R & D NOTES

Diffusion with Instantaneous Reaction in a Drop with Continuous-Phase Resistance

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In an earlier paper, Dutta et al. (1988) reported a theoretical analysis of mass transfer accompanied by an irreversible instantaneous chemical reaction in a rigid drop. The phenomenon, which is common to a number of industrial gas-liquid and liquid-liquid contacting operations, proceeds through a moving boundary mechanism. The reaction between a chemical species present in the drop and a second reactant species diffusing into the drop from a surrounding continuous phase occurs at a reaction front that progressively recedes away from the surface of the drop toward its center. While in their analysis Dutta et al. neglected the mass-transfer resistance in the continuous phase, its effects are shown here to be quite significant in many situations of practical importance, particularly during the initial stage of contact between phases.

Theoretical Analysis

Let us assume that the following irreversible instantaneous reaction occurs inside a rigid drop containing reactant B:

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

The reactant A diffuses from the continuous phase into the drop. In the following mathematical treatment we shall assume that the initial concentration of B in the drop, C_{B0}, is uniform and that the concentration of A in the bulk of the continuous phase, $C^c_{A\infty}$, remains constant in time. If the continuous phase mass-transfer resistance is small, the interfacial concentration of A in the drop rapidly approaches a constant value, $C^d_{A\infty}$, which is the solubility of A in the B-free dispersed phase. In this case the reaction front, initially positioned at the interface, is set in motion immediately after the phases come in contact.

The presence of significant mass-transfer resistance in the continuous phase leads to a different situation. Here mass transfer is controlled entirely by the continuous-phase resistance until the concentration of B at the drop surface is reduced to zero. During this initial period, whose duration will be denoted τ_0, the interfacial concentration of A remains zero. It is only after this period that the reaction front begins to recede away from the interface as A makes headway into the drop. The concentration profile of B in the drop during this initial period may be obtained from the following conservation equation:

$$\frac{\partial \bar{C}_B}{\partial \tau} = \frac{D}{\rho^2}\frac{\partial}{\partial \rho}\left(\rho^2 \frac{\partial \bar{C}_B}{\partial \rho}\right) \tag{2}$$

subject to the initial and boundary conditions,

$$\tau = 0, \quad \bar{C}_B = 1 \tag{3a}$$

$$\rho = 0, \quad \bar{C}_B \text{ finite} \tag{3b}$$

$$\rho = 1, \quad \frac{\partial \bar{C}_B}{\partial \rho} = -\frac{Bi}{D\beta} \tag{3c}$$

Equation 3c is based on the assumption that the continuous phase mass-transfer resistance may be simply represented by a constant mass-transfer coefficient which appears in the Biot number, Bi. Transients in the external film are thus neglected in this treatment. A solution of Eq. 2 with conditions 3 is given by

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(Carslaw and Jaeger, 1959)

$$\overline{C}_B = 1 - \frac{3Bi\tau}{\beta} - \frac{Bi}{10D\beta}(5\rho^2 - 3) + \frac{2Bi}{D\beta\rho}\sum_{n=1}^{\infty}\frac{\sin(\alpha_n\rho)}{\alpha_n^2 \sin\alpha_n} e^{-\alpha_n^2 D\tau} \tag{4}$$

This solution remains physically valid up to the time τ_0, when the concentration of B at the drop surface just reduces to zero. Thus, τ_0 may be found by equating Eq. 4 to zero at $\rho = 1$, yielding

$$1 - \frac{3Bi\tau_0}{\beta} - \frac{Bi}{5D\beta} + \frac{2Bi}{D\beta}\sum_{n=1}^{\infty}\frac{1}{\alpha_n^2} e^{-\alpha_n^2 D\tau_0} = 0 \tag{5}$$

Solution of Eq. 5 provides τ_0. The fractional conversion of B in the drop at $\tau = \tau_0$ can then be calculated by integrating Eq. 4, yielding

$$X_B = \frac{3Bi\tau_0}{\beta} \tag{6}$$

For times longer than τ_0, the reactant A is present at nonzero concentration within the drop, and the reaction occurs at a reaction plane that moves progressively toward the center of the drop. The mass-transfer process may then be represented by the same moving-boundary model presented by Dutta et al. (1988). Using the same notation, the continuity equations for A and B in the drop are the same as Eqs. 2 and 3 of that paper, provided that the dimensionless concentrations, C_A^* and C_B^*, are defined as follows:

$$C_A^* = \rho\overline{C}_A^d = \rho\frac{C_A^d}{C_{A\infty}^d} \tag{7}$$

$$C_B^* = \rho\overline{C}_B = \rho\frac{C_B}{C_{B0}} \tag{8}$$

Initial and boundary conditions are changed as follows to reflect the depletion of B that occurs for times $\tau < \tau_0$, and the presence of mass-transfer resistance in the continuous phase:

$$\tau = \tau_0, \quad C_A^* = 0, \quad C_B^* = \rho\overline{C}_B(\rho, \tau_0) \tag{9a}$$

$$\rho = 0, \quad C_B^* = 0 \tag{9b}$$

$$\rho = 1, \quad \frac{\partial C_A^*}{\partial\rho} = Bi(1 - C_A^*) + C_A^* \tag{9c}$$

Here, $\overline{C}_B(\rho, \tau_0)$ is the concentration profile of B in the drop at time τ_0, and is given by Eq. 4. At the moving reaction front, located within the drop, the fluxes of A and B must satisfy the stoichiometric requirement of reaction 1 as expressed by the "compatibility condition" introduced by Eq. 6 in the paper by Dutta et al. (1988).

A numerical algorithm is required for the solution of the continuity equations for A and B together with the initial and boundary conditions given by Eq. 9 and the compatibility condition at the moving boundary. For this purpose, the reaction front may be immobilized by making the transformation of the independent variables ρ and τ, shown by Dutta et al. (1988). The resulting transformed equations may then be solved numerically using an iterative finite difference technique.

Results and Discussion

Concentration profiles of A and B within the drop for values of τ greater than τ_0, were obtained numerically. Then, the instantaneous and time-average rates of diffusion of A into the drop were obtained from the calculated concentration profiles. The details of the numerical procedure are given by Dutta et al. (1988).

The results are presented here in terms of fractional conversion of B and enhancement factor. The enhancement factor, E_i, is defined here relative to the unsteady-state diffusion of A in a drop containing no B—i.e., for purely physical absorption of A with no mass-transfer resistance in the continuous phase. E_i is then given by

$$E_i = \frac{\tau_0 Bi + \int_{\tau_0}^{\tau}\left[\frac{\partial\overline{C}_A^d}{\partial\rho}\right]_{\rho=1} d\tau}{\frac{1}{3} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-n^2\pi^2\tau}} \tag{10}$$

The first term in the numerator represents the amount of A taken up by the drop over τ_0, the threshold time during which the reaction front remains at the drop interface. The fractional conversion of the dissolved reactant B during this period is given by Eqs. 5 and 6. It may be noted from these equations that X_B at τ_0 depends only upon the ratio, $Bi/D\beta$. This relationship is shown graphically in Figure 1. Here it is seen that, at low values of the ratio $Bi/D\beta$, approximately less than 0.3, the external resistance virtually controls mass transfer of A to the drop. For these conditions, X_B is about unity when $\tau = \tau_0$. Even when $Bi/D\beta = 1$, about 80% of B is consumed before the reaction front makes any progress inside the drop. For higher values of the $Bi/D\beta$ ratio, the fractional conversion of B achieved at $\tau = \tau_0$ gradually decreases.

The enhancement factor for times exceeding τ_0 depends upon three parameters individually, namely, Bi, β, and D. Computed values are presented in Figures 2–4 for ample ranges of parame-

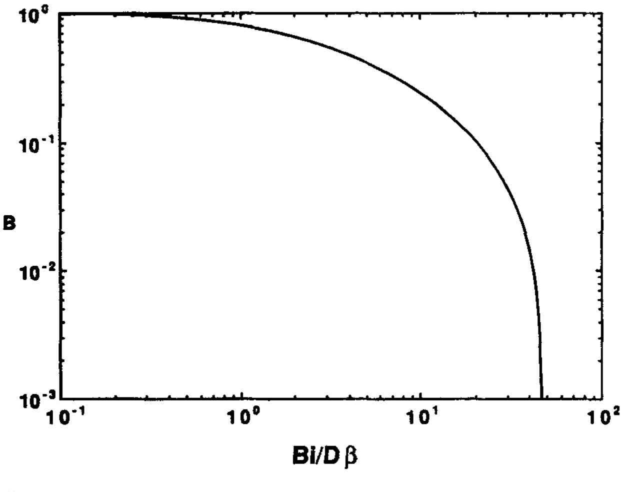

Figure 1. Fractional conversion of B in the drop at τ_0.

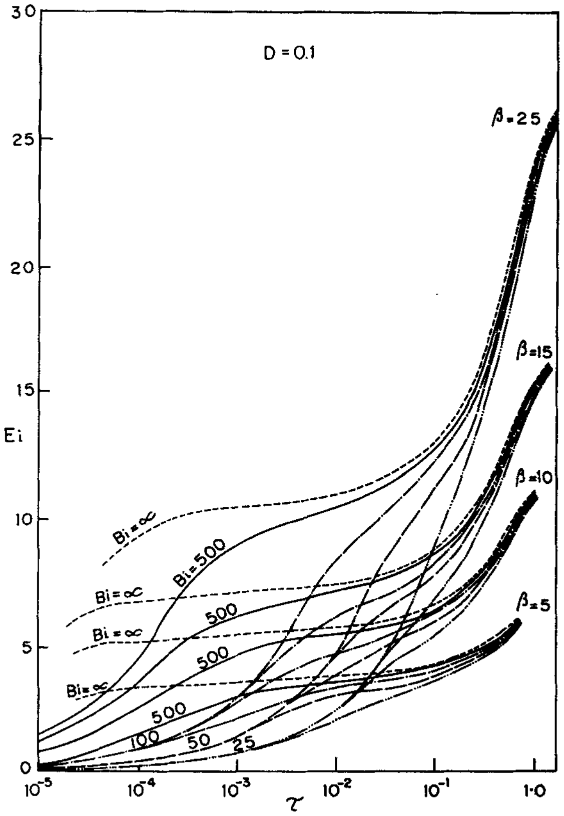

Figure 2. Enhancement factor vs. dimensionless contact time for $D = 0.1$.

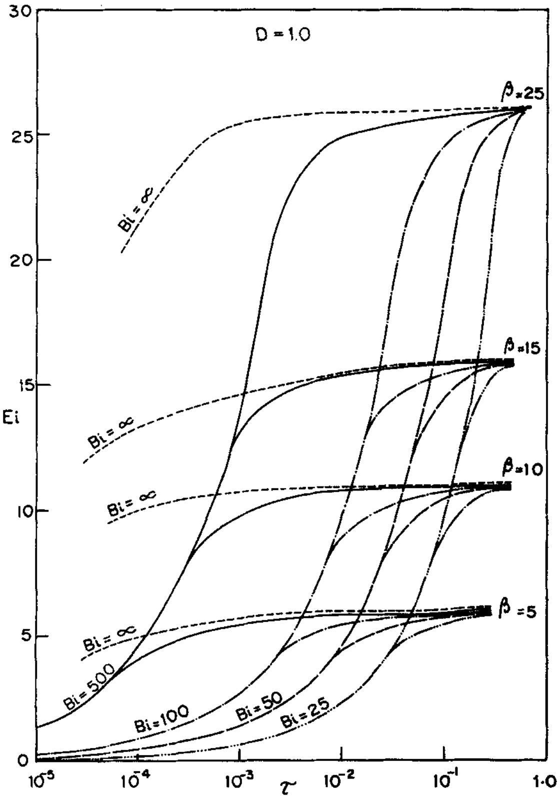

Figure 3. Enhancement factor vs. dimensionless contact time for $D = 1.0$.

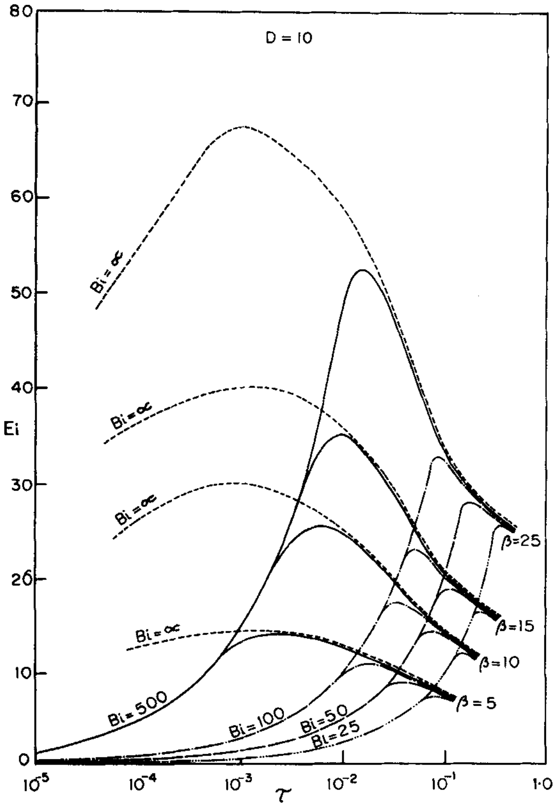

Figure 4. Enhancement factor vs. dimensionless contact time for $D = 10$.

ter values, along with curves calculated in the absence of mass-transfer resistance in the continuous phase ($Bi = \infty$). As seen in these figures, the enhancement factor predictably increases with the Biot number, because of a corresponding diminution of the continuous phase mass-transfer resistance. For vanishingly small times, the enhancement factor approaches zero because of the assumed reference condition of purely physical absorption of A in the drop in the absence of external mass-transfer resistance. As τ increases, the effects of the external mass-transfer resistance vanish and the calculated curves approach the asymptotic limit for $Bi = \infty$. For any finite Bi, the enhancement factor, E_i, is independent of β at small τ values, when the concentration of A in the drop is zero and the reaction front is located at the interface. Here, the rate of uptake of A is controlled by the continuous phase mass-transfer resistance.

The effects of the diffusivity ratio, D, on the enhancement factor are more complex since, as shown by Dutta et al. (1988), this parameter has a strong influence on the movement of the reaction plane. For small values of D (Figure 2), E_i increases monotonically with τ approaching the $Bi = \infty$ limiting curves. However, since here, D_B is considerably smaller than D_A, the initial period, τ_0, is rather short and B is rapidly depleted at the interface. Introduction of a finite external mass-transfer resistance has thus only a small effect in this case. Conversely, for values of D which exceed unity ($D_B > D_A$), the diffusion of B is fast enough to keep the reaction front near the drop interface. As seen in Figure 4, the enhancement factor increases with τ, reaching a maximum and then declining when conversion of B is essentially complete. In the declining branch of these curves, the mass-transfer process is virtually physical dissolution of A.

Finally, when $D = 1$ (Figure 3), the enhancement factor increases with τ and then reaches a plateau corresponding to the asymptotic value of $1 + \beta$ when τ is very large.

In all these cases, comparison of the E_i values obtained for finite values of the Biot number with the curves shown in Figures 2–4 for $Bi = \infty$, permits an assessment of the relative importance of the presence of mass-transfer resistance in the external continuous phase.

Notation

b, c = stoichiometric coefficients
A, B, C = reactants and products
Bi = Biot number, $mk_l^c R/D_A$
C_A, C_B = concentrations of A and B
$\overline{C}_A^d$ = dimensionless concentration of A in the drop
$\overline{C}_B$ = dimensionless concentration of B in the drop
D_A, D_B = diffusivity of A and B in the drop
D = diffusivity ratio, D_B/D_A
E_i = enhancement factor for instantaneous reaction
k_l^c = continuous phase mass-transfer coefficient
m = Henry's law constant, $C^c_{A\infty}/C^d_{A\infty}$
R = drop radius
t = time
X_B = fractional conversion of B

Greek letters

α_n = roots of $\alpha = \tan \alpha$
τ = dimensionless time, tD_A/R^2
ρ = dimensionless radial position, r/R
β = concentration ratios, $C_{B0}/bC^d_{A\infty}$
τ_0 = threshold time

Superscripts

c = continuous phase
d = dispersed phase

Subscripts

∞ = value in bulk continuous phase

Literature Cited

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