Gas Absorption with Zero-Order Chemical Reaction

The governing differential equation for gas absorption in laminar falling film with zero-order homogeneous reaction is solved analytically by the method of separation of variables, and subsequent solution with confluent hypergeometric function. The result for concentration profile was obtained in the forms of a sum of a polynomial and an infinite series of hypergeometric functions.

An enhancement factor, E, is defined as the ratio of the calculated absorption rates and the absorption rates found from a simple penetration model. When the Hatta number, $\sqrt{M'}$ is greater than 2, the enhancement factor is given by a simplified form with an error of less than 2%.

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SCOPE

The absorption of gases into liquid films is widely used as a separation technique in the chemical processing industry. The rates of absorption may be enhanced by simultaneous homogeneous reactions occurring in the liquid phase and have been extensively studied by Astarita (1967).

In general, the governing equation for the absorbed gas in the liquid is given by (see Figure 1 for the coordinate system used)

$$\bar{u}\frac{\partial \bar{C}}{\partial \bar{z}} = D\frac{\partial^2 \bar{C}}{\partial \bar{x}^2} - r \qquad (1)$$

where $\bar{u}$ is the dimensional velocity and r is the reaction rate. For $r = 0$ (physical absorption), an accurate solution has been published by Olbricht and Wild (1969). Best and Hoerner (1979) have studied the absorption rate and enhancement factors for the case of a first-order chemical reaction.

Here we represent the solution to Eq. 1 when the reaction is considered to be zero-order. Astarita and Marrucci (1963) have studied the problem of gas absorption with zero-order reaction in a stagnant liquid film. They have also discussed the conditions at which a reaction may be considered zero-order. For example, carbon dioxide absorption in aqueous monoethanolamine solutions may be regarded, under some conditions, as an absorption process with zero-order chemical reaction taking place in the liquid phase. In this paper we solve the governing equation analytically; then we use the concentration profiles to obtain enhancement factors when the gas phase resistance is negligible.

CONCLUSIONS AND SIGNIFICANCE

The analytical solution of mass transfer into laminar falling films with the effect of homogeneous zero-order chemical reaction has been presented. The enhancement of absorption, relative to the case of absorption into a stagnant film with no reaction has been evaluated and is plotted in the manner suggested by Best and Hoerner (1979). It is shown that when the modulus ($\sqrt{M'} = \sqrt{(\pi/4)\phi z}$) is greater than 2, the enhancement factor, E, can be calculated from the equation

$$E = \sqrt{\alpha M'} \qquad \alpha \le 2$$

$$E = \sqrt{2M'} \qquad \alpha > 2$$

with an error of less than 2%.

THEORY

We consider Eq. 1 where $\bar{u}$ is assumed to be a fully developed parabolic profile and r is a zero-order homogeneous reaction, i.e.:

$$\bar{u} = \bar{u}_o\left(1 - \frac{\bar{x}^2}{\delta^2}\right) \qquad (2)$$

and

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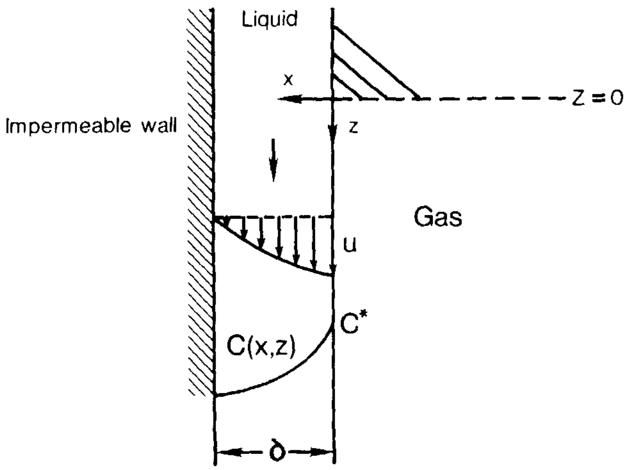

Figure 1. Schematic of a falling liquid film showing the coordinate system considered.

$$r = \text{constant} = k \tag{3}$$

Thus Eq. 1 becomes:

$$\bar{u}_o\left(1 - \frac{\bar{x}^2}{\delta^2}\right)\frac{\partial \bar{C}}{\partial \bar{z}} = D\frac{\partial^2 \bar{C}}{\partial \bar{x}^2} - k \tag{4}$$

Equation 4 can be written in a dimensionless form as follows

$$(1 - x^2)\frac{\partial C}{\partial z} = \frac{\partial^2 C}{\partial x^2} - \alpha \tag{5}$$

where

$$C = \bar{C}/\bar{C}^* \tag{6}$$

$$x = \bar{x}/\delta \tag{7}$$

$$z = D\bar{z}/\bar{u}_o\delta^2 \tag{8}$$

and

$$\alpha = k\delta^2/D\bar{C}^* \tag{9}$$

Neglecting the resistance to mass transfer in the gas phase, the boundary conditions associated with Eq. 4 are:
at

$$z = 0, 0 \leq x \leq 1, \qquad C = 0 \tag{10}$$

at

$$x = 0, z > 0 \qquad C = 1 \tag{11}$$

and at

$$x = 1, z > 0, \qquad \frac{\partial C}{\partial x} = 0 \tag{12}$$

It is important to note that the boundary condition given by Eq. 12 is correct only for low values of α due to low reaction rate, high solubility of gas in liquid, low film thickness, or high diffusion rate. Only under such conditions is the maximum depth of penetration greater than the film thickness; thus, Eq. 12 is correct. For zero-order reactions, the reactant can be depleted in the film, and there is a maximum depth of penetration by the dissolving gas, Δ. If this depth is less than the film thickness, the boundary condition given by Eq. 12 must be changed to

$$x = x^*, \quad C = 0; \quad \frac{\partial C}{\partial x} = 0 \tag{13}$$

where $x^* = \Delta/\delta$. Neglecting $\partial C/\partial z$ (steady-state condition) in Eq. 5 and solving Eq. 5 with boundary conditions given in Eqs. 11 and 13, one can obtain $x^* = \sqrt{2/\alpha}$. From this relation it is obvious that when $\alpha \leq 2$, $x^* \geq 1$ and the boundary condition given by Eq. 12 is correct; but if $\alpha > 2$, the boundary condition given by Eq. 13 must be used instead. When $\alpha \leq 2$, Δ is greater than δ, but due to the solid wall the maximum penetration depth, Δ, cannot exceed from the film thickness; therefore the maximum value for x^* is unity when α is less than or equal to 2. It would be appropriate to define the dimensionless maximum penetration depth, x^*, in the following form:

$$x^* = \begin{cases} 1 & \text{when } \alpha \leq 2 \\ \sqrt{\dfrac{2}{\alpha}} & \text{when } \alpha \geq 2 \end{cases} \tag{14}$$

Since Eq. 5 is nonhomogeneous, we assume the solution is in the following form:

$$C(x,z) = \omega(x,z) + \phi(x) \tag{15}$$

where functions $\omega(x,z)$ and $\phi(x)$ must be determined. Substitution of Eq. 15 into Eq. 5 results in the following equations for ϕ and ω:

$$\frac{d^2\phi}{dx^2} - \alpha = 0 \tag{16}$$

$$(1 - x^2)\frac{\partial \omega}{\partial z} = \frac{\partial^2 \omega}{\partial x^2} \tag{17}$$

The boundary conditions for Eq. 16 are:

$$x = 0 \qquad \phi(0) = 0 \tag{18}$$

and at

$$x = x^* \qquad \frac{d\phi}{dx} = 0 \tag{19}$$

The solution of Eq. 16 under these conditions is:

$$\phi(x) = \frac{\alpha}{2}x^2 - \alpha x^* x \tag{20}$$

The boundary conditions for Eq. 17 are:

$$z = 0 \qquad \omega(x,0) = -\phi(x) = -\frac{\alpha}{2}x^2 + \alpha x^* x \tag{21}$$

$$x = 0 \qquad \omega(0,z) = 1 \tag{22}$$

and at

$$x = x^* \qquad \frac{\partial \omega}{\partial x} = 0 \tag{23}$$

The boundary condition given by Eq. 22 is nonhomogeneous and the solution can be obtained as a linear combination of a particular solution of the nonhomogeneous condition and a general solution of the homogeneous problem. The method of separation of variables suggests:

$$\omega(x,z) = X(x)Z(z) \tag{24}$$

After separation, one obtains

$$\frac{1}{Z}\frac{dZ}{dz} = -\lambda^2 \tag{25}$$

and

$$\frac{1}{(1 - x^2)X}\frac{d^2X}{dx^2} = -\lambda^2 \tag{26}$$

TABLE I. EIGENVALUES λ_n AND INTEGRATION COEFFICIENTS A_n (EQS. 40 AND 46) FOR DIFFERENT α

	λ_n	A_n $\alpha = 0$	$\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.4$	$\alpha = 0.6$	$\alpha = 1$	$\alpha = 2$
1	2.26310730	−1.75041962	−1.68875122	−1.62708282	−1.50374889	−1.38040924	−1.13373566	−0.51705498
2	6.29768753	−0.94583791	−0.94779074	−0.94975090	−0.95366901	−0.95758766	−0.96541959	−0.98500973
3	10.30774117	−0.68508488	−0.68279725	−0.68050957	−0.67593431	−0.67135960	−0.66221058	−0.63933706
4	14.31281567	−0.53424400	−0.53475535	−0.53526646	−0.53629035	−0.53731215	−0.53935683	−0.54447240
5	18.31593323	−0.42852622	−0.42788619	−0.42724484	−0.42596477	−0.42468244	−0.42211741	−0.41571188

n	$\alpha = 3$ λ_n	A_n	$\alpha = 4$ λ_n	A_n	$\alpha = 6$ λ_n	A_n
1	2.38905811	−0.39503384	2.59138775	−0.34615232	2.99999714	−0.32509524
2	11.11647511	−0.60940564	12.28075695	−0.60196859	14.48623657	−0.38069564
3	19.88887024	−0.39239860	22.03276062	−0.32797408	26.02349304	−0.31857151
4	28.66842651	−0.24961549	31.79965210	−0.18004006	37.58782959	−0.15332603
5	37.30392456	−0.14320898	41.53424072	−0.10245061	49.10888672	0.00143038

For $\lambda = 0$, after integration of Eqs. 25 and 26 with the conditions given by Eqs. 22 and 23, one obtains the following particular solution of the nonhomogeneous problem:

$$\omega_p = 1 \tag{27}$$

The corresponding homogeneous problem is also stated by Eqs. 25 and 26 with λ generally different from zero. The homogeneous boundary conditions are
at

$$x = 0 \qquad \omega = 0 \tag{28}$$

and at

$$x = x^* \qquad \frac{\partial \omega}{\partial x} = 0 \tag{23}$$

Equation 25 can be resolved to give

$$Z_h = A_n \exp(\lambda^2 z) \tag{29}$$

Using the transformation

$$y = \lambda x^2 \tag{30}$$

$$Y = Xe^{y/2} \tag{31}$$

Eq. 26 transforms to Kummer's equation:

$$y\frac{d^2Y}{dy^2} + (1/2 - y)\frac{dY}{dy} - \left(\frac{1}{4} - \frac{\lambda}{4}\right)Y = 0 \tag{32}$$

The solution of this equation is

$$Y = BM\left(\frac{1-\lambda}{4}, \frac{1}{2}, y\right) + Dy^{1/2}M\left(\frac{3-\lambda}{4}, \frac{3}{2}, y\right) \tag{33}$$

where M is the confluent hypergeometric function. Cooney et al. (1974) discussed the method of evaluation for M.

In terms of the original variables the solution is

$$X_h = B\exp\left(-\frac{\lambda}{2}x^2\right)M\left(\frac{1-\lambda}{4}, \frac{1}{2}, \lambda x^2\right) + F\lambda\exp\left(-\frac{\lambda}{2}x^2\right)xM\left(\frac{3-\lambda}{4}, \frac{3}{2}, \lambda x^2\right) \tag{34}$$

From the boundary conditions given in Eqs. 28 and 23, one obtains $X(0) = 0$ and $(dX/dx)(x^* = 1) = 0$. The condition $X(0) = 0$ suggests that $B = 0$. The following characteristic equation is obtained upon application of the condition $(dX/dx)(x^* = 1) = 0$.

$$(1 - \lambda x^{*2})M\left(\frac{3-\lambda}{4}, \frac{3}{2}, \lambda x^{*2}\right) + \frac{\lambda(3-\lambda)}{3}x^{*2}M\left(\frac{7-\lambda}{4}, \frac{5}{2}, \lambda x^{*2}\right) \tag{35}$$

where x^* is defined by Eq. 14. The zeros of Eq. 35 were found by the numerical method of falsi (Carnahan et al., 1979), and a number of eigenvalues are given in Table 1. Therefore, the solution of homogeneous condition can be found by substitution of Z_h and X_h into Eq. 24. The function ω is the sum of the particular and homogeneous solutions

$$\omega = 1 + \sum_{n=1}^{\infty} A_n \exp(-\lambda_n^2 z)X_n(x) \tag{36}$$

where functions $X_n(x)$ are eigenfunctions of Eq. 26:

$$X_n(x) = \lambda_n^{1/2}x\exp\left(-\frac{\lambda_n}{2}x^2\right)M\left(\frac{3-\lambda_n}{4}, \frac{3}{2}, \lambda_n x^2\right) \tag{37}$$

Application of the boundary condition given by Eq. 21 leads to the requirement that

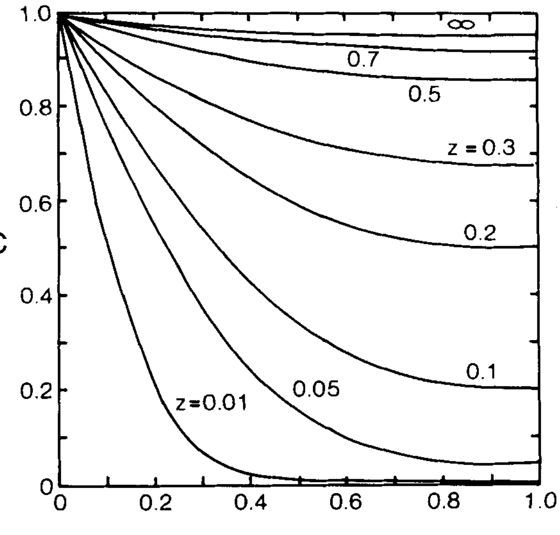

Figure 2. Development of the concentration profile for α = 0.1.

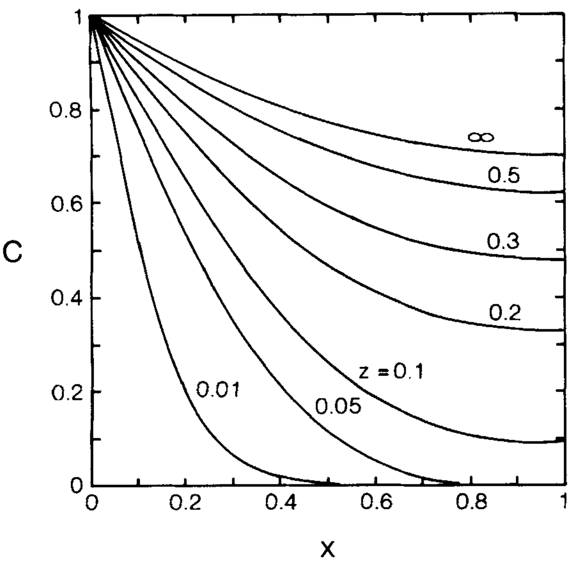

Figure 3. Development of the concentration profile for α = 0.6.

$$-\frac{\alpha}{2}x^2 + \alpha x^* x - 1 = \sum_{n=1}^{\infty} A_n X_n(x) \tag{38}$$

The condition of orthogonality of eigenfunctions with the weight function of $(1 - x^2)$ can be used to compute constants A_n; it follows that

$$A_n = \frac{\int_0^1 \left(-\frac{\alpha}{2}x^2 + \alpha x^* x - 1\right)(1 - x^2)X_n(x)dx}{\int_0^1 (1 - x^2)X_n^2(x)dx} \tag{39}$$

By substitution of Eqs. 20 and 36 into Eq. 15, the concentration profile can be obtained:

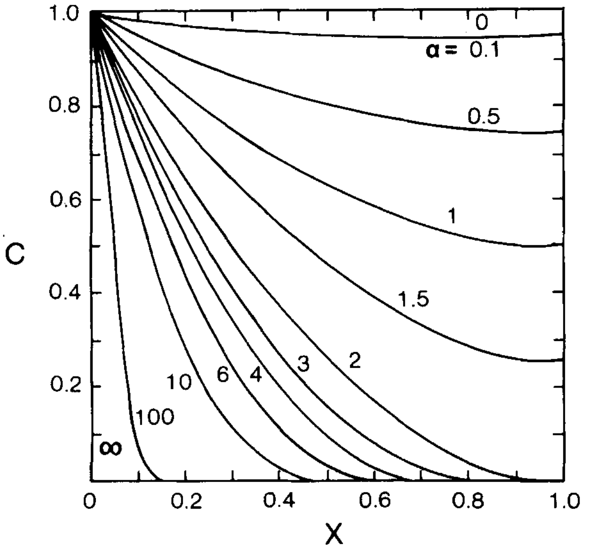

Figure 4. Development of the concentration profile for different values of α under steady-state conditions.

$$C = \frac{\alpha}{2}x^2 - \alpha x^* x + 1 + \sum_{n=1}^{\infty} A_n \lambda_n^{1/2} \exp(-\lambda_n^2 z) \times \exp\left(-\frac{\lambda_n}{2}x^2\right) x M\left(\frac{3 - \lambda_n}{4}, \frac{3}{2}, \lambda_n x^2\right) \tag{40}$$

$C = 0 \qquad$ when $x \geq x^*$

The total rate of gas absorption for a film of width W is

$$G = -W\bar{u}_o C^* \delta \int_0^z \frac{\partial C}{\partial x}\bigg|_{x=0} dz \tag{41}$$

In order to evaluate the influence of the chemical reaction, we compare the absorption rate, G, with the absorption, $G_\infty{}^o$, of an infinitely deep stagnant liquid with the same physical properties but in which there is no chemical reaction. The ratio $G/G_\infty{}^o$ is equivalent to the well-known enhancement factor E. $G_\infty{}^o$ for physical absorption has been given by Best and Hoerner (1979)

$$G_\infty^o = 2\bar{C}^* \delta \bar{u}_o W \sqrt{\frac{z}{\pi}} \tag{42}$$

If $\dot{m}$ and $\dot{m}_o$ are dimensionless absorption rates for G and $G_\infty{}^o$, we have

$$\dot{m} = \frac{G}{W\bar{u}_o \bar{C}^* \delta} = -\int_0^z \frac{\partial C}{\partial x}\bigg|_{x=0} dz \tag{43}$$

and

$$\dot{m}_o = \frac{G_\infty^o}{W\bar{u}_o \bar{C}^* \delta} = \sqrt{\left(\frac{4}{\pi}\right) z} \tag{44}$$

Substitution of the concentration profile from Eq. 40 into Eq. 43 yields the following relation for $\dot{m}$

$$\dot{m} = \alpha z - \sum_{n=1}^{\infty} \frac{A_n}{\lambda_n^{3/2}} (1 - e^{-\lambda_n^2 z}) \tag{45}$$

The enhancement factor, E, is then:

$$E = \frac{\dot{m}}{\dot{m}_o} = \frac{x^* \alpha z - \sum_{n=1}^{\infty} \frac{A_n}{\lambda_n^{3/4}} (1 - e^{-\lambda_n^2 z})}{\sqrt{\left(\frac{4}{\pi}\right) z}} \tag{46}$$

RESULTS

The coefficients A_n have been calculated from Eq. 39 by numerical methods; they are given in Table 1 for a range of α. The eigenvalues obtained from Eq. 34 are independent of the reaction parameter α. Our results for α = 0 agree exactly with those of Olbricht and Wild (1969), who have solved this problem for the case of no chemical reaction.

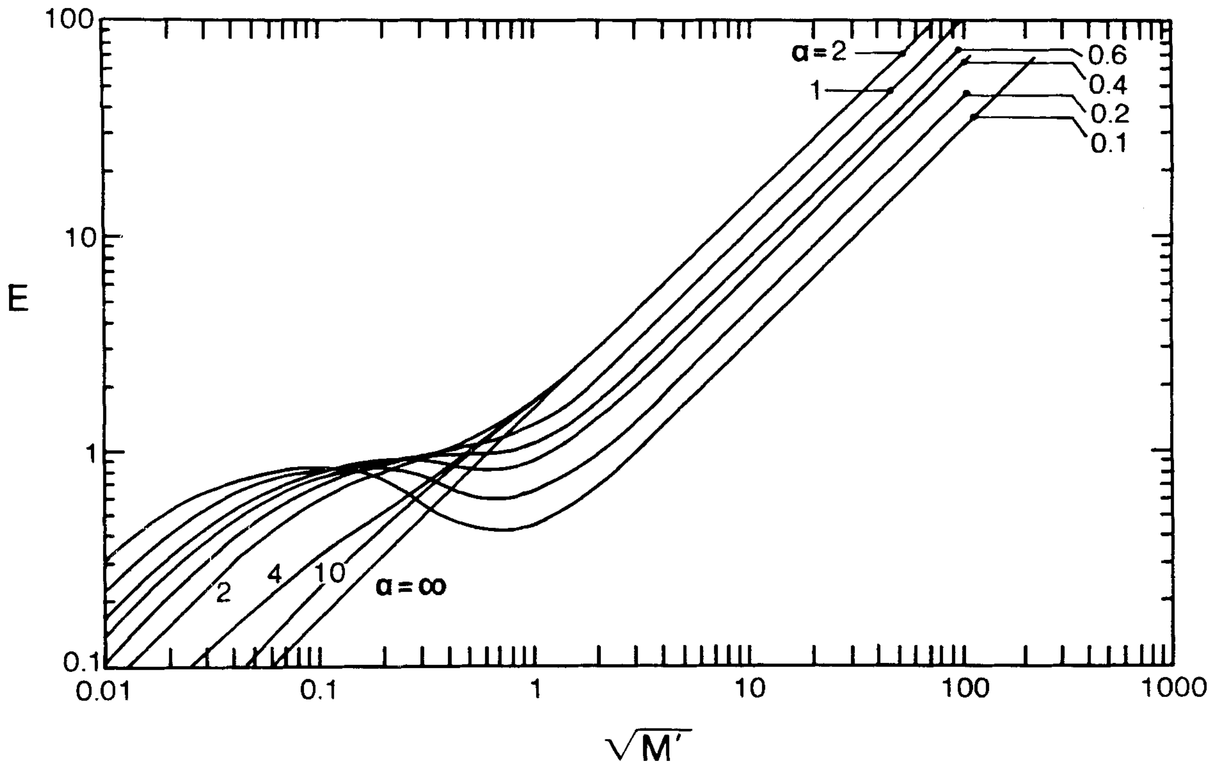

Figure 5. The enhancement of absorption, $\dot{m}/\dot{m}_o$, as a function of the modulus ($\sqrt{M'}$) with α as the parameter.

The concentration profiles obtained from Eq. 40 for $\alpha = 0.1$ and $\alpha = 0.6$ are shown in Figures 2 and 3, respectively. When the reaction parameter α increases, the concentration in the liquid phase decreases; this is also shown in our results. Figure 4 shows the development of the concentration profile at steady-state conditions for various values of α. At values of z greater than about 0.7, the summation term in Eq. 40 vanishes and the flow reaches steady-state conditions.

The enhancement factor, E, has been plotted as a function of the modulus $\sqrt{M'}$ (a form of Hatta number as used by Best and Hoerner) for various values of α; the results are reproduced in Figure 5. The modulus $\sqrt{M'}$ has been defined as

$$\sqrt{M'} = \sqrt{\left(\frac{\pi}{4}\right)az} \tag{47}$$

In Eq. 45, when z is greater than 2 the exponential term diminishes and $\dot{m}$ becomes a linear function of z. The reaction parameter α indicates the ratio of the rate of reaction to the rate of diffusion in relation to the thickness of the film. Thus a small value of α could be due to a very slow reaction, a very thin film, or a high rate of diffusion. It is seen that when α increases, its effect on the enhancement factor decreases. When $\sqrt{M'}$ is greater than 2, E has been successfully correlated to $\sqrt{M'}$ and α by the following simple relation:

$$(\sqrt{M'} > 2) \qquad E = \begin{cases} \sqrt{\alpha}\,\sqrt{M'} & \alpha \le 2 \\ \sqrt{2}\,\sqrt{M'} & \alpha > 2 \end{cases} \tag{48}$$

Equation 48 can predict values of E with an error of less than 2% and it is consistent with the results for steady-state conditions.

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NOTATION

A,B	= coefficients
C	= dimensionless concentration of dissolved gas in liquid phase, $= \bar{C}/\bar{C}^*$
$\bar{C}^*$	= dimensional concentration of dissolved gas at interface
D	= liquid phase diffusion coefficient
E	= enhancement factor, $= G/G_\infty{}^o$
F	= coefficient
G	= total gas absorption rate
$G_\infty{}^o$	= total gas absorption rate without reaction in an infinitely deep stagnant liquid
k	= zero-order reaction rate constant
M	= confluent hypergeometric function
$\sqrt{M'}$	= a form of Hatta number, $= \sqrt{(\pi/4)\alpha z}$
$\dot{m}$	= dimensionless absorption rate defined by Eq. 43
$\dot{m}_o$	= dimensionless absorption without reaction defined by Eq. 44
$\bar{r}$	= dimensional reaction rate
$\bar{u}$	= dimensional liquid velocity
$\bar{u}_o$	= dimensional liquid velocity at interface
W	= width of liquid film
X	= eigenfunction of Eq. 26
x	= dimensionless distance perpendicular to liquid surface, $= \bar{x}/\delta$
Y	= function defined by Eq. 31
y	= variable defined by Eq. 30
Z	= function defined in Eq. 24
z	= dimensionless axial distance, $= \bar{z}D/\bar{u}_o\delta^2$

Greek Letters

α = dimensionless reaction parameter, $= k\delta^2/D\bar{C}^*$
δ = liquid film thickness
λ_n = nth eigenvalue
ϕ = function defined by Eq. 15
ω = function defined by Eq. 15

Superscript

$-$ = dimensional quantities

Subscripts

h = homogeneous boundary conditions
p = particular solution
n = values corresponding to nth eigenvalue

LITERATURE CITED

Astarita, G., *Mass Transfer with Chemical Reaction*, Elsevier, Amsterdam (1967).

Astarita, G., and G. Marruci, "Gas Absorption with Zero-Order Chemical Reaction," *Ind. Eng. Chem. Fund.*, **2**, 4–7 (1963).

Best, R. J., and B. Hoerner, "Gas Absorption with First-Order Chemical Reaction in Laminar Falling Film—Calculation of Rates and Enhancement Factors," *Chem. Eng. Sci.*, **34**, 759 (1979).

Carnahan, B., H. A. Luther, and J. O. Wilkes, *Applied Numerical Methods*, Wiley, New York, 178 (1969).

Cooney, D. O., S. S. Kim, and E. J. Davis, "Analyses of Mass Transfer in Hemodialyzers for Laminar Blood Flow and Homogeneous Dialysate," *Chem. Eng. Sci.*, **29**, 1,731 (1974).

Olbricht, W. E., and J. D. Wild, "Diffusion from the Free Surface into a Liquid Film in Laminar Flow Over Defined Shapes," *Chem. Eng. Sci.*, **24**, 25 (1969).

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