclude that generally the maximum value that can be attained by C_s in the fourth quadrant is equal to

$$C_s^{\max} = \max \left(\frac{1}{\varepsilon \beta N} , \frac{1}{\varepsilon N}\right) \leq 1 .$$
(48)

The latter means that inside of the fourth quadrant one cannot realize the regime of instantaneous chemical reaction when $C_s(x) \simeq 1$ (i.e., the concentration of $[\text{RNH}_2]$ on the surface is equal to zero; see Eq. (2)), whereas the factor of chemical reaction acceleration is $\Phi \simeq N$ (i.e., at the maximum). This is the feature that distinguishes the solution in the considered region of the hydrodynamic plane from the corresponding solution for the second quadrant [1], where the above-indicated regime was always present, beginning from a certain length x. However, at the inner points of the second quadrant it was impossible to realize the regime of maximum absorption, because C_{gs} satisfied the inequality $C_{gs} > 0$ at any value of x (i.e., $[\text{CO}_2]$ at the interface from the side of the gas was always above zero).

From relation (48), it follows that at large values of the hydrodynamic parameters ($\varepsilon N \gg 1$, $\varepsilon \beta N \gg 1$) the concentration of carbamine at the phase interface satisfies the inequality $C_s(x) \ll 1$. Consequently, the solution of general problem (6)-(10) is simplified considerably, since the latter is reduced to a single-phase problem:

$$U_g \frac{\partial C_g}{\partial x''} = \frac{\partial^2 C_g}{\partial y_g^2},$$

$$\left(\frac{\partial C_g}{\partial y_g}\right) = -P_g C_g \quad \text{at} \quad y_g = 1,$$

(49)

$$\left(\frac{\partial C_g}{\partial y_g}\right) = 0 \quad \text{at} \quad y_g = 0, \quad C_g = 1 \quad \text{at} \quad x'' = 0.$$

In this case, the interaction between CO_2 and amine represents a chemical reaction of the pseudofirst order, since the amine is virtually not consumed ($[RNH_2] \simeq N'$ in any section of the channel). When $x' \gg 1/a^2$, problem (49) coincides with the asymptotic approximation for two-phase chemisorption with a first-order irreversible chemical reaction [5]; its solution depends only on the parameter P_g and it can be easily tabulated. In this case, we denote the dimensionless diffusion flux by $I_1(x)$. This function for small and large values of P_g was obtained analytically in [5, 6], respectively:

$$I_1 = \begin{cases} 1 - \exp(-Z) & \text{at} \quad P_g \ll 1, \\ \dfrac{2}{\sqrt{\pi}} \sqrt{Z} - (1 - \exp(-Z))\,\mathrm{erfc}\,(Z^{1/2}) & \text{at} \quad P_g \gg 1. \end{cases}$$

(50)

Confining ourselves to the 10% accuracy, we can say that approximation (49) takes place in the region of the hydrodynamic plane $X_N - Y_N$ located in the lower-right corner in Fig. 1 ($X_N \geq 1$, $Y_N \leq -1$). We can easily see that limiting problems (38)-(41) with $\varepsilon \beta N \gg 1$ and problems (46), (47) with $\varepsilon N \geq 1$ are reduced to Eq. (49).

CONCLUSIONS

1. The problem of two-phase absorption of a component (for example, CO_2) by a liquid phase in the case of the second-order chemical reaction depends on many variables, such as physicochemical (D_g, P_{liq}, ...), geometric (l, R, ...), and kinetic (k). In order to decrease the number of independent variables, the problem is investigated in dimensionless form. Two hydrodynamic (X_N, Y_N) and two chemisorption (a, P_g) parameters are introduced as dimensionless quantities.

2. The main objective of the work was to obtain a clear picture of the distribution of concentrations in both phases at arbitrary values of the determining variables. This made it possible to find conditions for the applicability of the following absorption regimes, well known from the literature: pseudo-first-order chemical reaction (the concentration of an absorber is not consumed); the resistance to chemisorption is concentrated in a gas ($C_{gs}' \ll C_0$) or in a liquid ($C_{liq.s}' \simeq kC_0$); kinetic regime where the concentration of an absorber is constant across the liquid film; regime of instantaneous chemical reaction in which the concentration of an absorber at the phase interface is equal to zero, while the factor of the chemical-reaction acceleration (Φ) is at a maximum, $\Phi \simeq N \gg 1$.

3. The conditions for the realization of the above regimes (in dimensionless variables) are obviously independent of the particular form of the velocity distribution of the phases (motion regimes); it is only necessary in these dimensionless variables to substitute the corresponding values of the transfer coefficients, D_g and D_{liq}.

4. In order to simplify the mathematical calculations, the piston motion of phases is studied, which is typical for turbulent regimes of motion.

5. The problem is investigated for an important practical case in which the chemical capacity of the liquid phase is large, $N' \gg kC_0$.

6. As a result of the theoretical analysis carried out, in the fourth quadrant of the hydrodynamic plane $X_N - Y_N$ (Fig. 1) a characteristic length of a mass-transfer device l_{chem} is found, whose magnitude depends mainly on the chemisorption parameter P_g. It is shown that in a two-phase system with $l \ll l_{chem}$, a regime of fast chemical reaction is realized on the condition that the resistance to mass exchange is exhibited in the liquid phase $(C'_g \simeq C_0)$. In the other limiting case $(l \gg l_{chem})$, the diffusion resistance is concentrated in the gas $(C_{gs} \simeq 0)$.

7. Generally, in the fourth quadrant the surface concentration C_{gs} decreases monotonically from unity to zero at the length $l \sim l_{chem}$.

8. As for the surface concentration of the reaction product C_s, in the general case it is a complex function of the length; inside the fourth quadrant it satisfies the inequality $C_s < 1$. This means that in the region of the hydrodynamic plane considered, the regime of instantaneous chemical reaction $([RNH_2]_s = 0)$ is impossible except for the points that belong to the boundary of this quadrant $(X_N = 0$ or $Y_N = 0)$.

9. The conditions for realization of the pseudo-first-order reaction regime are found for which $[RNH_2]_s \simeq N'$. This regime occurs at rather large values of the chemisorption capacities of the phases (virtually, $X_N \geq 1$, $Y_N \geq 1$); see the lower-right corner in Fig. 1.

10. Using the theoretical solutions obtained, it is possible to develop a procedure for calculating dimensionless fluxes $I(Z)$ at arbitrary values of the determining quantities $(D_g, D_{liq}, l, R, ...)$ in terms of the dimensionless parameters X_N, Y_N, P, a. In this case, it is sufficient to perform numerical calculations in the limited region of the fourth quadrant: $0 \leq X_N \leq 1, -1 \leq Y_N \leq 0$. Beyond this region the problem is simplified (the number of dimensionless complexes decreases), and the dimensionless flux $I(Z)$ coincides with one of the limiting solutions I_X, I_Y, or I_1. Such a procedure allows one to calculate mass-exchange devices without resorting to a computer.

NOTATION

C'_g, C'_{liq}, C', concentrations of CO_2 in a gas and in water and of carbamine in an aqueous solution, mole/liter; C_g, C_{liq}, C, same in dimensionless form; D, diffusion coefficient of particles, m^2/sec; k, Henry constant for CO_2; k, constant of reaction rate between CO_2 and amine, liter/mole·sec; l, channel length, m; $l_{liq} = l/hPe_{liq}$, $l_g = l/RPe_g$, dimensionless lengths; N', inlet concentration of amine, mole/liter; R, h, channel half-width and liquid film thickness, m; x, y, Cartesian coordinate system, m; x', y_{liq}, dimensionless Cartesian coordinates in liquid; x'', y_g, dimensionless Cartesian coordinates in gas; U', phase velocity, m/sec; $U = U'/\overline{U'}$, dimensionless phase velocity; $Pe_g = R\overline{U'_g}/D_g$, $Pe_{liq} = h\overline{U'_{liq}}/D_{liq}$, Peclet numbers for gas and liquid; $a, N, \varepsilon, \beta, X_N = \log \varepsilon N, Y_N = -\log \varepsilon N\beta$, dimensionless parameters; $\overline{C_g}$, $\overline{C_{liq}}$, mean-mass dimensionless concentrations of CO_2 in gas and liquid; $I, \Sigma = \overline{C}$, dimensionless diffusion fluxes in gas and liquid; cosh (x), tanh (x), hyperbolic cosine and tangent; erf (x), erfc $= 1 - $ erf (x), error functions. Subscripts: g, gas; liq, liquid; s, phase interface; 0, inlet section of channel; n, new coordinates.

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