A Diffusion Model For Reactions With Turbulent Mixing

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A diffusion model based on the simultaneous interdiffusion and reaction between alternate slabs of reactants is used to simulate the data of Vassilatos and Toor. After slab sizes are chosen to fit the conversion data for very rapid reactions in a stoichiometric mixture, reasonably good predictions are obtained of the effect of stoichiometry and reaction velocity constant on conversion. The results are close to the predictions of Kattan and Adler's stochastic mixing model, and the similar behavior of these disparate models implies that conversion is insensitive to the details of the mixing.

Chemical reactions in turbulent reactors can be divided into slow, rapid, and very rapid reactions (14), according to the relative rates between reaction and mixing. They correspond, respectively, to reaction rates much slower than the rate of mixing, reaction rates comparable to the rate of mixing, and reaction rates much faster than the rate of mixing. In general, slow reactions are not affected by turbulent concentration fluctuations. However, rapid and very rapid second-order reactions present a completely different problem due to nonhomogeneity. Here the reactants have to be brought together by molecular and turbulent diffusion, and concentration fluctuations do affect the reaction rate.

When the reaction is very rapid, the rate at which the reactants are brought together on the fine scale controls the reaction rate. This diffusion controlled reaction limit has been solved (*5, 13, 7, 14*), resulting in a relationship between the time average conversion, the scalar decay law of the mixer, and the stoichiometry.

The remaining problem is, as is common, the intermediate case of rapid reactions. In this range, it might be expected at first glance that a rather detailed knowledge of the effect of turbulence, reaction, and molecular diffusion would be required in order to predict the mean conversion.

Corrsin (*2*) has extended the statistical theory of turbulence to mass transfer with chemical reactions, but only first- and second-order reactions with single species (*2* to *4, 8* to *10*) have been analyzed.

Recently, Kattan and Adler (*6*) have simplified the problem by assuming random coalescence and redispersion of homogeneous fluid lumps. Their stochastic mixing model thus avoids molecular diffusion as an explicit step. By setting the rate of coalescence and redispersion to fit the data of Vassilatos and Toor (*14*) for very rapid reactions in a stoichiometric mixture, Kattan and Adler were able to predict reasonably well the conversion for nonstoichiometric mixtures as well as the conversion for rapid and slow reactions.

The fact that this simple model works as well as it does leads one to speculate that perhaps conversion is not a sensitive function of the details of the mixing, at least for the system of Vassilatos and Toor (*14*). Hence, another simple model which represents almost the opposite extreme of the Kattan and Adler model will be considered: a pure molecular diffusion model.

MATHEMATICAL MODEL

The diffusion model divides the fluid into slabs of thickness δ which are alternately arranged with reactants A and B at constant initial values of c_{A0} and c_{B0}. The stoichiometric equation is given by

$$A + nB \rightarrow \text{Product}$$

and the rate law by

$$r_A = -k\ c_A\ c_B$$

For the case of equal diffusivities, the model can be represented by the following two dimensionless equations:

$$\frac{\partial C_A}{\partial \Theta} = \frac{\partial^2 C_A}{\partial X^2} - \alpha\ C_A\ C_B \tag{1a}$$

$$\frac{\partial C_B}{\partial \Theta} = \frac{\partial^2 C_B}{\partial X^2} - \frac{\alpha}{\beta} C_A\ C_B \tag{1b}$$

With boundary conditions

$$\Theta = 0, \quad 0 < X < \tfrac{1}{2}, \quad C_A = 1, \quad C_B = 0$$
$$\tfrac{1}{2} < X < 1, \quad C_A = 0, \quad C_B = 1 \tag{1c}$$

$X = 0$ and 1:

$$\frac{\partial C_A}{\partial X} = \frac{\partial C_B}{\partial X} = 0 \tag{1d}$$

The dimensionless quantities are defined by

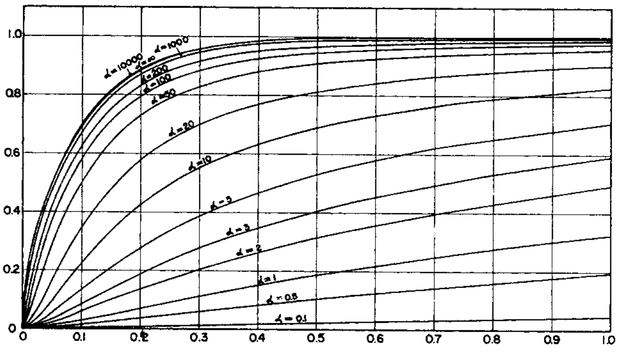

Fig. 1. Fractional conversion vs. time, $\beta = 1$.

$$X = \frac{x}{\delta}$$

$$\Theta = \frac{D\theta}{\delta^2}$$

$$C_i = \frac{c_i}{c_{io}}$$

$$\beta = c_{B0}/n\ c_{A0}$$

$$\alpha = k\delta^2\ c_{B0}/D$$

Equation (1*d*) follows from the symmetry of the problem.

The space mean concentration is given by

$$\overline{C}_A = \int_0^1 C_A\ dX \tag{2}$$

and the fractional conversion of species *A* by

$$F_A = 1 - 2\ \overline{C}_A \tag{3}$$

since $\overline{C}_{A0} = \dfrac{1}{2}$.

At the limit $\alpha \rightarrow 0$ there is no reaction, and the solution to Equation (1) is, of course, available in analytic form.

At the limit $\alpha \rightarrow \infty$ a reaction surface exists which allows construction of an analytic solution for this limit also (*13*). For $\beta = 1$, the reaction surface remains at $X = \dfrac{1}{2}$, and the solution is particularly simple. The conversion, for example, is given in this case by

$$F_A = 1 - \frac{8}{\pi^2} \sum_{n=1,3,5,..}^{\infty} \frac{1}{n^2} \exp(-\,n^2\,\pi^2\,\Theta) \tag{4}$$

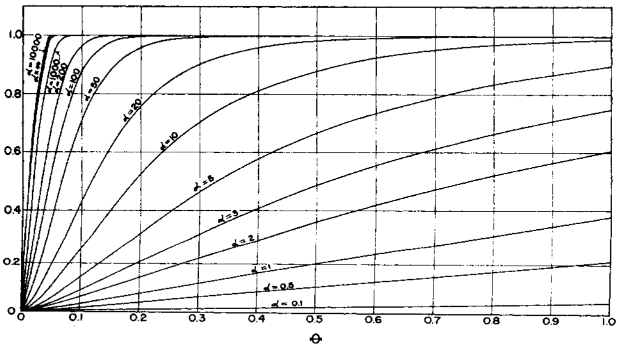

Fig. 2. Fractional conversion vs. time, $\beta = 10$.

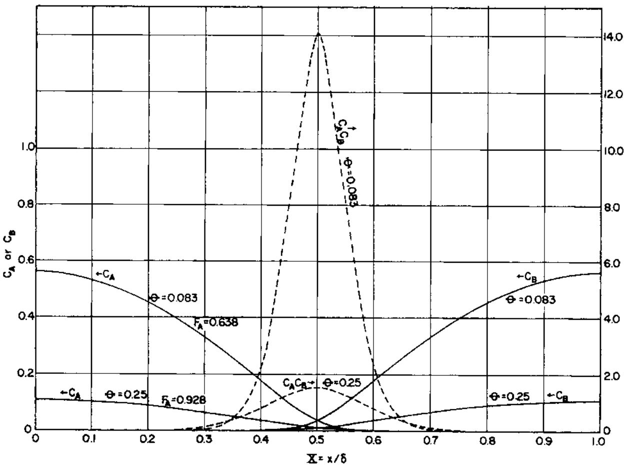

Fig. 3. Concentration profiles, $\beta = 1$, $\alpha = 10^4$.

Except for the limiting cases, Equation (1) must be solved numerically. Some solutions of the problem in a semi-infinite medium have been obtained by Perry and Pigford (*12*), Pearson (*11*), and Brian and his co-workers (*1*). Perry and Pigford used an explicit finite-difference method to solve their problems, yet Pearson and Brian chose two differently linearized implicit methods in order to avoid the difficulties encountered when an explicit method is used. Generally, explicit procedures are considered to be relatively easy, but they have critical stability limitations. For explicit schemes, the mesh size has to be decreased if α increases; hence, an exceedingly small size and a very large amount of computer time are required to obtain the results covering a wide range of α. However, it was found that for the diffusion model, solutions for $\alpha \geqq$ 10,000 were not really needed because they were almost equivalent to the limiting solutions for $\alpha = \infty$ (see Figures 1 and 2). Thus, a simple explicit method was chosen for this problem.

COMPUTATIONS

Equation (1) was solved in finite-difference form by using the increments

$$\Delta X = 1/20$$

$$\Delta\Theta = \frac{0.9}{\alpha + \dfrac{2}{(\Delta X)^2}}$$

These choices satisfy the necessary conditions for stability. Solutions for various values of β in the range $1 \leqq \beta \leqq 10$ were obtained, and at each value of β solutions were obtained for about twelve values of α in the range $0 < \alpha < 10^4$. The concentration profiles in each case were numerically integrated producing curves of F_A vs. Θ. Computation time on a Control Data G-21 computer was about 15 min. for each value of β. Data for $\beta = 1$ and $\beta = 10$ are shown in Figures 1 and 2. The values of F_A are accurate to about 0.1%. In almost all cases the concentrations are either zero or uniform in space for $\Theta \geqq 1$, so the conversion curves for $\Theta > 1$ can be obtained by following the homogeneous rate law.

The curves for $\alpha = \infty$ represent the analytic results mentioned earlier [in Figure 1 it is Equation (4)], and this diffusion controlled limit can be seen to be closely approached at $\alpha = 10^4$. It is interesting to observe that this limiting rate of reaction is closely approximated, even though the region in which the reaction is taking place is

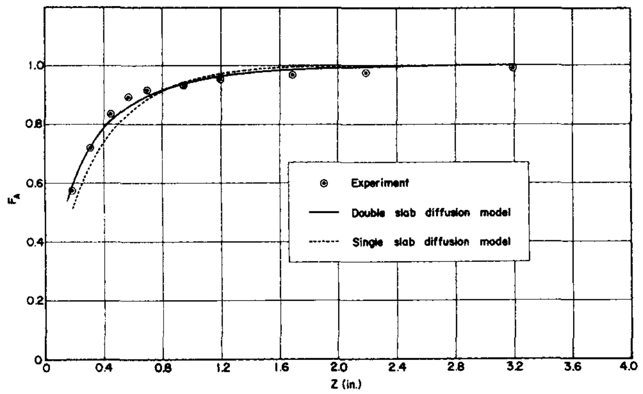

Fig. 4. Fractional conversion vs. distance, $\beta = 1$, $k = 10''$ liter/(mole) (sec.).

a significant fraction of the total region. Figure 3 shows, as an example, the instantaneous concentration profiles for two times with $\beta = 1$ and $\alpha = 10^4$. Also shown is the product $C_A\ C_B$ which is proportional to the reaction rate. It is seen that the reaction region occupies about 20% of the total space, even though F_A for this case is almost indistinguishable from the curve for $\alpha = \infty$ which assumes a delta function behavior for kC_AC_B. Similar behavior occurs for all values of β.

APPLICATION OF THE MODEL

In order to apply the diffusion model to the problems of reactions in turbulent flow, the slab thickness δ has to be determined. This can be accomplished during the process of simulating the experimental data for very rapid reactions. Since the slab size is assumed to be a function of the hydrodynamic conditions only, once δ is determined the conversions of other reaction systems at the same hydrodynamic conditions can be predicted from the F_A vs. Θ curves. The choice of δ effectively is a scaling of Θ into real time (or distance).

The diffusion model was employed to predict the experimental results of Vassilatos and Toor (*14*). Equal feed flow rates for the reactants were assumed for their experiments (actually $V_A/V_B = 0.8672$) (*15*); hence c_{A0} and c_{B0} were equal to $2\tilde{c}_{A0}$ and $2\tilde{c}_{B0}$, respectively. The data for very rapid reactions at $\beta = 1$ were simulated to determine the slab thickness δ. It was found by trial and error that the model's simulation of the $\beta = 1$ data could be improved by using two different slab sizes instead of one, but little progress could be made by increasing the different sizes from two to three. The best combination of two different values of δ was $\delta = \sqrt{D/3.3}$ and $\delta = \sqrt{D/10}$ for each half of the fluid. For a single slab size, the best value of δ was about $\sqrt{D/4.5}$. These curve fittings are shown in Figure 4. The experimental data are those of Vassilatos and Toor obtained by using acid-base systems with reaction velocity constants the order of 10^{11} liter/(mole) (sec.). These data correspond to the diffusion controlled limit; α is effectively ∞. Vassilatos and Toor's data at this same diffusion controlled limit for different values of β are shown in Figures 5 and 6, where the conversion at various values of β is plotted against the conversion for $\beta = 1$. The solid lines represent the predictions of a statistical model (*13*) which fits the data quite well and which is a much more realistic model than the present one. It is valid, however, only at the diffusion controlled limit.

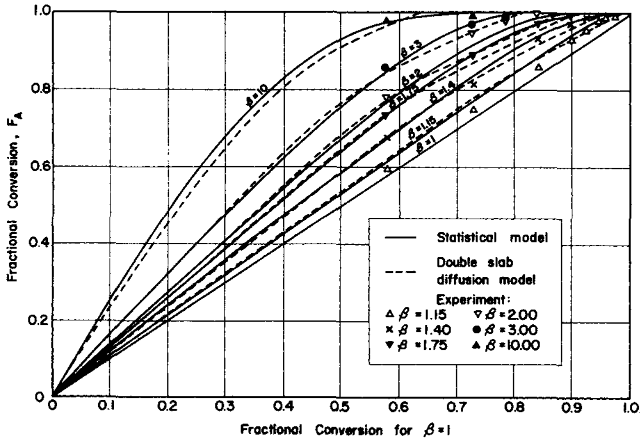

Fig. 5. Comparison between single slab diffusion model and statistical model.

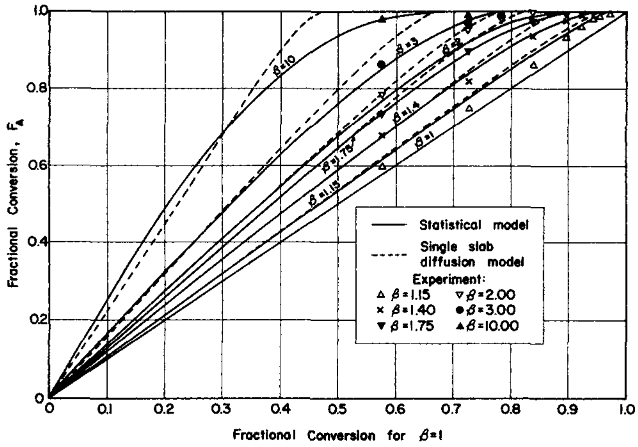

Fig. 6. Comparison between double slab diffusion model and statistical model.

The single slab model predictions are shown in Figure 5 and the double slab predictions in Figure 6. The double slab does a considerably better job of predicting the effect of β; it is about as good as the statistical model. Kattan and Adler's (*6*) prediction at $\beta = 1.4$ is indistinguishable from the statistical model on these graphs. It should be noted that this method of comparison is only a comparison

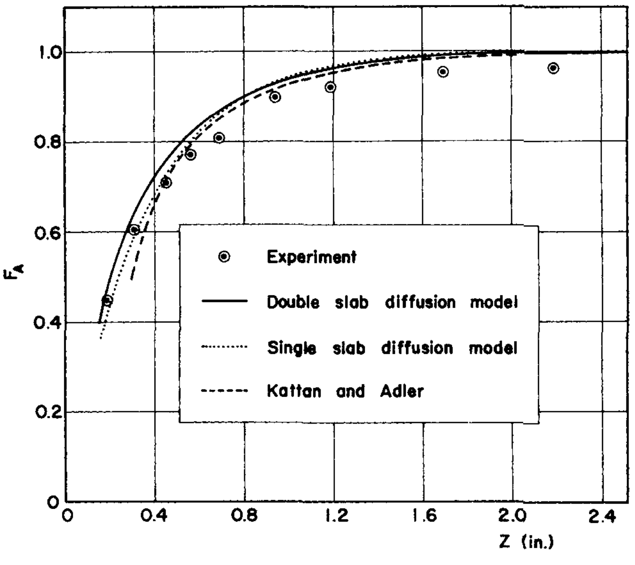

Fig. 7. Fractional conversion vs. distance, $k = 12{,}400$ liter/(mole) (sec.), $\beta = 1.26$.

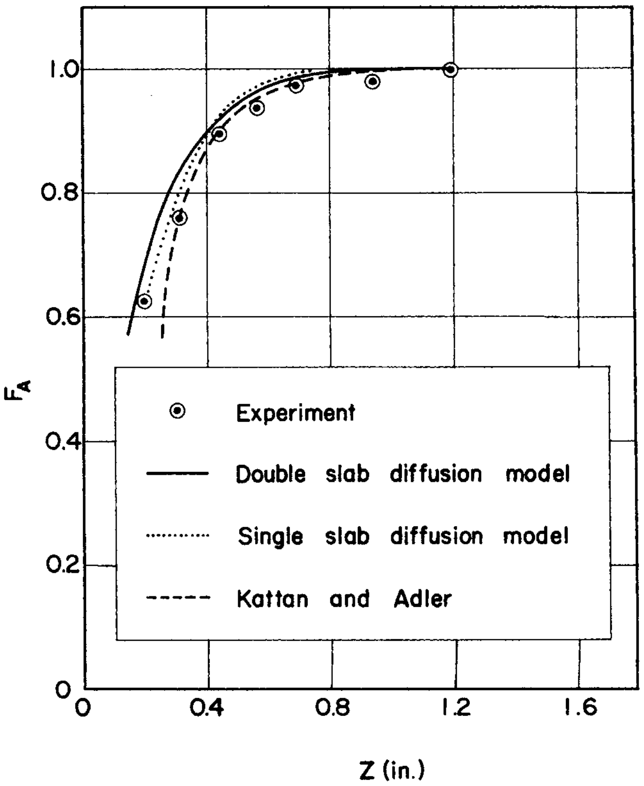

Fig. 8. Fractional conversion vs. distance, k = 12,400 liter (mole) (sec.), $\beta = 2.52$.

of the effect of stoichiometry; it ignores any discrepancy between the models and the measurements at $\beta = 1$.

The predictions of the two diffusion models and of Kattan and Adler (6) are compared with the carbon dioxide-sodium hydroxide data of Vassilatos and Toor in Figures 7 and 8. The reaction velocity here is 12,400 liter/(mole)(sec.), and the reaction and mixing are of comparable speed.

Figure 9 compares the predictions of the same models with the methylformate-sodium hydroxide data of Vassilatos and Toor which are reaction controlled.

These examples are typical of the results obtained for all the data of Vassilatos and Toor. In general, the double slab diffusion model and the stochastic mixing model are in close agreement, and both agree moderately well with the experimental data. Apparently either one can be used to predict the effect of stoichiometry and reaction velocity on the conversion if very rapid reaction data are available. The close agreement between the two disparate models implies that the conversion in a mixing process is not very sensitive to the details of the mixing.

The order of magnitude of the value of δ required to fit the data here was 10^{-3} cm., although we attribute little physical meaning to this quantity.

The model predictions are close to the diffusion controlled limit when α is in the range of 10^3 to 10^4. From the definition of α, using 10^{-3} cm. for δ and appropriate quantities for the other parameters, we conclude that under the conditions used by Vassilatos and Toor, the diffusion controlled limit should be closely approached for a reaction velocity constant in the range of 10^6 to 10^7 liter/(moles)(sec.). Further data are needed to check this prediction.

ACKNOWLEDGMENT

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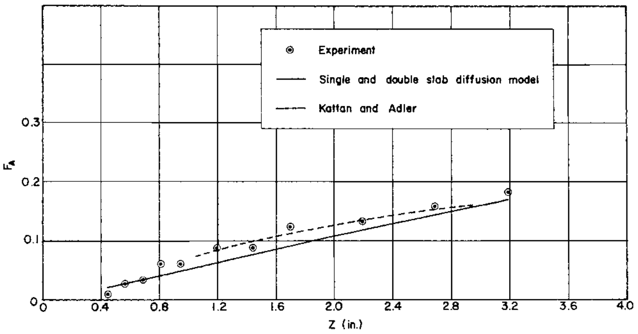

Fig. 9. Fractional conversion vs. distance, k = 47 liter/(mole)(sec.), $\beta = 1.56$.

NOTATION

A, B = species A, B
c_i = molar concentration of species i
C_i = c_i/c_{io}
D = molecular diffusivity
F_A = fractional conversion of secies A
k = reaction velocity constant
n = stoichiometric coefficient
r = reaction rate
V_i = feed flow rate for species i
x = distance in the direction of diffusion
X = x/δ
z = axial distance measured from reactor inlet

Greek Letters

α = $k\,\delta^2\,c_{B0}/D$, second Damköhler number
β = c_{B0}/nc_{A0}, initial stoichiometric ratio
δ = slab thickness
ΔX = increment in X
$\Delta\Theta$ = increment in Θ
θ = time
Θ = $D\theta/\delta^2$

Subscripts

i = species A or B
0 = initial value

Superscripts

$\overline{\ }$ = space average
$\sim$ = bulk average

LITERATURE CITED

1. Brian, P. L. T., J. F. Hurley, and E. H. Hasseltine, *AIChE J.*, **7**, 226 (1961).
2. Corrsin, S., *Phys. Fluids*, **1**, 42 (1958).
3. ———, *J. Fluid Mech.*, **11**, Pt. 3, 407 (1961).
4. ———, *Phys. Fluids*, **7**, 1156 (1964).
5. Hawthorne, W. R., D. S. Weddell, and H. C. Hottel, "Third Symposium on Combustion and Flame and Explosion Phenomena," p. 266, Williams and Wilkin, Baltimore, Md. (1949).
6. Kattan, Abraham, and R. J. Adler, *AIChE J.*, 13, 580 (1967).
7. Keeler, R. N., E. E. Petersen, and J. M. Prausnitz, *ibid.*, **11**, 221 (1965).
8. Lee, J., *Phys. Fluids*, 9, 1753 (1966).
9. O'Brien, E. E., *ibid.*, 215.
10. *Ibid.*, 1561.
11. Pearson, J. R. A., *Appl. Sci. Res.*, **A11**, 321 (1963).
12. Perry, R. H., and R. L. Pigford, *Ind. Eng. Chem.*, **45**, 1247 (1953).
13. Toor, H. L., *AIChE J.*, **8**, 70 (1962).
14. Vassilatos, George, and H. L. Toor, *ibid.*, **11**, 666 (1965).
15. Vassilatos, G., Ph.D. thesis, Carnegie-Mellon University, Pittsburgh, Pa. (1964).

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