The method applied here has been used for the analysis of several other cases, namely mass transfer between a spherical drop and the continuous phase, mass transfer into a turbulent liquid (5), and mass transfer between a bubble and a pulsed liquid (6). In all these cases the convective-diffusion equation has form (4) and the similarity variable $\eta = y_1/[\delta(x_1, t)]$ enables it to be reduced to an ordinary differential equation for the concentration c and to a first-order partial-differential equation for $\delta = \delta(x_1, t)$.

NOTATION

c = concentration
c_0 = value of c_0 for $y_1 = 0$
D = diffusion coefficient
h = film thickness
k = wave number
R = curvature radius
t = time
u = x component of velocity
u_1 = x_1 component of velocity
v_1 = y_1 component of velocity
w = wave velocity
z = $x_1 - wt$
Z = function defined by Equation (12)
x, y = coordinates in a fixed system of reference; distance along the wall and distance to the wall in the case of a thin liquid film in wave motion
x_1 = coordinate along the interface
y_1 = distance to the interface
α = ratio of the wave amplitude to the average value of h
β = ratio of propagation velocity to the average velocity $\bar{u}$
δ = penetration depth by diffusion
Δ = $\equiv (\delta/\epsilon)^2$
$\bullet$ = arbitrary numerical constant
η = y_1/δ

Subscript and Superscript

o = the values of the quantities at $y_1 = 0$
$-$ = time and y average values

LITERATURE CITED

1. Higbie, Ralph, *Trans. Am. Inst. Chem. Engrs.*, 31, 365 (1935).
2. Angelo, J. R., E. N. Lightfoot, and D. W. Howard, *AIChE J.*, 12, 751 (1966).
3. Kapitza, P. L., *Zh. Eksperim i Teor. Fiz. SSSR*, 18, 3 (1948); *see also* V. G. Levich, "Physicochemical Hydrodynamics," pp. 386-689, Prentice-Hall, New York (1962).
4. Ruckenstein, Eli and C. P. Berbente, *Chem. Eng. Sci.* 20, 795 (1965).
5. Ruckenstein, Eli, *Intl. J. Heat Mass Transfer* in press.
6. ———, and Ovidiu Muntean (paper in preparation).

Film-Penetration Models for Mass Transfer with Chemical Reaction

JOEL LEE SMITH and JACK WINNICK

University of Missouri, Columbia, Missouri

The film-penetration model for mass transfer was developed by Toor and Marchello (6) on the assumption that the average thickness of the liquid element had a finite value, L. Toor and Marchello showed that the film (7), penetration (2), and surface-renewal (1) models were merely limiting conditions of their film-penetration model. Huang and Kuo (3) revised the film-penetration theory to include a first-order or pseudofirst-order chemical reaction. Two further applications of the film-penetration theory are presented here to describe mass transfer through a surface resistance with chemical reaction and mass transfer with chemical reaction in spherical drops.

MODEL I—MASS TRANSFER THROUGH A SURFACE RESISTANCE WITH CHEMICAL REACTION

The following model was postulated to describe the mass-transfer process across a place surface with a surface resistance by applying the film-penetration concept.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - KC \tag{1}$$

$$C = C_o; \quad x \gtrless L; \quad t > 0$$

$$C = C_o; \quad x \gtrless 0; \quad t = 0 \tag{2}$$

$$-D\left(\frac{\partial C}{\partial x}\right)_{x=0} = k_s (C_i - C); \; x = 0; \; t > 0 \tag{3}$$

Equation (3) is the surface-resistance condition which is used instead of surface equilibrium because it is nearer the actual situation encountered in mass transfer operations. The quantity $(C_i - C)$ is the departure from surface equilibrium due to the surface resistance.

The average rate of mass transfer over the entire surface is found by combining the rate for surfaces of age t with the age distribution function and by integrating over all ages:

$$R = \int_o^\infty \psi(t)\, \phi(t)\, dt \tag{4}$$

For this situation these functions are described as

Joel Lee Smith is with the Shell Chemical Company, Houston, Texas.

$$\psi(t) \equiv -D\left(\frac{\partial C}{\partial x}\right)_{x=0} \tag{5}$$

$$\phi(t) \equiv se^{-st} \tag{6}$$

When the transform of Equation (2) is taken, the solution to the resulting ordinary differential equation readily yields the desired result for the average rate:

$$R = \frac{s\,k_s\,G(1-F)\,(1+e^{-2GL}) - 2\,s\,G\,k_s(E-F)e^{-GL}}{(G+H) + (G-H)e^{-2GL}} \tag{7}$$

The complete solution is shown by Smith (5).

As in the case of Toor and Marchello's and Huang and Kuo's film-penetration models, it is possible to show the generality of this model by finding the limiting conditions: (1) as the thickness of the liquid element approaches infinity, the limiting condition must correspond to Danckwerts's surface-renewal theory; and (2) as the surface renewal rate approaches zero, the limiting condition must correspond to the film theory. These conditions are shown by Smith (5).

The Effects of Surface Resistance

The effect of surface resistance with no chemical reaction on the proposed model is investigated by means of the dimensionless group γ. Figure 1 shows the plots of the reduced mass transfer coefficients, $\frac{k_l'\,(\sqrt{Ds}+k_s)}{k_s\sqrt{Ds}}$ and $\frac{k_l'\,(D+k_sL)}{k_sD}$, versus γ at various values of surface-resistance coefficient, k_s, with $K = 0$. The curves shown are those for which the liquid-phase resistance is controlling, ($k_s = 1.0$ cm./sec.) [equivalent to that reported by Huang and Kuo (3)], and the two resistances are approximately equal ($k_s = 0.005$ cm./sec.). The third case, for which the surface resistance is controlling ($k_s = 0.0001$ cm./sec.), is a horizontal line with a value of unity for any γ value. It is not presented. In all cases the value used for $\sqrt{DS}$ or D/L was 0.005 cm./sec.

As may be seen from Figure 1, there is a zone of γ values for which there is considerable disagreement in mass transfer coefficients predicted by the simpler theories (film and surface renewal) and transfer coefficients predicted by the film-penetration concept. Figure 1 can be used as a qualitative guide as to which model may be used to calculate mass transfer coefficients.

Effect of Chemical Reaction on Mass Transfer Rates

The effect of chemical reaction on mass transfer rates is of considerable interest and may be discussed in terms of the ratio of the chemical mass transfer coefficient to the physical mass transfer coefficient, k_l/k_l'. Many of the models predict practically the same values for this ratio. For the model presented here the ratio of transfer coefficients is

$$\frac{k_l}{k_l'} = \frac{\sqrt{1+MU^2}\,(Z+1)}{Z(\sqrt{1+MU^2}) + \tanh\,(\sqrt{1+MU^2}\,\sqrt{1/\gamma})}$$

$$= \frac{\sqrt{1+MU^2}\left(\frac{N}{\sqrt{\gamma}}+1\right)}{\frac{N}{\sqrt{\gamma}}(\sqrt{1+MU^2}) + \coth\,(1/\sqrt{\gamma})\tanh(\sqrt{1+MU^2}\,\sqrt{1/\gamma})} \tag{8}$$

The ratio of k_l/k_l' for both the film theory and the surface-renewal theory can be found by combining the rate equations for mass transfer with and without a chemical reaction.

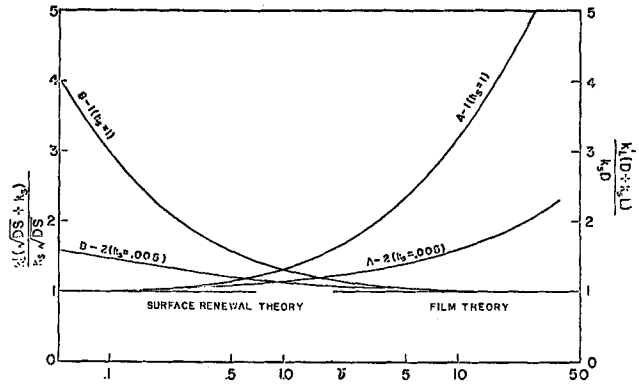

Fig. 1. Effect of dimensionless group γ.

Film theory:

$$\frac{k_l}{k_l'} = \frac{1}{\frac{N}{N+1} + \sqrt{1/M}\,\tanh\left(\sqrt{M}\left[\frac{1}{1+N}\right]\right)} \tag{9}$$

with

$$N \equiv \frac{R_s}{R_l'} = \frac{D/L}{k_s}$$

Surface renewal theory:

$$\frac{k_l}{k_l'} = \frac{\sqrt{1+M\left[\frac{1}{Z+1}\right]^2}\,(1+1/Z)}{\sqrt{1+M\left[\frac{1}{Z+1}\right]^2} + \frac{1}{Z}} \tag{10}$$

with

$$Z \equiv \frac{R_s}{R_l''} = \frac{\sqrt{Ds}}{k_s}$$

To test the sensitivity of Equation (8), values of k_l/k_l' were found for the film-penetration model, the film model, and the surface-renewal model at various values of M, Z, (or N), and γ. However, since the surface-renewal model contains the dimensionless parameter, Z, and the film model contains N, the values of which differ by the square root of γ, the ratios of mass transfer coefficients were compared only at $\gamma = 1$.

The ratios of mass transfer coefficients were compared at M values from 0.1 to 2,500 and at a Z value of unity. This shows the variation of k_l/k_l' with M for the situation of the liquid film and interfacial resistances equal. For M values below 0.1 and above 50, all three theories predict the same values for the effect of chemical reaction on mass transfer. For M values lying between 0.1 and 50, the maximum deviation is 1.7% occurring at $M = 5.0$. All three models predict a limiting value of 2 at high M values for the rate of mass transfer coefficients (at $Z = 1$); whereas the limit of this ratio is equal to the square root of M for Z very small.

Two other conditions of resistances were examined: (1) liquid-film resistance controlling ($k_s = \infty$) and (2) interfacial resistance controlling ($k_s = 0$). The former case was investigated by finding the limit of Equation (8) as $Z \rightarrow 0$. The resulting expression was identical to that reported by Huang and Kuo (3). The latter case was ex-

amined by finding the limit of Equations (8) to (10) as Z (or N) approaches ∞. The limit, in all three equations, for any value of M was equal to 1. In other words, the chemical mass transfer coefficient is equal to the physical mass transfer coefficient since both depend only on the coefficient of surface resistance. For any k_s, the curve from the film-penetration model lies between the curves of the simpler models.

MODEL II—MASS TRANSFER WITH CHEMICAL REACTION IN SPHERICAL DROPS

The most difficult problem in developing a theoretical model which will allow the prediction of mass transfer coefficients into a drop is the unknown internal-circulation pattern. Some success might be achieved if the exact circulation pattern can be ignored and only its effect on the volume near the surface is considered. The model presented here is an attempt to apply the film-penetration concept to drops which are assumed to be spherical over a time-averaged period. Mass is assumed to penetrate into the outer region of the drop, which is composed of small fluid elements. These fluid elements in the outer shell of the drop are assumed to be constantly replaced by the circulation pattern inside the drop caused by the movement of the drop. The lifetime of each element is assumed to be independent of its age. Zero resistance in the continuous phase is assumed.

The model can be described by

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) - KC; \qquad (a-L) \leq r \leq a \quad (11)$$

$$C = C_i; \qquad r = a; \qquad t > 0$$
$$C = 0; \qquad r \leq (a-L); \qquad t > 0$$
$$C = 0; \qquad r \leq a; \qquad t = 0$$

with the mass transfer rate found from Equation (4) with

$$\psi(t) = D\left(\frac{\partial C}{\partial r}\right)_{r=a} \qquad (12)$$

The solution to Equations (11) and (12) yields

$$R = \frac{DC_i}{a}\left[\frac{aG(1+e^{-2GL})}{(1-e^{-2GL})} - 1\right] \qquad (13)$$

Rearranging and solving for the physical mass transfer coefficient ($K = 0$) gives

$$\frac{k_l' a}{D} = \frac{1}{W\sqrt{\gamma}}\left(\coth\frac{1}{\sqrt{\gamma}}\right) - 1 \qquad (14)$$

Equation (14) is in the form of a Sherwood number in terms of the dimensionless groups γ and W. The group γ, defined as D/sL^2, is the ratio of turbulent to stagnant mass transfer resistances.

In the limit of $s = 0$, or no surface renewal, Equation (14) becomes identical to the solution for a hollow, stagnant sphere with a radius of (a) and $(a - L)$.

$$k_l' = \frac{D(a-L)}{aL} \qquad (15)$$

In the limit of very high renewal rates, Equation (14) becomes

$$k_l' = \sqrt{Ds} \qquad (16)$$

This result is obtained for any surface-renewal model if the renewal rate becomes high enough to prohibit complete penetration by the solute of any of the surface elements.

Skelland and Wellek found experimentally (*4*) that their mass transfer coefficient varied with the diffusivity of the solute raised to the 0.787 power. This was within the range predicted by Equation (14) and indicated an average value of γ of about 2.

Effect of Chemical Reaction

Important insights may be obtained by comparing the results of a mass transfer model with and without a chemical reaction. For the present case, this ratio can be defined as

$$\frac{k_l}{k_l'} = \frac{\sqrt{1+MV^2}}{V}\coth\sqrt{\frac{1+MV^2}{\gamma}} - \frac{W\sqrt{\gamma}}{V} \qquad (17)$$

In the limit of low renewal rates, Equation (17) becomes

$$\frac{k_l}{k_l'} = \sqrt{M}\coth\left[\sqrt{M}(1-W)\right] - \frac{W}{(1-W)} \qquad (18)$$

and for high renewal rates

$$\frac{k_l}{k_l'} = \sqrt{1+M} \qquad (19)$$

The effect of γ on the ratio of mass transfer coefficients is small unless the element thickness, L, is nearly half the drop radius. This situation, however, would not seem to be physically possible.

ACKNOWLEDGMENT

The authors wish to acknowledge the aid of the University of Missouri Engineering Experiment Station.

NOTATION

a = drop radius, cm.
C = concentration of diffusing species, g.-moles/liter
C_i = equilibrium concentration of diffusing species, g.-moles/liter
C_o = concentration of diffusing species in bulk liquid, g.-moles/liter
D = molecular diffusivity, sq.cm./sec.
E = C_o/s
F = $C_o/(K+s)$
G = $\sqrt{\frac{K+s}{D}}$
H = k_s/D
I = C_i/s
K = reaction rate constant, sec.$^{-1}$
k_l = chemical mass transfer coefficient, cm./sec.
k_l' = physical mass transfer coefficient, cm./sec.
k_s = surface resistance coefficient, cm./sec.
L = average thickness of liquid element, cm.
M = $KD/(k_l')^2$
N = $Z\sqrt{\gamma}$, (film penetration)
N = D/Lk_s, (film)
r = radial distance, cm.
R = average mass transfer rate, g.-moles/sq.cm. sec.
R_l = resistance in liquid element (film penetration), sec./cm.
R_l' = resistance in liquid element (film), sec./cm.
R_l'' = resistance in liquid element (surface renewal), sec./cm.
s = surface renewal rate, sec.$^{-1}$
t = time, sec.
U = $\coth(1/\sqrt{\gamma})/(Z+1)$
V = $\coth(1/\sqrt{\gamma}) - W\sqrt{\gamma}$
W = L/a
x = linear distance, cm.
Z = ratio of surface to liquid film resistances

Greek Letters

γ = D/sL^2
$\phi(t)$ = element-age distribution function
$\psi(t)$ = mass transfer rate for an element of age t, g.-moles/sq.cm.-sec.

LITERATURE CITED

1. Danckwerts, P. V., *Ind. Eng. Chem.*, **43**, 1460 (1951).
2. Higbie, R., *Trans. Am. Inst. Chem. Engrs.*, **31**, 365 (1935).
3. Huang, C. J., and C. H. Kuo, *AIChE J.*, **9**, 161 (1963).
4. Skelland, A. H. P., and R. M. Wellek, *AIChE J.*, **10**, 491 (1964).
5. Smith, J. L., M. S. thesis, Univ. Missouri, Columbia, (1966).
6. Toor, H. L., and J. M. Marchello, *AIChE J.*, **4**, 97 (1958).
7. Whitman, W. G., *Chem. Met. Eng.*, **29**, No. 4, 166 (1923).