

Gas Absorption Accompanied by a Second-Order Chemical Reaction Modeled According to the Danckwerts Surface Renewal Theory

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In the work reported here, gas absorption accompanied by a second-order irreversible reaction was modeled by the Danckwerts surface renewal theory. The partial differential equations describing the unsteady state diffusion and reaction of gas A and liquid-phase reactant B were solved numerically, and the results of these numerical calculations were integrated over time according to the surface renewal theory to obtain the enhancement factor. The stoichiometry considered in this work, $A + 2B \rightarrow \text{products}$, corresponds to the industrially important case of carbon dioxide absorption in aqueous hydroxide solutions.

Solutions to this problem based on the penetration theory have been obtained by Brian et al. (1961) and by Pearson (1963). The predicted enhancement factors of this work were found to differ only slightly from those calculated from the Higbie penetration theory. The numerical results were also found to be in good agreement with the approximate analytical formula of DeCoursey (1974) over a wide range in the parameters. The DeCoursey equation is a simple, explicit relationship for the enhancement factor based on the Danckwerts model.

DEVELOPMENT OF NUMERICAL SOLUTION

The physical situation for the absorption of gas A followed by subsequent irreversible reaction with liquid phase reactant B ($A + 2B \rightarrow \text{products}$) can be represented by a pair of time-dependent diffusion equations:

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - k C_A C_B \quad (1)$$

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} - 2k C_A C_B \quad (2)$$

The initial boundary conditions are taken to be:

$$t = 0 \quad x > 0 \quad C_B = C_{Bi} \quad C_A = 0$$

$$t > 0 \quad x = 0 \quad \frac{\partial C_B}{\partial x} = 0 \quad C_A = C_{Ao} \quad (3)$$

$$t > 0 \quad x \rightarrow \infty \quad C_B = C_{Bi} \quad C_A = 0$$

Equations (1) and (2) with boundary conditions given by Equations (3) were solved numerically in dimensionless form using the Crank-Nicolson finite-difference procedure.

The amount of gas A absorbed into the liquid per unit area in contact time τ is given by

$$Q(\tau) = D_A \int_0^\tau \left(\frac{-\partial C_A}{\partial x} \right)_{x=0} dt \quad (4)$$

The enhancement factor based on a penetration theory model is obtained by dividing $Q(\tau)$ by the amount of gas absorbed per unit area for physical absorption as predicted by penetration theory:

$$E_P(\tau) = Q(\tau) \sqrt{\frac{\pi}{D_A \tau}} / (2C_{Ao}) \quad (5)$$

Thus, the enhancement factor may be calculated from the results of the numerical calculations through Equations (4) and (5). Figure 1 shows some typical results of the calculations for $D_B/D_A = 1$ and for $0.2 \leq C_{Bi}/C_{Ao} \leq 10.0$.

ENHANCEMENT FACTOR BASED ON SURFACE RENEWAL THEORY

Pearson (1963) has obtained a large time asymptotic solution to Equations (1) and (2). Equation (6) expresses the rate of gas absorption at time τ per unit area as determined from the large time asymptotic solution of Pearson:

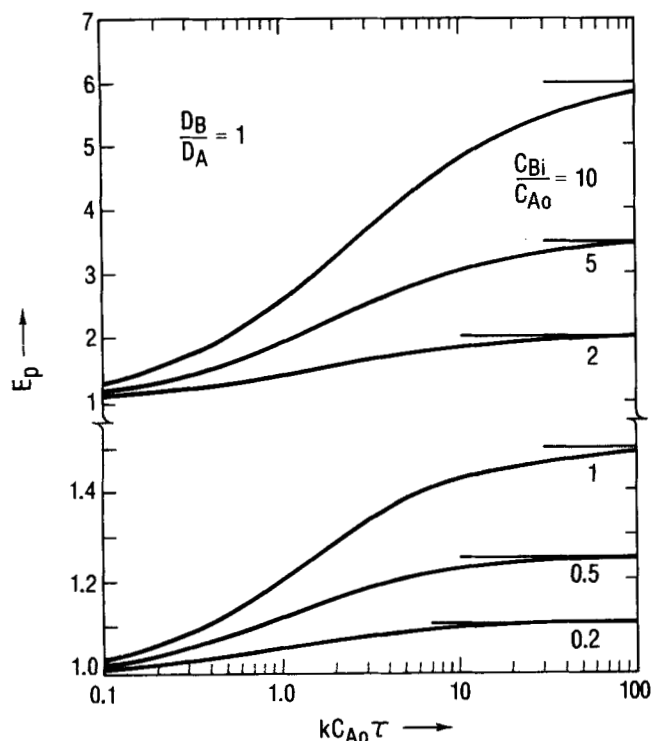


Fig. 1. Enhancement factor based on the penetration theory model as a function of contact time. $A + 2B \rightarrow \text{products}$.

$$R(\tau) = R_o(\tau_o) + \frac{C_{Ao}}{\text{erf } B} \left(\frac{D_A}{\pi} \right)^{1/2} \left| (\tau - \tau_o)^{1/2} \right| \quad (6)$$

In Equation (6), τ_o corresponds to the time at which the asymptotic solution is applicable, and B is given by the solution of the nonlinear Equation (7):

$$\frac{1}{2} \left(\frac{C_{Bi}}{C_{Ao}} \right) \left(\frac{D_B}{D_A} \right)^{1/2} \text{erf } B \exp B^2$$

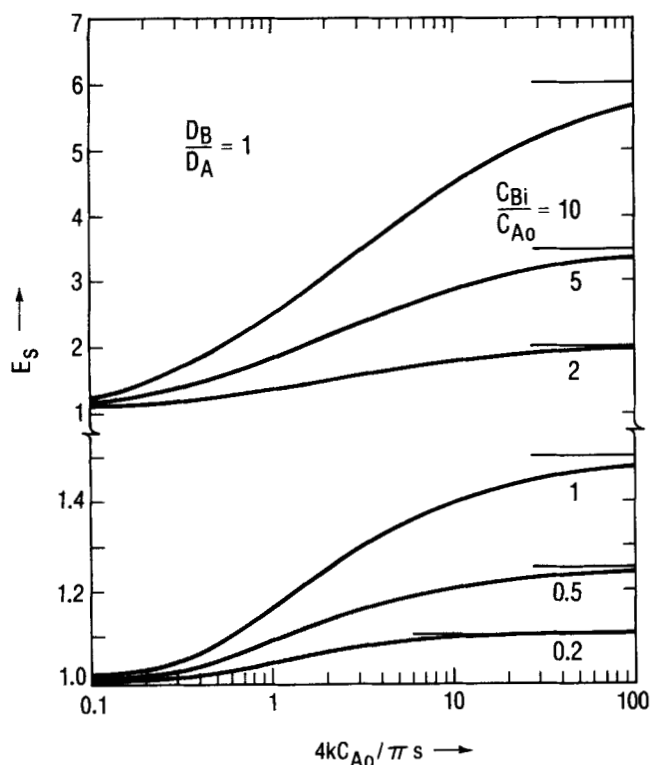


Fig. 2. Enhancement factor based on the surface renewal theory model as a function of surface renewal rate. $A + 2B \rightarrow \text{products}$.

$$= \text{erfc} \left[B \left(\frac{D_A}{D_B} \right)^{1/2} \right] \exp \left(\frac{B^2 D_A}{D_B} \right) \quad (7)$$

The mass transfer coefficient according to the Danckwerts surface renewal theory is expressed as

$$k_c = \frac{1}{C_{Ao}} \int_0^\infty s e^{-st} R(t) dt \quad (8)$$

The expression for the enhancement factor for the surface renewal theory is obtained by dividing Equation (8) by the mass transfer coefficient for physical absorption, $k_c^o = \sqrt{D_A s}$:

$$E_s(s) = \frac{1}{C_{Ao} \sqrt{D_A s}} \int_0^\infty s e^{-st} R(t) dt \quad (9)$$

The integral in Equation (9) may be split into two parts, so that for the first part, for $0 \leq t \leq \tau_o$, the integrand in Equation (9) may be determined from the numerical solution of the differential equations, and for the second part, $\tau_o \leq t < \infty$, the asymptotic expression of Pearson may be used in the integrand. In this case, the second term may be evaluated exactly to give

$$E_s(s) = \frac{1}{C_{Ao} \sqrt{D_A s}} \int_0^{\tau_o} s e^{-st} R(t) dt + (1/\text{erf } B) \text{erfc} \left(s \sqrt{\frac{\tau_o}{k C_{Ao}}} \right) \quad (10)$$

Thus, for a given rate of surface renewal s , the enhancement factor may be calculated from Equation (10) using the values of $R(t)$ determined from the numerical solution of Equations (1) and (2). τ_o is taken to be sufficiently large so that the numerical calculations agree with the asymptotic solution of Pearson.

Figure 2 shows some typical results for the enhancement factor based on the surface renewal theory.

Figure 3 compares the enhancement factors based on the penetration theory and surface renewal theory models. The abscissa scales in Figure 3 were chosen in such a way that both models predict the same mass transfer coefficient in the limit of no reaction. It may be seen in Figure 3 that the predictions of the surface renewal theory are in all cases slightly higher than for the penetration theory. However, the differences in the predictions of the two models are relatively insignificant over the complete range in penetration time or surface renewal rate.

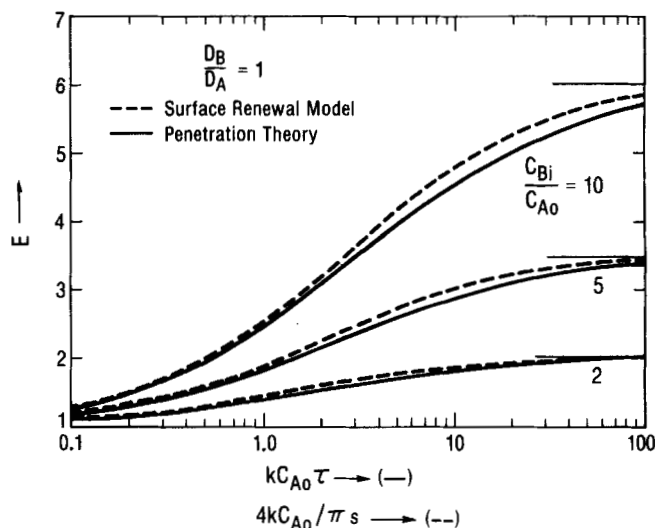


Fig. 3. Comparison of enhancement factor as predicted by surface renewal and penetration theory models. $A + 2B \rightarrow \text{products}$.

TABLE 1. ASYMPTOTIC VALUES OF THE ENHANCEMENT FACTOR FOR AN INSTANTANEOUS CHEMICAL REACTION

$\frac{C_{Bi}}{C_{Ao}} \backslash \frac{D_B}{D_A}$	0	0.2	0.5	0.75	1	1.5	2	5
0	1	1	1	1	1	1	1	1
0.2	1.0816	1.0861	1.0918	1.0961	1.1000	1.1072	1.1137	1.1457
0.5	1.1892	1.2044	1.2234	1.2373	1.2500	1.2732	1.2942	1.3978
1	1.3469	1.3865	1.4341	1.4685	1.5000	1.5572	1.6090	1.8648
2	1.6143	1.7178	1.8371	1.9223	2.0000	2.1404	2.2671	2.8834
3	1.8424	2.0233	2.2260	2.3697	2.5000	2.7343	2.9446	3.9503
4	2.0449	2.3127	2.6064	2.8132	3.0000	3.3340	3.6319	5.0376
5	2.2290	2.5910	2.9813	3.2544	3.5000	3.9371	4.3249	6.1353
6	2.3989	2.8612	3.3523	3.6939	4.0000	4.5424	5.0215	7.2390
7	2.5575	3.1252	3.7204	4.1322	4.5000	5.1492	5.7205	8.3462
8	2.7067	3.3843	4.0862	4.5696	5.0000	5.7571	6.4211	9.4560
9	2.8482	3.6394	4.4504	5.0064	5.5000	6.3658	7.1229	10.567
10	2.9829	3.8912	4.8132	5.4426	6.0000	6.9751	7.8256	11.680

INSTANTANEOUS REACTION CASE

The large time asymptotic solution of Equations (1) to (3) obtained by Pearson (1963) is equivalent to the result which would be obtained for the case of an instantaneous reaction. The enhancement factor for the instantaneous reaction case is expressed as

$$E_a = 1/\text{erf } B \quad (11)$$

where B is given by the implicit relation, Equation (7). Table 1 gives the asymptotic values of the enhancement factor for the instantaneous reaction case as calculated from Equations (7) and (11) over a range in the parameters C_{Bi}/C_{Ao} and D_B/D_A . The asymptotic results in Table 1 agree with the approximate expression for large E_a given by Equation (12) to within 4% for $C_{Bi}/C_{Ao} > 3$ and for $D_B/D_A > 0.75$:

$$E_a = \sqrt{\frac{D_A}{D_B}} + \frac{C_{Bi}}{2C_{Ao}} \sqrt{\frac{D_B}{D_A}} \quad E_a \gg 1 \quad (12)$$

The asymptotes in Figures 1 to 3 are given by Equation (11).

COMPARISON WITH THE APPROXIMATE ANALYTICAL RESULTS OF DeCOURSEY

DeCoursey (1974) carried out an approximate analytical integration of Equations (1) and (2) for the Danckwerts surface renewal theory. The DeCoursey formula for the enhancement factor is given as

$$E_D = -\frac{M}{2(E_a - 1)} + \left(\frac{M^2}{4(E_a - 1)^2} + \frac{E_a M}{(E_a - 1)} + 1 \right)^{1/2} \quad (13)$$

where E_a is the asymptotic value of the enhancement factor for instantaneous reactions as given by Equation (11). A comparison of this simple explicit relation for the enhancement factor with the results of the numerical calculations of this work showed very good agreement over a wide range of variables. For $0.2 \leq D_B/D_A \leq 5$ and for $0.2 \leq C_{Bi}/C_{Ao} \leq 10$, the maximum discrepancy in the enhancement factor was less than 7%. Thus, owing to the simplicity and accuracy of Equation (13), its use can be recommended for enhancement factor predictions based on either the penetration or surface renewal theories.

NOTATION

- B = constant determined by solving Equation (7)
 C_A = concentration of dissolved gas, g mole/cm³
 C_{Ao} = interfacial concentration of dissolved gas, g mole/cm³
 C_B = concentration of liquid phase reactant, g mole/cm³
 C_{Bi} = concentration of liquid phase reactant in the bulk liquid, g mole/cm³
 D_A = diffusivity of dissolved gas, cm²/s
 D_B = diffusivity of liquid phase reactant, cm²/s
 E = enhancement factor $\equiv k_c/k_c^o$
 E_a = asymptotic value of the enhancement factor given by Equation (11)
 E_D = enhancement factor predicted by the DeCoursey formula, Equation (13)
 E_p = enhancement factor based on penetration theory
 E_s = enhancement factor based on surface renewal theory
 k = second-order reaction rate constant, cm³/g mole s
 k_c = mass transfer coefficient for chemical absorption, cm/s
 k_c^o = mass transfer coefficient for physical absorption, cm/s
 M = $D_A k C_{Bi} / (k_c^o)^2$
 Q = amount of gas absorbed per unit area, g mole/cm²
 R = rate of gas absorption per unit area, g mole/cm²s
 s = rate of surface renewal, s⁻¹
 x = distance measured into the liquid from the free surface, cm
 τ = contact time, s
 τ_o = contact time at which the large time asymptotic solution is applicable, s

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