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GAS ABSORPTION ACCOMPANIED BY FIRST-ORDER REVERSIBLE AND IRREVERSIBLE REACTIONS IN TURBULENT LIQUID FILMS

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Abstract—The problem of absorption with a chemical reaction in a turbulent falling film is theoretically analyzed by assuming that the mass transport normal to the interface takes place as a combined molecular and turbulent mechanism. It is assumed that the eddy diffusivity is a function of the distance to the gas–liquid interface.

A very simple and accurate approximate solution is obtained when chemical reactions are of first-order, reversible and irreversible, type. The main result is the expression for predicting the rate of mass transfer at the interface. When compared with results obtained from the surface renewal school it is found that most of them are encompassed by our final result using this eddy diffusivity model. Moreover it is shown that when the convective transport term, parallel to the interface, is neglected the resulting expression coincides exactly with that given by the pioneering work of Danckwerts [1] using his surface replacement idea. Since the eddy diffusivity can be related to hydrodynamic parameters so should the rate of surface renewal, since a simple relation linking both parameters is found.

It is concluded that surface renewal and eddy diffusivity models should not be considered as two different approaches to describe the same phenomenon since they are simply related.

NOMENCLATURE

b_1,	dimensionless parameter equal to 1;
b_2,b_3,	dimensionless parameter given by equation (A-14) or equation (17);
B,	dimensionless auxiliary variable satisfying equation (29b) and subject to conditions (30a,b,c);
B^*,	dimensionless auxiliary variable satisfying equation (29b) and subject to conditions (29a,b) and $B^* = 1$ at $\xi = 0$;
$\bar{B}^*$,	denotes Laplace transform of B^*;
$\bar{B}^{*\prime}(0)$,	denotes $(\mathrm{d}\bar{B}^*/\mathrm{d}\xi)$ evaluated at the interface;
C_A,	dimensionless concentration of species A equal to $(\bar{C}_A/\bar{C}_{A_S})$;
$\bar{C}_A$,	dimensional concentration of species A;
$\bar{C}_{A_S}$,	dimensional concentration of species A at $\xi = 0$;
C_B,	dimensionless concentration of species B equal to $(\bar{C}_B/\bar{C}_{A_S})$;
C_{B_S},	dimensionless concentration of species B at $\xi = 0$;
$\bar{C}_B$,	dimensional concentration of species B;
d,	dimensional film thickness;
D_A,	modified dimensionless Damköhler number defined by equation (6b);
D,	molecular diffusivity (dimensional) assumed equal for species A and B;
D^*,	dimensional eddy diffusivity assumed equal for species A and B and given by equation (3);
G,	dimensionless eddy diffusivity given by equation (5a);
G',	denotes $(\mathrm{d}G/\mathrm{d}\xi)$ [see equation (5b)];
h,	auxiliary dimensionless function of ξ, used with WBK approximation, solution to equation (A-4);
h',	denotes $(\mathrm{d}h/d\xi)$;
$h_0,h_1,h_2,\ldots$,	functions of ξ used to solve equation (A-4) approximately;
H^*,	dimensionless auxiliary variable satisfying equation (29a) and subject to conditions (29a,b) and $H^* = 1$ at $\xi = 0$;
$\tilde{H}^*$,	denotes Laplace transform of H^*;
$\tilde{H}^{*\prime}_{(0)}$,	denotes $(\mathrm{d}\tilde{H}^*/\mathrm{d}\xi)$ evaluated at the interface;
k,	dimensional pseudo-first-order kinetic constant;
k_L,	dimensional film mass transfer coefficient;
M,	dimensionless parameter defined by equation (28);
p,	auxiliary parameter either equal to D_A or to $S+D_A$;
s,	Laplace transform dimensionless parameter;
S^*,	auxiliary parameter defined as $S^* = S+b_3$;
Sh,	dimensionless Sherwood number for the case of first-order irreversible chemical reactions defined by equation (15);
Sh_P,	dimensionless Sherwood number given by penetration theory expression for first-

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	order irreversible chemical reactions [see equation (18)];
Sh_{SR},	denotes Sherwood number for surface renewal theory;
Sh^0,	dimensionless Sherwood number for physical absorption;
Sh^0_∞,	denotes Sherwood number for physical absorption when $\tau \to \infty$;
Sh^r,	dimensionless Sherwood number for the case of first-order reversible chemical reactions;
Sh^r_P,	dimensionless Sherwood number for the case of first-order reversible reactions as given by the penetration theory;
t,	dimensional contact time equal to (x/U_S);
t^*,	dimensionless contact time (Fourier number) $= td^2/D$;
U_S,	surface liquid film velocity;
w,	rate of surface renewal when $t = 0$;
x,	parallel coordinate to the interface;
y,	normal coordinate to the interface;
y^*,	dimensionless coordinate to the interface equal to (y/d).

Greek symbols

α,	dimensionless variable defined as $(C_A + C_B)$;
β,	dimensionless eddy diffusivity equal to $(\varepsilon/D)d^2$;
γ,	dimensionless parameter defined as the asymptotic expression of the reaction factor when $D_A \to \infty$, for first-order irreversible reactions as given by equation (22);
γ_r,	denotes γ for first-order reversible reactions given by equation (38);
δ,	auxiliary dimensionless parameter taken as $\simeq 0.8$;
δ_M,	dimensional mass transfer boundary-layer thickness [see equation (39)];
ε,	dimensional eddy diffusivity parameter defined by equation (3);
ξ,	dimensionless normal coordinate defined by equation (6c);
τ,	modified dimensionless contact time defined by equation (6b);
φ,	modified Laplace transform of C_A;
φ_0,	first term of the expansion of φ when $p \to 0$;
φ_n,	nth term of the expansion of φ when $p \to 0$;
φ_∞,	denotes the asymptotic solution for φ when $p \to \infty$;
Φ,	reaction factor for first-order irreversible reactions defined as (Sh/Sh^0);
Φ_{SR},	denotes reaction factor for first-order irreversible reactions given by surface renewal theory [see equation (23)];
Φ^r,	denotes reaction factor for first-order reversible reactions;
Φ^r_{SR},	denotes reaction factor for first-order reversible reactions given by surface renewal theory [see equation (37)];
χ,	inverse of the chemical equilibrium constant for reaction $A \rightleftharpoons B$;
Ω,	per cent differences between the actual reaction factor and that given by surface renewal theory [see equation (24)].

INTRODUCTION

SINCE turbulent films are commonly encountered in many industrial absorption processes, a great number of theoretical and experimental contributions with the aim of predicting the rate of absorption have been presented in the chemical engineering literature.

Due to the rather poor knowledge of the fluid mechanics of the turbulent liquid stream with a free interface there are two main approaches to simplify calculations for predicting the rate of mass transfer with and without chemical reaction through the interface. After Danckwerts [1] and his main idea relating to the "surface renewal" model a number of authors, as discussed later by Danckwerts [2] himself, presented other similar models which basically propose other expressions for the rate of surface renewal. In this line of reasoning the following should be included: Dobbins [3], Toor and Marchello [4], and Marchello and Toor [5] models also known as "film-penetration renewal" models. Basically this first approach postulates that the governing mass balance differential equation, for each piece of the interface replaced, is that of the penetration theory. The crucial point is the justification of the expression of the rate of replacement which must be intuitively accepted with at least an empirical parameter which must be experimentaly measured. The main advantage is the very simple form of the resulting expression for the rate of mass transfer and the main disadvantage is the difficulty that arises when such a parameter must be related to the hydrodynamic parameters such as Reynolds, Froude and eventually Weber numbers which characterize the flow pattern.

The other approach is also an oversimplification of the actual mechanism of mass transport. It is based on the time averaged technique of the governing differential equations when the flow pattern is turbulent. As a consequence an eddy diffusivity must be introduced in the time averaged mass balance differential equation. The crucial point here is the expression for the eddy diffusivity which is also empirical and must be intuitively accepted. Levich [6], for instance, postulates an expression where the eddy diffusivity is a growing function of the distance measured from the interface. As shown below in this case at least an empirical parameter must also be introduced. However the advantage with this approach, as shown by King [7], is that this parameter is directly related to hydrodynamic parameters and also to viscous dissipation. The main disadvantage, as pointed out by Danckwerts [2], is that this model would be much more difficult to use than those of the surface renewal school since the resulting mass balance differential equation, when the chemical reaction must be taken into account, is not easily solved. In fact the only case presented in the literature, where this second approach was used and the chemical reaction was taken into account, was solved by Menez and Sandall [8] using numerical techniques.

The purpose of this work is to analyze theoretically the whole problem of mass transfer with chemical reaction assuming as valid this second approach. In the first part the main assumptions that support the model are explicitly stated. In the second part the main steps, leading to a rather simple and accurate expression for the rate of mass transfer, are developed leaving the algebraic details for the Appendix. The analysis is divided in two sections: one to consider first order irreversible reactions and the other for first order reversible reactions.

It is shown that the final analytical expression for the rate of mass transfer coincides, in the limiting case of relatively large contact times, with the corresponding expression derived from Danckwerts [1] surface renewal model. This is a very important finding, since at least the main disadvantages of both approaches are eliminated after this contribution. Moreover a relationship between the specific rate of surface renewal and the eddy diffusivity parameter is established.

DESCRIPTION OF THE SYSTEM

The schematic diagram of the system to be analyzed is presented in Fig. 1. It is shown that x and y denote the coordinates parallel and normal to the interface respectively.

It is assumed that the flow is incompressible and that the only component of the time averaged velocity vector is U which is a function of y. The value of U at the interface ($y = 0$) is denoted by U_S.

Furthermore it will be assumed that the penetration depth (i.e. the distance from the interface where the concentration of the species A decays to almost zero) is small in comparison with the corresponding thickness where U changes substantially. With this assumption, which can be verified afterwards, U can be replaced by U_S in the mass balance equation for the absorbing species A. Moreover the usual boundary-layer assumptions will be used here: the order of magnitude of the time averaged concentration changes in the y direction are much larger than the corresponding changes in the x direction. With these assumptions, the steady-state time-averaged mass balance for species A in a dilute solution can be written in the following form:

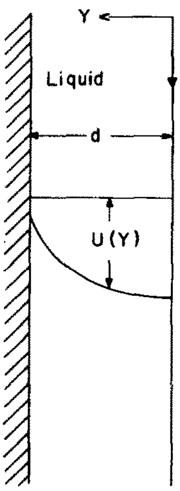

FIG. 1. Schematic diagram of the gas absorption studied.

$$U_S\left(\frac{\partial \bar{C}_A}{\partial x}\right) = \frac{\partial}{\partial y}\left[(D+D^*)\frac{\partial \bar{C}_A}{\partial y}\right] + \Gamma_A. \qquad (1)$$

$\bar{C}_A$ being the time averaged concentration of species A, D and D^* the molecular and eddy diffusivity and Γ_A the net rate of generation of species A, due to chemical reaction, expressed in moles per unit volume.

The crucial point is the form assumed for D^* in equation (1). Following previous works (Levich [6], King [7], Menez and Sandall [8] and Sandall [9]) it will be assumed that:

$$D^* = \varepsilon y^2. \qquad (2)$$

When expression (2) is replaced into equation (1) we can write:

$$U_S\left(\frac{\partial \bar{C}_A}{\partial x}\right) - 2\varepsilon y\left(\frac{\partial \bar{C}_A}{\partial y}\right) = (D+D^*)\frac{\partial^2 \bar{C}_A}{\partial y^2} + \Gamma_A. \qquad (3)$$

A close inspection to equation (3) shows that its second term on the LHS produces a similar effect to that of a normal velocity component directed to the interface. This is a direct consequence of the expression chosen for D^*. Moreover equation (3) resembles very much the governing differential mass balance for stagnation flow. Thus it should be expected that, when $x \to \infty$, an asymptotic value of the boundary-layer mass-transfer thickness will be obtained even in the absence of a chemical reaction. This in fact was the case analyzed by King [7] who neglected the term multiplied by U_S in equation (1) and the effect of the chemical reaction. The extension of King's [7] work to include the case of a first-order chemical reaction was studied both theoretically and experimentally by Menez and Sandall [8] who solved equation (1) numerically and succeeded in correlating their experimental results. In their model $\partial \bar{C}_A/\partial x = 0$.

Sandall [9] has also solved numerically equation (1) but neglecting the effect of the chemical reaction. Moreover Lamourelle and Sandall [10] have carefully carried out experiments in turbulent liquid films to correlate ε as a function of the Reynolds number of the system.

Subramanian [11] has recently presented an approximate solution for the case analyzed by Sandall [9]. However his final results are in good agreement with numerical estimates of Sandall [9] in a very limited range of contact time (x/U_S) values.

More recently Gottifredi and Quiroga [12] have succeeded in obtaining an approximate expression which predicts the rate of mass transfer, in the absence of chemical reaction, in close agreement (maximum deviation is about 2%) with Sandall's [9] numerical results over the whole range of contact times.

In this work the effect of the chemical reaction will be studied assuming that species A reacts in the liquid phase according to first-order irreversible and reversible reactions. It will be shown that our analytical approximate results can be expressed in almost exactly the same form as if they were given by a surface renewal model. In this way it will be possible to establish a relation between ε and the main parameter for the rate of surface renewal.

The results deduced here are only valid for first-order reversible and irreversible reactions in the absence of a finite initial concentration of the absorbing species but they can easily be extended to second-order irreversible reactions by the method proposed by Yeramian *et al.* [13] and also, for the case of finite initial concentration, through the work of Gottifredi *et al.* [14].

ANALYSIS

Irreversible first-order reactions

In this case it is assumed that species A reacts in the liquid phase according to a first order irreversible chemical reaction. So equation (3) can be written in the following dimensionless form:

$$\frac{\partial C_A}{\partial \tau} = G(\xi)(\partial^2 C_A/\partial \xi^2) + G'(\xi)(\partial C_A/\partial \xi) - D_A C_A, \quad (4)$$

where

$$G(\xi) = 1+\xi^2; \quad G'(\xi) = 2\xi \quad (5a,b)$$

and

$$C_A \equiv (\bar{C}_A/\bar{C}_{As}); \quad \tau \equiv (tD/d^2)\beta = t^*\beta = \varepsilon t$$
$$\xi \equiv (y/d)\beta^{1/2} = y^*\beta^{1/2}; \quad D_A \equiv (k/\varepsilon),$$
$$t \equiv (x/U_S); \quad \beta \equiv (\varepsilon/D)d^2. \quad (6a,b,c,d,e,f)$$

d being the film thickness (see Fig. 1). According to the assumption stated in the previous section equation (4) must be solved subject to the following initial and boundary conditions:

$$\begin{aligned} C_A &= 0, \quad \tau = 0, \quad \xi > 0, \\ C_A &= 0, \quad \tau \geqslant 0, \quad \xi \to \infty, \\ C_A &= 1, \quad \tau \geqslant 0, \quad \xi = 0, \end{aligned} \quad (7a,b)$$

so that $\bar{C}_{As}$ is the equilibrium concentration of the absorbing species at the interface.

A general analytical solution to equation (1) subject to conditions (7a,b) does not exist but here an approximate one will be presented. By defining

$$\varphi = s\int_0^\infty C_A(\tau, \xi)\exp(-s\tau)\mathrm{d}\tau.$$

Equation (4) is reduced to:

$$G(\xi)(d^2\phi/\mathrm{d}\xi^2)+G'(\xi)(\mathrm{d}\varphi/\mathrm{d}\xi) - (D_A+s)\varphi = 0 \quad (8)$$

subject to the following boundary conditions:

$$\varphi = 0, \quad \xi \to \infty, \varphi = 1, \quad \xi = 0. \quad (9a,b)$$

In order to find the approximate solution the following procedure will be used. First, asymptotic solutions to equation (8) for small and large values of s will be found and then they will be matched to obtain an approximate valid solution for the whole range of s values.

As $s \to 0(\tau \to \infty)$ the following series can be assumed as solution to equation (8):

$$\varphi = \varphi_0(\xi)+s\varphi_1(\xi)+\ldots, \quad (10)$$

which after being replaced into equation (8) and collecting terms in like power of s gives:

$$G(\xi)\varphi_0''+G'(\xi)\varphi_0'-D_A\varphi_0 = 0, \quad (11)$$

where the upper prime denotes differentiation with respect to ξ. Since we are mainly interested in the estimation of the rate of mass transfer at the interface an approximate expression for φ_0' at $y = O[\varphi_0'(0)]$ is deduced in the Appendix. Thus:

$$-\varphi_0'(0) = [D_A+(2/\pi)^2]^{1/2} \quad (12)$$

and when it is compared with results of Menez and Sandall [8] who solved equation (11) by numerical techniques an excellent agreement is found. Maximum deviation is about 2% (see Gottifredi and Quiroga [12]). It should be noted that equation (11) is the mass balance for the species A when the convective transport parallel to the interface is neglected in equation (4).

On the other hand when $s \to \infty(\tau \to 0)$ (see Appendix) an approximate expression for φ' at the interface $[\varphi_\infty(0)]$ can also be deduced:

$$-\varphi_\infty'(0) = (s+D_A)^{1/2}+\tfrac{1}{4}(s+D_A)^{-1/2}+\ldots, \quad (13)$$

which exactly coincides with Subramanian (11) results when $D_A = 0$. By matching equations (12) and (13) by the method described in the Appendix it is finally found:

$$-\varphi'(0) = \{s+(2/\pi)^2+D_A\}^{1/2} = (s^*+D_A)^{1/2}, \quad (14)$$

where $s^* = s+(2/\pi)^2$ was defined. Equation (14) is now valid on the whole range of s values as shown by Gottifredi and Quiroga [12].

The form of expression (14) is really compact and surprising due to its similarity with the known expression that would have been obtained if the penetration model had used. Indeed the only difference is s^* instead of s. By defining now the Sherwood number:

$$Sh = \left(\frac{k_L d}{D}\right) = -\left.\frac{\partial C_A}{\partial y^*}\right|_{y^*=0} = \beta^{1/2}\mathscr{L}^{-1}\left\{\frac{1}{s}[-\varphi'(0)]\right\} \quad (15)$$

and performing the antitransform ($\mathscr{L}^{-1}$) operation in equation (15) it is finally found:

$$Sh = b_3\int_0^\tau Sh_p(\tau')\exp(-b_3\tau')\,d\tau' + Sh_p\exp(-b_3\tau), \qquad (16)$$

where

$$b_3 = (2/\pi)^2 \qquad (17)$$

and

$$Sh_p = \beta^{1/2}\left\{\frac{1}{(\pi\tau)^{1/2}}\exp(-D_A\tau) + \mathrm{erf}[(D_A\tau)^{1/2}]D_A^{1/2}\right\} \qquad (18)$$

were defined. However it should be noted that equation (18) is exactly the expression for the Sherwood number given by the penetration theory. Thus the first conclusion is that when $\tau \leqslant 0.05$ the model here analyzed produces almost the same results as the penetration theory model. Since, according to experimental results of Lamourelle and Sandall [10] typical values of ε are 0.1–1s^{-1}, it is very unlikely that penetration theory would be helpful under these circumstances [see equation (6b)].

The other interesting feature of equation (16) is its remarkable similarity with the result that would have been obtained if Danckwerts' [1] surface renewal model had been applied:

$$Sh_{SR} = \int_0^\infty wSh_p\exp(-wt^*)\,dt^*, \qquad (19)$$

diffusivity model had been analytically solved. In fact this particular case was solved numerically by Menez and Sandall [8] but the equivalence between the two models could not be established since Menez and Sandall [8] did not find an analytical expression for the Sherwood number.

Thus it can be concluded that the surface renewal model can be described, after this work, in the form of a mass balance differential equation in which an eddy diffusivity is introduced, which in turn describes a hydrodynamic model of the stagnation type flow in the neighbourhood of the interface with an increasing diffusivity in the direction normal to the interface.

On the other hand if it is admitted (see King [7]) that ε is directly related to hydrodynamic parameters so will w, through equation (20). Thus the main disadvantages of both models, pointed out in the introduction, have been removed.

All the models derived from the surface renewal school are also encompassed by equation (16) since they produce results which are in the intermediate region between the penetration model and the surface replacement idea of Danckwerts [1].

For comparison purposes it is better to express the results in terms of the reaction or enhancement factor (Φ) (this being the ratio of the Sherwood numbers calculated with and without chemical reaction) as a function of the parameter γ (this being the asymptotic expression of Φ when $D_A \to \infty$). Thus in the present case:

$$\Phi = \frac{(D_A+b_3)^{1/2}\mathrm{erf}\{[(D_A+b_3)\tau]^{1/2}\} + (\pi\tau)^{-1/2}\exp[-(D_A+b_3)\tau]}{(\pi\tau)^{-1/2}\exp(-b_3\tau) + (2/\pi)\mathrm{erf}[(b_3\tau)^{1/2}]} \qquad (21)$$

and

$$\gamma = D_A^{1/2}/\{(\pi\tau)^{-1/2}\exp(-b_3\tau) + (2/\pi)\mathrm{erf}[(b_3\tau)^{1/2}]\}. \qquad (22)$$

where, according to equation (6b), $t^* = (\tau/\beta)$ and w is the rate of surface replacement at $t^* = 0$. Expression (16) coincides exactly with equation (19) when $\tau \to \infty$ and if

$$w = (2/\pi)^2\beta = Sh_\infty^{0^2}, \qquad (20)$$

where Sh_∞^0 is the Sherwood number in the absence of chemical reaction when $\tau \to \infty$. From a practical point of view equations (16) and (19) give the same numerical results when $\tau \geqslant 4(\sim\tau\to\infty)$ and when the relationship between β and w given by equation (20) is assumed. Since both β and w are empirical parameters they must be fitted with experimental results and because they are directly related with Sh_∞^0, such a relation can be assumed as valid. Moreover we can conclude that the surface renewal model is equivalent to the eddy diffusivity model when convective transport parallel to the interface is neglected. It should be stressed that this important finding would have never have been obtained unless the governing differential equation for the eddy

Once again it can be shown that when $\tau \to 0$ classical penetration theory results are found and as $\tau \to \infty$, Φ is given by Danckwerts surface renewal model:

$$\Phi_{SR} = (1+\gamma^2)^{1/2}. \qquad (23)$$

In Fig. 2, Ω defined as:

$$\Omega = (\Phi_{SR}-\Phi)\cdot 100/\Phi_{SR}, \qquad (24)$$

is plotted as a function of γ with τ as parameter. Once again it is shown that the differences that arise from different fluid dynamic models are smoothed out when the calculated results are expressed in terms of the reaction factor. Nevertheless, except in a small region of γ around 1, when $\tau \geqslant 1.5$ the eddy diffusivity and the surface renewal models almost coincide exactly. In a lot of industrial equipment values of τ of the order of 1.5 are not unusual. So for most practical situations of mass transfer with chemical reaction, the convective mass transport term in equation (3) can be neglected and then this

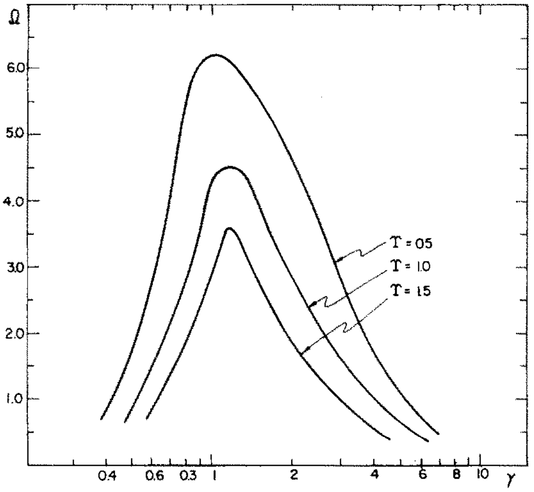

FIG. 2. Percent differences between the reaction factor Φ given by equation (21) and the corresponding value given by the surface renewal theory (Φ_{SR}) [see equation (23)]. Ω and γ being defined by equations (24) and (22) respectively.

eddy diffusivity model gives, almost exactly, equal results as the surface renewal model.† In other words both models are equivalent.

Reversible first-order reactions

In this case species A is absorbed in a turbulent film and by reacting with species C in excess, produces a new substance B which is not initially present in the liquid phase. It is further assumed that the interface is impermeable to species B. Thus, the chemical reaction can be represented by

$$A \rightleftharpoons B$$

and mass balance for species A and B can be written in the following dimensionless form, after assuming equal molecular diffusivities for both species:

$$\frac{\partial C_A}{\partial \tau} = \frac{\partial}{\partial \xi}\left[G(\xi)\frac{\partial C_A}{\partial \xi}\right] - D_A(C_A - \chi C_B),$$
$$\frac{\partial C_B}{\partial \tau} = \frac{\partial}{\partial \xi}\left[G(\xi)\frac{\partial C_B}{\partial \xi}\right] + D_A(C_A - \chi C_B), \qquad (25a,b)$$

where the new variable C_B is given as the ratio of the dimensional concentration of B to $\bar{C}_{A_S}$, while χ is the inverse of the equilibrium constant for the reaction considered. Equations (25a,b) are subject to the following initial and boundary conditions:

$$\begin{aligned} &C_A = 0, \quad C_B = 0, \qquad \tau = 0, \quad \xi > 0;\\ &C_A = 0, \quad C_B = 0, \qquad \tau \geqslant 0, \quad \xi \to \infty; \qquad (26a,b,c)\\ &C_A = 1, \quad \partial C_B/\partial \xi = 0, \quad \tau \geqslant 0, \quad \xi = 0. \end{aligned}$$

By defining two dependent variables

$$\alpha = (C_A + C_B), \qquad B = C_A - M\alpha, \qquad (27a,b)$$

where

$$M = \chi(1+\chi)^{-1} \qquad (28)$$

it can be shown that α and B must satisfy the following partial differential equations:

$$\frac{\partial \alpha}{\partial \tau} = \frac{\partial}{\partial \xi}\left[G(\xi)\frac{\partial \alpha}{\partial \xi}\right],$$
$$\frac{\partial B}{\partial \tau} = \frac{\partial}{\partial \xi}\left[G(\xi)\frac{\partial B}{\partial \xi}\right] - D_A(1+\chi)B, \qquad (29a,b)$$

subject to the following initial and boundary conditions:

$$\begin{aligned} &\alpha = 0, \quad B = 0, \quad \tau = 0, \quad \xi > 0;\\ &\alpha = 0, \quad B = 0, \quad \tau \geqslant 0, \quad \xi \to \infty;\\ &\alpha = 1 + C_{B_S}(\tau),\\ &B = (1-M) - MC_{B_S}(\tau), \quad \tau \geqslant 0, \quad \xi = 0. \qquad (30a,b,c) \end{aligned}$$

Let us denote the solutions to equation (29a,b) with homogeneous boundary conditions (let us say that $\alpha = 1$ and $B = 1$ at $\xi = 0$), as H^* and B^* respectively, which were derived above. Thus, by using the original boundary conditions (25a,b,c) in the Laplace transformed field, it can be shown that:

$$-\frac{\mathrm{d}\tilde{C}_A}{\mathrm{d}\xi}\bigg|_{\xi=0} = -\frac{\mathrm{d}\tilde{H}^*}{\mathrm{d}\xi}\bigg]_{\xi=0}(1 + s\tilde{C}_{B_S}) \qquad (31)$$

and

$$s\tilde{C}_{B_S} = \frac{[-\tilde{B}^{*\prime}(0)] - [\tilde{H}^{*\prime}(0)]}{\{\chi[-\tilde{B}^{*\prime}(0)] + [-\tilde{H}^{*\prime}(0)]\}}, \qquad (32)$$

where

$$-\hat{B}^{*\prime}(0) = -\frac{\mathrm{d}\hat{B}^*}{\mathrm{d}\xi}\bigg|_{\xi=0}$$
$$= \frac{1}{s}[s + b_3 + (1+\chi)D_A]^{1/2}, \qquad (33)$$
$$-\hat{H}^{*\prime}(0) = -\frac{\mathrm{d}\hat{H}^{*\prime}}{\mathrm{d}\xi}\bigg|_{\xi=0} = \frac{1}{s}(s+b_3)^{1/2} \qquad (34)$$

according to the results derived in the previous section. By replacing (33) and (34) into equation (31) we found:

$$-\frac{\mathrm{d}\tilde{C}_A}{\mathrm{d}\xi}\bigg|_{\xi=0} = \frac{s^{*1/2}}{s} \times \left\{\frac{[s^* + D_A(1+\chi)]^{1/2} - s^{*1/2}}{\chi[s^* + D_A(1+\chi)]^{1/2} + s^{*1/2}} + 1\right\} \qquad (35)$$

and once again if this result is compared with that given by the penetration theory (let us say $s^* = s$), it can be shown that

$$Sh^r = b_3 \int_0^{\tau} Sh_p^r \exp(-b_3\tau')\,\mathrm{d}\tau' + Sh_p^r \exp(-b_3\tau) = \left(\frac{k_L d}{D}\right), \qquad (36)$$

where the upper index r is to denote the Sherwood number for reversible reactions and the lower index p to denote penetration theory results.

Once again equation (36) encompasses all results derived from the surface renewal school for the case here analyzed. Danckwerts' [1] surface replacement

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†It must be stressed that the conclusion is the same even if the results are compared in terms of Sherwood numbers.

model is a particular case which can be exactly derived if the convective transport terms in equations (29a,b) are neglected. Thus Danckwerts' [1] very well known model can be represented in this case by equations (29a,b) with $\partial C_A/\partial \tau = \partial C_B/\partial \tau = 0$. Equation (36) shows that the Sherwood number is given by penetration theory results, derived by Sherwood and Pigford [15], when the unlikely situation of $\tau \leqslant 0.05$ is met. On the other hand when $\tau \geqslant 4$, the asymptotic result derived from Danckwerts [1] surface renewal model is found. Expressed in terms of the reaction factor:

$$\Phi^r_{SR} = \frac{[b_3 + D_A(1+\chi)]^{1/2} - b_3^{1/2}}{\chi[b_3 + D_A(1+\chi)]^{1/2} + b_3^{1/2}} + 1. \qquad (37)$$

In deducing equation (37) the relation between w and β given by equation (20) was used. From (37) it can be shown that the asymptotic expression of $\Phi^r_{SR}(\gamma^r)$ as $D_A \to \infty$ is:

$$\gamma_r = \left(\frac{1}{\chi} + 1\right) \qquad (38)$$

which is in agreement with Sherwood and Pigford's [15] predictions since as $D_A \to \infty$, the hydrodynamic model is immaterial.

Expression (37) is also given by Danckwerts [2], in his well-known book, and reduces to the corresponding result for first order irreversible reactions when $\chi \to 0$.

There is no need to carry out calculations in this case since from a practical point of view the eddy diffusivity and surface renewal models produce almost the same expression for the rate of mass transfer provided $\tau \geqslant 1.5$.

Such a conclusion would have not been achieved if the system of governing differential equations for the eddy diffusivity model had not been analytically solved.

CONCLUSIONS

A theoretical analysis of the absorption of a gas in a reacting turbulent liquid film is presented. An eddy diffusivity model previously studied by Sandall [9] for the case of physical absorption was used. The main assumptions leading to the governing differential mass balance equations for the case of first-order reversible and irreversible reactions were pointed out. One of them must however still be proven. It was assumed that the penetration thickness was sufficiently small to replace the time-averaged velocity component in the flow direction by its interfacial value. From expression (20) the penetration depth can be approximately calculated as:

$$(\delta_M/d) \simeq \frac{D}{k_L d} = \frac{\pi}{2\beta^{1/2}} \qquad (39)$$

and since, according to Lamourelle and Sandall [10], typical values of β are 1000–10 000 the assumption seems justified.

A very simple, approximate and accurate expression to estimate the rate of mass transfer in the presence of a first-order reversible and irreversible reaction was deduced. The comparison of our predicted results with numerical estimates of Sandall [9] for the case of physical absorption shows a maximum deviation of about 2% as analyzed elsewhere [12]. Since the case of a first-order chemical reaction is a superposition based on the corresponding results for the case without chemical reaction, the accuracy of the expressions presented in this work to predict the rate of absorption is expected to be as good as for the case of physical absorption. Since the mathematical procedure is extremely simple it is expected that this work will be used, in the future, for the analysis of more complex systems of reaction than those studied here.

As pointed out above the results deduced here are only valid in the case of zero initial concentration of the absorbing species and for first-order reversible and irreversible reactions. However it can be easily extended to cases of finite initial concentration and second-order irreversible reactions following the ideas of Gottifredi *et al.* [14] and Yeramian *et al.* [13] respectively.

However, the most important achievement of this work is related to finding out the connection between the surface renewal and the eddy diffusivity models which, up until now, were treated by many authors as two different approaches to the same problem. Moreover in this form the main disadvantages of both schools of reasoning are eliminated.

Moreover it is shown that, with only one empirical parameter, most of the results derived by modifications of Danckwerts' [1] pioneering idea of surface replacement are encompassed by our final analytical expressions (18) and (36) that predict the rate of mass transfer in the presence of first-order irreversible and reversible reactions respectively. Furthermore it is shown that Danckwerts' [1] surface renewal model can be exactly described by the time-averaged mass balance governing system of differential equations when the convective mass transport parallel to the interface can be neglected and when the eddy diffusivity is expressed, after the pioneer work of Levich [6], by equation (2). A limit in terms of the eddy diffusivity parameter and the actual contact time is established as a criterium for neglecting the convective transport parallel to the interface. ($\tau \geqslant 1.5$). Also, through equation (20) a relation between the specific rate of surface renewal and the eddy diffusivity parameter is established. It must be stressed that none of these conclusions would have been derived if the approximate solutions of the eddy diffusivity model had not been found.

In his book Danckwerts [2] pointed out that the model presented in this work would be much more difficult to use than other models (such as film or surface renewal and associate models) to predict the rate of mass transfer and to study the effect of the chemical reaction. This limitation can be removed after this contribution.

Lastly it should be mentioned that most of the analysis presented in this work can be applied to other situations such as the unsteady mass transfer in turbulent agitated vessels. In this sense it can be regarded as an extension of the work of King [7] who assumed that the mass-transfer process takes place at steady state conditions.

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APPENDIX

Here we are concerned with the solution of an ordinary differential equation of the form:

$$G(\xi)\left(\frac{d^2\varphi}{d\xi^2}\right)+G'(\xi)\left(\frac{d\varphi}{d\xi}\right)-p\varphi=0 \qquad \text{(A-1)}$$

subject to:

$$\varphi(0)=1;\quad \varphi(\infty)=0, \qquad \text{(A-2)}$$

where $G(\xi)$ is given by expression (5). p is a parameter which is encompassed between 0 and ∞. It is easy to verify that $p=s+D_A$ and $p=D_A$ in equations (8) and (11) respectively.

When p is large ($p\to\infty$), a solution can be obtained with WBK approximation. In fact, by letting

$$\varphi=\exp\left[\int_0^{\xi} h(\xi')\,d\xi'\right] \qquad \text{(A-3)}$$

and substituting this expression into $(A-1)$, $h(\xi)$ is found to satisfy the following differential equation:

$$G(\xi)(h^2+h')+G'(\xi)h=0. \qquad \text{(A-4)}$$

Thus a solution for large values of p can be written in by the following series:

$$h=h_0p^{1/2}+h_1+h_2p^{-1/2}+h_3p^{-1}+\ldots. \qquad \text{(A-5)}$$

By introducing the last expression in (A-4) and collecting terms in like powers of p, a system of ordinary differential (rather algebraic) equations is found, which can be easily solved, yielding

$$h_0(0)=1,\quad h_1(0)=0,\quad h_2(0)=-1/4, \qquad \text{(A-6)}$$

so that

$$-\varphi'_{\infty}(0)=p^{1/2}+\tfrac{1}{4}p^{-1/2}+\ldots. \qquad \text{(A-7)}$$

On the other hand, for small values of $p(p\to 0)$ a power series of the form:

$$\varphi=\varphi_0+p\varphi_1+\ldots \qquad \text{(A-8)}$$

can be used, which once substituted in equation (A-1), and after matching like powers of p gives:

$$\frac{d}{d\xi}\left\{G(\xi)\frac{d\varphi_0}{d\xi}\right\}=0, \qquad \text{(A-9)}$$

for p^0 and

$$\frac{d}{d\xi}\left\{G(\xi)\frac{d\varphi_n}{d\xi}\right\}=\varphi_{n-1}, \qquad \text{(A-10)}$$

for p^n with $n\geqslant 1$. However, equation (A-9) is identical to the steady-state case solved by King (7), namely:

$$-\varphi_0(0)=\frac{2}{\pi}. \qquad \text{(A-11)}$$

Thus a valid solution for the whole range of p can be constructed using the method proposed by Rosenzweig [16], by letting

$$-\varphi'(0)=b_1\frac{(p+b_2)}{(p+b_3)^{1/2}} \qquad \text{(A-12)}$$

and expanding expression (A-12) for small and large values of p, conditions for b_1 and b_3 are found:

$$\begin{aligned} b_1b_2b_3^{-1/2}&=(2/\pi),\\ b_1&=1,\\ b_1(b_2-\tfrac{1}{2}b_3)&=\tfrac{1}{4}\delta. \end{aligned} \qquad \text{(A-13)}$$

It should be noted that we found it necessary to introduce $\delta\simeq 0.8$ to allow b_2 and b_3 to be real and positive values. Under these conditions,

$$b_1=1,\quad b_2=b_3=(2/\pi)^2. \qquad \text{(A-14)}$$

Thus,

$$-\varphi'(0)=[p+(2/\pi)^2]^{1/2}. \qquad \text{(A-15)}$$

Since equation (A-1), (under the same conditions and with $p=D_A$) was solved by Menez and Sandall [8], the results given by expression (A-15) can be compared with their numerical results, showing a very good agreement (maximum deviation less than 2%).

ABSORPTION GAZEUSE AVEC REACTION CHIMIQUE DU PREMIER ORDRE, REVERSIBLE OU IRREVERSIBLE, DANS UN FILM LIQUIDE TURBULENT

Résumé—On analyse par voie théorique le problème de l'absorption avec réaction chimique dans un film turbulent et tombant, en supposant que le transport massique normal à l'interface se fait selon un mécanisme combiné moléculaire et turbulent. On suppose que la diffusivité turbulente est fonction de la distance à l'interface gaz–liquide.

On obtient une solution approchée très simple lorsque les réactions chimiques sont du premier ordre, réversibles ou irréversibles. Le résultat principal est l'expression du flux massique à l'interface. Quand on compare avec les résultats obtenus par la théorie du renouvellement de la surface, on trouve que la plupart d'entre eux sont entourés par notre résultat final à partir du modèle de la diffusivité turbulente. On montre que lorsque le terme de transport parallèle à l'interface est négligé, l'expression résultante coïncide exactement avec celle donnée par le premier travail de Danckwerts (1) avec l'idée du remplacement de surface. Puisque la diffusivité thermique peut être reliée aux paramètres hydrodynamiques, on pourrait espérer cela pour le taux de renouvellement des surfaces, car une relation simple entre les deux paramètres est trouvée.

Les modèles de renouvellement de surface et de diffusivité turbulente ne doivent pas être considérés comme deux approches différentes pour décrire le même phénomène puisqu'ils sont simplement reliés.

GASABSORPTION IN VERBINDUNG MIT UMKEHRBAREN UND NICHTUMKEHRBAREN REAKTIONEN ERSTER ORDNUNG IN FLÜSSIGKEITSFILMEN

Zusammenfassung—Das Problem der Absorption mit chemischer Reaktion in einem turbulenten Rieselfilm wird theoretisch untersucht, wobei angenommen wird, daß der Stofftransport normal zur Phasengrenzfläche als kombinierter molekularer und turbulenter Mechanismus abläuft. Es wird angenommen, daß die scheinbare Temperaturleitfähigkeit eine Funktion der Entfernung von der Gas-Flüssigkeits-Grenzfläche ist. Eine sehr einfache und genaue Näherungslösung wird erreicht, wenn die umkehrbaren und nichtumkehrbaren Reaktionen vom Typ erster Ordnung sind. Das Hauptergebnis ist die Funktion zur Voraussage der Stofftransportrate an der Phasengrenzfläche. Vergleicht man dieses Resultat mit Ergabnissen, die man nach der Vorstellung der Oberflächenerneuerung erhält, dann zeigt sich, daß unsere Ergebnisse, die mit dem Modell der scheinbaren Temperaturleitfähigkeit gefunden wurden, die meisten davon enthalten. Weiter wird gezeigt, daß bei Vernachlässigung des konvektiven Transportterms parellel zur Phasengrenzfläche die entstehenden Ausdrüche exakt mit denen übereinstimmen, die sich aus der bahnbrechenden Arbeit von Danckwerts [1] ergeben, wenn man seiner Idee der Oberflächenerneuerung folgt. Da die scheinbare Temperaturleitfähigkeit mit hydrodynamischen Parametern in Beziehung gesetzt werden kann, ist das auch für die Oberflächenerneuerungsrate zu erwarten, zumal eine einfache Beziehung zwischen den beiden Parametern besteht. Abschließend wird festgestellt, daß die Modelle der Oberflächenerneuerung und des scheinbaren Temperaturleitfähigkeit nicht als zwei verschiedene Möglichkeiten zur Beschreibung des gleichen Phänomens betrachtet werden sollten, weil sie in einfacher Weise untereinander verknüpft sind.

АБСОРБЦИЯ ГАЗА, СОПРОВОЖДАЮЩАЯСЯ ОБРАТИМЫМИ И НЕОБРАТИМЫМИ РЕАКЦИЯМИ ПЕРВОГО ПОРЯДКА В ЖИДКОСТИ ПРИ НАЛИЧИИ ТУРБУЛЕНТНОСТИ

Аннотация — Проблема абсорбции при наличии химической реакции в турбулентной стекающей плёнке анализируется теоретически при допущении, что перенос массы по нормали к поверхности раздела происходит в результате совместного действия механизмов молекулярного и турбулентного переноса. Предполагается, что коэффициент турбулентной диффузии является функцией расстояния до поверхности раздела газ-жидкость. Получено очень простое приближенное решение для случая, когда химические реакции являются реакциями первого порядка обратимого и необратимого типов. Основным результатом анализа является выражение для расчёта скорости переноса массы на поверхности раздела. При сравнении с результатами, полученными на основе теории обновления поверхности, найдено, что большинство из них входит в наш окончательный результат, полученный с помощью модели турбулентной диффузии. Кроме того, показано, что при пренебрежении конвективным переносом параллельно границе раздела фаз, полученное выражение полностью совпадает с выражением, приведенным в первоначальной работе Дэнквертса [1] и выведенным на основе его теории смены поверхности. Поскольку коэффициент турбулентной диффузии можно отнести к гидродинамическим параметрам, то так же можно поступить и со скоростью обновления поверхности, поскольку получено простое соотношение, связывающее оба эти параметра.

Сделан вывод о том, что модели обновления поверхности и турбулентной диффузии не должны рассматриваться как два различных подхода к одному явлению, поскольку они являются взаимосвязанными.