Journal of Engineering Physics and Thermophysics, Vol. 65, No. 1, 1993

TWO-PHASE CHEMISORPTION OF CARBON DIOXIDE BY AMINE SOLUTIONS IN PLANE SPRAYED PACKINGS WITH GAS AND LIQUID UNIFLOW

V. N. Babak, T. B. Babak, and L. P. Kholpanov

UDC 66.071.7

We investigated theoretically the two-phase problem of chemisorption with a second-order chemical reaction in a liquid phase, taking absorption by amines as an example. We considered the behavior of carbon dioxide and carbamine concentrations at the interface and found the conditions under which the chemisorption resistance is concentrated entirely in the liquid.

One of the basic stages in producing synthetic ammonia is separating the original gases from CO_2 [1-3]. This stage, in turn, involves the chemisorption of CO_2 by organic solvents, which is carried out in adsorption columns. The most commonly used chemisorbents are aqueous solutions of alkalamines (monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), NH_3) [3, 4]. Current approaches to predicting similar chemisorption processes, which may be reduced at carbonization degrees of $\alpha \leq 0.5$ to studying absorption, complicated by a second-order chemical reaction proceeding in a liquid phase between amine and CO_2 molecules, are developed in [5-7]. All these studies, however, are performed under the following assumptions: approximation of the boundary layer in the liquid, constancy of the CO_2 concentration at the interface, etc. The above assumptions may be justifiable in predicting packed columns because of the small sizes of the standard packings generally employed (Raschig's and Pall's rings of ≃25-50 mm); however, in the general case and, specifically, for more efficient plane-parallel packings tolerating large phase loadings with small pressure drops [8-10], the validity of such assumptions must be checked. A fixed value of the interface sets up favorable conditions for theoretically analyzing such chemisorption columns.

In the present study, mass transfer in a single vertical sprayed channel is investigated, which is a part (an elementary cell) of a plane-parallel packing. Differential equations of transfer in the gas and liquid phases under the condition of flow and concentration conjugation on the surface of the liquid film are considered.

It is well known that, for a carbonization degree of $\alpha \leq 0.5$, the CO_2 and liquid molecules react with alkalamine molecules by the scheme (for example, for monoethanolamine) [5, 6]:

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

where $R = CH_2\text{-}CH_2\text{-}OH^-$ is the neutral group. The CO_2 gas is present in the solution in physically dissolved states of $[CO_2]$ and chemically bound states, in the form of $[RNCOO^-]$. The following linear relationship exists between $[RNH_2]$ and $[RNHCOO^-]$:

$$[RNH_2] = N' - 2[RNHCOO^-].$$

This allows one to examine, in the liquid phase, only two transfer equations, namely, for CO_2 (C'_l) and $RNHCOO^-$ (C') particles. The two-phase problem is formulated as follows:

$$U_g \frac{\partial C'_g}{\partial x} = D_g \frac{\partial^2 C'_g}{\partial y^2}, \quad U_l \frac{\partial C'_l}{\partial x} = D_l \frac{\partial^2 C'_l}{\partial y^2} - kC'_l (N' - 2C'),$$

$$U_l \frac{\partial C'}{\partial x} = D_l \frac{\partial^2 C'}{\partial y^2} + kC'_l (N' - 2C').$$

Institute of New Chemical Problems, Russian Academy of Sciences, Chernogolovka. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 65, No. 1, pp. 63-75, July, 1993. Original article submitted March, 18, 1992.

Taking into account that C' is a nonvolatile component, additional conditions for these equations are written as

$$D_l\left(\frac{\partial C'_l}{\partial y}\right)_s = D_g\left(\frac{\partial C'_g}{\partial y}\right)_s,\quad \left(\frac{\partial C'}{\partial y}\right)_s = 0,\quad C'_{ls} = kC'_{gs}\quad \text{for}\quad y = R - h,$$

$$\left(\frac{\partial C'}{\partial y}\right) = \left(\frac{\partial C'_l}{\partial y}\right) = 0 \quad \text{for}\quad y = R,\quad \left(\frac{\partial C'_g}{\partial y}\right) = 0 \quad \text{for:}\quad y = 0,$$

$$C'_g = C_0,\quad C'_l = C' = 0 \quad \text{for}\quad x = 0.$$

The system of Cartesian coordinates (x-y) is chosen such that the constraints $y = 0$, $y = R-h$, and $y = R$ are satisfied at the channel center, on the film surface, and at one of the walls, respectively, and the equality $x = 0$, at the gas inlet to the packing.

Such a statement of the problem is, obviously, idealized, since it disregards many factors involved in practice, viz., development of the gas profile in the gas, wave formation, nonisothermicity, high concentration of the solution, etc. For example, in real industrial packed apparatuses, the temperature drops between the upper and the lower sections may reach a few tens of degrees because reaction (1) is exothermal [8]. It is perfectly clear that a complete consideration of all these factors will markedly complicate solving the problem of two-phase chemisorption. In the first approximation, the temperature will be assumed invariable, and the gas and liquid motion, pistonwise. These simplifications will not affect the qualitative pattern of the two-phase chemisorption, clarification of which is one of the tasks of this work.

Let us introduce the dimensionless coordinates and function

$$y = (R - h)\, y_g,\quad y = hy_l,\quad x = (h\,\mathrm{Pe}_l)\, x' = (R\,\mathrm{Pe}_g)\, x'',$$
$$C'_g = C_0C_g(x'', y_g),\quad C'_l = kC_0C_l\,(x', y_l),\quad C' = (N'/2)\, C\,(x', y_l).$$

The two-dimensional problem in dimensionless form is formulated as

$$\frac{\partial C_g}{\partial x''} = \frac{\partial^2 C_g}{\partial y_g^2},\quad \frac{\partial C_l}{\partial x'} = \frac{\partial^2 C_l}{\partial y_l^2} - a^2C_l\,(1 - C),$$
$$\frac{\partial C}{\partial x'} = \frac{\partial^2 C}{\partial y_l^2} + a^2\left(\frac{2kC_0}{N'}\right)C_l\,(1 - C); \tag{2}$$

$$\left(\frac{\partial C_l}{\partial y_l}\right)_s = -\frac{1}{\varepsilon\beta^2}\left(\frac{\partial C_g}{\partial y_g}\right)_s,\quad C_{gs} = C_{ls}, \tag{3}$$
$$\left(\frac{\partial C}{\partial y_l}\right)_s = 0 \quad \text{for}\quad y_l = 1,$$

$$\left(\frac{\partial C_g}{\partial y_g}\right) = 0 \quad \text{for}\quad y_g = 0;\quad \left(\frac{\partial C_l}{\partial y_l}\right) = \left(\frac{\partial C}{\partial y_l}\right) = 0 \quad \text{for}\quad y_l = 0; \tag{4}$$

$$C_g = 1,\quad C = C_l = 0 \quad \text{for}\quad x' = 0. \tag{5}$$

Henceforth we will consider the most important case in practice, when the amine concentration N' greatly exceeds the maximum CO_2 concentration in the liquid (kC_0):

$$N' \gg kC_0 = \frac{kP_0}{RT} \quad \text{or} \quad N = \frac{N'}{kC_0} \gg 1. \tag{6}$$

Here, P_0 is the partial pressure of CO_2 at the inlet. It was shown previously [9] that, with conditions (6) fulfilled, a noticeable change in the RNH_2 concentration is observed only at fairly large packings that satisfy the constraint

$$l' \gg 1/a^2. \tag{7}$$

At moderate lengths ($a^2 l \leq 10$) the chemical interaction between CO_2 and RNH_2 may be regarded as a reaction of pseudofirst order. Given this, it is possible to set $C = 0$ in Eqs. (2)-(4) and, therefore, the two-phase problem reduces to a previously studied case [10].

It follows from a theoretical analysis [10, 11] that, with fairly long packings ($a^2 l' \gg 1$), regardless of the values of the parameters a^2 and N ($N \gg 1$), it is possible to neglect the term $U_l(\partial C_l/\partial x')$ in the equation for CO_2 transfer (2) in the liquid and the source term in the relevant equation for carbamine. Moreover, in the region of the main variation in the CO_2 concentration, the concentration C may be regarded as constant, equal to its value at the interface $C_s(x)$. Consequently, the following analytic relation [10] holds for the distribution of CO_2 over the film:

$$C_l\,(x',\, y_l) = C_{ls}\,\frac{\mathrm{ch}\,[a y_l \sqrt{1-C_s(x')}]}{\mathrm{ch}\,[a \sqrt{1-C_s(x')}]}\,. \tag{8}$$

Physically, this means that a fast-reaction mode takes place in the liquid, in which all carbon dioxide coming from the gas is expended on the formation of carbamine [5]. With consideration of the foregoing, the dimensional formulation of problem (2)-(4) simplifies:

$$\frac{\partial C_g}{\partial x''} = \frac{\partial^2 C_g}{\partial y_g^2}, \quad \frac{\partial C}{\partial x'} = \frac{\partial^2 C}{\partial y_l^2}; \tag{9}$$

$$\left(\frac{\partial C}{\partial y_l}\right)_s = -\frac{a}{N}\sqrt{1-C_s(x')}\,\mathrm{th}\,(a\sqrt{1-C_s(x')}),$$
$$\left(\frac{\partial C_g}{\partial y_g}\right)_s = -(\varepsilon N)\,\beta^2\left(\frac{\partial C}{\partial y_l}\right)_s, \quad C_{gs} = C_{ls}\;(x'). \tag{10}$$

Conditions (4)-(5) remain unchanged. The subscript indicates that the corresponding quantity is taken at the interface.

The dimensionless integral equation of material balance for chemisorption in the new variables actually takes the same form as for two-phase absorption, with allowance for the obvious substitution $\varepsilon \Rightarrow \varepsilon N$, $C_l \Rightarrow C(x', y_l)$

$$I \equiv (1 - \bar{C}_g) = (\varepsilon N)\,\Sigma. \tag{11}$$

In the general case, the solution for problem (9)-(10) is four-parametric, depending on the complexes ε, β^2, a^2, and N. Subsequently, however, with allowance made for the explicit analogy between absorption of CO_2 by water and amines, the following quantities will be used as independent dimensionless parameters

$$(\varepsilon N), \quad (\varepsilon\beta N), \quad a^2, \quad N.$$

For a clear representation of the solution we introduce the rectangular Cartesian system of the "hydrodynamic" variables X_N-Y_N, where

$$X_N = \lg(\varepsilon N), \quad Y_N = -\lg(\varepsilon\beta N). \tag{12}$$

The coordinates $X = \log \varepsilon$, $Y = -\log(\varepsilon\beta)$, introduced when considering two-phase absorption [12], and X_N, Y_N, are related linearly by

$$X_N = X + \lg N, \quad Y_N = Y - \lg N.$$

Graphically, the latter equations mean that the planes (X-Y) and (X_N-Y_N) are displaced relative to each other by log N along the axes X_N and Y_N, as Fig. 1 shows.

By analogy with two-phase absorption, the solution will be studied in various parts of the "hydrodynamic" plane (X_N-Y_N). With fixed X_N and Y_N, the parameter a^2 will "traverse" all admissible values from zero to infinity.

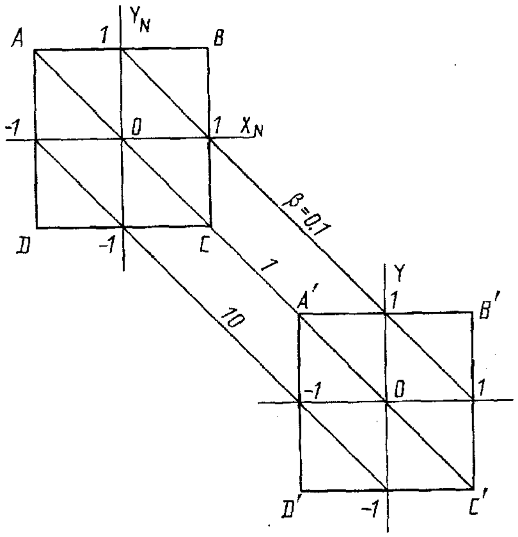

Fig. 1. Hydrodynamic plane for chemisorption X_N-Y_N.

Forestalling the results obtained below, we note that it is sufficient to consider the solution in the limited region $-1 \leq X_N \leq 1$, $-1 \leq Y_N \leq 1$ of the plane (in the so-called "chemisorptional" square).

It is readily seen (Fig. 1) that, for N >> 1, all of this square is located at the left-hand corner of the "hydrodynamic" plane X-Y, that is, in the region where the following inequalities hold:

$$\varepsilon \ll 1, \quad \varepsilon\beta \ll 1.$$

The latter implies that, for moderate (εN) and ($\varepsilon\beta N$), the diffusional resistance in the case of physical absorption [12] is actually entirely concentrated in the liquid phase, whereas the dimensionless surface concentration of CO_2 at the interface is

$$C_{ls}^{\mathrm{abs}}(x') \simeq 1 \tag{13}$$

at any x'.

Most of the up-to-date methods of predicting mass transfer that is complicated by chemical reactions occurring in the liquid phase are based on the basic mass transfer equation [13]. Here, in predicting the mass transfer coefficient k_g from the additivity equation, instead of the mass transfer β_l the product $\beta_l \phi$ is used, where ϕ is the local acceleration factor of the chemical reaction. In the general case, ϕ is a function of the packing length. The latter hampers its determination and, especially, representation, not to mention that the design of apparatuses is made much more difficult.

With the theoretical approach developed in this study, there is no need to find ϕ because it can be obtained just by solving the general problem. The apparatus dimensions are calculated using the efficiency functions, which are the dimensionless flows I(x) or $\sum(x)$. By analogy with absorption, in the left half of the plane X_N-Y_N ($X_N \leq 0$) it is convenient to use, the dependence $\sum(x)$ as the efficiency function, and in the right half ($X_N > 0$)—I(x).

Alongside the local coefficient ϕ, the integral acceleration coefficient Φ is sometimes used, which shows how many times larger the total flux $I(\sum)$ is than the corresponding quantity in absorption I^{abs}. Taking into account that the transfer equations (9) coincide with the corresponding absorption equations, with allowance for the substitution $C_l \Rightarrow C$ in the liquid phase, by the order of magnitude for the points in the "chemisorption" square it is possible to write

$$\Phi \simeq NC_s(x'). \tag{14}$$

This relation results from the conditions N >> 1 and (13). Thus, the dimensionless concentration $C_s(x')$ has acquired yet another physical meaning. The surface concentrations $C_s(x')$ and $C_{ls}(x')$ are considered in the present study, and, based on this, the important question of limiting the transfer processes from the side of gas ($C_{ls} \simeq 0$) or liquid ($C_{ls} \simeq 1$) phases is clarified.

The relations for C_s and C_{ls} behave qualitatively differently depending on which of the four quadrants, the first ($X_N \geq 0$, $Y_N \geq 0$, the second ($X_N \leq 0$, $Y_N \geq 0$), the third ($X_N \leq 0$, $Y_N \leq 0$), or the fourth ($X_N \geq 0$, $Y_N \leq 0$), the point (X_N, Y_N) belongs to. Therefore, solutions for the two-phase problem (2)-(4) should be treated separately in each of the four quadrants.

A distinctive feature of two-phase problems is the presence of characteristic dimensions hPe_l and RPe_g and corresponding dimensionless lengths l' and l''. The transfer equations are parabolic partial differential ones. In conformity with the general theory, regardless of the specific type of conjugation conditions, at small l' (l'') in the liquid (gas) phase a diffusional boundary layer δ' of the order of $\sqrt{l'}$($\delta'' \simeq \sqrt{l''}$) exists, intergrowing throughout the whole thickness of the film (the channel) at distances from the outlet of the order of $l' \simeq 1$ ($l'' \simeq 1$), so that at $l' \gg 1$ ($l'' \gg 1$) the carbamine (CO_2) concentration in the film (the channel) is C_s (C_{ls}). The relationship between hPe_l and RPe_g (or their ratio β^2) determines in which of the phases, gas ($\beta^2 \leq 1$) or liquid ($\beta^2 \geq 1$), the boundary layer intergrows faster. The latter follows from the equality

$$\delta' \simeq \beta\delta''.$$

It is easy to verify that, on straight lines parallel to the straight line AC (the bisectrix of the second quadrant), β^2 assunes a constant value (Fig. 1). Here, $\beta^2 \geq 1$ below AC and $\beta^2 \leq 1$ above AC.

The solution for the problem is investigated in the current study only for the points of quadrant II of the plane X_N-Y_N, where $\varepsilon N \leq 1$ and $\varepsilon\beta N = EN \leq 1$. In this region, the parameter β^2 can be both smaller and larger than unity (Fig. 1). Taking into account that the behavior of C_{ls} depends substantially on β^2, the regions $\beta^2 \leq 1$ and $\beta^2 \geq 1$ are treated separately.

Before proceeding to the general consideration of the problem we obtain two limiting solutions corresponding to "low" and "high" rates of chemical interaction (formally, when $k \Rightarrow 0$ and $k \Rightarrow \infty$). For $k \Rightarrow 0$, the boundary layers intergrow in both phases, and hence,

$$C_s \simeq \Sigma, \quad C_{ls} \simeq 1 - (\varepsilon N)\Sigma. \tag{15}$$

In this case, by integrating the equations of transfer in the liquid phase with respect to y_l from zero to unity, we derive the ordinary differential equation determining Σ

$$\frac{d\Sigma}{dz} = \sqrt{1-\Sigma}\left[\frac{\operatorname{th}(a\sqrt{1-\Sigma})}{\operatorname{th} a}\right][1-(\varepsilon N)\Sigma]; \quad \Sigma(0) = 0, \tag{16}$$

where $P_2 = a \tanh a/N$ is the chemisorption parameter and $z = P_2x'$ is the dimensionless coordinate. Henceforth, the mean concentration of carbamine, determined from Eq. (16), is denoted by $\Sigma_0(a^2, \varepsilon N, z)$.

The dependence $\Sigma_0(z)$ in the selected variables is two-parametric. It will be proved subsequently that the solution for two-phase chemisorption throughout quadrant II coincides with Eq. (16) at fairly small values of the chemisorption parameter P_2 (actually, when $P_2 \ll 1$). In view of $N \gg 1$, the inequality $P_2 \equiv a \tanh a/N \ll 1$ is fulfilled when $a \ll N$; therefore, it is sufficient to investigate the chemisorption problem in the general formulation (4)-(5), (9)-(10) only for $a^2 \gg 1$ because the solution coincides with $\Sigma_0(a^2, X_N, z)$ at moderate values of a^2 ($a \ll N$). Substituting $\tanh(a\sqrt{1-C_s}) \Rightarrow 1$ in the boundary conditions (9)-(10), we obtain the dimensionless formulation for $a^2 \gg 1$

$$\frac{\partial C_g}{\partial x''} = \frac{\partial^2 C_g}{\partial y_g^2}, \quad \frac{\partial C}{\partial x'} = \frac{\partial^2 C}{\partial y_l^2}; \tag{17}$$

$$\left(\frac{\partial C}{\partial y}\right)_s = P_2\sqrt{1-C_s(x')}\,C_{ls}\,(x'); \tag{18}$$

$$\left(\frac{\partial C_g}{\partial y_g}\right)_s = -(\varepsilon N)\,\beta^2\left(\frac{\partial C}{\partial y_l}\right)_s, \quad C_{gs} = C_{ls}\,(x'). \tag{19}$$

Conditions (4)-(5) remain unchanged. Consequently, it is possible to decrease the number of parameters of the general chemisorption problem in the approximation of $N \gg 1$ to three:

$$P_2 = a/N, \quad X_N \text{ и } Y_N,$$

here $a^2 >> 1$.

With moderate $a << N$, as was noted above, the solution reduces to the two-parametric problem (15)-(16). Equation (16) admits separation of the variables and can be solved in implicit form with respect to $\sum_0$ in quadratures:

$$\int_0^{\Sigma_0} \frac{\mathrm{th}\,(a)\, d\Sigma_0}{\sqrt{1-\Sigma_0}\,[\mathrm{th}\,(a\sqrt{1-\Sigma_0})][1-(\varepsilon N)\,\Sigma_0]} = z.$$

The value of this integral for $a >> 1$ is easily calculated [14]:

$$(1-\Sigma_0)^{1/2} = \frac{1-\left(\frac{1-\varepsilon N}{\varepsilon N}\right)^{1/2} \mathrm{tg}\,[(\varepsilon N)^{1/2}(1-\varepsilon N)^{1/2} z/2]}{1+\left(\frac{1-\varepsilon N}{\varepsilon N}\right)^{1/2} \mathrm{tg}\,[(\varepsilon N)^{1/2}(1-\varepsilon N)^{1/2} z/2]}. \tag{20}$$

Thus, the solution for the problem (4)-(5), (17)-(19) and, therefore, the efficiency function $\sum_0$ at fairly small values of P_2 depend solely on the parameter X_N. We will show that the number of governing parameters of the general chemisorption problem in the other limiting case ($P_2 >> 1$) can also be reduced to unity. Let us introduce new variables along the axes y_g, y_l, and x' by the formulas

$$(1-y_g) = \frac{1}{P_2\beta}\, y_{gn}, \quad 1-y_l = \frac{1}{P_2}\, y_n, \quad z = P_2^2 x' = (P_2\beta)^2 x'',$$

whereupon the dimensionless formulation (17)-(18), (4)-(5) is transformed as follows:

$$\frac{\partial C_g}{\partial z} = \frac{\partial^2 C_g}{\partial y_{gn}^2}, \quad \frac{\partial C}{\partial z} = \frac{\partial^2 C}{\partial y_n^2}; \tag{21}$$

$$\left(\frac{\partial C}{\partial y_n}\right)_s = \sqrt{1-C_s(z)}\, C_{ls}; \quad \left(\frac{\partial C_g}{\partial y_{gn}}\right)_s = (EN)\sqrt{1-C_s(z)}\, C_{ls}; \tag{22}$$

$$\left(\frac{\partial C}{\partial y_n}\right)_\infty = \left(\frac{\partial C_g}{\partial y_{gn}}\right)_\infty = 0, \quad y_n \Rightarrow \infty, \quad y_{gn} \Rightarrow \infty, \quad C=0, \; C_g = 1 \quad \text{for} \quad z=0. \tag{23}$$

This formulation is formally derived from Eqs. (17)-(18), (4)-(5) for $P_2 \Rightarrow \infty$. In this case, there are diffusion boundary layers in the gas and the liquid. The material balance equation in the new variables takes the form

$$I_{gn} \equiv \int_0^\infty (1-C_g)\, dy_{gn} = (\varepsilon\beta N)\int_0^\infty C\, dy_n \equiv (EN)\,\Sigma_n \tag{24}$$

where the mean dimensionless concentration $\sum_n$ is defined by

$$\Sigma_n = P_2 \Sigma(z). \tag{25}$$

Clearly, the efficiency function $\sum_n(z)$ depends only on the parameter Y_N at rather large P_2. We now turn to the general consideration of the problem (4)-(5), (17)-(19) in various regions of quadrant II of the "hydrodynamic" plane (Fig. 1).

Relationships of the Solution for $\beta^2 \leq 1$. We derive a set of analytic equations on the straight line AC (Fig. 1). In this case, $\beta^2 = 1$ and the boundary layers in the gas and the liquid intergrow to the width of the corresponding phase when $x' \simeq x'' \simeq 1$. Hence, when the inequality $P_2 << 1$ is fulfilled, the solution is determined by the analytic equations (15) and (20). In the other limiting case ($P_2 >> 1$), the boundary layers ($\delta_g'' \simeq \delta_l'$) can be assumed to exist in both phases. Subsequently, the initial section will mean column packing dimensions for which the constraints $C_{ls} \simeq 1$ and $C_s << 1$ are fulfilled. Then, the solution of Eq. (17) in the boundary layer approximation obviously exists in the form

$$1 - C_g = (x'')^{1/2} f_{1/2}(\eta_g)[(-\varepsilon N\beta^2 P_2)/f'_{1/2}(0)] + \ldots, \tag{26}$$

$$C \simeq x^{1/2} f_{1/2}(\eta_l)(-P_2/f'_{1/2}(0)) + \ldots, \tag{27}$$

where the similarity variables η_g and η_l are introduced

$$\eta_g = (1 - y_g)/\sqrt{x''}, \quad \eta_l = (1 - y_l)/\sqrt{x'},$$

and the function $f_{1/2}(\eta)$ satisfies the ordinary differential equation resulting from substitution of expansions (26) and (27) into Eq. (17):

$$\frac{d^2 f_\gamma}{d\eta^2} + \frac{\eta}{2}\frac{d}{dz} f_\gamma - \gamma f_\gamma = 0; \quad f_\gamma(0) = 1; \quad f_\gamma(\infty) = 0. \tag{28}$$

The solution for this equation for $\gamma = 1/2$ is of the form [15]

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

Therefore, concentrations on the initial section vary as follows

$$C_s \simeq -\frac{P_2}{f'_{1/2}(0)}\sqrt{x'} = \frac{2\sqrt{z}}{\sqrt{\pi}}, \quad C_{ls} \simeq 1 - (EN)\frac{2\sqrt{z}}{\sqrt{\pi}}, \tag{29}$$

where the dimensionless coordinate with respect to x is $z \equiv P_2 x'$.

From the inequality $C_s \le 1$ (18) it is inferred that, for $z \ge 1$, the concentration is $C_s \Rightarrow 1$ and hence [5, 6]

$$\Sigma \Rightarrow 1 - \sum_{n=0}^{\infty} \frac{2}{\pi^2 (n + 1/2)} \exp[-\pi^2 (n + 1/2)^2 x'], \quad x' \gg 1/P_2^2. \tag{30}$$

The constant concentration C_{ls} can be obtained by using analytic distributions in the liquid and the gas [5]:

$$C(x', y_l) = \operatorname{erfc}(\eta_l), \quad C_g = 1 - (1 - C_{ls})\operatorname{erfc}(\eta_g), \quad x' = x'' \ll 1. \tag{31}$$

Substituting these distributions into the conjugation conditions (18) yields

$$C_{ls} \Rightarrow 1 - EN. \tag{32}$$

It should be pointed out that, for $P_2 \gg 1$, the solution on the section $z \simeq 1$ (in the region of the main variations in C_s) depends on the parameter EN alone in full accordance with Eqs. (21)-(23) (compare Eqs. (29) and (32)). As an example, Fig. 2 gives a numerical calculation of the surface concentrations C_s and C_{ls} on the straight line $A\underset{\prime}{C}$ (see Fig. 1) for various values of X_N. All calculations for the problem (17)-(20), (4)-(5) were performed on the BESM-6 computer by a forward-marching method with the conditions of flow and concentration conjugation at the interface in much the same manner as was done for a two-phase problem of direct-flow physical absorption in [12].

For convenience of representing the numerical solution at arbitrary values of the governing parameters, subsequently a dimensionless length z is introduced everywhere:

$$z = \begin{cases} x' P_2 & (P_2 \leqslant 1), \\ x' P_2^2 & (P_2 > 1). \end{cases} \tag{33}$$

The basic advantage of the variable z is that, for $z \Rightarrow 0$ (the so-called initial section with $C_{ls} \simeq 1$ and $C_s \ll 1$), the efficiency functions $\sum$ (when $P_2 \le 1$) and $\sum_n$ (when $P_2 > 1$) are virtually linear:

$$\Sigma \Rightarrow P_2 x' = z \quad \text{or} \quad \Sigma_n \Rightarrow P_2^2 x' = z. \tag{34}$$

The equality (34) results from integrating, over the entire film thickness, the second transfer equation (2) with appropriate boundary conditions (3)-(4) for the concentration C(x, y). Another advantage of the coordinate z is that $C_s \Rightarrow 1$ (and, therefore, $\sum$ is determined by the analytic formula (30)) at any point of quadrant II when $z > 1$.

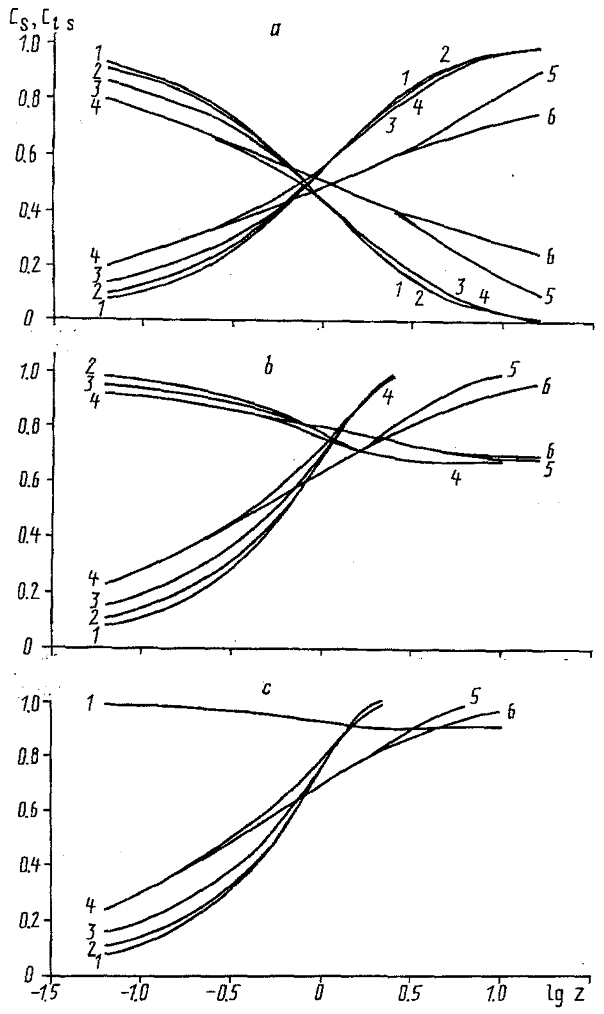

Fig. 2. The surface concentrations C_s and C_{ls} at $\beta = 1$ at the points: a) $X_N = Y_N = 0$; b) $X_N = -0.5$, $Y_N = 0.5$; c) $X_N = -1$, $Y_N = 1$; 1) $\log P_2 = -1.2$; 2) -0.8; 3) -0.4; 4) 0.5; 5) 0.4; 6) $\log P_2 \geq 0.8$.

In view of the above, C_s and C_{ls} were calculated on the section of the main variations in the concentration C_s, i.e., in the interval $-1 \leq \log z \leq 1$.

Analyzing the relations plotted in Fig. 2 makes it clear that the concentrations $C_s(z)$ and $C_{ls}(z)$ are monotonic functions: the first increases from zero to unity, and the second falls from unity to a minimum value $(1 - \varepsilon N)$. At fairly small values of the chemisorption factor P_2 (practically, when $\log P_2 \leq -1$), approximations (15) and (20) are valid, and the latter means that the solution is dependent solely on the parameter X_N.

It is easy to see that, at rather large P_2 (actually, when $\log P_2 \geq 1$), in conformitywith the general theory (see the formulation of the problem (21)-(23)) the solution in the interval $-1 \leq \log z \leq 1$ is also one-parametric, depending on the quantity $EN = \varepsilon N$ alone (because $\beta = 1$). In particular, with "small" z ($\log z \leq 0$) and $\log P_2 \geq 0$, approximations (29) are valid with a high degree of accuracy (curves 4-6 in Fig. 2).

Studying the Solution for $\beta^2 \Rightarrow 0$. In this case transverse variations in the gas concentration can be disregarded, since $RPe_g \Rightarrow 0$. With small values $P_2 \ll 1$ in the region of the main variations in C_2, the boundary layers intergrow in both phases and, therefore, the solution is determined by Eqs. (15) and (20). We now derive analytic relations for $P_0 \gg 1$. Because $\sqrt{z}/P_2 \ll 1$ on the initial section, as previously (see Eqs. (27) and (28)), approximation (29) holds true for the surface concentration C_s, From the material balance equation it is possible to obtain Eq. (15) for C_s, taking into account that $RPe_g \Rightarrow 0$, whereas, since the efficiency function is $\sum \ll 1$ because of the small thickness of the boundary layer δ' in the region of the main variations in C_s, the concentration C_{ls} is determined analytically with uniform accuracy with respect to x' (see Eq. (30)) by:

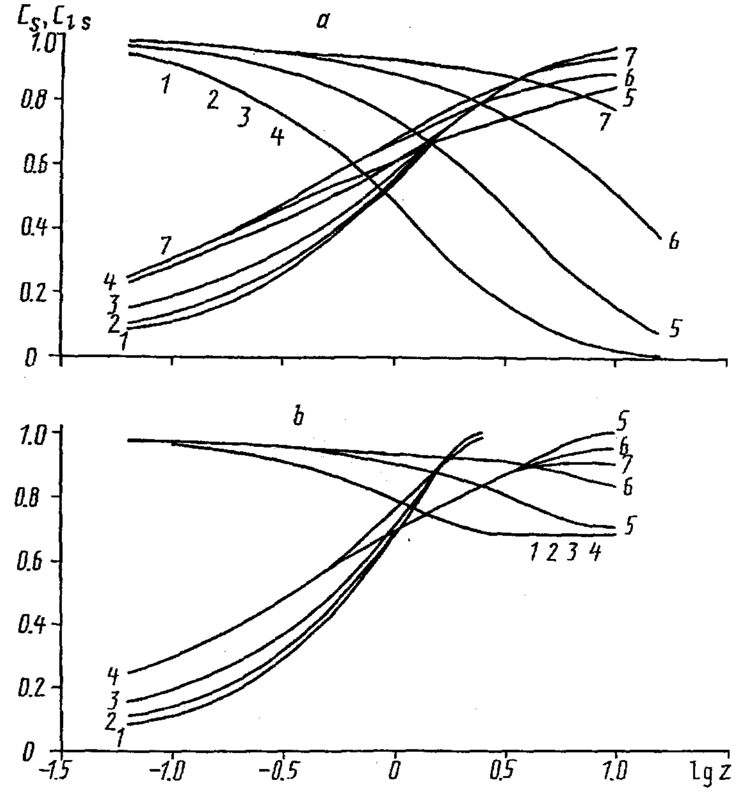

Fig. 3. The concentrations C_s and C_{1s} for 1 at the points: a) $Y_N = 1$, $X_N = 0$; b) $Y_N = 1$, $X_N = -0.5$. Curves 1-6) as in Fig. 2; 7) $\log P_2 = 1.2$.

$$C_{ls} = 1-(\varepsilon N)\left\{1-\sum_{n=0}^{\infty}\frac{2}{\pi^2(n+1/2)^2}\exp[-\pi^2(n+1/2)^2x']\right\}. \tag{35}$$

This function decreases with increasing x' and tends to a constant value $(1-\varepsilon N)$ when $x' \geq 1$. Figure 3 presents the calculation of the concentrations $C_s(z)$ and $C_{ls}(z)$ in the interval $-1 \leq \log z \leq 1$ for small β at the points $Y_N = 1$, $X_N = 0$ ($\beta = 10^{-1}$) and $Y_N = 1$, $X_N = -0.5$ ($\beta = 0.316$). It is easily seen that the solution becomes one-parametric, depending on the parameter X_N alone, at small P_2, actually with $\log P_2 \leq 0$, for C_{ls}, and with $\log P_2 \leq -1$ for C_s.

At rather large P_2 ($\log P_2 \geq 1.2$), the concentrations C_{ls} and C_s obtained for various X_N also actually do not differ in the interval $-1 \leq \log z \leq 1$ (curve 7 in Fig. 3), since the solution must depend solely on the value $Y = 1$ in full accordance with Eqs. (21) - (23). Here, at "large" $z \geq 1$, the function $C_{ls}(z)$ "goes out" to a constant value $(1-EN) = 0.9$ (see Eq. (32)). It should be noticed, however, that this value is not an asymptote for C_{ls}, as it may seem in Fig. 3 (curves 7). In fact, Eq. (32) holds in the region $\beta \leq 1$ if the following two conditions are fulfilled: $C_s \Rightarrow 1$ and $\delta' \leq 1$ (this follows immediately from deriving Eq. (32)). Obviously, these conditions can be fulfilled only at fairly large P_2 ($1/\beta \ll P_2$) and, in addition, in a limited range of packing lengths: $1 \leq z \leq P_2^2\beta^2$($1 \leq z$, $x'' \leq 1$). Subsequently ($1 \ll x''$ or $P_2^2\beta^2 \leq z$), the relation of C_{ls} will depart from the intermediate value $(1-EN)$, "passing" into Eq. (35), and, at the distances from the entrance $x' \simeq 1$ ($z \simeq P_2^2$), $C_{ls} \Rightarrow (1-\varepsilon N)$ (in Fig. 3, C_{ls} tends to zero and 0.68, respectively).

Evidently, at moderate values of P_2, satisfying the inequalities $1 \leq P_2 \leq 1/\beta$, the boundary layer in the gas intergrows completely prior to to the onset of saturation at the interface $C_s \Rightarrow 1$. In this case, there are no constant-concentration sections on the curve $C_{ls}(x)$, and relation (35) holds when $z \geq 1$, i.e., immediately on saturation (curves 6 and 7 in Fig. 3b).

With small values of the chemisorption factor ($P_2 < 1$), the concentration C_{ls} also changes rather monotonically from unity to $(1-\varepsilon N)$ in the interval $-1 \leq \log z \leq 1$ (see the corresponding plots in Figs. 2 and 3). Thus, the concentration C_{ls} is a decreasing function of the coordinate x in the region $\beta \leq 1$, its minimal value being equal to $(1-\varepsilon N)$.

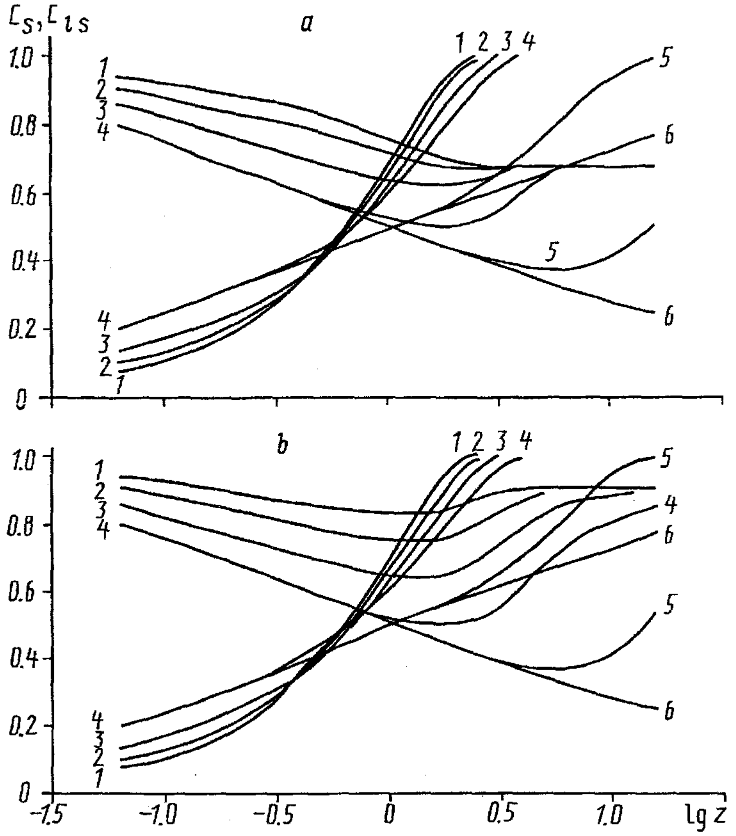

Fig. 4. The concentrations C_s and C_{ls} for $\beta > 1$. Designations as in Fig. 2.

Studying the Solution for $\beta^2 \geq 1$. In this region (the points lying beneath AC (see Fig. 1)), with $P_2 \leq 1/\beta^2$ in the interval of the main C_s variations the boundary layer intergrows in both phases, and, therefore, the concentration is determined from Eqs. (15) and (20). With a further increase in the parameter P_2 ($1/\beta^2 \leq P_2 \leq 1$), the case when at $z \simeq 1$ the boundary layer exists only in the gas phase is realized; here only the first of Eqs. (15) is valid. On the initial section, obviously,

$$C_s \simeq \Sigma = P_2 x' = z, \; C_{ls} = 1 - (EN)\sqrt{P_2}\,\frac{2\sqrt{z}}{\sqrt{\pi}}. \tag{36}$$

The expression for C_{ls} is derived from Eq. (29), where the dimensionless coordinate was determined from Eq. (33), taking into account that $P_2 \leq 1$. The first of Eqs. (36) shows that the carbamine concentration in the liquid phase volume tends to saturation ($C_s \simeq \sum \Rightarrow 1$) and, as follows from the material balance equation (11), $I \Rightarrow (\varepsilon N) \leq 1$. With such packing dimensions, the solution can be obtained from the following uniphase formulation:

$$\frac{\partial C_g}{\partial x''} = \frac{\partial^2 C_g}{\partial y_g^2}, \quad C_g = 1 \quad \text{for} \quad y_g = 0, \quad 1 - \int_0^1 C_g dy_g = \varepsilon N.$$

The solution of the problem for $x'' \ll 1$ exists in the form

$$1 - C_g = \frac{\varepsilon N}{\int_0^\infty f_{-1/2} d\eta} \, \frac{f_{-1/2}(\eta)}{\sqrt{x''}},$$

where the function $f_{-1/2}$ satisfies Eq. (28) at $\gamma = -1/2$ [15]:

$$f_{-1/2}(\eta) = \exp(-\eta^2/4).$$

Hence, when $z \gg 1$, C_{ls} is an increasing function:

$$C_{ls} \simeq 1 - \frac{1}{\int\limits_0^\infty f_{-1/2}(\eta)} \frac{\varepsilon N}{\sqrt{x''}} = 1 - \frac{1}{\sqrt{\pi}} \frac{EN\sqrt{P_2}}{\sqrt{z}}, \quad x'' \ll 1. \tag{37}$$

Comparing Eqs. (36) and (37) for small and large z suggests that for $z \simeq 1$ there is a minimum of the order of $1 - (EN)\sqrt{P_2}$ on the curve $C_{ls}(z)$. Evidently, as the packing length increases still more ($x'' \geq 1$), when the boundary layers intergrow in both phases (see Eq. (20)), C_{ls} tends to the limiting value:

$$C_{ls} \Rightarrow 1 - \varepsilon N, \quad 1 \leqslant x''. \tag{38}$$

We now present the solution for $P_2 >> 1$. In this case, in the interval of the main C_s variations the boundary layers exist in both phases ($x' \simeq z/P_2^2 \leq 1$); hence the concentration distribution is determined from Eqs. (26) and (27) and, therefore, from Eqs. (29)-(33). With a subsequent packing lengthening ($1 \leq x'$) or ($P_2^2 \leq z$), relations (37) and (38) hold for $C_{ls}(x')$.

Figure 4 gives the calculation of the surface concentrations for two points of the hydrodynamic plane: $Y_N = 0$, $X_N = -0.5$ and $Y_N = 0$, $X_N = -1$. The two points belong to the region $\beta > 1$. It is easily seen that, in full accordance with the above theoretical results, at fairly small values of the chemisorption parameter (actually, when $\log P_2 \leq -1.2$) the concentrations cease to depend on P2 and are determined by Eqs. (15) and (20). Accordingly, at large P_2 (practically, with $\log P_2 \geq 1$), the functions $C_s(z)$ and $C_{ls}(z)$ in the interval $-1 \leq \log z \leq 1$ also do not depend on P_2 because they coincide with the solution for the limiting problem (21)-(23). It is clear in the figure that C_{ls} at $\log z \simeq 1.5$ tends to the intermediate value $(1-EN) = 0$. All curves in Fig. 4 (except for small P_2) pass through a minimum and tend to the asymptotic value (38) in the region $1 \leq x'$ (or $\beta^2 P_2^2 \leq z$). Thus, the minimum value that $C_{ls}(x)$ assumes at a fixed level of Y_N is equal to (32), this value being attained only at sufficiently large P_2 (actually, when $\log P_2 \geq 1$).

Summing up the results obtained permits the conclusion that the minimum value of C_{ls} throughout quadrant II ($EN \leq 1$, $\varepsilon N \leq 1$) is

$$C_{ls\,\min} = \min(1 - EN, 1 - \varepsilon N). \tag{39}$$

It is often assumed a priori in the literature (especially in designing packed devices) [6-8] that the chemisorption resistance is concentrated entirely in the liquid phase ($C_{ls} \simeq 1$) regardless of the rate. From the results (39), we deduce that the conditions sufficient for such a mode are simultaneous fulfillment of the inequalities

$$\varepsilon N \ll 1 \text{ and } EN \ll 1. \tag{40}$$

This region is situated at the upper left-hand corner of the "hydrodynamic" plane X_N-Y_N (see Fig. 1). It should be emphasized that conditions (40) are sufficient in the sense that, when fulfilled, $C_{ls} \simeq 1$ irrespective of the packing length. Apparently, the boundaries of this region can be defined more precisely only from numerical calculations of the efficiency functions $\sum(x)$ of the general two-phase problem (2)-(5) and by comparing them with appropriate relations for the uniphase chemisorption problem with the condition $C_{ls} \simeq 1$ at the interface. The latter problem was treated in [5, 6, 10, 11]. We note that, with fairly small packing dimensions ($z << 1$), the condition $C_{ls} \simeq 1$ is always fulfilled (Figs. 2-4).

There are regions in quadrant II where the chemisorption resistance is fully concentrated in the liquid phase when some additional conditions are imposed on the rates of the chemical reactions. Indeed (see Figs. 2c and 4), in the left half of quadrant II for the points located to the left of the vertical straight line AD ($X_N \leq -1$), the equality $C_{ls} \simeq 0$ holds for any x at rather small P_2 (actually, at $\log P_2 \leq -1$).

On the other hand (see Fig. 2), in the upper part of quadrant II (the points above the horizontal straight line AB), the chemisorption resistance is concentrated in the liquid phase, provided P_2 is fairly large ($\log P_2 \geq 1$), which is the case when the packing dimensions are small ($x'' << 1$ or $z << P_2^2$).

The above results permit finding the conditions under which the mass transfer resistance is independent of the chemical reaction rate, i.e., is concentrated entirely in the gas phase. In this case, $C_{ls} \simeq 0$, and the efficiency function I(x) is determined from Eq. (30), where the substitution $x' \Rightarrow x''$. should be made [16]. This is the mode of the most intense CO_2 absorption; therefore, finding the conditions of its realization is also of practical interest, aside from theoretical. Obviously, at all inside points of quadrant II, where $\varepsilon N < 1$ and $EN < 1$, the above-mentioned mode cannot be realized under any conditions whatsoever because the stringent inequality $C_{ls} > 0$ (39) is always fulfilled. However, near the boundary of this region on the vertical straight line $X_N = 0$ and on the horizontal straight line $Y_N = 0$, $C_{ls} = 0$ can be realized under certain conditions.

In the first case ($X = 0$, $Y > 0$), this occurs when $C_{ls}(x)$ approaches its asymptotic value $C_{l\mathrm{smin}} = 1 - \varepsilon N \simeq 0$: for small $P_2 \leq 1$, this requires that the inequality $z \geq 1$ be fulfilled; for large $P_2 > 1 - x' \geq 1$ or $z \geq P_2^2$ (Figs. 2 and 3). In the second case ($Y = 0$, $X < 0$), the intense absorption mode is observed when C_{ls} assumes an intermediate minimum value: $C_{l\mathrm{smin}} = 1 - EN \simeq 0$. The latter is possible only for sufficiently large values of the chemisorption factor (actually, when $\log P_2 \geq 1$) (Fig. 4) in the limited interval of packing lengths $1/P_2^2 \leq x' \leq 1$.

As follows from the above analysis, the characteristic property of the solution for the two-phase chemisorption problem (2)-(5) in quadrant II is that the surface concentration of carbamine $C_s(x)$ is a monotonically increasing function, changing from zero to unity on a confined section, whose magnitude in the coordinates z generally satisfies the inequality $\log z \leq 1$. This inequality is approximate in the sense that "going out" to the limiting straight line $C_s \Rightarrow 1$ depends not only on the position of the point X_N, Y_N on the hydrodynamic plane but also on the chemisorption factor P_2 (Figs. 2-4).

Thus, with fairly long mass transfer packings ($\log z \geq 1$), the carbamine concentration at the interface approaches saturation and, therefore, the efficiency function $\sum(x)$ coincides with the analytic equation (30). This is the so-called mode of instantaneous chemical reaction with the acceleration factor $\Phi \Rightarrow N$ [5, 6].

NOTATION

C', dimensional concentration, mole/liter; C_0, constant CO_2 concentration at the entrance, mole/liter; D, diffusion coefficient, m^2/sec; k, constant of the reaction between CO_2 and amine, $m^3/mole \cdot sec$; N', total amine concentration in the solution, mole/liter; k, Henry constant; R, gas constant; T, temperature, K; U, rate, m/sec; h, film thickness, m; l, packing length, m; $a^2 = kN'h^2/D_l$; $N = N'/2kC_0$; $\varepsilon = qk/RU_g$, $E = \varepsilon\beta$, $\beta^2 = RPe_g/hPe_l$, dimensionless complexes; $\mathrm{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}}\int_0^x \exp(-t^2)dt$, error function. Subscripts: l, g, liquid and gas; s, value on the surface.

REFERENCES

1. V. P. Semenov, Ammonia Production [in Russian], Moscow (1985).
2. A. M. Kutepov, T. I. Bondareva, and M. G. Berengarten, General Chemical Technology: Manual for Technical Universities [in Russian], Moscow (1985).
3. A. M. Kutepov, Khimiya i Zhizn', No. 4, 2-8 (1987).
4. USA Patent 1783901 (cl. 23-2), "Process for separation of acidic gases" (R. R. Bottoms), 7.10.30, Public 2.12.30.
5. I. Astarita, Mass Transfer with a Chemical Reaction [Russian translation], Leningrad (1971).
6. P. V. Dankverts, Gas-Liquid Reactions [Russian translation], Moscow (1973).
7. Yu. V. Aksel'rod, Gas-Liquid Chemisorption Processes [in Russian], Moscow (1989).
8. Yu. G. Pikulik, Regeneration of Carbogassed Monoethanolamine Solutions in Cleaning Technological Gases [in Russian], Moscow (1988).
9. V. N. Babak, in: Heat and Mass Transfer in Surface Combustion [in Russian], Minsk (1986), pp. 138-144.
10. V. N. Babak, L. P. Kholpanov, V. A. Malyusov, and N. M. Zhavoronkov, Teor. Osn. Khim. Tekhnol., **11**, No. 1, 28-32 (1977).
11. V. N. Babak, T. B. Babak, L. P. Kholpanov, V. A. Malyusov, and N. M. Zhavoronkov, Teor. Osn. Khim. Tekhnol., **15**, No. 2, 170-176 (1981).

12. V. N. Babak, T. B. Babak, L. P. Kholpanov, V. A. Malyusov, and N. M. Zhavoronkov, Teor. Osn. Khim. Tekhnol., **12**, No. 11, 3-9 (1988).
13. V. N. Ramm, Gas Absorption [in Russian], Moscow (1976).
14. I. S. Gradshtein and I. M. Ryzhik, Table of Integrals, Sums, Series, and Products [in Russian], Moscow (1963).
15. E. Kamke, Manual on Ordinary Differential Equations [in Russian], Moscow (1961).
16. V. V. Vyazovov, Zh. Tekh. Fiz., **10**, Issue 18, 1519-1523 (1940).