Mass Transfer Inside Liquid Droplets and Gas Bubbles Accompanied by a Second-Order Chemical Reaction

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Mass transfer accompanied by chemical reaction inside falling or rising fluid spheres is of interest as a means of using the reaction to enhance the rate of mass transfer or as a means of bringing together two reactants initially in mutually insoluble phases. This work considers a second-order, irreversible chemical reaction within the dispersed phase, which is related by the following stoichiometric equation:

$$\mathrm{a} + z\ \mathbf{b} \rightarrow \text{products} \tag{1}$$

The **a** reactant diffuses into the sphere from the continuous phase, and the **b** reactant, which is initially within the dispersed phase, is insoluble in the continuous phase. In order to focus attention on mass transfer and chemical reaction within the dispersed phase, it is assumed that there is no resistance to mass transfer in the continuous phase.

The most useful quantitative means of presenting results for mass transfer with chemical reaction is through the use of the variable, the total mass transferred $\overline{A}_{mt}$, which is defined as follows:

$$\overline{A}_{mt} = (\overline{C}_a + C_{ar})/C_{as} \tag{2}$$

Previous investigators (*9, 10, 12, 13*) have presented their results in terms of an enhancement factor ϕ.

$$\phi = \frac{\overline{A}_{mt}\ (\text{for } k_R \neq 0)}{\overline{A}_{mt}\ (\text{for } k_R = 0)} \tag{3}$$

The results of these investigators are presented in the next section.

EXISTING MODELS

It was possible in this work to adapt certain existing theories to the problem of mass transfer with chemical reaction inside fluid spheres, even though the existing theories are based on much simpler physical models. The existing models are based on the following simultaneous, differential solute balance equations:

$$\delta \frac{\partial C_a}{\partial t} = D_a \frac{\partial^2 C_a}{\partial h^2} - k_2 C_a C_b \tag{4a}$$

$$\delta \frac{\partial C_b}{\partial t} = D_b \frac{\partial^2 C_b}{\partial h^2} - z k_2 C_a C_b \tag{4b}$$

and the boundary conditions

$$C_a(0,h) = 0 \qquad C_b(0,h) = C_{b0}$$

$$C_a(t,0) = C_{as} \qquad \frac{\partial C_b}{\partial h}(t,0) = 0 \tag{5}$$

$$C_a(t,H) = 0 \qquad C_b(t,H) = C_{b0}$$

For the film theory, $\delta = 0$ and H is the film thickness. For the penetration theory, $\delta = 1$ and H approaches infinity.

Van Krevelen and Hoftijzer (*15*) found an approximate solution for film theory mass transfer accompanied by a second-order reaction. Their relation for the enhancement factor ϕ is

$$\phi = \frac{Y}{\tanh Y}\left\{1 - \frac{\dfrac{Y}{\sinh Y \cosh Y}}{\dfrac{k_R(\pi\tau)}{6} + \dfrac{Y}{\tanh Y}}\right\} \tag{6}$$

where

$$Y = \sqrt{\pi\ k_{R\tau}\ (1 + R_c - \phi R_c)/4} \tag{7}$$

Equations (6) and (7) were obtained by approximating film theory mass transfer without reaction by the penetration theory relation. This type of approximation was suggested by Astarita (*1*).

Perry and Pigford (*13*) numerically solved the simultaneous partial differential equations for the penetration theory, mass transfer rate expression accompanied by a reversible second-order reaction. This included, as a special case, mass transfer with an irreversible second-order chemical reaction. Brian et al. (*2*) later resolved the penetration model for irreversible chemical reaction and presented results for a greater range of parameters. Finally, Pearson (*12*) resolved the differential equations numerically and supplemented his work with analytical solutions for asymptotic cases in order to present results for the complete range of independent variables.

Kishinevskii (9) obtained an approximate solution for the penetration theory approach with a second-order reaction. Later Kishinevskii and Kornienko (*10*) empirically corrected this analytical solution to fit the solution of Brian et al (*2*). Their corrected expression for the enhancement factor is

$$\phi = 1 + \frac{W\,[1 - f(0.85\sqrt{W^2 R_c + W})]}{R_c W + \exp(-0.35\,W R_c)} \tag{8}$$

where the function f is defined by

$$f(x) = \frac{\exp(-x^2)}{x}\int_0^x \exp(x')^2\,dx' \tag{9}$$

and

$$W = \frac{\pi\ k_{R\tau}}{4} \tag{10}$$

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The total mass transferred $\overline{A}_{mt}$ can be found from either Equation (6) or (8) by the following relation:

$$\overline{A}_{mt} = 6\phi \sqrt{\frac{\tau}{\pi}} \qquad (11)$$

Both the film theory and the penetration theory assume that the **b** reactant is always present at some distance H away from the interface. This is not true at large contact times inside a sphere surrounded by a continuous phase. Thus it becomes necessary to use a physical model which can account for the complete depletion of the **b** reactant. The development of such a model is given in the next section.

THEORETICAL DEVELOPMENT

Johns and Beckmann (*8*) recently presented a solution for unsteady state mass transfer without chemical reaction inside a circulating fluid sphere using the equation of continuity and the Hadamard (*6*) stream functions. The assumptions introduced in their development which are used in this work are summarized as follows:

All solutions are dilute so that the flow and diffusion equations are uncoupled.
The dispersed phase is a viscous sphere in linear or creeping motion.
The continuous phase resistance to solute diffusion is negligible.

In addition, we assume in this work that the heat of reaction is low enough so that heat effects do not cause variations in any of the physical properties of the solutions.

The velocity components which follow from the Hadamard derivation are

$$V_r = -\frac{V_t}{2}\,\frac{\mu_c}{\mu_c+\mu_d}\,(1-R^2)\,\cos\theta \qquad (12)$$

$$V_\theta = \frac{V_t}{2}\,\frac{\mu_c}{\mu_c+\mu_d}\,(1-2R^2)\,\sin\theta \qquad (13)$$

The streamlines are shown in Figure 1. Strictly speaking, Equations (12) and (13) are valid only for Reynolds numbers less than 1; however, Horton, Fritsch, and Kintner (*7*) measured velocity profiles within liquid droplets and found that their results compared favorably with the Hadamard theory relations for Reynolds numbers as high as 19. There is evidence that the Hadamard velocity profile is valid at least qualitatively for much higher Reynolds numbers for liquid droplets (*14*).

Substituting the expressions for the velocity components into the equations of continuity for components **a** and **b** inside the dispersed phase and introducing certain dimensionless terms, one obtains the following relations describing dispersed phase mass transfer with a second-order chemical reaction:

$$\frac{\partial A}{\partial \tau} = \frac{\partial^2 A}{\partial R^2} + \frac{2}{R}\frac{\partial A}{\partial R} + \frac{1}{R^2}\frac{\partial^2 A}{\partial \theta^2} + \frac{\cot\theta}{R^2}\frac{\partial A}{\partial \theta} + N_{Pe}\left[(1-R^2)\cos\theta\frac{\partial A}{\partial R} - \frac{(1-2R^2)}{R}\sin\theta\frac{\partial A}{\partial \theta}\right] - k_R\,AB \qquad (14a)$$

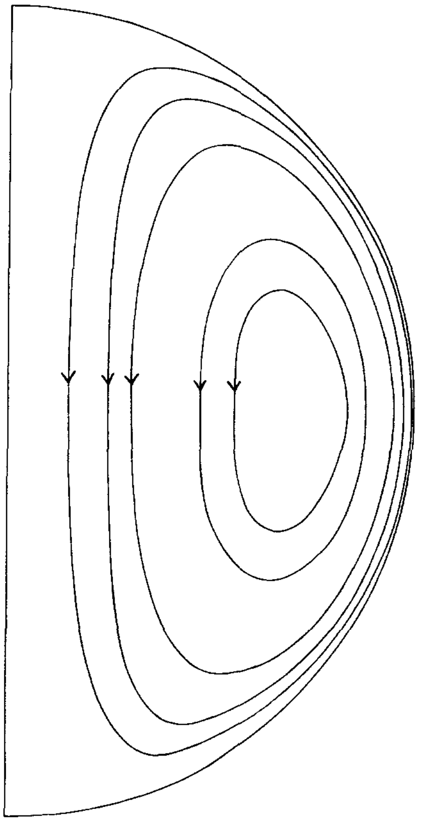

Fig. 1. Hadamard streamlines.

and

$$\frac{\partial B}{\partial \tau} = R_D\left[\frac{\partial^2 B}{\partial R^2} + \frac{2}{R}\frac{\partial B}{\partial R} + \frac{1}{R^2}\frac{\partial^2 B}{\partial \theta^2} + \frac{\cot\theta}{R^2}\frac{\partial B}{\partial \theta}\right] + N_{Pe}\left[(1-R^2)\cos\theta\frac{\partial B}{\partial R} - \frac{(1-2R^2)}{R}\sin\theta\frac{\partial B}{\partial \theta}\right] - R_c\,k_R\,AB \qquad (15a)$$

with the boundary conditions

$$A(0,R,\theta) = 0 \quad (14b) \qquad B(0,R,\theta) = 1 \quad (15b)$$

$$\frac{\partial A}{\partial R}(\tau,0,\theta) = 0 \quad (14c) \qquad \frac{\partial B}{\partial R}(\tau,0,\theta) = 0 \quad (15c)$$

$$A(\tau,1,\theta) = 1 \quad (14d) \qquad \frac{\partial B}{\partial R}(\tau,1,\theta) = 0 \quad (15d)$$

$$\frac{\partial A}{\partial \theta}(\tau,R,0) = 0 \quad (14e) \qquad \frac{\partial B}{\partial \theta}(\tau,R,0) = 0 \quad (15e)$$

$$\frac{\partial A}{\partial \theta}(\tau,R,\pi) = 0 \quad (14f) \qquad \frac{\partial B}{\partial \theta}(\tau,R,\pi) = 0 \quad (15f)$$

where the dimensionless terms are

$$A = C_a/C_{as}$$

$$B = C_b/C_{b0}$$

$$R = r/a$$

$$\tau = \frac{D_a t}{a^2}$$

$$N_{Pe} = \frac{a\,V_t}{2\,D_a}\,\frac{\mu_c}{\mu_d+\mu_c}$$

$$k_R = \frac{k_2\,a^2\,C_{b0}}{D_a}$$

$$R_D = \frac{D_b}{D_a}$$

$$R_c = \frac{zC_{as}}{C_{b0}}$$

Equations (14) and (15) were solved by an explicit finite-difference method. Employing the DuFort and Frankel (5) substitution, we obtain the following for the a component:

$$\begin{aligned}
&\left[\frac{1}{2} + S + \frac{P}{R_i^2} + \frac{k_R}{2} B_{i,j,k}\right] A_{i,j,k+1} \\
&= \left[S + \frac{2S_2}{R_i} + N_{Pe}\,(1 - R_i^2)(\cos\theta_j)S_2\right] A_{i+1,j,k} \\
&+ \left[S - \frac{2S_2}{R_i} - N_{Pe}\,(1 - R_i^2)(\cos\theta_j)S_2\right] A_{i-1,j,k} \\
&+ \left[\frac{P}{R_i^2} + \frac{(\cot\theta_j)P_2}{R_i^2} + N_{Pe}\frac{(2R_i^2 - 1)}{R_i}(\sin\theta_j)P_2\right] A_{i,j+1,k} \qquad (16) \\
&+ \left[\frac{P}{R_i^2} - \frac{(\cot\theta_j)P_2}{R_i^2} - N_{Pe}\frac{(2R_i^2 - 1)}{R_i}(\sin\theta_j)P_2\right] A_{i,j-1,k} \\
&+ \left[\frac{1}{2} - S - \frac{P}{R_i^2} - \frac{k_R}{2} B_{i,j,k}\right] A_{i,j,k-1}
\end{aligned}$$

and for component **b**:

$$\begin{aligned}
&\left[\frac{1}{2} + R_D S + \frac{R_D P}{R_i^2} + \frac{R_c k_R}{2} A_{i,j,k}\right] B_{i,j,k+1} \\
&= \left[R_D S + \frac{2R_D S_2}{R_i} + N_{Pe}(1 - R_i^2)(\cos\theta_j)S_2\right] B_{i+1,j,k} \\
&+ \left[R_D S - \frac{2R_D S_2}{R_i} - N_{Pe}(1 - R_i^2)(\cos\theta_j)S_2\right] B_{i-1,j,k} \qquad (17) \\
&+ \left[\frac{(2R_i^2 - 1)}{R_i}(\sin\theta_j)P_2 N_{Pe} + \frac{R_D P}{R_i^2} + R_D\frac{(\cot\theta_j)P_2}{R_i^2}\right] B_{i,j+1,k} \\
&+ \left[\frac{R_D P}{R_i^2} - R_D\frac{(\cot\theta_j)P_2}{R_i^2} - N_{Pe}\frac{(2R_i^2 - 1)}{R_i}(\sin\theta_j)P_2\right] B_{i,j-1,k} \\
&+ \left[\frac{1}{2} - R_D S - \frac{R_D P}{R_i^2} - \frac{R_c k_R}{2} A_{i,j,k}\right] B_{i,j,k-1}
\end{aligned}$$

Applying the boundary conditions at the surface of the dispersed phase, one obtains the following:

$$A_{n,j,k+1} = 1 \qquad (18)$$

$$\begin{aligned}
&[1 + 2R_D S + 2R_D P + R_c k_R \Delta\tau]\, B_{n,j,k+1} \\
&= [1 - 2R_D S - 2R_D P - R_c k_R \Delta\tau] B_{n,j,k-1} + 4R_D S B_{n-1,j,k} \\
&+ [2\,R_D P + R_D \cot\theta_j\, P_2 + N_{Pe} \sin\theta_j\, P_2] B_{n,j+1,k} \qquad (19) \\
&+ [2\,R_D P - R_D \cot\theta_j\, P_2 - N_{Pe} \sin\theta_j\, P_2] B_{n,j-1,k}
\end{aligned}$$

At the center of the dispersed phase all angular dependence of concentration vanishes. By using L'Hospital's method to find the limit of terms which become indeterminant in the differential equation and then making the finite-difference substitutions, one obtains the following finite-difference equations:

$$\begin{aligned}
&A_{0,j,k+1}\,[1 + 6S + k_R \Delta\tau B_{0,j,k}] \\
&= A_{0,j,k-1}\,[1 - 6S - k_R \Delta\tau B_{0,j,k}] + 12S\; A_{1,j,k} \qquad (20)
\end{aligned}$$

$$\begin{aligned}
&B_{0,j,k+1}\,[1 + 6R_D S + R_c k_R \Delta\tau A_{0,j,k}] \\
&= B_{0,j,k-1}\,[1 - 6R_D S - R_c k_R \Delta\tau A_{0,j,k}] + 12R_D S\; B_{1,j,k} \qquad (21)
\end{aligned}$$

Again applying L'Hospital's rule and the boundary conditions (14*e*), (14*f*), (15*e*), and (15*f*) to Equations (14*a*) and (15*a*), one obtains the following finite-difference equations at the angular boundaries:

$$\begin{aligned}
&\left[1 + 2S + \frac{4P}{R_i^2} + k_R \Delta\tau B_{i,j,k}\right] A_{i,j,k+1} \\
&= \left[1 - 2S - \frac{4P}{R_i^2} - k_R \Delta\tau B_{i,j,k}\right] A_{i,j,k-1} \\
&+ \left[2S + \frac{4S_2}{R_i} \pm 2N_{Pe}(1 - R_i^2)S_2\right] A_{i+1,j,k} \\
&+ \left[2S - \frac{4S_2}{R_i} \mp 2N_{Pe}(1 - R_i^2)S_2\right] A_{i-1,j,k} \\
&+ \frac{8P}{R_i^2} A_{i,j\pm1,k} \qquad (22)
\end{aligned}$$

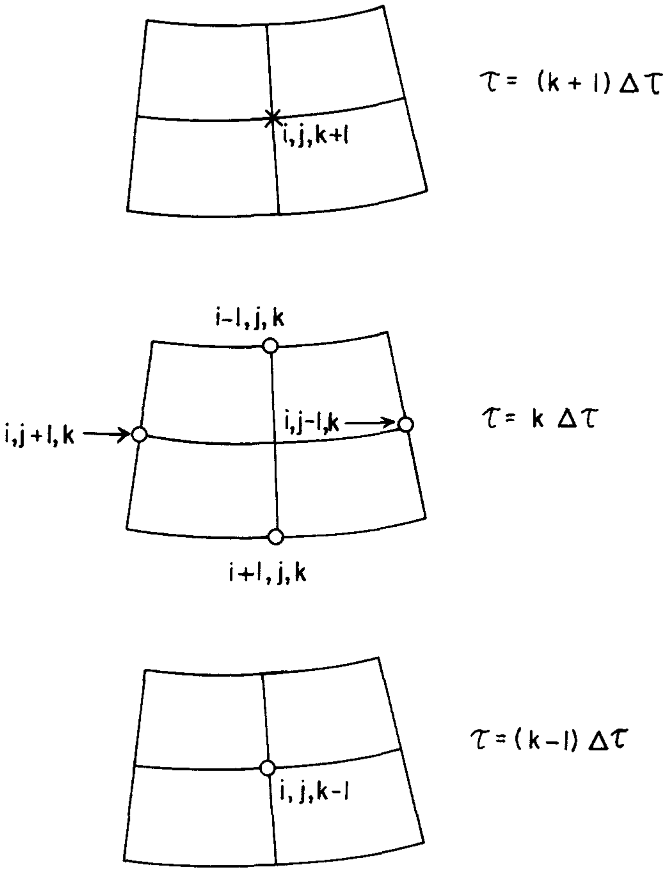

Fig. 2. Calculation scheme for the numerical solution of the partial differential equations.

Table 1. The Dependent Variables Studied in Dimensionless Form

Symbol	Variable	Method of calculation*
$\overline{A}$	Volume averaged concentration of **a**	$=\frac{1}{V}\int_0^V AdV'$
$\overline{B}$	Volume averaged concentration of **b**	$=\frac{1}{V}\int_0^V BdV'$
$\overline{A}_{mt}$	Total mass of **a** transferred	$=A+(1-\overline{B})/R_c=\frac{3}{2S_0}\int^{\tau}\int_0^{S_0}\left.\frac{\partial A}{\partial R}\right\|_{R=1} dS_0'd\tau'$
		$=\frac{3}{2}\int_0^{\tau} Nd\tau'$
N	Flux of **a**	$=\frac{2}{3}\frac{d\overline{A}_{mt}}{d\tau}$
$\overline{N}$	Time average flux of **a**	$=\frac{2}{3}\frac{\overline{A}_{mt}}{\tau}$
N_{Sh}	Sherwood number	$=N/(1-\overline{A})$
$\overline{N}_{Sh}$	Time average Sherwood number	$=\frac{1}{\tau}\int_0^{\tau} N_{Sh}d\tau'$
ϕ	Enhancement factor	$=\frac{\overline{A}_{mt}\text{ (for }k_R\neq 0)}{A_{mt}\text{ (for }k_R=0)}=\frac{\overline{N}\text{ (for }k_R\neq 0)}{\overline{N}\text{ (for }k_R=0)}$

* $\overline{A}_{mt}$ was in general calculated by the first method indicated. See Appendix A for the derivation of this equation.

$$\left[1+2R_DS+\frac{4R_DP}{R_i^2}+R_c\,k_R\Delta\tau A_{i,j,k}\right]B_{i,j,k+1}$$
$$=\left[1-2R_DS-\frac{4R_DP}{R_i^2}-R_c\,k_R\Delta\tau A_{i,j,k}\right]B_{i,j,k-1}$$
$$+\left[2R_DS+2S_2\left\{\frac{2R_D}{R_i}\pm N_{Pe}(1-R_i^2)\right\}\right]B_{i+1,j,k}$$
$$+\left[2R_DS-2S_2\left\{\frac{2R_D}{R_i}\pm N_{Pe}(1-R_i^2)\right\}\right]B_{i-1,j,k}$$
$$+\frac{8R_DP}{R_i^2}B_{i,j\pm 1,k} \quad (23)$$

where the top sign in the above equations is for θ equal to zero ($j = 0$), and the bottom sign is for θ equal to π($j = m$). The complete details for the development of these finite-difference equations are given elsewhere (*4*).

The calculation scheme for solving the finite-difference equations is briefly indicated in Figure 2. The grid points indicated by circles were used to calculate the point at a future time step. The future time step is indicated by a cross.

For most computer solutions of the finite-difference equations, the increments used were $\Delta\tau = 2(10^{-4})$, $\Delta R = 1/40$, and $\Delta\theta = \pi/31$. However, when the reaction number exceeded 160, the concentration gradients became so large that it was necessary to reduce the radial increment to 1/80 and the time increment to 10^{-4}, leaving the angular increment as before. To perform calculations for Peclet numbers as high as 500, the angular and radial increments were kept as originally stated, and the dimensionless time increment was reduced to 2×10^{-5}. To check the accuracy of the numerical solution, the increments were reduced until further reduction did not affect the concentration profile.

The finite-difference substitutions used to solve Equations (14) and (15) involve the central difference approximation for the time derivative. This is more accurate than the forward difference approximation used in most explicit finite-difference equations. The use of the central difference approximation allowed the use of larger time increments than would have been possible with other explicit methods.

DISCUSSION AND RESULTS

The concentration profiles for reactants **a** and **b** depend on four dimensionless parameters (k_R, R_D, R_c, and N_{Pe}) in addition to the dimensionless time, radius, and angle. The dependent variables calculated from the concentration profiles are shown in Table 1. All eight of the dependent variables shown in Table 1 were calculated for the complete range of dimensionless parameters and for dimensionless times encountered in both liquid extractions and gas absorptions. See Table 2 for the range of parameters used.

Table 2*a*. Values of Dependent Variables Studied

(all possible combinations)

R_D	1				
N_{Pe}	0	40	100		
R_c	0	0.2	1	∞	
k_R	0	40	160	640	∞

Table 2*b*. Special Combinations of Variables Studied

Special study number	1	2	3	4	5	6
R_D	5	0.2	5	0.2	0	∞
N_{Pe}	100	100	0	0	0	0
R_c	0.2	0.2	0.2	0.2	0.2	0.2
k_R	640	640	640	640	640	640

TABLE 2c. A SPECIAL STUDY OF HIGH PECLET NUMBERS

For $R_D = 1$, $R_c = 0.2$, $k_R = 40$, and $N_{Pe} = 150$, 200, 300, 400, 500

Table 1 defines the instantaneous flux of a both in terms of the radial derivative of the concentration at the surface and as the time derivative of the total mass transferred. As an internal check of the accuracy of the program, both methods were used to calculate the flux. The deviation between the two calculated fluxes did not exceed 2%.

The most important dependent variable for use in comparing theoretical results with experimental data or for use in designing reactor-contactors is the total mass transferred $\overline{A}_{mt}$. The total mass transferred is the moles of component a present in the sphere (in the reacted and unreacted states) divided by the product of the volume of the sphere and the surface concentration of component a. Figures 4 through 7 show representative curves of $\overline{A}_{mt}$ versus dimensionless time for various parametric values. Tabular values for $\overline{A}_{mt}$ and the seven other dependent variables given in Table 1 are deposited elsewhere for the complete range of independent variables.*

Figure 3 shows the effect of reaction number on the total mass transferred. When the reaction number is zero, the solution reduces to mass transfer without reaction as presented by Johns and Beckmann (*8*). This reference solution was used as a check for the program written for this article.

For an infinitely fast reaction ($k_R \to \infty$) and a diffusivity ratio of 1, the expression for the enhancement factor developed by Brunson and Wellek (*3*) and Toor (*20*) applies. Thus the total mass transferred to the dispersed phase when the reaction is instantaneous is equal to the product of the mass transferred without reaction and ($1 + 1/R_c$). The relation developed by the above authors was checked for $R_c = 5$, $R_D = 1$, $k_R = 640$, and $N_{Pe} = 0$. For dimensionless times larger than 10^{-2}, the maximum deviation between the analytic relation of Brunson and Wellek and the numerical solution is less than 1%.

Curves for some intermediate values of reaction number k_R are shown to allow interpolation. The mass flux to the sphere is proportional to the slope of the graphical relation of total mass transferred versus dimensionless time. Thus, from Figure 3 it can be seen that at small dimensionless times, the flux increases with increasing reaction number. At large times the **b** reactant inside the dispersed phase has been depleted if the reaction is rapid but some **b** reactant is still present for slow reactions. Thus the flux for mass transfer with a slow reaction is larger than the flux for mass transfer with a fast reaction; however, the total mass transferred at any given time increases with increasing reaction number.

Figure 4 shows the dependence of the total mass transferred on parametric values of concentration ratio R_c. For a concentration ratio of zero the **b** reactant is in such excess that the reaction is pseudo first-order. At the other extreme when the concentration ratio becomes infinite, there is no **b** reactant present, and the total mass transferred can be found from the problem for mass transfer with no reaction as originally solved by Johns and Beckmann (*8*). Each of the curves in Figure 4 for intermediate values of the concentration ratio approaches an asymptotic value of $1 + 1/R_c$.

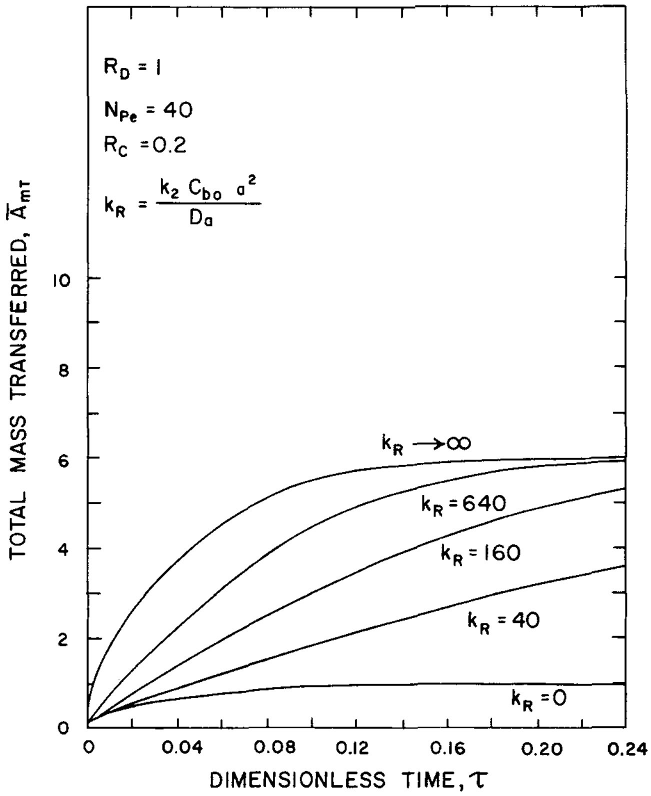

Fig. 3. Total mass transferred $\overline{A}_{mt}$ as a function of dimensionless time τ for parametric values of the reaction number k_R.

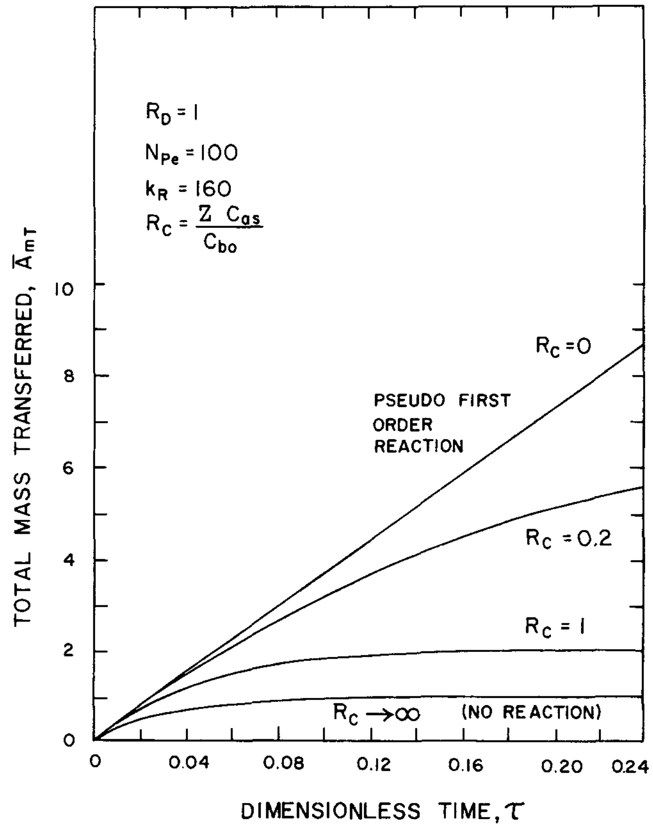

Fig. 4. Total mass transferred $\overline{A}_{mt}$ as a function of dimensionless time τ for parametric values of the concentration ratio R_c.

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The dependence of the total mass transferred $\overline{A}_{mt}$ on the diffusivity ratio R_D is indicated in Figure 5. For a given value of dimensionless time, the total mass transferred increases with increasing diffusivity ratio R_D, because the rate of reaction is fastest if the **b** reactant is mobile enough to maintain a large concentration near the surface of the sphere. The two extremes of diffusivity ratio equal to zero and approaching infinity may not be of practical importance; however they are included in the figure to show the complete range of parameters. The solution for an infinite diffusivity ratio was obtained numerically by setting the concentration of **b** at each grid point equal to the average concentration of **b** after each time interaction.

For a pseudo first-order reaction, the concentration of component **b** remains constant; therefore the effect of the diffusivity ratio disappears when the concentration ratio becomes zero. The importance of the diffusivity ratio is also small for large concentration ratios, because the total mass transferred $\overline{A}_{mt}$ approaches an asymptotic value within the time range studied For a concentration ratio R_c of unity and a diffusivity ratio R_D of unity, the total mass transferred is within 1% of its asymptotic value at a dimensionless time τ of 0.24. This does not allow a larger diffusivity ratio to greatly increase the total mass transferred. Thus the effect of the diffusivity ratio is most important for concentration ratios R_c between 0 and 1.

The effect of the diffusivity ratio increases with increasing reaction number. This is due to the fact that as the reactants become depleted by a faster reaction, it becomes more important how rapidly the reactants diffuse toward each other.

The effect of the diffusivity ratio decreases as the Peclet number increases. As the Peclet number increases, transfer by bulk flow becomes more important than solute transfer by diffusion. For example, when $R_c = 0.2$, $k_R = 640$, and $N_{Pe} = 100$, the total mass transferred changes by less than one part in four thousand when the diffusivity ratio is increased from 0.2 to 5.

Figure 6 shows the effect of internal circulation on the total mass transferred predicted by the model. The complete extensions of all of the curves are not shown in Figure 6, to avoid unnecessary clutter. The curves for the empirical solution of the penetration theory by Kishinovskii and Kornienko (*10*) and the film theory approximate solution by Van Krevelen and Hoftijzer (*15*) both asymptotically approach the curve for the numerical solution of the penetration theory obtained by Pearson (*12*). For the example used in Figure 6, the curve of $\overline{A}_{mt}$ as a function of τ for a Peclet number equal to 40 approaches the curve for a Peclet number equal to 100 at both large and small values of dimensionless time.

For dimensionless times less than 10^{-3}, the total mass transferred calculated from Equations (14) and (15) differs from that predicted by either the film theory or the penetration theory by less than 5%. This is the range of dimensionless time important in many liquid extraction applications. Thus the correlations by Van Krevelen and Hoftijzer (*15*) or by Kishinevskii and Kornienko (*10*) [that is, Equations (2) and (4), respectively] are sufficiently accurate for most work in liquid extraction with irreversible, second-order chemical reactions. At higher contact times, the assumption of a flat interface which is basic to both of the above applications of the film theory and penetration theory is no longer valid. At large dimensionless times ($\tau > 0.02$), which include dimensionless times important for gas absorption, both the film theory and the penetration theory predict values of the total mass transfer greater than is possible. This is due to the inability of either theory to allow for the eventual depletion of the **b** reactant within the sphere.

No attempt was made in this work to solve analytically for mass transfer with reaction for a Peclet number approaching infinity as was done by Kronig and Brink (*11*)

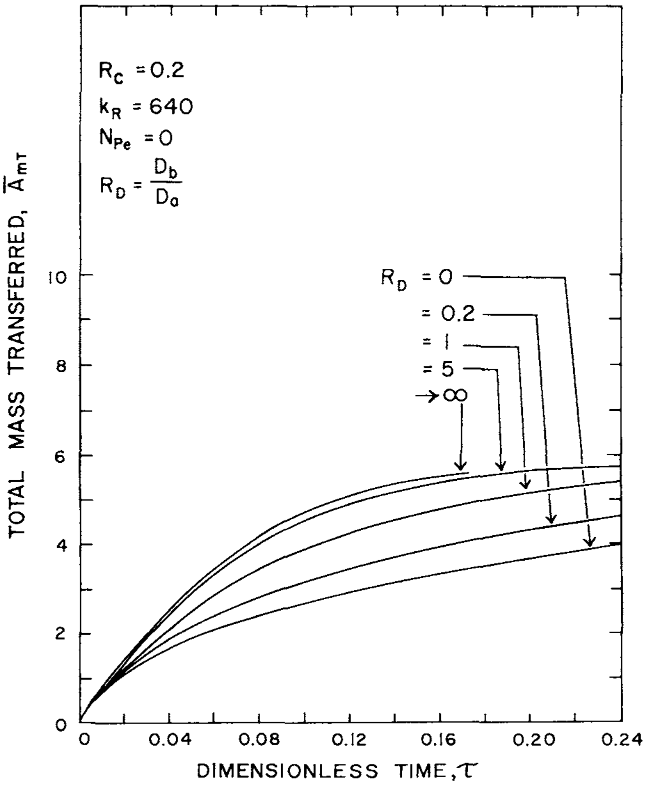

Fig. 5. Total mass transferred $\overline{A}_{mt}$ as a function of dimensionless time τ for parametric values of the diffusivity ratio R_D.

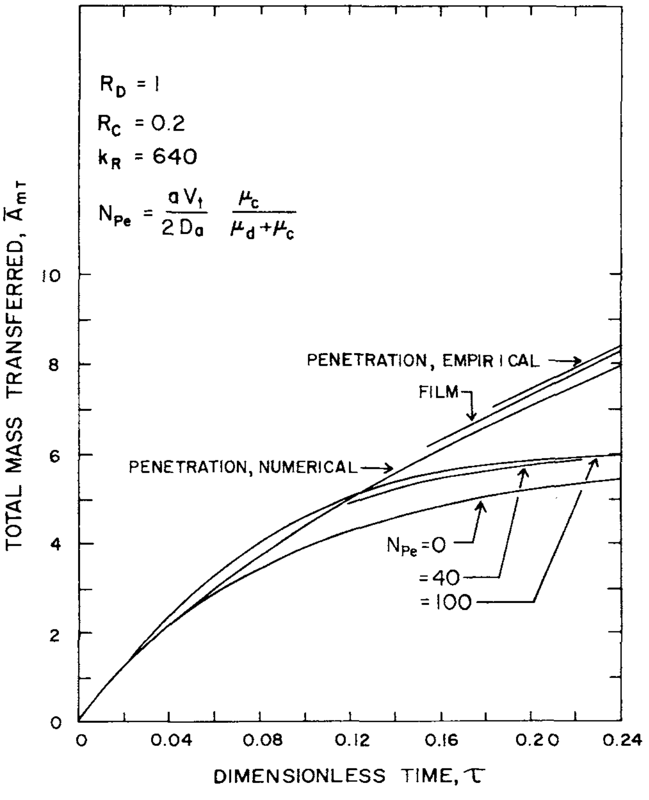

Fig. 6. Total mass transferred $\overline{A}_{mt}$ as a function of dimensionless time τ showing effect of the Peclet number N_{Pe}.

for mass transfer without chemical reaction. However, it was possible to increase the Peclet number until the total mass transferred $\overline{A}_{mt}$ approached a constant value. This occurred at a Peclet number about equal to 100 for both mass transfer without reaction and for mass transfer with a rapid chemical reaction. Larger Peclet numbers were required to reach the asymptotic effect of Peclet number for intermediate reaction numbers, especially if the concentration ratio was small. Mass transferred at a given dimensionless time increased with increasing Peclet number up to a Peclet number of 500 for the following example where $k_R = 40$, $R_c = 0.2$, $R_D = 1.0$, and $\tau = 0.05$:

N_{Pe}	0	100	200	300	400	500
$\overline{A}_{mt}$	1.0026	1.1816	1.2863	1.3350	1.3616	1.3762

Although it was not emphasized earlier in this paper, the solution of this model was dependent upon the assumption that the multicomponent molecular diffusivities D_a and D_b are constant. Thus, when applying the model, one would probably have to use good space and time average estimates of the diffusivities. The model considers a wide range of values of C_a and C_b in the dispersed phase ($C_a = 0 \rightarrow C_{as}$; $C_b = C_{b0} \rightarrow 0$, respectively); and hence if solutions are not dilute, the diffusivities would have to be averaged over the concentration changes expected.

COMMENTS ON APPLICATIONS

Industrial second-order reactions which involve two liquid phases include saponification of esters, nitration, and sulfonation (*16*). Danckwerts (*17*) lists several gas-liquid, second-order, reacting systems. Reactions are also used to enhance the rate and extent of liquid extraction and gas absorption.

Johnson and Bliss (*19*) concluded from their study of nonreacting spray towers that unless the flow rate of the extracting phase is much less than the flow rate of the other phase, it is better to disperse the extracting phase. The work presented in this paper describes and solves a mathematical model for mass transfer into and simultaneous reaction within the dispersed phase.

As with any model the results of this work are limited by the assumptions made in the section entitled Theoretical Development. However, several guidelines can be drawn from this work, and the results of this work may apply qualitatively or even quantitatively beyond the limitations imposed by the assumptions incorporated in the mathematical model.

Materials

If reaction is used to enhance the rate of solute transfer to a separating phase, the designer is usually free to choose both the identity and the concentration of reactant **b**.

The most important factors to consider in selecting component **b** are cost and rate of reaction. From Figure 3 it can be seen that even a moderate reaction rate is sufficient in gas bubbles, whereas for a liquid droplet, it is important to have as high a reaction rate as possible. As an approximate rule of thumb, one can conclude from this work that it is advantageous to pay twice as much for a reactant if the reaction rate constant can be increased by an order of magnitude (see Figure 3).

Since the total mass transferred becomes insensitive to the diffusivity ratio at large Peclet numbers, the diffusivity of component **b** is not important. However, it is important that component **b** does not greatly increase the viscosity of the dispersed phase. In many cases it will be important that component **b** can be regenerated and used again.

The effect of the concentration of the **b** reactant is related to both the dimensionless reaction number and the concentration ratio; however the effect is most pronounced as a result of changes in the concentration ratio shown in Figure 4. In general, the total mass transferred increases as C_{b0} is increased. However, a large concentration of reactant **b** could greatly change the viscosity of the dispersed phase. Therefore, if possible, C_{b0} should be just large enough to approach a pseudo first-order reaction. For the complete range of variables studied, the total mass transferred could not be increased by as much as 5%, no matter how much the concentration ratio was reduced below two-tenths for dimensionless times less than 0.01, which is the time region of interest if the dispersed phase is a liquid.

Equipment

After the chemicals and concentrations for a contactor are selected, the size of the drops formed depends on the nozzle design and operating conditions. Reducing the drop size increases the dimensionless time but reduces the dimensionless reaction constant and the Peclet number. Because of the way the dimensionless reaction constant varies with drop size, the reduction of drop size is not as important for mass transfer with reaction as it is for mass transfer without reaction. Despite this effect it is still desirable to form small drops. Although the drops formed will not be of uniform size, work by Gal-Or and Hoelscher (*18*) for transfer from drops with and without reaction indicates that there is little error if the mean drop size is used.

Reaction inside the fluid sphere keeps the driving force for mass transfer from decreasing rapidly with time. For example, at a Peclet number of 100, if there is no chemical reaction, the dimensionless flux of **a** reduces from 29.77 at a dimensionless time of 0.001 to 0.02 at a dimensionless time of 0.24. However, if there is a chemical reaction (for example, $R_c = 0$ and $k_R = 160$) the dimensionless flux of **a** has a value of 35.89 at a dimensionless time of 0.001 and has only reduced to 23.79 at a dimensionless time of 0.24. This can be seen graphically by examining Figure 4. The slope of the graph of the total mass transferred versus dimensionless time (which is proportional to the flux of **a**) is initially large for all values of R_c. At large times the slope of the graph for $R_c = 0$ is still large, but the curve representing no reaction is almost horizontal. Since the presence of a chemical reaction reduces the effect of the time of contact on the flux of **a**, it is not necessary to redisperse the extracting phase as often as must be done when there is no reaction present. This means that if backmixing can be tolerated (as is the case with nitration, sulfonation, and saponification), fewer perforated plates are needed per unit length of column. This fact also makes the spray tower feasible for more applications.

CONCLUSIONS

This work examined mass transfer with a second-order, irreversible chemical reaction inside circulating fluid spheres. The velocity components inside the dispersed phase were described by the Hadamard relations for the laminar flow regime. It was found that the mass transfer indices (listed in Table 1) were a function of five dimensionless parameters: a diffusivity ratio, a concentration ratio, a reaction number, the Peclet number, and the dimensionless contact time. A range of the dimensionless parameters was studied to determine their effect on eight different dispersed phase mass transfer indices.

In addition to using more accurate geometrical and fluid flow descriptions than the theories previously available, this work allows for the complete depletion of the reactant initially in the dispersed phase. None of the previously available theories are able to predict accurately mass transfer after the **b** reactant has been depleted.

If the fluid sphere is a liquid, either the film theory or the penetration theory may be used with confidence. However, the numerical solutions obtained in this work must be used if the dispersed phase is a spherical gas bubble.

The analytic enhancement factor relation for infinitely fast chemical reactions developed by Toor and others was verified by the results of the numerical solution for mass transfer with chemical reaction inside fluid spheres. Since the diffusivity ratio was found in this work to have little effect on the mass transfer rate at high Peclet numbers, the relation can be used for very high Peclet numbers even if the diffusivity ratio is not close to 1.

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NOTATION

a = radius of sphere, cm.
$\mathbf{a}$ = reactant initially in continuous phase
A = dimensionless concentration of $\mathbf{a}$, C_a/C_{as}
A_r = dimensionless amount of solute reacted in the sphere, C_{ar}/C_{as}
$\overline{A}_{mt}$ = total mass transferred (see Table 1), dimensionless
$\mathbf{b}$ = reactant soluble only in dispersed phase
B = dimensionless concentration of $\mathbf{b}$, C_b/C_{b0}
C_a = concentration of $\mathbf{a}$, moles/liter
C_{ar} = moles of $\mathbf{a}$ reacted per volume of sphere, moles/liter
C_{as} = surface concentration of $\mathbf{a}$, moles/liter
C_b = concentration of $\mathbf{b}$, moles/liter
C_{b0} = initial concentration of $\mathbf{b}$, moles/liter
D_a = diffusivity of component $\mathbf{a}$, sq.cm./sec.
D_b = diffusivity of component $\mathbf{b}$, sq.cm./sec.
h = distance from the interface, cm.
H = distance from interface wherein diffusion is important: film thickness for film theory and approaching infinity for penetration theory, cm.
i = index of grid point in radial direction
j = index of grid point in angular direction
k = index of grid point in time dimension
k_2 = second-order reaction constant, liter/mole/sec.
k_R = dimensionless reaction number, $k_2a^2C_{b0}/D_a$
m = number of grid points in angular direction
n = number of grid points in radial direction
N_{Pe} = Peclet number, $(aV_t/2D_a)\ [\mu_c/(\mu_d + \mu_c)]$
P = $\Delta\tau/(\Delta\theta)^2$
P_2 = $\Delta\tau/(2\Delta\theta)$
r = radial distance, cm.
R = dimensionless radius, r/a
R_c = concentration ratio, $z\ C_{as}/C_{b0}$
R_D = diffusivity ratio, D_b/D_a
S = $\Delta\tau/(\Delta R)^2$
S_2 = $\Delta\tau/(2\Delta R)$
S_0 = surface area of sphere, sq.cm.
t = contact time, sec.
V = volume of sphere, cu.cm.
V_r = velocity in radial direction, cm./sec.
V_θ = velocity in angular direction, cm./sec.
V_t = terminal velocity of sphere relative to surrounding fluid, cm./sec.
W = parameter in Equation (8) as defined by Equation (10)
x = parameter in Equation (9) $= 0.85\sqrt{W^2R_c + W}$
Y = parameter in Equation (6) and defined by Equation (7)
z = stoichiometric coefficient in Equation (1)

Greek Letters

μ_c = viscosity of continuous phase, poise
μ_d = viscosity of dispersed phase, poise
ϕ = enhancement factor, $[\overline{A}_{mt}(k_R \neq 0)]/[\overline{A}_{mt}(k_R = 0)]$
τ = dimensionless time, $t\ D_a/a^2$
θ = angle
δ = Kronecker delta (one for penetration theory and zero for film theory)

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APPENDIX A: CALCULATION OF THE TOTAL MASS TRANSFERRED $\overline{A}_{mt}$

Equation (2) can be rewritten as

$$\overline{A}_{mt} = \overline{C}_a/C_{as} + C_{ar}/C_{as}$$

The first term on the right-hand side of the above equation is, by definition, $\overline{A}$. Therefore the first term can be found by averaging A over the volume of the sphere. The second term on the right-hand side can be found by a material balance on component $\mathbf{b}$. The total amount of $\mathbf{b}$ which has reacted per unit volume is the initial concentration less the amount of $\mathbf{b}$ still present, $C_{b0} - \overline{C}_b$. Then, according to the stoichiometry of Equation (1), the moles of $\mathbf{a}$ reacted per volume of sphere C_{ar} are $(C_{b0} - \overline{C}_b)/z$. Thus

$$C_{ar}/C_{as} = \frac{C_{b0} - \overline{C}_b}{z\,C_{as}}$$

$$= \frac{C_{b0}/C_{b0} - \overline{C}_b/C_{b0}}{z\,C_{as}/C_{b0}}$$

$$= (1 - \overline{B})/R_c$$

Therefore

$$\overline{A}_{mt} = \overline{A} + (1 - \overline{B})/R_c$$

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