Simultaneous Mass Transfer and Chemical Reaction in a Case of Time-Dependent Interfacial Area

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In recent years there have been a number of important theoretical studies (Beek and Kramers, 1962; Rose and Kintner, 1966; Angelo et al., 1966; Ruckenstein, 1968) on fluid-liquid mass transfer with a time dependent interfacial area reported in the literature. These studies considered no reaction in the liquid phase. This note extends these studies and presents the analytical results for the fluid-liquid mass transfer rates in the presence of a first order irreversible and an instantaneous second-order liquid phase reactions.

THEORY

First-Order Liquid Phase Reaction

When both fluids are Newtonian and isothermal and transport and reaction coefficients are constant, the governing mass balance equations for the fluid and the liquid phases for this case can be expressed as (Beek and Kramers, 1962; Angelo et al., 1966):

$$\frac{\partial C_i}{\partial t} - y\beta(t)\frac{\partial C_i}{\partial y} = D_i\frac{\partial^2 C_i}{\partial y^2} - R_i \qquad \begin{matrix} i = 1 \text{ fluid} \\ i = 2 \text{ liquid} \end{matrix} \tag{1}$$

where $R_1 = 0$; $R_2 = KC_2$

Equation (1) neglects axial convection. The quantity $\beta(t)$ can be related to time dependent interfacial area $A(t)$ as (Beek and Kramer, 1962)

$$\beta(t) = \frac{d \ln\left(\frac{dA}{dt}\right)}{dt} \tag{2}$$

or as (Angelo et al., 1966)

$$\beta(t) = \frac{d \ln A(t)}{dt} \tag{3}$$

When the diffusional resistances of both phases are important the boundary and initial conditions to Equation (1) are

$$C_1 = C_{10} \text{ and } C_2 = C_{20}\,; \quad t = 0 \tag{4}$$

$$C_1 = HC_2 \text{ and } D_1\frac{\partial C_1}{\partial y} = D_2\frac{\partial C_2}{\partial y}\,; \quad y = 0,\ t > 0 \tag{5}$$

$$C_1 \rightarrow C_{10}\,; \qquad y \rightarrow -\infty \tag{6}$$

$$C_2 \rightarrow C_{20}\,e^{-Kt}\,; \qquad y \rightarrow +\infty \tag{7}$$

An analytical solution to Equation (1) can be obtained by first introducing a variable $\tilde{U}$ such that $C_2 = \tilde{U}e^{-Kt}$ and then applying Duhamel theorem (Carslaw and Jaeger, 1959). The resulting equations can be solved in a straight forward manner using the method of Angelo et al. (1966). The final results* for C_i thus obtained are

$$C_i = e^{-(i-1)Kt}\frac{\partial}{\partial t}\int_0^t Z_i\,(\lambda, t-\lambda, y)\,d\lambda \quad i = 1, 2 \tag{8}$$

where

$$Z_i = A_i\int_0^{\xi_i} e^{-x^2dx + B_i} \tag{9}$$

$$\xi_i = \frac{y\,S(t)}{\sqrt{4D_i\int_0^t S^2(x)\,dx}} \tag{10}$$

The quantity $S(t) = A(t)$ if β is defined by Equation (3) and $S(t) = dA/dt$ if β is defined by Equation (2). The constants A_i and B_i are

$$A_1 = \frac{2}{\sqrt{\pi}}\left[\frac{C_{20}\,e^{-k\lambda} - C_{10}/H}{\frac{1}{H} + \sqrt{\frac{D_1}{D_2}}}\right],$$

$$B_1 = \left[\frac{C_{20}\,e^{-k\lambda} + C_{10}\sqrt{\frac{D_1}{D_2}}}{\frac{1}{H} + \sqrt{\frac{D_1}{D_2}}}\right]$$

$$A_2 = \frac{2}{\sqrt{\pi}}\left[\frac{C_{20} - C_{10}/He^{-k\lambda}}{1 + \frac{1}{H}\sqrt{\frac{D_2}{D_1}}}\right],$$

$$B_2 = \left[\frac{C_{10}\,e^{k\lambda} + C_{20}\sqrt{\frac{D_2}{D_1}}}{H + \sqrt{\frac{D_2}{D_1}}}\right] \tag{11}$$

The expression for mass transfer rate N can be obtained from Equations (8), (9), and (11) as

$$N = -D_1\frac{\partial C_1}{\partial y}\bigg|_{y=0} = -D_1\frac{\partial}{\partial t}\int_0^t \frac{2}{\sqrt{\pi}}\left[\frac{C_{20}\,e^{-k\lambda} - C_{10}/H}{\frac{1}{H} + \sqrt{\frac{D_1}{D_2}}}\right]\frac{S(t-\lambda)}{\sqrt{4D_1\int_0^{t-\lambda} S^2(x)\,dx}}\,d\lambda \tag{12}$$

The enhancement factor Φ for the present case can be defined as

$$\Phi = \frac{\int_0^t N(t)\,A(t)\,dt}{\int_0^t N^*(t)\,A(t)\,dt} \tag{13}$$

where $N^*(t)$ is the mass transfer rate in the absence of liquid phase chemical reaction. If the mass transfer resistance of the fluid phase is negligible and $C_{20} \rightarrow 0$, then using the above analysis one can show that

$\Phi =$

$$\frac{\int_0^t \left[e^{-k\tau} \frac{\partial}{\partial \tau} \int_0^\tau e^{k\lambda} \frac{S(\tau-\lambda)}{\sqrt{\int_0^{\tau-\lambda} S^2(x)\,dx}}\,d\lambda \right] A(\tau)\,d\tau}{\int_0^t \frac{S(\tau)}{\sqrt{\int_0^\tau S^2(x)\,dx}} A(\tau)\,d\tau} \tag{14}$$

ENHANCEMENT FACTOR FOR AN EXPANDING SURFACE

If $A = A_0 t^p$, where A_0 is some constant, then from Equations (2) and (10) $S(t) = A_0 p t^{p-1}$. Thus, from Equation (14)

$$\Phi = \frac{(p + 1/2)\sqrt{\pi}}{\theta^{p+1/2}} \int_0^\theta \left[\operatorname{erf}\sqrt{\tau} + \frac{e^{-\tau}}{\sqrt{\pi\tau}} \right] \tau^p\,d\tau \tag{15}$$

where $\theta = Kt$

For $p = 1$, 2, and 3 the above equation can be re-expressed as

$$\Phi = \frac{3}{2}\frac{\sqrt{\pi}}{\theta^{3/2}}\left[\frac{\theta^{3/2}}{2}\left(\sqrt{\theta}\operatorname{erf}\sqrt{\theta} + \frac{1}{\sqrt{\pi}}e^{-\theta}\right) - \frac{5}{8\sqrt{\pi}}\sqrt{\theta}\,e^{-\theta} + \frac{5}{16}\operatorname{erf}\sqrt{\theta}\right] \quad \text{for} \quad p = 1 \tag{16}$$

$$\Phi = \frac{5\sqrt{\pi}}{2\theta^{5/2}}\left[\frac{\theta^{5/2}}{3}\left(\sqrt{\theta}\operatorname{erf}\sqrt{\theta} + \frac{1}{\sqrt{\pi}}e^{-\theta}\right) - \frac{1}{6}\frac{\theta^{3/2}}{\sqrt{\pi}}e^{-\theta} - \frac{1}{4}\frac{\theta^{1/2}}{\sqrt{\pi}}e^{-\theta} + \frac{1}{8}\operatorname{erf}\sqrt{\theta}\right] \quad \text{for} \quad p = 2 \tag{17}$$

$$\Phi = \frac{7\sqrt{\pi}}{2\theta^{7/2}}\left[\frac{\theta^{7/2}}{4}\left(\sqrt{\theta}\operatorname{erf}\sqrt{\theta} + \frac{1}{\sqrt{\pi}}e^{-\theta}\right) - \frac{\theta^{5/2}e^{-\theta}}{8\sqrt{\pi}} - \frac{5\theta^{3/2}e^{-\theta}}{16\sqrt{\pi}} - \frac{15\theta^{1/2}e^{-\theta}}{32\sqrt{\pi}} + \frac{15}{64}\operatorname{erf}\sqrt{\theta}\right] \quad \text{for} \quad p = 3 \tag{18}$$

The results of Φ predicted from Equations (16) to (18) as a function of $\sqrt{M} = \sqrt{\frac{\pi}{4}\theta}$ are compared in Figure 1 with the ones obtained from well-known Higbie's model of constant surface area ($p = 0$). It is rather interesting that the effect of p on Φ versus $\sqrt{M}$ plot is qualitatively very similar to the similar effect of order of the reaction with respect to transferring species.

ENHANCEMENT FACTOR FOR LARGE OSCILLATING BUBBLE

For large oscillating bubbles, Angelo et al. (1962) have suggested the relationship $S(\tau) = A(\tau) = A(0)\ (1 + \delta \sin^2 \tau)$. For this $S(\tau)$, the plots of Φ versus $\sqrt{M}$ for $\delta = 0.2$ and 0.5 (Angelo et al., 1962) were obtained by numerical integration of Equation (14). These results are described in Figure 2. Interestingly, the results indicate that the enhancement factor for this case is a very mild function of an amplitude of oscillation δ.

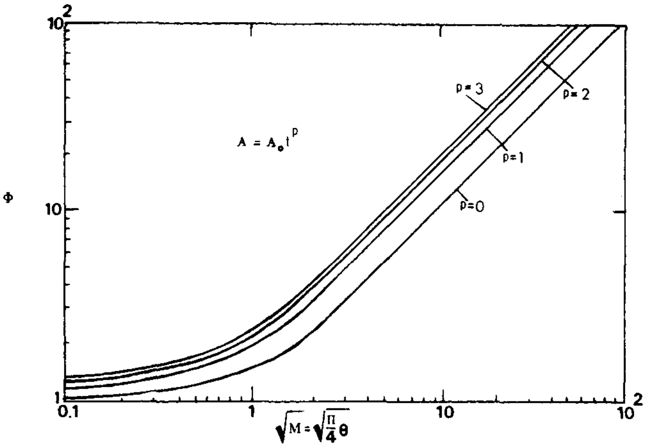

Fig. 1. Enhancement factors for an expanding surface, first-order reaction.

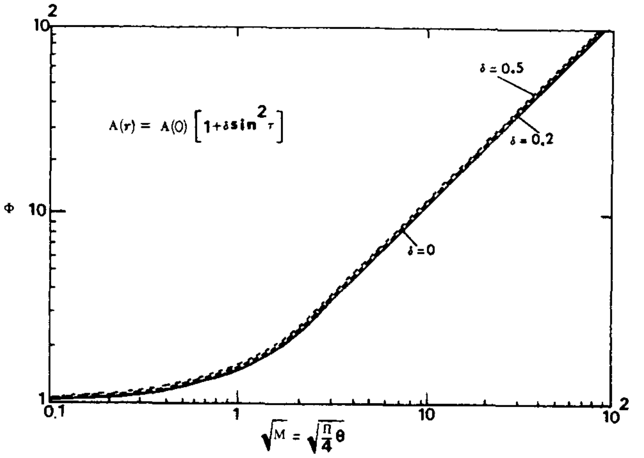

Fig. 2. Enhancement factors for a large oscillating bubble, first-order reaction.

Second-Order Instantaneous Reaction in the Liquid

The mass balance equation for species A in the fluid phase for this case is the same as one described earlier. The governing mass balance equations in the liquid phase are

$$D_{2A}\frac{\partial^2 C_{2A}}{\partial y^2} - y\,\beta(t)\frac{\partial C_{2A}}{\partial y} = \frac{\partial C_{2A}}{\partial t} \tag{19}$$

$$\text{for} \quad 0 < y < y'$$

$$D_{2B}\frac{\partial^2 C_{2B}}{\partial y^2} - y\,\beta(t)\frac{\partial C_{2B}}{\partial y} = \frac{\partial C_{2B}}{\partial t} \tag{20}$$

$$\text{for} \quad y' < y < \infty$$

These equations are subjected to the boundary and initial conditions (4) to (6) and the ones described by Sherwood and Pigford (1952). Following the above method of analysis, a solution to these equations can be shown to be

$$C_{1A} = A_1 + B_1 \operatorname{erf} \xi_{1A} \tag{21}$$

and

$$C_{2A} = A_2 + B_2 \operatorname{erf} \xi_{2A}, \quad 0 < \xi_{2A} < \xi'_{2A} \tag{22}$$

$$C_{2B} = A_2' + B_2' \operatorname{erf} \xi_{2B}, \quad \xi'_{2B} < \xi_{2B} < \infty \tag{23}$$

where

$$\xi_{2A} = y\,f_{2A}(t) = \frac{y\,S(t)}{\sqrt{4D_{2A}\int_0^t S^2(x)\,dx}} = \sqrt{\frac{D_{2A}}{D_{2B}}}\,\xi_{2B}$$

$$= \sqrt{\frac{D_{2A}}{D_{1A}}}\,\xi_{1A} = \frac{y}{y'}\,\xi'_{2A} = \frac{y}{y'}\sqrt{\frac{D_{2A}}{D_{2B}}}\,\xi'_{2B} \quad (24)$$

The constants in Equations (21) to (23) can be expressed as

$$A_1 = \frac{H\,C_{1A,0}\sqrt{\dfrac{D_{1A}}{D_{2A}}}\operatorname{erf}\xi'_{2A}}{1 + H\sqrt{\dfrac{D_{1A}}{D_{2A}}}\operatorname{erf}\xi'_{2A}},$$

$$B_1 = \frac{-C_{1A,0}}{1 + H\sqrt{\dfrac{D_{1A}}{D_{2A}}}\operatorname{erf}\xi'_{2A}}, \quad A_2' = \frac{-q\operatorname{erf}\xi'_{2B}}{\operatorname{erfc}\xi'_{2B}}$$

$$A_2 = \frac{C_{1A,0}\sqrt{\dfrac{D_{1A}}{D_{2A}}}\operatorname{erf}\xi'_{2A}}{1 + H\sqrt{\dfrac{D_{1A}}{D_{2A}}}\operatorname{erf}\xi'_{2A}},$$

$$B_2 = \frac{-C_{1A,0}\sqrt{\dfrac{D_{1A}}{D_{2A}}}}{1 + H\sqrt{\dfrac{D_{1A}}{D_{2A}}}\operatorname{erf}\xi'_{2A}}, \quad B_2' = \frac{q}{\operatorname{erfc}\xi'_{2B}} \quad (25)$$

The time dependence of location of reaction zone y' can be shown to be expressed as*

$$y' = 2\alpha_1\sqrt{\int_0^t S^2(x)\,dx}\Big/S(t) \quad (26)$$

where constant α_1 is obtained from the solution of the equation

$$\sqrt{D_{2A}}\,B_2\,e^{-(\alpha_1^2/D_{2A})} + \sqrt{D_{2B}}\,B_2'\,e^{-(\alpha_1^2/D_{2B})} = 0 \quad (27)$$

The mass transfer rate for this case is

$$N = -D_{2A}\,B_2\,f_{2A}(t) \quad (28)$$

and the enhancement factor Φ can be shown to be

$$\Phi = 1/\operatorname{erf}(\alpha_1/\sqrt{D_{2A}}) \quad (29)$$

a value independent of time-dependence of interfacial area.

NOTATION

C_i = concentration of transferring species in ith phase
D_i = diffusion coefficient of transferring species in ith phase
H = equilibrium dissolution constant
K = intrinsic reaction rate constant
q = initial concentration of species B in the liquid phase
t = time
y = distance normal to fluid-liquid interface

Subscripts

i	refers to phase $i = 1$ fluid; $i = 2$ liquid
A, B,	refers to the transferring species A and B respectively
0	refers to condition at time $t = 0$

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* Supplementary material has been deposited as Document No. 01928 with the National Auxiliary Publications Service (NAPS), c/o CCM Information Corp., 866 Third Ave., New York 10022 and may be obtained for \$2.00 microfiche and \$5.00 for photocopies.

Notes on Transfer in Turbulent Pipe Flow

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A recent paper by Hughmark (1971) proposes models for heat and mass transfer for the wall region and the core of turbulent pipe flow. The core model includes an empirical correlation for transfer by eddy diffusion that is a function of the Reynolds number. The data shown by Figure 6 of the paper can also be represented as a function of the friction factor by the equation

$$k^+_{EC} = 2\sqrt{f/2} \quad (1)$$

which represents the heat transfer, mass transfer, momentum relationship for the fully turbulent core region

$$\frac{h_{EC}}{\rho C_p} = k_{EC} = U\,f \quad (2)$$

It is interesting to observe that Equation (2) does not include molecular diffusion properties.

The wall region analysis includes a correlation for eddy diffusion transfer that is based upon the pipe solution mass transfer data of Harriott and Hamilton (1965). The Mizushino et al. (1971) analysis of wall region data indicates that the pipe solution method may give high mass transfer coefficients because of surface roughness associated with the dissolving pipe wall. The authors report mass transfer data with reduction of ferricyanide ions at a nickel cathode in the presence of a large excess of sodium and potassium hydroxide. Shaw and Hanratty (1964), and Hubbard and Lightfoot (1966), also report data for ferricyanide reduction. Lin et al. (1951) used a number