Mass Transfer with Instantaneous Chemical Reaction in a Rigid Drop

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Mass transfer between liquid drops and a surrounding fluid with an accompanying chemical reaction is important in a number of industrial processes such as spray absorption, liquid-liquid extraction, separation using liquid membranes, and others. The reaction may occur either in the continuous phase or in the dispersed phase, depending on the nature of the particular system. Theoretical analyses of mass transfer with chemical reaction to or from liquid drops have been reported by a number of workers. Ruckenstein et al. (1971) developed a similarity solution for the concentration distribution in the continuous phase and obtained the rate of mass transfer from a drop, in the presence of a first-order reaction, based on a suitable stream function for the external velocity field. Mass transfer to the dispersed phase was also considered for internally circulating drops, and it was observed that a steady state mass transfer rate is attained within a very small time of contact. Dang and Ruckenstein (1973) subsequently extended the analysis to the case of fast-moving circulating drops. Ramachandran et al. (1985) presented a theoretical investigation of mass transfer with chemical reaction to a single drop using the boundary layer concept for the gas phase and film theory for the liquid phase. An extension to the case of absorption in a string of circulating drops was reported by Kleinstreuer et al. (1985).

In many situations of practical interest, however, mass transfer to drops is associated with an instantaneous reaction. Here the solute diffuses from the continuous phase into the drop and reacts with a reagent present in it. As a result there develop two regions inside the drop, each containing only one of the reactants, which react at the moving reaction front that demarcates the two regions. Despite its practical importance, the problem does not appear to have received attention. Theoretical analysis of this moving-boundary problem has been reported in this work, including computation of reaction front position, rate of mass transfer, and the enhancement factor for different values of the system parameters. The results of this investigation are applicable to small drops, which may be considered to behave as rigid spheres (Levich, 1962).

Formulation of the Problem

Let us consider a noncirculating liquid droplet containing a solute B with uniform initial concentration of C_{Bo}, absorbing another solute A from the surrounding continuous phase, where A and B react instantaneously according to:

$$A + bB \longrightarrow cC \tag{1}$$

The bulk concentration of A in the continuous phase is assumed to remain constant and the corresponding equilibrium concentration at the drop surface is C_{Ai}. Mass transfer resistance in the continuous phase is neglected. The relevant governing equations in nondimensional form are:

$$\frac{\partial C_A^*}{\partial \tau} = \frac{\partial^2 C_A^*}{\partial \rho^2} \tag{2}$$

$$\frac{\partial C_B^*}{\partial \tau} = D\frac{\partial^2 C_B^*}{\partial \rho^2} \tag{3}$$

where

$$C_A^* = \rho \overline{C}_A = \rho \frac{C_A}{C_{Ai}}$$

$$C_B^* = \rho \overline{C}_B = \rho \frac{C_B}{C_{Bo}} \tag{4}$$

The following initial and boundary conditions may be prescribed.

$$\tau = 0, \quad C_A^* = 0 \quad C_B^* = \rho$$

$$\rho = 1, \quad C_A^* = 1$$

$$\rho = 0, \quad C_B^* = 0$$

$$\rho = \phi, \quad C_A^* = 0 = C_B^* \tag{5}$$

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Here $\rho = \phi$ is the location of the moving reaction front at any time τ, where the following compatibility condition relating the fluxes of A and B should be satisfied:

$$\rho = \phi, \quad \frac{\partial C_A^*}{\partial \rho} = -\beta D \frac{\partial C_B^*}{\partial \rho} \tag{6}$$

No analytical solution of the above set of equations exists, and a direct numerical approach becomes complicated because the position of the reaction front is not known *a priori*. The analogous but simpler problem in heat transfer—the Stefan problem—involving solidification of a sphere of liquid initially at the fusion temperature has been considered by Pedroso and Domoto (1973), Stewartson and Waechter (1976), and Soward (1980). In all these investigations a singular perturbation technique was used to find an asymptotic solution of the moving-boundary problem for large latent heat of solidification. However, such a technique does not appear to be suitable for the present problem. Instead, an appropriate coordinate transformation has been sought, one that immobilizes the reaction front so that the resulting equations may be solved numerically on regular, fixed finite-difference grids for the two regions containing A and B, respectively. Accordingly, if the following new variables are introduced,

$$\eta = \frac{\rho - \phi}{1 - \phi}, \quad 1 \le \rho \le \phi \tag{7a}$$

$$\bar{\eta} = 1 - \frac{\rho}{\phi}, \quad 0 \le \rho \le \phi \tag{7b}$$

Eqs. 2–4 and 6 reduce to:

$$\frac{\partial C_A^*}{\partial \tau} - \frac{1 - \eta}{1 - \phi} \frac{d\phi}{d\tau} \frac{\partial C_A^*}{\partial \eta} = \frac{1}{(1 - \phi)^2} \frac{\partial^2 C_A^*}{\partial \eta^2} \tag{8}$$

$$\frac{\partial C_B^*}{\partial \tau} + \frac{1 - \bar{\eta}}{\phi} \frac{d\phi}{d\tau} \frac{\partial C_B^*}{\partial \bar{\eta}} = \frac{D}{\phi^2} \frac{\partial^2 C_B^*}{\partial \bar{\eta}^2} \tag{9}$$

$$\begin{aligned} &\tau = 0; \quad C_A^* = 0, \quad C_B^* = 1 - \bar{\eta} \\ &\eta = 1; \quad C_A^* = 1 \\ &\bar{\eta} = 1; \quad C_B^* = 0 \\ &\eta = 0 = \bar{\eta}; \quad C_A^* = 0 = C_B^* \end{aligned} \tag{10}$$

and

$$\frac{\partial C_A^*}{\partial \eta} = \beta D \left(\frac{1 - \phi}{\phi} \right) \frac{\partial C_B^*}{\partial \bar{\eta}} \tag{11}$$

Computational Method

Equations 8 and 9, subject to the corresponding boundary conditions, Eq. 10, and the compatibility condition, Eq. 11, were solved numerically using an iterative finite-difference technique. A central difference scheme was used for integration along η and $\bar{\eta}$ grids and the Euler method for integration along τ. Each step in τ, however, required iteration because of nonlinear involvement of ϕ in the relevant equations. The computational steps are as follows:

1. Assume a value for ϕ at the $i + 1$ location of the τ grid.
2. Solve for C_A^* and C_B^* over the η and $\bar{\eta}$ grids by the usual procedure.
3. Check whether the compatibility condition, Eq. 11, is satisfied. If not, make a new estimate for ϕ using the secant method and repeat the process from step 2 until the matching is satisfactory.

The ratio of grid sizes in the τ and η (and also $\bar{\eta}$) directions was chosen by trial and error for efficient convergence. Convergence was fairly rapid even near $\tau = 0$, and it improved with increase in τ. The absorption rate of A and other relevant quantities may be calculated easily from the solution for concentration distribution.

It may be noted that the numerical integration cannnot be extended to zero time and hence evaluation of time integrals, Eqs. 12 and 14, will always entail a small error. This error, however, could be kept small by choosing a sufficiently small length of interval for τ near $\tau = 0$.

Results and Discussion

The computational procedure described above has been used to find the solution to the system of Eqs. 8–11 for different sets of values of the system parameters—namely, β, the concentration ratio weighted by the stoichiometric coefficient in the reaction, and D, the diffusivity ratio—in order to obtain the nature of propagation of the reaction front, the instantaneous as well as cumulative mass flux of A, and the enhancement factor for mass transfer. The computational accuracy is checked indirectly by the following mass balance equation, at time τ, relating the amounts of A absorbed, B consumed, and physically absorbed A in the outer region that contains no B:

$$\int_o^\tau \left(\frac{\partial \bar{C}_A}{\partial \rho} \right)_{\rho=1} d\tau = \int_\phi^1 \bar{C}_A \rho^2 \, d\rho + \beta \left(\frac{1}{3} - \int_o^\phi \bar{C}_B \rho^2 \, d\rho \right) \tag{12}$$

The maximum matching error remains fairly well below 1%.

It is particularly useful to find the mass transfer enhancement factor E_i. Using the solution of unsteady state diffusion equation in a sphere (Carslaw and Jaeger, 1959),

$$E_i = \frac{\int_o^\tau \left(\frac{\partial \bar{C}_A}{\partial \rho} \right)_{\rho=1,\,\text{chem}} d\tau}{\int_0^\tau \left(\frac{\partial \bar{C}_A}{\partial \rho} \right)_{\rho=1,\,\text{phys}} d\tau} = \frac{3Q}{1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \bar{e}^{n^2\pi 2_\tau}} \tag{13}$$

where

$$Q = \int_0^\tau \left(\frac{\partial \bar{C}_A}{\partial \rho} \right)_{\rho=1,\,\text{chem}} d\tau \tag{14}$$

Here Q is the cumulative mass flux over the time τ. It may easily be verified that the limiting values of Q and E_i at large time are ⅓ $(1 + \beta)$ and $(1 + \beta)$, respectively.

From physical considerations it appears that propagation of the reaction front will be governed by three factors: the diffusion rates of A and B, and the relative amount of B present in the droplet. Larger concentration of B will have a decelerating effect on the movement of the reaction front. The effect of

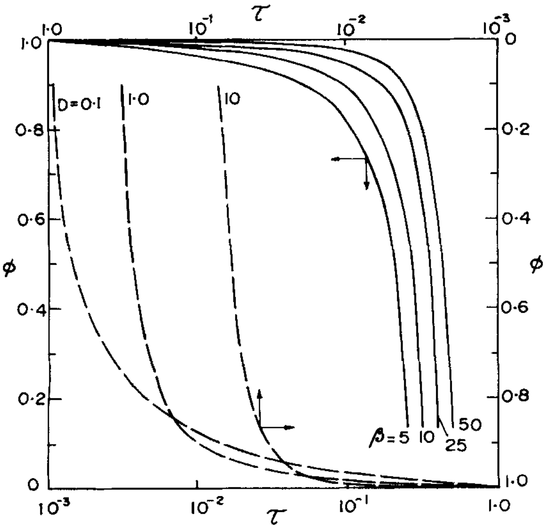

Figure 1. Progress of reaction front.
——— Effect of β for $D = 1$
- - - Effect of D for $\beta = 10$

higher diffusivity of species B will be similar. However, the nature of the retardation will differ qualitatively. For slow-diffusing B, the retardation will be more uniform, whereas if B is highly mobile or quick-diffusing, there will be an initial period of large retardation—a period when the reaction front can make very little progress, but most of B gets consumed. Thereafter the reaction front will proceed fairly rapidly.

The computed results are in conformity with the physical interpretation given above. Figure 1 shows the movement of the reaction front with time. The diffusivity ratio D remaining the same, larger β will cause slower movement of the reaction front, resulting in a sharper knee. Similarly, for constant β, the larger the diffusivity of B, the slower is the initial movement of the reaction front, followed by a rapid progress at later time. This also explains the intersection of the $\phi - \tau$ curves at different values of D.

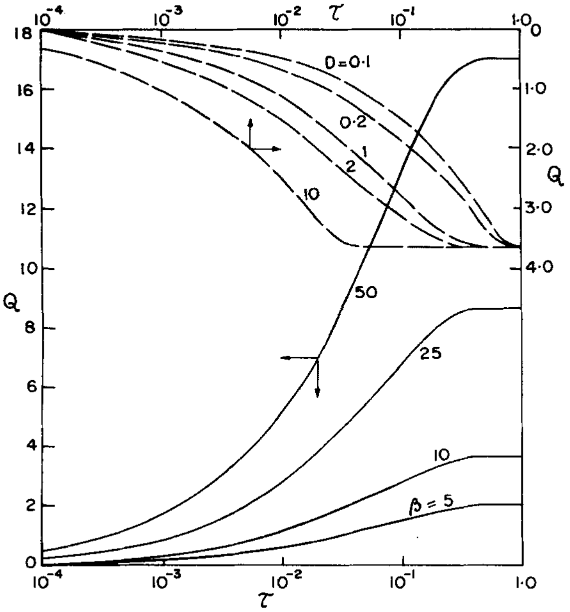

Figure 2. Variation of cumulative mass flux with τ.
——— Effect of β for $D = 1$
- - - Effect of D for $\beta = 10$

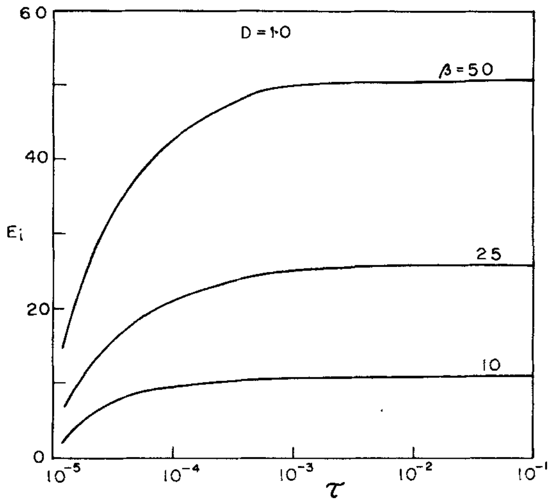

Figure 3. Enhancement factor plot, effect of β.

The time integral of absorption rate or the total amount of A absorbed per unit area over a time span τ is shown in Figure 2. Here also it is observed that with increase of β at constant D, the amount absorbed predictably increases. Consequently the enhancement factor will increase with β. But at large time the asymptotic value of the enhancement factor, $(1 + \beta)$, is reached, which is independent of D, Figure 3. Again, at constant β, if the diffusivity of B becomes larger, a greater amount of A is absorbed at small time, but all the curves must tend to the final asymptotic value at large time.

This behavior causes the interesting phenomenon shown in Figure 4. Here it is seen that for larger values of D_B, the enhancement factor shows a maximum, and then drops down to the limiting value. This is because most of the B is consumed in the early stage, followed by virtually simple physical absorption at later time. For small values of D_B the curves show a steplike

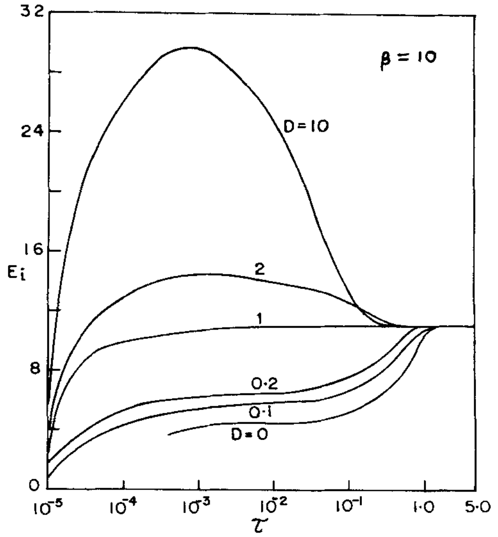

Figure 4. Enhancement factor plot, effect of D.

behavior. In the initial stage there is a sharp rise as a steeper concentration gradient of the absorbed species A is set up due to reaction with B and is maintained for some time, resulting in the plateau of the enhancement factor curves. Thereafter the enhancement factor gradually increases and the limiting value is reached asymptotically. The diffusivity ratio $D = 1$ demarcates the boundary between these two types of behavior. When D becomes extremely small, a pseudosteady-state solution, valid for not very small time, for the concentration of A exists. The plots of enhancement factor of $D < 1$, including the one corresponding to this limiting case, are similar in nature.

Notation

b, c = stoichiometric coefficients
A,B,C = reactions and product
C_A, C_B = concentrations of A and B
C_{Ai} = concentration of A at drop surface
C_{Bo} = initial concentration of B in drop
$\overline{C}_A, \overline{C}_B$ = dimensionless concentrations of A and B, Eq. 4
C_A^*, C_B^* = transformed concentrations of A and B, Eq. 4
D = diffusivity ratio, D_B/D_A
E_i = enhancement factor for instantaneous reaction
Q = cumulative mass flux, Eq. 17

Greek letters

$\beta = C_{Bo}/bC_{Ai}$
ϕ = dimensionless position of reaction front
$\eta, \overline{\eta}$ = variables defined by Eqs. 10a, 10b
ρ = dimensionless radial position, r/R
τ = dimensionless time, tD_A/R^2

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