Int. J. Heat Mass Transfer. Vol. 24, pp. 299–304
Pergamon Press Ltd. 1981. Printed in Great Britain

0017-9310/81/0201-0299 $02.00/0

GAS ABSORPTION IN LAMINAR FALLING FILMS WITH FIRST ORDER HOMOGENEOUS REACTION AND GAS PHASE MASS TRANSFER RESISTANCES

HENRIK PEDERSEN* and JIRI E. PRENOSIL
Technisch-chemisches Laboratorium ETH, CH-8092 Zurich, Switzerland

(*Received* 1 *February* 1980 *and in revised form* 20 *March* 1980)

Abstract – An analytical solution of the governing differential equation for gas absorption in laminar falling films with the first order homogeneous reaction and external gas phase mass transfer resistance is shown. The analysis is simplified by introducing a phenomenological mass transfer coefficient, *Bi*, that is a Biot number. An enhancement factor is defined as the ratio of the calculated absorption rates and the absorption rates found from a simple penetration model. It is shown also that external gas phase mass transfer resistances can significantly lower the absorption rates compared with those found when gas phase resistances are not present.

NOMENCLATURE

a_n,	parameter in the confluent hypergeometric function defined in equation (11);
A_n,	*n*th coefficient required in the solution for the developing concentration profile;
b,	parameter = 1/2 used in equation (10);
Bi,	Biot number ($= h\delta/D$);
C,	dimensionless liquid phase concentration;
D,	liquid phase diffusion coefficient [m^2/s];
E,	enhancement factor defined in equation (21);
h,	gas phase mass transfer coefficient [m/s];
H_i,	Henry's law constant;
k,	first order reaction rate constant [1/s];
$\dot{m}$,	dimensionless absorption rate;
$M(a, b; y)$,	confluent hypergeometric function [13];
p_i,	partial pressure in the gas phase of species *i*;
$p_{i,o}$,	partial pressure at the gas–liquid interface;
Pe,	Peclet number for mass transfer ($= v_o\delta/D$);
$\dot{r}$,	dimensionless reaction rate;
t,	characteristic time [s];
v_o,	interfacial liquid velocity [m/s];
v_z,	velocity profile (dimensionless);
y,	dimensionless penetration distance ($= \bar{y}/\delta$);
z,	dimensionless axial distance [$= \bar{z}/(\delta\, Pe$].

Greek symbols

α^2,	reaction rate constant ($= k\delta^2/D$);
δ,	film thickness [m];
λ_n,	*n*th eigenvalue;
ϕ_n,	*n*th eigenfunction defined by equation (10).

Superscripts

$'$,	local value;
∞,	value obtained for $Bi = \infty$, no gas phase resistance;
$-$,	dimensional quantity.

Subscripts

d,	developing solution;
o,	evaluated for physical absorption only;
p,	penetration;
r,	reaction;
s,	stationary solution.

INTRODUCTION

THE ABSORPTION of gases into liquid films has numerous practical applications and is a widely used separation technique in the chemical processing industry. That the absorption rates are enhanced by simultaneous homogeneous reactions occurring in the liquid phase is well known and has been extensively studied both theoretically and experimentally (see [1], Chapter 8).

In general, the governing equation for the absorbed species in the liquid phase is given, in dimensionless form, by [2], p. 11):

$$\frac{\partial^2 C}{\partial y^2} = v_z \frac{\partial C}{\partial z} - \dot{r} \tag{1}$$

where v_z is the dimensionless velocity profile and $\dot{r}$ is the dimensionless reaction rate. The penetration and axial coordinates are y and z, respectively. When v_z is

---

* Permanent address: Department of Chemical and Biochemical Engineering, Rutgers – The State University, New Brunswick, NJ 08903, U.S.A.

constant (plug flow assumption), equation (1) describes the equivalent situation of unsteady state diffusion into a stagnant liquid; in this case, z is a dimensionless penetration time. Subject to this simplification, various 'penetration models' have been described that assume an infinitely deep liquid phase and solutions have been published for different reaction rate expressions. For example, Astarita and Marruci [3] have considered absorption with a zeroth order reaction, and Danckwerts has treated the case of first order reaction as well as second order reactions with one non-volatile reactant in the liquid phase [4]. When v_z is given by a parabolic profile [5] and, therefore, finite film thicknesses considered, solutions to equation (1) have been obtained for purely physical absorption, $\dot{r} = 0$, by various investigators [6–8]. Absorption with a first order reaction for this case has been treated by Stepanek and Achwal [9] and, recently, by Best and Hoerner [10].

In most instances, the existence of significant gas side mass transfer resistances on the rate of absorption was neglected. As pointed out by Tamir and Taitel [11], however, the effect of gas side resistance on the absorption rates can be appreciable, particularly when fast chemical reaction takes place in the liquid phase. In fact, gas side mass transfer will limit the absorption rates when the liquid phase homogeneous reaction is infinitely fast. Of course, when absorption occurs from a pure (one component) gas, this effect is not present. In practice, however, absorption is from a multicomponent mixture.

In this report, we consider the effect of gas side mass transfer on the absorption of a single volatile species from a multicomponent mixture. The analysis is simplified by neglecting variations in the bulk gas phase reactant concentration and by introducing a macroscopic mass transfer coefficient rather than solving the complicated boundary layer equations in the gas phase [11]. We also compare our results for no gas phase mass transfer resistances with those recently published [10] and point out some discrepancies.

THEORY

We consider equation (1) where v_z is assumed to be a parabolic profile and $\dot{r}$ is a first order homogeneous reaction, i.e.:

$$v_z = 1 - y^2 \tag{2}$$

and

$$\dot{r} = -\alpha^2 C. \tag{3}$$

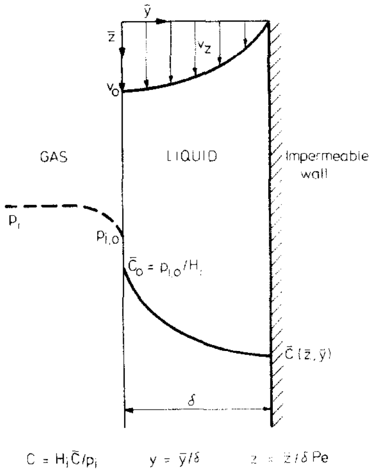

FIG. 1. Schematic of a falling liquid film showing the coordinate system considered and the dimensionless coordinates.

The coordinate system used and the physical description of the absorbing film are shown in Fig. 1. The interfacial concentration of the absorbing species is assumed to be in equilibrium with the prevailing partial pressure in the adjacent gas phase and is given in terms of a constant Henry's law coefficient, H_i (see Fig. 1). The concentration is normalized to the equilibrium concentration evaluated at the bulk partial pressure. The dimensionless coordinates z and y are defined in Fig. 1 where the Peclet number is $Pe = v_0\delta/D$. The rate constant in equation (3) is $\alpha^2 = k\delta^2/D$, where k is the first order dimensional rate constant. The boundary conditions are:

$$C = 0; \quad z = 0; \quad 0 \le y \le 1 \tag{4}$$

$$\frac{\partial C}{\partial y} = -Bi(1 - C); \quad z > 0; \quad y = 0 \tag{5}$$

$$\frac{\partial C}{\partial y} = 0; \quad z > 0; \quad y = 1, \tag{6}$$

where the Biot number is $Bi = h\delta/D$ and h is the dimensional mass transfer coefficient for the gas phase. Best and Hoerner [10] have solved equations (1)–(6) for the case of no gas phase mass transfer resistances, $Bi = \infty$.

The solution for any value of the Biot number is formulated in terms of a stationary solution, C_s, that satisfies the inhomogeneous boundary condition given by equation (5) and a developing solution, C_d, that satisfies the homogeneous boundary condition:

$$\frac{\partial C_d}{\partial y} = BiC_d; \quad z > 0; \quad y = 0. \tag{7}$$

The concentration is then obtained as the sum of the stationary and developing solutions. As shown by Stepanek and Achwal [9], C_s is a function only of y, such that:

$$C_s = \frac{\cosh[\alpha(1 - y)]}{\cosh\alpha + (\alpha \sinh\alpha)/Bi}. \tag{8}$$

The developing concentration profile can be evaluated using the transformations of equations (1)–(4), (6) and (7) described by Davis [12]. The solution satisfying equation (7) is found in this manner to be:

$$C_d = \sum_{n=1}^{\infty} A_n \phi_n(y) \exp(-\lambda_n^2 z), \tag{9}$$

where:

$$\phi_n(y) = [M(a_n, b; \lambda_n y^2) + Bi\, y\, M \times (a_n + b, 2 - b; \lambda_n y^2)] \exp(-\lambda_n y^2/2). \tag{10}$$

The function $M(a, b; y)$ is the confluent hypergeometric function [13] and is easily evaluated using simple numerical techniques [14]. In equation (10):

$$a_n = (1 - \lambda_n + \alpha^2/\lambda_n)/4 \tag{11}$$

$$b = 1/2. \tag{12}$$

The eigenvalues, λ_n, and coefficients, A_n, are determined by evaluating the solution for the concentration profile at the boundary conditions equations (6) and (4), respectively. When the Biot number is infinite, the solution for ϕ_n is given by [10]:

$$\phi_n^\infty = \lambda_n^{1/2} y M(a_n + b, 2 - b; \lambda_n y^2) \exp(-\lambda_n y^2/2). \tag{13}$$

The local dimensionless absorption rate, $\dot{m}'$, is:

$$\dot{m}' = \partial C/\partial y \bigg|_{y=0}. \tag{14}$$

When the Biot number is finite, equation (5) can be used to evaluate the gradient. From the solution, equation (8) plus (9), we obtain that:

$$\dot{m}' = \frac{Bi\, \alpha \tanh \alpha}{Bi + \alpha \tanh \alpha} - Bi \sum_{n=1}^{\infty} A_n \mathrm{e}^{-\lambda_n^2 z}. \tag{15}$$

When $Bi = \infty$:

$$\dot{m}'^{\infty} = \alpha \tanh \alpha - \sum_{n=1}^{\infty} A_n \lambda_n^{1/2} \mathrm{e}^{-\lambda_n^2 z}. \tag{16}$$

The absorption rate associated with the stationary part of the concentration profile satisfies an additivity relation. If we let $\dot{m}'_s$ be the absorption rate for the stationary solution, then:

$$\frac{1}{\dot{m}'_s} = \frac{1}{Bi} + \frac{1}{\alpha \tanh \alpha}. \tag{17}$$

The first term on the RHS of equation (17) is a resistance to mass transfer in the gas phase and the second term can be thought of as a resistance to mass transfer due to finite reaction rates in the liquid phase.

The total absorption of the volatile species into the liquid film, $\dot{m}$, is found by integrating equations (15) or (16) along the film length, z:

$$\dot{m} = \frac{Bi\, \alpha \tanh \alpha}{Bi + \alpha \tanh \alpha} z - Bi \sum_{n=1}^{\infty} \frac{A_n}{\lambda_n^2} (1 - \mathrm{e}^{-\lambda_n^2 z}) \tag{18}$$

and for $Bi = \infty$:

$$\dot{m}^{\infty} = \alpha \tanh \alpha\, z - \sum_{n=1}^{\infty} \frac{A_n}{\lambda_n^{3/2}} (1 - \mathrm{e}^{-\lambda_n^2 z}). \tag{19}$$

In order to compare the absorption rates evaluated with the combined influence of gas phase mass transfer resistances and finite film thicknesses, we introduce the absorption rate found from the simple penetration model, that assumes no reaction ([1], p. 71):

$$\dot{m}_o^{\infty} = (4z/\pi)^{1/2}. \tag{20}$$

RESULTS AND DISCUSSION

The eigenvalues and coefficients in equations (10) and (11) have been numerically evaluated for different values of the Biot number and reaction rate parameter, α, and are shown in Table 1. The results for infinite *Bi* agree exactly with those recently published by Best and Hoerner [10].

An enhancement factor, E, is defined for the absorption system as the ratio of absorption rates using equations (18) or (19) and (20):

$$E = \dot{m}/\dot{m}_o^{\infty}. \tag{21}$$

The enhancement factor is plotted in Fig. 2 as a function of the modulus $[(\pi/4)(t_p/t_r)]^{1/2}$, where t_p is a characteristic time for penetration (a residence time), and t_r is the characteristic time for reaction. They are defined as:

$$t_p = \bar{z}/v_o \tag{22}$$

$$t_r = 1/k \tag{23}$$

The interpretation of the figure is facilitated by recognizing that the modulus can be rewritten as:

$$[(\pi/4)(t_p/t_r)]^{1/2} = (\alpha z)/\dot{m}_o^{\infty}. \tag{24}$$

The linear regions of the graph, observed for small and large t_p/t_r, represent regimes of diffusion and reaction control of absorption, respectively. At either region $\dot{m}$ = constant (αz), as seen from equations (21) and (24). In the diffusion regime, the curves are approximately separated by a distance corresponding to the log of their α^2 ratios provided that α is not too large. This implies that the reaction rate has no influence on the absorption rate. At the other extreme, the reaction will control the absorption rate since the developing concentration profile is almost zero. From equation (19) we see that the curves should correspond to $\dot{m} = \tanh \alpha\, (\alpha z)$. Best and Hoerner [10] have derived a more general expression for the enhancement factor at large values of the modulus for which $\tanh \alpha$ is the leading term. They have also presented the same graph shown in Fig. 2; however, the curves drawn imply that the enhancement factor is unity for values of the modulus less than 0.1. Also, the lines corresponding to large α values are not correct.

The existence of a diffusion controlled regime for absorption disappears for large α values. Figure 2 is typical of absorption rate behaviour in the presence of homogeneous reaction ([1], p. 308), and similar curves are observed for different values of the Biot number.

Figure 3 shows how the enhancement factor varies with the modulus for $\alpha^2 = 0.1$ when the Biot number is

Table 1. Eigenvalues (λ) and integration constants [A_n (equation 9)], for different α^2 and Bi numbers

Bi		0.1		1.0		10		∞	
α^2	n	λ_n	$-A_n$	λ_n	$-A_n$	λ_n	$-A_n$	λ_n	$-A_n$
0.1	1	0.54534703	0.48507710	1.1677075	0.70837461	2.0417514	0.22513893	2.3068112	1.7254050
	2	4.3396001	0.01332433	4.5822822	0.10889729	5.6542638	0.17685774	6.3135470	1.0195501
	3	8.3310152	0.00365510	8.4652172	0.03438905	9.3575181	0.12728627	10.317425	0.79481651
	4	12.329047	0.00167256	12.420944	0.01625526	13.146464	0.08920281	14.319780	0.67390169
	5	16.328446	0.00095428	16.398174	0.00938754	16.997622	0.06340570	18.321387	0.59547690
	6	20.328281	0.00061590	20.384419	0.00609392	20.890400	0.04637296	22.322569	0.53932774
	7	24.328287	0.00043010	24.375254	0.00426911	24.810840	0.03496425	26.323484	0.49657183
	8	28.328364	0.00031724	28.368730	0.00315506	28.750051	0.02711035	30.324218	0.46260689
	9	32.328472	0.00024361	32.363861	0.00242583	32.702369	0.02154060	34.324823	0.43478097
	10	36.328592	0.00019292	36.360095	0.00192279	36.664107	0.01747775	38.325331	0.41144275
1.0	1	1.2769490	0.09458431	1.6661768	0.37569217	2.4153346	0.17615441	2.6632791	1.3112038
	2	4.5416378	0.01189395	4.7697358	0.09891533	5.8046712	0.16900581	6.4547756	0.97561769
	3	8.4384581	0.00353972	8.5701733	0.03335789	9.4503490	0.12486954	10.404437	0.78159244
	4	12.401908	0.00164807	12.493005	0.01602305	13.213321	0.08825503	14.382573	0.66803231
	5	16.383520	0.00094628	16.452899	0.00930990	17.049708	0.06297682	18.370493	0.59229782
	6	20.372538	0.00061256	20.428494	0.00606114	20.932975	0.04615687	22.362882	0.53738565
	7	24.365275	0.00042847	24.412135	0.00425303	24.846796	0.03484575	26.357674	0.49528440
	8	28.360132	0.00031636	28.400431	0.00314627	28.781144	0.02704078	30.353898	0.46170212
	9	32.356311	0.00024308	32.391655	0.00242065	32.729743	0.02149702	34.351045	0.43411683
	10	36.353367	0.00019260	36.384838	0.0019154	36.688549	0.01744964	38.348817	0.41093909
10	1	3.6615132	0.01669890	3.8900275	0.10783496	4.5188384	0.09386905	4.7722752	0.56444570
	2	6.1639339	0.00571991	6.3168680	0.05149008	7.1294561	0.12061528	7.7230764	0.69674837
	3	9.4528167	0.00266099	9.5642224	0.02539967	10.341609	0.10482719	11.245471	0.67084511
	4	13.115230	0.00143103	13.198973	0.01395815	13.870808	0.07961771	15.001812	0.61432140
	5	16.929100	0.00087123	16.995129	0.00858124	17.566482	0.05891190	18.858345	0.56210940
	6	20.813079	0.00058043	20.867255	0.00574600	21.357046	0.04406917	22.764699	0.51859172
	7	24.734300	0.00041257	24.780109	0.00409621	25.205634	0.03368802	26.699015	0.48269980
	8	28.677462	0.00030763	28.717090	0.00305992	29.091775	0.02635595	30.650484	0.45280575
	9	32.634578	0.00023792	32.669468	0.00236934	33.003388	0.02106966	34.613204	0.42756160
	10	36.601098	0.00018934	36.632249	0.00188720	36.932965	0.01717026	38.583685	0.40594624

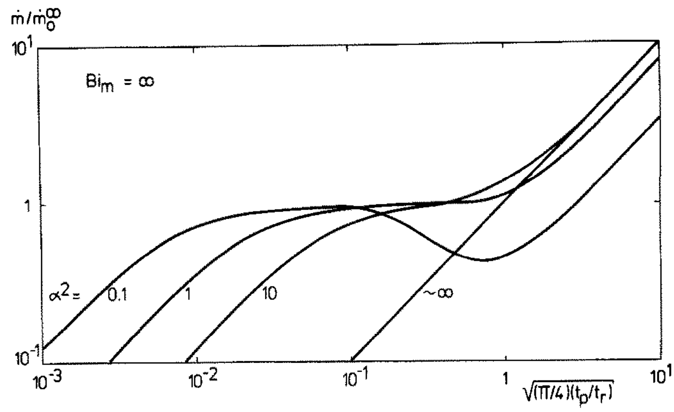

FIG. 2. The enhancement of absorption, $\dot{m}/\dot{m}_o^\infty$, as a function of the modulus, $[(4/\pi)(t_p/t_r)]^{1/2}$ used by Best and Hoerner [10], with the dimensionless reaction constant as the parameter. Note that the modulus can also be written as $\alpha z/\dot{m}_o^\infty$.

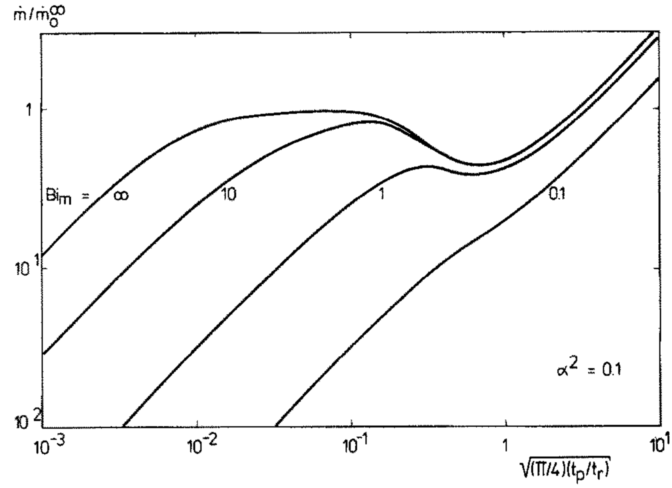

FIG. 3. The effect of finite gas phase mass transfer resistances on the enhancement of absorption for $\alpha^2 = 0.1$.

the parameter. In all cases, the enhancement is less than that observed in the absence of external diffusion limitations. The effect is most pronounced at low values of the modulus. At large values of the modulus, the curves will be given by $\dot{m} = [\tanh \alpha/(1 + \alpha \tanh \alpha/Bi)][\alpha z]$ as seen from equation (18). The increase in mass transfer resistances in the gas phase, characterized by decreasing values of the Biot number, results in a more rapid transition to the reaction controlled absorption regime which is now modified by external gas transfer. When the Biot number is small relative to α, the absorption rate will be entirely controlled by the rate of transport from the gas phase to the gas-liquid interface.

CONCLUSIONS

The analytical solution for mass transfer into laminar falling films with the combined effects of homogeneous first order reaction and gas phase mass transfer resistance has been presented. The enhancement of absorption, relative to the case of absorption into a stagnant film with no reaction or gas phase resistance, has been shown to display two linear regimes corresponding to the liquid phase diffusion control and the reaction control of absorption when the enhancement factor is plotted in the manner suggested by Best and Hoerner [10]. With gas phase mass transfer resistance, the absorption rates can be significantly smaller than those observed for the case of no resistance, particularly when the Biot number and the modulus given by equation (24) are small.

Acknowledgement—This work was carried out while the first author was a visiting scientist in the laboratory of Prof. J. R. Bourne, whose support is gratefully acknowledged.

REFERENCES

1. T. K. Sherwood, R. L. Pigford and C. R. Wilke, *Mass Transfer*. McGraw-Hill, New York (1975).
2. G. Astarita, *Mass Transfer with Chemical Reaction*. Elsevier, Amsterdam (1967).
3. G. Astarita and G. Marruci, Gas absorption with zero-order chemical reaction, *Ind. Engng Chem. Fundl.* **2**, 4–7 (1963).

4. P. V. Danckwerts, (a) Absorption by simultaneous diffusion and chemical reaction, (b) Unsteady-state diffusion or heat conduction with moving boundary, *Trans. Faraday. Soc.* **46,** 300–304, 701–712 (1950).
5. J. O. Wilkes and R. M. Nedderman, The measurement of velocities in thin films of liquid, *Chem. Engng Sci.* **17,** 177–187 (1962).
6. R. E. Emmert and R. L.-Pigford, A study of gas absorption in falling liquid films, *Chem. Engng Prog.* **50**(2), 87–93 (1954).
7. J. F. Davidson and E. J. Cullen, The determination of diffusion coefficients for sparingly soluble gases in liquids, *Trans. Instn. Chem. Engrs* **35,** 51–60 (1957).
8. W. E. Olbricht and J. D. Wild, Diffusion from the free surface into a liquid film in laminar flow over defined shapes, *Chem. Engng Sci.* **24,** 25–32 (1969).
9. J. B. Stepanek and S. K. Achwal, Absorption with first-order chemical reaction into a liquid film in laminar flow, *Can. J. Chem. Engng* **54,** 545–550 (1976).
10. R. J. Best and B. Hoerner, Gas absorption with first-order chemical reaction in laminar falling films — calculation of rates and enhancement factors, *Chem. Engng Sci.* **34,** 759–762 (1979).
11. A. Tamir and Y. Taitel, The effect of the gas side resistance on absorption with chemical reaction from binary mixtures, *Chem. Engng Sci.* **30,** 1477–1482 (1975).
12. E. J. Davis, Exact solutions for a class of heat and mass transfer problems, *Can. J. Chem. Engng* **51,** 562–572 (1973).
13. M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions.* Dover, New York (1965).
14. D. O. Cooney, S. S. Kim and E. J. Davis, Analyses of mass transfer in hemodialyzers for laminar blood flow and homogeneous dialysate, *Chem. Engng Sci.* **29,** 1731–1738 (1974).

ABSORPTION DE GAZ DANS DES FILMS TOMBANTS LAMINAIRES AVEC DES REACTIONS HOMOGENES DU PREMIER ORDRE ET DES RESISTANCES DE TRANSFERT MASSIQUE

Résumé—On donne une solution analytique de l'équation représentant l'absorption de gaz dans les films tombants laminaires avec une réaction homogène du premier ordre et une résistance au transfert massique. L'analyse est simplifiée en introduisant un coefficient phénoménologique de transfert massique *Bi* qui est un nombre de Biot. Un facteur d'amélioration est défini comme le rapport du flux d'absorption calculé au flux obtenu à partir du modèle simple de pénétration. On montre aussi que les résistances au transfert massique en phase gazeuse peuvent abaisser nettement les flux d'absorption par rapport à ceux obtenus en l'absence de résistance.

GASABSORPTION IN LAMINAREN RIESELFILMEN MIT HOMOGENER REAKTION ERSTER ORDNUNG UND STOFFÜBERGANGSWIDERSTAND IN DER GASPHASE

Zusammenfassung – Eine analytische Lösung der beschreibenden differentiellen Gleichung für Gasabsorption in Rieselfilmen mit Reaktion erster Ordnung und externem Stoffüberganswiderstand in der Gasphase wird gezeigt. Durch das Einführen eines phänomenologischen Faktors, *Bi*, d.h. Biot-Nummer,wird die Analyse vereinfacht. Ein Verstärkungsfaktor wird als Verhältnis der berechneten Absorptionsraten und derjenigen aus dem einfachen Penetrationsmodell definiert. Weiter wird gezeigt, dass der Stoffübergangswiderstand in der Gasphase die Absorptionsraten erheblich reduzieren kann, verglichen mit derjenigen ohne Gasphasenwiderstand.

АБСОРБЦИЯ ГАЗА В ЛАМИНАРНЫХ СТЕКАЮЩИХ ПЛЕНКАХ ПРИ НАЛИЧИИ ОДНОРОДНОЙ РЕАКЦИИ ПЕРВОГО ПОРЯДКА И СОПРОТИВЛЕНИЯ ПЕРЕНОСУ МАССЫ СО СТОРОНЫ ГАЗОВОЙ ФАЗЫ

Аннотация — Дано аналитическое решение основного дифференциального уравнения для абсорбции газа в ламинарных стекающих пленках при наличии однородной реакции первого порядка и сопротивления переносу массы, оказываемого внешней газовой средой. Анализ упрощен за счет ввода феноменологического массообменного коэффициента Bi, т. е. числа Био. Интенсифицирующий фактор определяется как отношение расчетной скорости поглощения к скорости поглощения, определяемой с помощью простой модели проницания. Показано также, что сопротивление переносу массы со стороны внешней газовой фазы может значительно снизить интенсивность абсорбции.