$$+ \frac{1}{\dfrac{3.58\mathcal{D}}{Ru^*} + 2\sqrt{f/2}} \qquad (2)$$

This equation is consistent with the experimental observation of Popovich and Hummel (1967) that $y^+ = 1.6$ is the limit of the laminar sublayer, and $y^+ = 34.6$ is the limit of the transition region. Hughmark (1973) has shown that the eddy term for the transition region is consistent with the penetration model and the mean period of fluctuation near the wall. The eddy term for the transition region was also shown to be consistent with experimental data for the eddy diffusivities of heat and mass. Hughmark (1971) has also shown that the two-thirds exponent for the laminar region is consistent with developing laminar boundary-layer model. The core term and the molecular diffusion term for the transition region represent a negligible contribution with high Schmidt numbers. Thus, for this case, Equation (2) reduces to

$$\frac{1}{k^+} = \frac{1}{\dfrac{1}{1.6\,N_{Sc}} + \alpha N_{Sc}^{-2/3}} + \frac{1}{0.0615\,N_{Sc}^{-1/2}} \qquad (3)$$

Equation (3) with the Shaw and Hanratty data provides an average value of $\alpha = 0.047$. Comparison of Equation (3) with this value and the data shows an average absolute deviation of about 2%, and comparison of Equation (1) with the data shows an average absolute deviation of about 3.6%. Thus, both equations represent excellent correlations of these experimental data.

Equation (3) provides an estimate of the relative contributions of the laminar and transition regions. At a Schmidt number of 100 000, about 12% of the total resistance would appear to be in the transition region, and molecular diffusion represents about 20% of the laminar layer resistance. These estimated values are consistent with Shaw and Hanratty's conclusion that the commonly proposed relations $N_{Sc}^{-2/3}$ or $N_{Sc}^{-3/4}$ are incorrect for the Equation (1) model with high Schmidt numbers.

## NOTATION

$\mathcal{D}$ = molecular diffusivity
$f$ = friction factor
$k$ = mass transfer coefficient
$k^+$ = dimensionless transfer coefficient, $k/u^*$
$N_{Sc}$ = Schmidt number
$R$ = core radius for circular pipe
$u^*$ = shear velocity
$y^+$ = $yu^*/\nu$
$y$ = radial distance from pipe wall
$\nu$ = kinematic viscosity

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*Manuscript received February 10, and accepted April 12, 1977.*

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# Simple Criteria for Mixing Effects in Complex Reactions

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Detailed modeling of an incompletely mixed reactor is complex and usually calls for data and parameter values which are inaccurately known or possibly inaccessible. These difficulties are particularly marked when we consider complex (that is, multistep) reactions. In this case, only knowledge of the reaction mechanism and a few kinetic data are usually available, and the effort required to obtain all the kinetic and hydrodynamic parameters required by a full modeling can probably be justified for only a few frequently occurring reactions. Furthermore, no model has been sufficiently well tested to allow its general application.

With knowledge of the reaction mechanism, but without the kinetics, a simple method can be applied which does not determine quantitatively the extent of a mixing effect but rather indicates qualitatively how partial segregation and feed configuration influence the rates of formation of the desired and undesired products and hence the selectivity. This method was previously applied in the detailed development for a second-order reaction (Toor, 1962; Vassilatos and Toor, 1965; Toor, 1975). It will be illustrated here for some complex reactions, where the objective is to produce an intermediate. (It is also applicable in other situations, for example, when producing the final product of a sequence of reactions.) In this note we consider both incompletely mixed continuous stirred-tank reactors (CSTR) and turbulent tubular reactors together.

The concentration $X$ of a substance at any point in an inhomogeneous reactor is set equal to the time averaged concentration $\overline{X}$ of $X$ at a point plus a concentration deviation $X'$, due to incomplete mixing: $X = \overline{X} + X'$. Applications follow.

### COMPETITIVE (PARALLEL) REACTIONS

When the reactions differ in their kinetic orders, mixing influences not only the reaction rates but also the selectivity. The simplest of these cases is considered here:

$$A \xrightarrow{k_1} P \quad r_P = k_1 A$$

$$A + A \xrightarrow{k_2} A_2 \quad r_{A2} = k_2 A^2$$

$$\overline{r}_P = k_1(\overline{\overline{A} + A'}) = k_1\overline{A}$$

$$\overline{r}_{A2} = k_2\overline{(\overline{A} + A')^2} = k_2(\overline{A}^2 + \overline{A'^2})$$

The product forming reaction, being first order, is not influenced by incomplete mixing, while the rate of dimerisation is increased; the selectivity ($\overline{r}_P/\overline{r}_{A2}$) therefore falls.

Reactions involving two or more reactants can be realized using either a premixed stream containing all reactants or separate feed streams:

$$A + B \xrightarrow{k_1} P \quad r_P = k_1 AB$$

$$A + A \xrightarrow{k_2} A_2 \quad r_{A2} = k_2 A^2$$

$$\overline{r}_P = k_1(\overline{A}\,\overline{B} + \overline{A'B'})$$

$$\overline{r}_{A2} = k_2(\overline{A}^2 + \overline{A'^2})$$

Premixed feed: $A'$ and $B'$ will be positively correlated at all points in an incomplete mixture (Appendix A). $A'$ will always be completely positively correlated with itself. In an incompletely mixed reaction, both reactions will proceed faster than in the ideally mixed case, but relatively little change in selectivity should result because of the similar signs of the fluctuation terms.

Separate feeds: $A'$ and $B'$ exhibit negative correlations (Appendix A). With incomplete mixing, the rates of product formation and dimerization will be decreased and increased, respectively, and a significant loss of selectivity may occur. This loss will depend upon the relative magnitude of the products of the fluctuations which will depend upon the incompleteness of the mixing. It will be significant when the reaction is rapid compared to the mixing.

### CONSECUTIVE (SERIES) REACTIONS

Mixing effects are absent when first-order reactions follow each other. For a first-order reaction followed by a second-order step:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \quad \overline{r}_B = k_1\overline{A} - k_2(\overline{B}^2 + \overline{B'^2})$$

$$\overline{r}_C = k_2(\overline{B}^2 + \overline{B'^2})$$

Segregation retards the formation of $B$ by accelerating the reaction of $B$ to $C$.

### SERIES-PARALLEL REACTIONS

$$A + B \xrightarrow{k_1} C \quad C + B \xrightarrow{k_2} D$$

$$\overline{r}_C = k_1(\overline{A}\,\overline{B} + \overline{A'B'}) - k_2(\overline{B}\,\overline{C} + \overline{B'C'})$$

$$\overline{r}_D = k_2(\overline{B}\,\overline{C} + \overline{B'C'})$$

Premixed feed: $A'$ and $B'$ are positively correlated (Appendix A) as are $B'$ and $C'$ (Appendix B). Since both reaction rates are increased, the selectivity is increased or decreased depending upon whether $\overline{A'B'}/\overline{A}\,\overline{B}$ is greater or less than $\overline{B'C'}/\overline{B}\,\overline{C}$. The resolution of this point requires a detailed model.

Separate feeds: $A'$ and $B'$ exhibit negative correlation, while $B'$ and $C'$ are only weakly correlated (Appendixes A and B). With segregation, the rate of product ($C$) formation would fall, while the rate of by-product ($D$) formation would remain relatively unchanged; imperfect mixing lowers selectivity.

### AUTOCATALYSIS

$$A + B \xrightarrow{k} B + B \quad \overline{r}_B = k(\overline{A}\,\overline{B} + \overline{A'B'})$$

Premixed feed: $A'$ and $B'$ are negatively correlated (Appendix C); the reaction rate is reduced by imperfect mixing.

Separate feeds: $A'$ and $B'$ are probably negatively correlated (Appendix C); segregation probably reduces the reaction rate in this case as well as in the former case.

When, after the reaction is initiated, $B$ is no longer fed to the reactor, mixing is still vital for the progress of the reaction. Freshly entering $A$ must mix with the $B$ present in the tank, and this case can be regarded as if separate feed streams of $A$ and $B$ were being used.

### COPOLYMERIZATION

$x$ and $y$ are the ratios of the monomer concentrations $A$ to $B$ in the solution and in the freshly formed copolymer, respectively. They are related in the classical theory of copolymerization by

$$y = \frac{x(1 + \rho_A x)}{x + \rho_B} \tag{1}$$

where $\rho_A$ and $\rho_B$ are the reactivity ratios. A perfectly mixed CSTR holds $x$ constant, so that $y$ remains constant, and the spread of composition in the copolymer is a minimum.

In an imperfectly mixed reactor, the local value of $x$ is $(\overline{A} + A')/(\overline{B} + B')$. The variation in solution monomer ratio $x$ is clearly higher when separate feed streams are used than for a premixed feed. This variation in $x$ generates greater variation in the copolymer composition ($y$) when the feed streams are separated.

### ELEMENTARY STEPS

$$2A + B \to A_2B \quad r_{A_2B} = \frac{0.72\,A^2B}{1 + 2A}$$

The above example from Levenspiel (1964) has the elementary steps

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} AB^*$$

$$AB^* + A \xrightarrow{k_3} A_2B$$

which, with the steady state approximation, yield the above overall rate expression. By time averaging each step and then invoking the steady state approximation, we get

$$\overline{r}_{A_2B} = \frac{0.75\,\overline{A}(\overline{A}\,\overline{B} + \overline{A'B'})}{1 + 2\overline{A}}$$

Premixed feed: $A'$ and $B'$ are positively correlated. In an incompletely mixed reactor, the reaction will proceed faster than in the ideally mixed case.

Separate feeds: $A'$ and $B'$ are negatively correlated. Incomplete mixing slows down the reaction compared to the ideal case. There is no selectivity issue here. Since $AB^*$ is small, it can be shown that $\overline{A'B'}$ is related quantitatively to the segregation as in reactions of the type considered by Toor (1975).

## NOTATION

$A, B, \ldots$ = chemical substances $A, B, \ldots$ or concentrations of substances $A, B, \ldots$
$k_i$ = reaction velocity constant for reaction $i$
$r_i$ = reaction rate of substance $i$
$x$ = ratio of monomer concentrations in solution
$X$ = concentration of substance $X$
$y$ = ratio of monomer in freshly formed copolymer
$\rho_A, \rho_B$ = reactivity ratios
$'$ = fluctuation
— = local time average
$^*$ = reaction intermediate

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## APPENDIX A: CORRELATIONS OF REACTANTS WITH EACH OTHER: $A + B \rightarrow P$

This is an expansion of an earlier argument by Vassilatos and Toor (1965).

The reaction decreases $A$ (and $B$) in an element of fluid as it moves away from the feed. Hence, an instantaneous excess of $A$ at a given point and time can only occur if an element of fluid which originated in the $A$ rich feed arrives at that point and time, unless there is a process which can concentrate $A$ in an element of fluid as it moves from its point of origin in the feed to the point in question. This concentration can occur only by a molecular process like a cross-diffusion effect in a multicomponent mixture, but this would require such an unusual combination of circumstances that it can be ruled out for practical purposes. Both reaction and diffusion decrease the concentration of $A$ in the element after it enters the reactor.

Premixed feeds: Thus, if $B$ is premixed with $A$, then an instantaneous excess of $A$ will also cause an instantaneous excess of $B$, since $B$ and $A$ originate together. When there is a deficiency of $A$, then there will be a deficiency of $B$. Hence, $\overline{A'B'} > 0$.

Separate feed: If $A$ and $B$ are fed separately, an excess of $A$ requires an insufficiency of $B$ and vice-versa, since fluid elements originating in the $A$ feed and $B$ feed cannot both be at the same point at the same time. Thus, nonpremixed feeds lead to a negative correlation, $\overline{A'B'} < 0$.

With separate feeds, a slightly different viewpoint (local spatial average) is as follows:

The fine scale concentration profiles will look like Figure 1. The fluctuations at a point occur as fluid elements with those profiles in them sweep by the point. Since they sweep by randomly, all parts of the fine scale profiles spend equal amounts of time at the point. Hence, $\overline{A'B'}$ at a point is the spatial average of $A'B'$ within the element, $\overline{A}$ is the spatial average of $A$, and $\overline{B}$ is the spatial average of $B$. But, on the left, $A' > 0$ and $B' < 0$, so $A'B' < 0$; on the right, $A' < 0$ and $B' > 0$, so again $A'B' < 0$. Hence, $\overline{A'B'} < 0$.

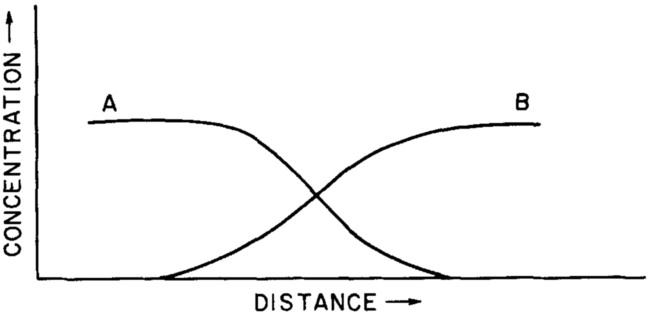

Fig. 1. Fine scale concentration profiles, $A + B \rightarrow P$.

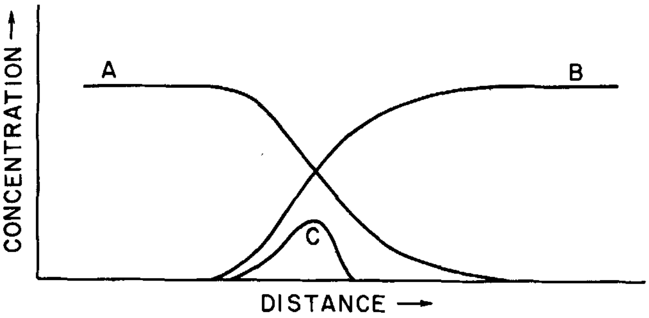

Fig. 2. Fine scale concentration profiles for a series-parallel reaction.

## APPENDIX B: CORRELATION OF REACTION INTERMEDIATE WITH REACTANTS: $A + B \rightarrow C \qquad C + B \rightarrow D$

Premixed feeds: The intermediate is produced in the regions where the reactant concentrations are high; hence, the intermediate product is positively correlated with the reactants, $\overline{B'C'} > 0$.

Separate feed: We adopt the local spatial average viewpoint used in Appendix A. The intermediate $C$ is produced in the reaction zone regions, where $A$ and $B$ are mixed together at the molecular level by diffusion. Hence, $C$ must have its highest concentration in this region. The concentration profiles on a fine scale will look qualitatively like Figure 2. On the right of the reaction zone, $C' < 0$ and $B' > 0$, so $B'C' < 0$. On the left of the reaction zone, $C' < 0$ and $B' < 0$, so $B'C' > 0$. In the reaction zone itself there will be a region where $B'C'$ is negative, but there may also be a region where $B'C'$ is positive as well. Because of the differences in sign throughout the volume of the element, the local spatial average will be relatively small, $\overline{B'C'} \approx 0$.

An entirely different viewpoint comes from examining Figure 2. $A$ and $B$ must interdiffuse to react, but $C$ is produced in the immediate vicinity of $B$. Hence, segregation should slow down the first reaction more than the second, which is consistent with the conclusion that $\overline{B'C'}$ is relatively small.

## APPENDIX C: CORRELATIONS WITH AN AUTOCATALYTIC REACTION: $A + B \rightarrow 2B$

Premixed feeds: If there is an instantaneous excess of $A$, at a point less reaction took place in the element which is present at that point and time than the average element which passes that point. Hence, there must be less $B$ in the element than in the average element which passes that point since the reaction which consumes $A$ produces $B$. Hence, $A' > 0$ and $B' < 0$, so $A'B' < 0$. Similarly, if $A' < 0$, then $B' > 0$, so in both cases $A'B' < 0$; therefore, $\overline{A'B'} < 0$.

Separate feeds: If one uses the local spatial average viewpoint and examines the fine scale concentration profiles in a manner similar to Appendix B, one finds that $A'B' < 0$ everywhere except possibly in the reaction zone where $A'B'$ can be greater than zero. $\overline{A'B'}$ is probably $< 0$.

*Manuscript received February 4, and accepted March 7, 1977.*