# Selectivity in Experimental Reactors

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**Unpacked pipes or tubes, commonly called *flow reactors,* are often desirable for carrying out homogeneous reactions. Unless these reactors are properly designed and operated, axial mixing will alter both the rate of conversion and the distribution of products from successive reactions. Several hypothetical reaction schemes are analyzed here to show how axial mixing affects the production of an intermediate. The analysis represents mixing by an axial diffusion coefficient and is valid when mixing is not extreme. Results from several particular cases are compared, showing that reactor-product distribution is generally distorted in proportion to a reactor Peclet number. G. I. Taylor's theory of axial mixing is used to relate this Peclet number to the physical characteristics of the reactor.**

**Although the effects of axial mixing are concluded to be negligible in most commercial or large-scale equipment, they are serious in the case of experimental or pilot-scale apparatus. Charts are drawn to illustrate design problems for these reactors.**

## PURPOSE AND SCOPE

The successful scale-up of a process requires accurate knowledge of yields and reaction rates in the range of operation of the scaled-up process. To this end, a method is given here for designing experimental flow reactors in which good selectivity can be maintained, that is, reactors in which the products formed are characteristic of the reaction chemistry, concentrations, etc., and not characteristic of the peculiarities of the experimental reactor.

Excessive axial mixing, or backmixing, in an experimental reactor makes the interpretation of results on yields and by-products highly uncertain. It is especially detrimental with integrated processes wherein recycle rates, separation procedures, etc., are based on the composition of the effluent obtained in experiments. Unrealistic amounts of by-products from a faulty experimental reactor may lead to establishment of a false optimum in operating conditions for the integrated process; and even if this mishap is later discovered, most of the experiments may involve conditions near the false optimum, thus yielding little information for the operating conditions of ultimate interest. Despite these pitfalls flow reactors are necessary in the study of certain reactions which cannot be explored with accuracy in bombs or continuous well-stirred vessels because of physical problems associated with the reaction mixture.

Although there have been past studies of backmixing in homogeneous reactors (*4, 5, 6, 7, 8, 9, 10*) most efforts have been directed toward the effect of mixing on conversion of a reactant and not on selectivity for production of an intermediate in a series of reactions.

Because of its complexity, an exact analysis of the effects of axial mixing on the course of a reaction was not attempted here. Instead an approximate analysis was used which is valid for all kinds of reactions when the effect of mixing on the overall performance is not excessive. Therefore, the methods developed are useful not for interpreting data from reactors in which there has been excessive mixing, but rather for selecting reactor dimensions and operating conditions which make backmixing effects tolerably small. The product from the reactor is then substantially the same as from a batch reactor.

## THE EFFECT OF AXIAL MIXING

Axial mixing in an unpacked tube is caused by variation of axial velocity across the radius. Fluid elements near the center move more rapidly than the average; thus they penetrate into downstream material near the walls and eventually mix with it. The magnitude of this effect depends greatly on the shape of the velocity profile and the rate of mixing in the radial direction. Contrary to first instinct, radial mixing inhibits axial mixing; this interrelation formed the basis for Taylor's analysis, (*1*) later extended by Tichacek, Barkelew, and Baron. (*2*) Taylor's analysis showed that under certain conditions (sufficiently large Renyolds number, straight pipes, small concentration gradients) the degree of axial mixing is proportional to the axial concentration gradient, permitting description of the intensity of mixing in terms of an axial diffusion coefficient.

Axial mixing has been the subject of much experimental work, some in laboratories but most in pipe lines. Many data have been taken under conditions expressly forbidden by Taylor for comparison with his theory, and the incompatibility of results in these cases has led to some disregard for the theory. Data taken under the conditions prescribed by Taylor, however, do confirm his analysis. The results of Taylor's theory as extended (*2*) are used in this work, but only in the range of validity, hence the restrictions against application of this method to reactors with severe axial mixing.

As a reacting fluid element passes through a pipe, two effects occur which cause the reactor product to differ from what would result if each fluid element were isolated and allowed to react for the nominal residence time of the reactor. The first is a variation of residence times from one fluid element to another. Elements spending most of their time near the center of the pipe move through more quickly than others and are thus allowed less than average time for reaction. The second effect is the intimate mixing of fluid elements having different histories and thus different compositions, each time forming a new element of a new composition. In the newly formed element the driving force for reaction is sometimes less than the average driving force would have been had the original elements not mixed. The first effect can result from macroscopic interpenetration; the second results only from molecular scale mixing or diffusion. Both effects are experienced in varying degree by every fluid element. Both can influence the gross reactor product in a different way, depending upon the kinetics of the reactions involved.

The combined effects of interpenetration and molecular mixing are estimated by simulating the actual reactor by either a plug-flow reactor on which is superimposed a type of relative axial mixing that can be described by the simple diffusion equation, or by a series of well-mixed stages, the number of stages being chosen to give approximately the same axial-mixing effect as in the actual reactor. These models are a more or less successful representation of the actual system depending upon the kinetics of the reactions involved and upon the relative amounts of macroscopic and microscopic mixing which contribute to the axial mixing. Both models are exact if all reactions have first order kinetics; in that case the product distribution depends only on the residence time distribution if the reactor irrespective of the mechanism which has caused it. Regardless of kinetics, both models become exact

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representations in the limiting case where the axial spreading of material becomes very small when compared to the length of the reactor. In this case macroscopic convection and microscopic diffusion cannot exert discernibly different influences on the reactor product.

The exactness of the method in this limiting case is particularly fortunate. It allows the design of reactors in which selectivity losses will be tolerably small. Furthermore, in this case a single parameter, a type of Peclet number, can be used to characterize both the degree of axial mixing and its effect on the reactor products.

Since axial mixing affects selectivity when successive reactions are involved, the following reaction scheme was analyzed:

$$A + R \xrightarrow{k_1} B \qquad \text{(A)}$$

$$B + R \xrightarrow{k_2} C \qquad \text{(B)}$$

The influence of axial mixing on product distribution was calculated for various types of reaction kinetics in the above system. The differential equations describing this system in a flow reactor operating at the steady state and with axial mixing described as diffusion are

$$V \frac{\partial A}{\partial x} = E \frac{\partial^2 A}{\partial x^2} - k_1 A^m R^{m'} \qquad (1)$$

$$V \frac{\partial B}{\partial x} = E \frac{\partial^2 B}{\partial x^2} + k_1 A^m R^{m'} - k_2 B^n R^{n'} \qquad (2)$$

$$V \frac{\partial R}{\partial x} = E \frac{\partial^2 R}{\partial x^2} - k_1 A^m R^{m'} - k_2 B^n R^{n'} \qquad (3)$$

Three methods of solution are used, depending on the reaction orders. In the first case treated, the kinetics are first order in $A$ and $B$ and zero order in $R$ ($m = n = 1$; $m' = n' = 0$); the equations are integrated directly. In the second case only the first reaction is second order, such that $m = 2$, $n = 1$, $m' = n' = 0$. A perturbation solution based on small values of $E$ is used. In the third case both reactions are second order, so that $m = n = m' = n' = 1$. Equations (1), (2), and (3) are not used in this case; the physical system is simulated by a series of well-stirred vessels for which the product distribution is calculated. The series of well-stirred vessels causes a residence time distribution characteristic of flow with axial mixing. The number of stages corresponding to a certain degree of axial mixing has been studied by others (3).

Figure 1 illustrates qualitatively the effect of axial mixing on the conversion of compound $A$ and the production of compound $B$. It is seen that axial mixing retards the conversion of compound $A$, and for any chosen conversion of $A$ the yield of compound $B$ is smaller because of mixing. The reduction in the maximum amount of compound B obtainable from the reactor is taken as an index of the loss of selectivity for $B$. Quantitatively, we define the loss in selectivity, $\delta$, as the difference between the maximum amount of desired product produced with and without axial mixing divided by the maximum amount which would be produced without axial mixing.

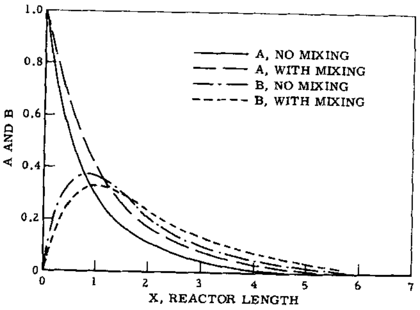

**Fig. 1. Concentrations of A and B with and without axial mixing for the first order reactions $A \xrightarrow{k} B \xrightarrow{k} C$.**

## SOLUTION OF THE DIFFERENTIAL EQUATIONS

### First-Order Reactions

When the reaction rates are proportional to the concentrations of components $A$ or $B$ only, the equations are linear and can be solved directly. The solution to Equation (1) is

$$A(x) = k' \exp\left[\frac{Vx}{2E}\left(1 - \sqrt{1 + \frac{4k_1 E}{V^2}}\right)\right] + k'' \exp\left[\frac{Vx}{2E}\left(1 + \sqrt{1 + \frac{4k_1 E}{V^2}}\right)\right] \qquad (4)$$

where $k'$ and $k''$ are constants to be determined. The boundary conditions used are

$$A(\infty) = 0, \; VA_o = VA(0) - EA'(0) \qquad (5)$$

where the prime represents the derivative with respect to $x$. The latter condition represents mass conservation across the boundary. The first boundary condition is applied to make constants in the solution independent of location of the downstream end of the reactor; that end is by the nature of axial mixing incapable of affecting what happens upstream. This boundary condition would not be applied in the case of true diffusion, but yields a solution which is a successful approximate description of a reactor in which there is axial mixing.

Application of these boundary conditions to Equation (4) gives

$$A(x) = \frac{2A_o}{1 + \sqrt{1 + \frac{4k_1 E}{V^2}}} \exp\left[\frac{Vx}{2E}\left(1 - \sqrt{1 + \frac{4k_1 E}{V^2}}\right)\right] \qquad (6)$$

Equation (2) can subsequently be solved to give

$$B(x) = \frac{2A_o}{1 + \sqrt{1 + \frac{4k_1 E}{V^2}}} \frac{k_1}{k_2 - k_1} \left. \exp\left[\frac{Vx}{2E}\left(1 - \sqrt{1 + \frac{4k_1 E}{V^2}}\right)\right] + k''' \exp\left[\frac{Vx}{2E}\left(1 - \sqrt{1 + \frac{4k_2 E}{V^2}}\right)\right] + k'''' \exp\left[\frac{Vx}{2E}\left(1 + \sqrt{1 + \frac{4k_2 E}{V^2}}\right)\right]\right\} \qquad (7)$$

The boundary conditions used are

$$B(\infty) = 0, \quad B(0) - \frac{E}{V} B'(0) = 0 \qquad (8)$$

The first condition has been explained above. The second boundary condition sets the net flow of $B$ equal to 0 at the reactor inlet; the flux of $B$ thus remains positive over the entire reactor. The alternate boundary condition, setting $B(0) = 0$, results in a net upstream flux of compound $B$ at the reactor inlet. The boundary conditions are thus chosen to render a more accurate description of reactor product than average concentration across the reactor tube. The values of the constants are

$$k''' = -\frac{1 + \sqrt{1 + \frac{4k_1 E}{V^2}}}{1 + \sqrt{1 + \frac{4k_2 E}{V^2}}} \qquad k'''' = 0 \qquad (9)$$

The flux of component A as a function of reactor length, $x$, is given by $VA_o \, F_A(x)$ where*

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* Some authors refer to this term, "F," as the *mean-flow concentration* or *mixing-cup concentration*, its value being calculated according to

$$A_o F_A = \int_0^1 A(r) \frac{u}{v}(r) \, 2r dr \qquad \text{(a)}$$

where $u$ is the time averaged axial velocity in the pipe at the radial position $r$. The two conceptions of $F$ in Equations (10) and (a) are for all practical purposes identical because of the physical origin of the term $E/V$. The mean cross-sectional concentration, on the other hand, is given by

$$A = \int_0^1 A(r) \, 2r dr \qquad \text{(b)}$$

and it is this type of mean concentration that has been employed here as the driving force for chemical reaction.

$$F_A(x) = \frac{1}{A_o}\left[ A(x) - \frac{E}{V} A'(x) \right] \tag{10}$$

and a similar expression applies for component $B$. These quantities are found to be

$$F_A\left(\frac{k_1 E}{V^2}, \frac{k_1 x}{V}\right) = \exp\left[\frac{Vx}{2E}\left(1 - \sqrt{1 + \frac{4k_1 E}{V^2}}\right)\right]$$

$$F_B\left(\frac{k_2}{k_1}, \frac{k_1 E}{V^2}, \frac{k_1 x}{V}\right) = \frac{k_1}{k_2 - k_1}\left\{ \exp\left[\frac{Vx}{2E}\left(1 - \sqrt{1 + \frac{4k_1 E}{V^2}}\right)\right] - \exp\left[\frac{Vx}{2E}\left(1 - \sqrt{1 + \frac{4k_2 E}{V^2}}\right)\right]\right\} \tag{11}$$

Since the maximum value of $F_B$ and the alteration of this value because of axial mixing both depend on the relative values of the rate constants involved, calculations were made for three cases:

$$\frac{k_2}{k_1} = 0.2,\ 1.0,\ \text{and}\ 5.0$$

### Combinations of First- and Second-Order Reaction Rates

The differential equations for the system wherein a second-order reaction is followed by one of first order is

$$\frac{\partial^2 A}{\partial x^2} - \frac{V}{E}\frac{\partial A}{\partial x} - \frac{k_1}{E} A^2 = 0 \tag{12}$$

$$\frac{\partial^2 B}{\partial x^2} - \frac{V}{E}\frac{\partial B}{\partial x} - \frac{k_2}{E} B = \frac{-k_1}{E} A^2 \tag{13}$$

A direct analytic solution of these equations cannot be obtained. For small values of the ratio $E/V$, however, a perturbation solution can be obtained. The concentration $A$ is set equal to the value it would have if there were no axial mixing plus a small correction term due to axial mixing and proportional to the value of $E/V$:

$$A = A_1 + \frac{E}{V} a; \quad B = B_1 + \frac{E}{V} b \tag{14}$$

The new variables of Equation (14) are substituted into Equations (12) and (13). The values of $A_1$ and $B_1$ are found by neglecting all terms containing $E/V$ and solving the remaining equations:

$$\frac{\partial A_1}{\partial x} + \frac{k_1}{V} A_1^2 = 0 \tag{15}$$

$$\frac{\partial B_1}{\partial x} + \frac{k_2}{V} B_1 = \frac{k_1}{V} A_1^2 \tag{16}$$

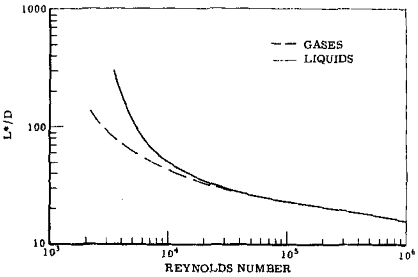

Fig. 2. *Minimum L*/D for prevention of selectivity loss greater than 0.01.*

The solution of these equations is

$$\frac{A_1}{A_o} = \frac{1}{1 + \dfrac{k_1 A_o x}{V}} \tag{17}$$

$$\frac{B_1}{A_o} = \frac{k_2}{k_1 A_o} \exp\left(\frac{-k_2}{k_1 A_o} - \frac{k_2 x}{V}\right)\left\{ E_i\left(\frac{k_2}{k_1 A_o} + \frac{k_2 x}{V}\right) - E_i\left(\frac{k_2}{k_1 A_o}\right)\right\} + \exp\left(\frac{-k_2 x}{V}\right) - \frac{1}{1 + \dfrac{k_1 A_o x}{V}} \tag{18}$$

where $E_i$ represents the exponential integral defined by

$$E_i(y) = \int_{-\infty}^{y} \frac{\exp y'}{y'} dy' \tag{19}$$

Values of this function can be obtained from tables. These values for $A_1$ and $B_1$ are substituted into the perturbation Equations

$$\frac{\partial a}{\partial x} + 2\frac{k_1}{V} A_1 a = \frac{\partial^2 A_1}{\partial x^2} \tag{20}$$

$$\frac{\partial b}{\partial x} + \frac{k_2}{V} b = 2\frac{k_1}{V} A_1 a + \frac{\partial^2 B_1}{\partial x^2} \tag{21}$$

which can then be solved for $a$ and $b$. The value of $a$ is given by

$$\frac{a}{A_o} = 2\frac{k_1 A_o}{V}\,\frac{\ln\left(1 + \dfrac{k_1 A_o x}{V}\right) - 1/2}{(1 + k_1 A_o x/V)^2} \tag{22}$$

where the boundary conditions which have been applied are

$$A(\infty) = 0 = A_1(\infty) + \frac{E}{V} a(\infty) \tag{23}$$

$$A_o = A(0) - \frac{E}{V} A'(0) = A_1(0) - \frac{E}{V} A_1'(0) + \frac{E}{V} a(0) - \frac{E^2}{V^2} a'(0) \tag{24}$$

These conditions are chosen because of the same arguments which led to Equations (5). The term involving $E^2/V^2$ in the boundary condition is neglected as are terms of this small order in the perturbation equations. The solution to Equation (21) is

$$\frac{b}{A_o} = \frac{k_1 A_o}{V} \exp\left(-\frac{k_2 x}{V}\right) \int_1^{1 + \frac{k_1 A_o x}{V}} \exp\left[\frac{k_2}{k_1 A_o}(y - 1)\right]\left[ 4\frac{\ln y - 1}{y^3} - \frac{k_2}{k_1 A_o y^2} + \frac{k_2^2 B_1}{k_1^2 A_o^3}\right] dy + \frac{k_1 A_o}{V} \exp\left(-\frac{k_2 x}{V}\right) \tag{25}$$

where the boundary conditions have been set following the reasoning of Equations (8), (23), and (24). Equation (25) must be evaluated numerically. Equations (17), (18), (22), and (25) were evaluated for the following ratios of $k_2/k_1A_o$: 0.2, 1, and 5.

### Second-Order Reaction Systems

If both reaction rates depend on the first power of the concentration of each reactant involved, Equations (1), (2), and (3) cannot be solved analytically. Thus assume that a reactor in which there is axial mixing can be approximated by a series of continuous well-stirred reactors. Kramers and Alberda (3), considering residence time distribution in the two systems, arrive at the following relation between number of stages and axial Peclet number:

$$\frac{1}{N - 1} \approx \frac{2E}{LV} \tag{26}$$

The approximation is good for values of $N$ greater than about 5 to 10.

The concentrations of the products and reactants leaving the *ith* stage can be calculated from the concentrations entering from the preceding stage by using the relations

$$A_{i-1} - A_i = k_1 \tau_i A_i R_i \tag{27}$$

$$B_{i-1} - B_i = k_2 \tau_i B_i R_i - k_1 \tau_i A_i R_i \tag{28}$$

$$R_{i-1} - R_i = \tau_i R_i (k_1 A_i + k_2 B_i) \tag{29}$$

The case with no axial mixing was solved first as indicated below, and an estimate made of the total residence time necessary in all stages in order to obtain the maximum amount of compound $B$. Since it was desired to minimize computations by making this calculation for only ten stages, the total residence time was divided by a number near 10 chosen to simplify numerical work. A value of $k_1\tau$/stage was thus obtained. Each stage requires a trial and error solution in order to determine the value of $R_i$ for that stage. The values of $A$ and $B$ can then be calculated directly. In carrying out

TABLE 1. KINETIC AND REACTOR PARAMETERS FOR $B$ AT $A$ MAXIMUM

| $m$ | $n$ | $m'$ | $n'$ | $\frac{k_2}{k_1 A_o^{m-n}}$ | $F_{B\max}$ | $\frac{k_1 L_B}{V} A_o^{m-n}$ | $\frac{k_1 E}{V^2} A_o^{m-n}$ | $\frac{E}{VL_B}$ | $\delta$ | $\frac{\delta}{E/VL_B}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 0 | 0 | 0.2 | 0.669 | 2.12 | 0.01 | 0.0047 | 0.0037 | 0.80 |
| 1 | 1 | 0 | 0 | 1.0 | 0.368 | 1.00 | 0.01 | 0.010 | 0.010 | 1.00 |
| 1 | 1 | 0 | 0 | 5.0 | 0.134 | 0.402 | 0.01 | 0.0249 | 0.020 | 0.80 |
| 2 | 1 | 0 | 0 | 0.2 | 0.512 | 2.12 | 0.01 | 0.0047 | 0.0048 | 1.01 |
| 2 | 1 | 0 | 0 | 1.0 | 0.284 | 0.88 | 0.01 | 0.0114 | 0.0115 | 1.01 |
| 2 | 1 | 0 | 0 | 5.0 | 0.1126 | 0.33 | 0.01 | 0.0305 | 0.0273 | 0.83 |
| 1 | 1 | 1 | 1 | 0.2 | 0.669 | 1.56 | $N = 12.8$ | 0.0424 | 0.0347 | 0.82 |
| 1 | 1 | 1 | 1 | 1.0 | 0.368 | 0.675 | $N = 8.3$ | 0.0685 | 0.065 | 0.95 |
| 1 | 1 | 1 | 1 | 5.0 | 0.134 | 0.232 | $N = 11.0$ | 0.050 | 0.041 | 0.82 |

these calculations, the initial concentrations assumed were $A(0) = A_o$, $B(0) = 0$, and $R(0) = 2A_o$.

For the comparison case with no axial mixing in the reactor, that is, for $E = 0$, an analytic solution of Equations (1), (2), and (3) can be obtained. The equations are simplified by introducing a new parameter, $\theta$:

$$\theta = \frac{1}{V} \int_o^x R\, dx' \qquad (30)$$

The system of equations then has the following simple solution:

$$A = A_o \exp(-k_1 \theta) \qquad (31)$$

$$B = \frac{A_o k_1}{k_2 - k_1} [\exp(-k_1 \theta) - \exp(-k_2 \theta)] \qquad (32)$$

$$R = R_o - 2A_o + 2A + B \qquad (33)$$

The variable $x$ can subsequently be retrieved as a function of $\theta$ by

$$x = V \int_o^\theta \frac{d\theta'}{R} \qquad (34)$$

The maximum value of $B$ was calculated for rate constants with the ratios $k_2/k_1$: 0.2, 1.0, 5.0.

## RESULTS

Pertinent characteristics calculated for the reactor at the point where the production of $B$ is a maximum are summarized in Table 1. Parameters listed are the four concentration exponents of the kinetic equations; the ratio of reaction-rate constants made dimensionless by inclusion of starting concentration $A_o$ when necessary; the maximum concentration of $B$ attained when there is no mixing; value of the conversion coordinate for the reactor length at which the maximum occurs with no mixing; a combination of the diffusion coefficient with a ratio characteristic of the concentration gradient to give a term which had been arbitrarily chosen in starting the calculation; a Peclet number based on $L_B$; the selectivity loss, $\delta$, and the ratio of $\delta$ to the Peclet number.

It is evident from this table that the selectivity loss is roughly equal to $E/VL_B$, and the closeness of this proportionality depends no more on kinetic order than on relative magnitudes of the reaction-rate constants. This suggests that axial mixing reduces selectivity for $B$ primarily by the premature transport of material out of the reaction zone rather than by interference with the reaction rate through mixing of differing fluid elements. In other words, the reactor product is affected mostly by residence time distribution and very little by intermingling so long as the effect of axial mixing is small. This conclusion is possible because $E/LV$ uniquely fixes the normalized variance of residence time.

An extension of this analysis (*11*) to the case with another reaction destroying compound $C$ indicates that selectivity loss for $C$ is likewise roughly equal to $E/LV$ provided $C$ appears in reasonable quantities. In this case $L$ is the distance between points in the reactor where maxima in $B$ and $C$ would occur.

Results of this investigation can thus be summarized by a rule of thumb: when $\delta$ is small, it can be estimated by

$$\delta \approx \frac{E}{VL_B} \qquad (35)$$

where $E$ is estimated by the methods of reference 2. Equation (35) is accurate within 20% for all cases studied. A considerable simplification in applying this rule can be obtained at the expense of usually increased conservatism: in all cases $E/LV$ is an upper limit on the fractional reduction in the flux of compound $B$ if the extent of reaction is less than that required for attaining maximum $B$. In this case $L$ is the actual reactor length.

In development work reaction-rate constants are often measured in experimental flow reactors. It becomes necessary not only to consider maintaining the selectivity of the reactor but also to design the reactor for negligible errors in the determination of reaction rates. Errors caused by axial mixing in measurement of rate constants are estimated by considering how a reduction, $\delta$, in the maximum concentration of an intermediate compound is reflected in the values of the rate constants deduced therefrom. For many cases the percentage of error in determining the relative values of rate constants is approximately $300\delta$. A more accurate estimate of the relation between peak concentrations and relative values of the rate constants can be made if the reaction rates are known approximately when the experimental reactor is being designed.

Since the degree of mixing which causes a 1% loss in selectivity generally leads to errors of several percent in the determination of reaction-rate constants, quite stringent limitations are placed on the design and operation of an experimental reactor if accurate rate constants are desired. Furthermore, an experimental reactor usually must be designed to operate over a range of flow velocities so that residence time can be varied easily; the reactor must be designed for those residence times at which mixing is most disadvantageous: long residence times for turbulent flow reactors and short residence times for laminar flow reactors.

### Design of Reactors with Tolerably Small Axial Mixing Effects

For turbulent flow reactors a limitation on $L/D$, the ratio of length to diameter, arises in the following way. Consider designing a reactor to be operated at a chosen Reynolds number with a reactant mixture of given Schmidt number; the ratio $E/DV$ is then fixed (*1, 2*). If an upper limit is set for $\delta$, and thereby for $E/LV$, the minimum allowable $L/D$ becomes

$$L/D = \frac{E/DV}{E/LV} \qquad (36)$$

For maintaining $\delta \leq 0.01$ the minimum $L/D$ is shown in Figure 2 as a function of Reynolds number for two cases: typical gases ($N_{Sc} \approx 1$) and typical liquids ($N_{Sc} > 100$). Low Reynolds numbers are clearly undesirable.

TABLE 2. VALUES OF CHARACTERISTIC GROUPS IN THE SAMPLE CALCULATION

| $\tau$, sec. | $(\nu^3\tau\delta)^{1/2}$ cc./sec. × $10^5$ | $(\nu^3\tau\delta)^{1/2}$ 1/min. × $10^6$ | $(\tau\nu\delta)^{1/2}$ cm. | $(\tau\nu/\delta)^{1/2}$ cm. | $(\tau\nu/\delta)^{1/2}$ m. |
|---|---|---|---|---|---|
| 10 | 2.83 | 1.70 | 0.01414 | 1.414 | 0.01414 |
| 60 | 6.93 | 4.16 | 0.0346 | 3.46 | 0.0346 |
| 600 | 21.9 | 13.14 | 0.1095 | 10.95 | 0.1095 |

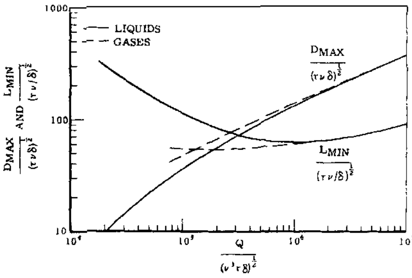

**Fig. 3. Design chart for experimental reactors: effects of axial mixing.**

For calculating the necessary dimensions of flow reactors the parameters found convenient as independent variables are $Q$, $\tau$, $\nu$, and $\mathfrak{D}$. Ordinarily the physical properties of the system and the residence time are determined by conditions under which the experiments must be performed, conditions such as temperature, pressure, and catalyst concentration. The disposable design variables are then the reactor geometry and flow rate. The following parametric equations relate maximum reactor diameter, minimum reactor length and flow rate:

$$D_{\max} = (\tau\,\nu\,\delta)^{1/2}\,N_{Re}{}^{1/2}\left(\frac{E}{DV}\right)^{-1/2} \tag{37}$$

$$L_{\min} = \left(\frac{\tau\,\nu}{\delta}\right)^{1/2} N_{Re}{}^{1/2}\left(\frac{E}{DV}\right)^{1/2} \tag{38}$$

$$Q = \frac{\pi}{4}\,(\nu^3\tau\delta)^{1/2}\,N_{Re}{}^{3/2}\left(\frac{E}{DV}\right)^{-1/2} \tag{39}$$

These equations can be written using the definition of Reynolds number, the fact that residence time is $L/V$, and by setting $\delta = E/LV$. The set is sufficient because of the unique relation between $E/DV$ and $N_{Re}$ for a given $N_{Sc}$ as already mentioned.

The dependence of $D_{\max}$ and $L_{\min}$ on $Q$ for a turbulent flow reactor has been calculated from Equations (37) to (39) and illustrated in Figure 3. Geometric limitations do not appear as severe at high flow rates as at low flow rates; the design is most constrained in experimental reactors where high flow rates cannot be maintained. It should be noted that the curves in Figure 3 cannot be extrapolated to values of the abscissa lower than $2 \times 10^4$ because this becomes a region wherein the flow is metastable, possibly turbulent, but without a well-defined turbulence pattern.

For laminar flow the value of $E/DV$ is given by *(1)*

$$\frac{E}{DV} = \frac{DV}{192\mathfrak{D}} = \frac{N_{Re}\,N_{Sc}}{192} \tag{40}$$

If the selectivity loss must be less than $\delta$, then $D_{\max}$ can be calculated from Equation (41):

$$D_{\max} = (192\,\delta\mathfrak{D}\tau)^{1/2} \tag{41}$$

The maximum tolerable diameter in this case depends not on flow rate but on the molecular-diffusion coefficient and the shortest residence time anticipated. With the diameter fixed, the length necessary for the laminar flow reactor is set by the flow rate desired at the longest residence times:

$$L = \frac{4\tau Q}{\pi D^2} \tag{42}$$

Specifications for little axial mixing in a laminar flow reactor can therefore be met even if the residence time is long and the flow rate is small. The reactor diameter, however, must usually be rather small as shown below.

## EXAMPLE OF APPLICATION OF RESULTS

The methods developed here can be illustrated by application to a typical problem. Consider the process

$$A + R \xrightarrow{k_1} B$$

$$B + R \xrightarrow{k_2} C$$

where $B$ is the desired product. These reactions are to be studied with combinations of catalyst concentrations and conversions such that residence times between 10 sec. and 10 min. are necessary.

Preliminary experiments indicate that the first reaction is approximately three times as rapid as the second. At maximum expected catalyst concentration $A$ is one-half converted within 30 sec. What would be a practical reactor design with regard to the flow rates generally feasible in an experimental study?

A reactor design is chosen to maintain selectivity for $B$ when it is producing $B$ at maximum possible concentration. However, the flow rate through the reactor will be varied in order to vary the conversion. For conversions insufficient to produce the maximum amount of $B$ this assumption leads to a slightly conservative design as previously stated.

The average physical properties of the reaction mixture are estimated as

$\nu = 0.2$ centistokes $= 0.002$ sq. cm./sec.
$\rho = 0.6$ g./cc.
$\mathfrak{D} = 1.0 \times 10^{-4}$ sq.cm./sec.

A limit of 0.01 on the selectivity loss, $\delta$, is chosen to insure against errors larger than 3% in the rate constants. If values of $\tau$ equal to 10, 60, and 600 sec. are chosen for calculations, then with $\nu = 0.002$ sq.cm./sec. and $\delta = 0.01$, the values of the required characteristic groups are as shown in Table 2. The values of these characteristic groups can be used to calculate $D_{\max}$ and $L_{\min}$ as a function of $Q$ by using Figure 3. The results are shown in Figure 4.

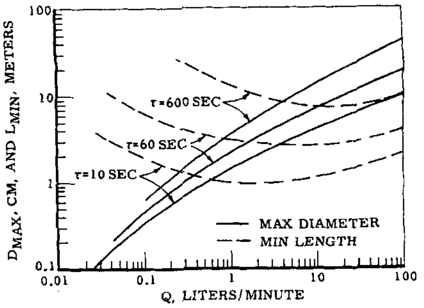

**Fig. 4. Design limitations for an experimental reactor for the example problem.**

In Figure 4 many of the limitations of a turbulent flow reactor become apparent. First, long residence times make a flow reactor inconvenient unless the laboratory is suitable for the erection of long straight pipes. In this example, the minimum length of the reactor is 7.88 meters if a residence time of 10 min. is desired. Secondly, only a very long reactor will be satisfactorily operable with flow rates which are reasonable for laboratory-scale experiments. Decreasing the reactor length can be accomplished only at the expense of increasing flow rate and reactor diameter. Finally, one of the severest limitations of flow reactors appears: lack of flexibility of operation. It is difficult to build one reactor which will be operable over a considerable range of residence times. For instance, a reactor of 12 meters length and 3.75 cm. diam. would be operable with a flow rate of 1.31 liters/min. to give residence times of 10 min. If this reactor were to be operated with residence times of 10 sec., the flow rate would have to be increased to 600/10 × 1.31 or 79 liters/min. The alternative to increasing the flow rate excessively is to shorten the reactor for smaller residence times, or, for that matter, to construct a different reactor. In this example, if the 3.75 cm. diam. reactor is to be shortened, its length would be 1.2 meters and the flow rate approximately 8 l/min. for a residence time of 10 sec. A design such as this, however, is meaningless because entrance effects grow to overriding proportions when the ratio $L/D$ becomes less than 100.

If use of a turbulent flow reactor is unavoidable and the required length is intolerable, the reactor might be built up of a few long sections. By no means could the reactor be coiled, nor should the straight sections be connected by gentle bends or curves. A sharp 180 deg. reversal of flow by close-turning elbows is far less harmful, even though the pressure drop may be greater.

In preference to a sectional turbulent flow reactor a laminar flow reactor might be used. For laminar flow, the values of $D_{\max}$ calculated according to Equation (41) are 0.438 mm. for $\tau = 10$ sec., 1.07 mm. for $\tau = 60$ sec., and 3.4 mm. for $\tau = 10$ min. This reactor need only be long enough to give the desired flow rate at the longest residence time, according to Equation (42).

The analysis thus far has indicated no convenient reactor design for carrying out accurate experiments; a compromise can be investigated. The most nearly practical design was the laminar flow reactor so a modification of this design might be acceptable. Assume it possible to construct a reactor 1 mm. in diam. and to vary catalyst concentrations in a way which eliminates the need for residence times less than 30 sec. What error would be introduced into such experiments?

Rearrangement of Equation (41) yields the relation

$$\delta = \frac{D^2}{192\mathcal{D}\tau} \qquad (41a)$$

For $D = 0.1$ cm. $\mathcal{D} = 10^{-4}$ sq.cm./sec., and $\tau = 30$ sec., the loss in selectivity, $\delta$, is 0.0174. If the maximum concentration of $B$ is to be used in determining the ratio of $k_2/k_1$, this error of 1.74% in $B_{\max}$ will introduce an error of about 5% in the ratio of $k_2/k_1$ for the case where $k_2/k_1 \approx 3$ and the reaction kinetics are first order with respect to all reactants. If this 5% error is tolerable, then for a 1 mm. diam. reactor residence times as short as 30 sec. may be used.

The length of the reactor can be calculated from Equation (42). If 25 cc./hr. is a sufficiently large flow rate for analysis, the length necessary for the longest residence time, 600 sec., is 530 cm. from Equation (42). At the shortest residence time, 30 sec., the flow rate will be 500 cc./hr. based on 25 cc./hr. at 600 sec.

This peculiarity of flow reactors is clear: for reactor lengths equal to the normal dimensions of a laboratory, the flows must be either very small in the case of laminar flow or very large in the case of turbulent flow.

## LIMITATIONS OF THE ANALYSIS

The complexity of the physical system being studied prevented an exact analysis of the way in which axial mixing affects the course of a reaction. Instead, the problem was treated in terms of an effective axial diffusivity superimposed on an idealized plug-flow reactor. When the parameter $E/LV$ is small (on the order of 0.01), slight but significant differences from the idealized reactor are predicted. The solutions presented are therefore in the nature of perturbations to the idealized reactor. They are expected to be valid approximations for small values of $E/LV$. Unfortunately, no definitive experiments have been performed to mark the limitations of this analysis.

For the case of a laminar flow reactor, Cleland and Wilhelm (*4*) have carried out an exact solution of the problem of reaction with axial mixing. Their calculations were, however, concerned only with the conversion of one reactant. The values calculated by their exact method agree well with those found by the approximate method developed here as long as the value of $E/LV$ is equal to 0.05 or less.

It is evident from the foregoing that the methods used in this report are useful for designing reactors in which axial mixing is to be held within certain limits, rather than in interpreting data from reactors in which there has been excessive axial mixing.

It should also be borne in mind that the methods presented here are limited to straight pipe reactors and are invalid for reactors which have curves or bends. In curved pipes, mixing is known to be much more severe and is difficult to analyze quantitatively.

## NOTATION

$A$, $B$ = concentrations of compounds $A$ and $B$
$A_o$ = concentration of $A$ in the reactor feed
$A_1$, $B_1$ = concentrations of compounds $A$ and $B$ in the first approximation, neglecting the effects of axial mixing
$a$, $b$ = concentration perturbations for compounds $A$ and $B$ which give the first approximation to the effects of axial mixing
$D$ = diameter of reactor tube
$D_{\max}$ = maximum allowable reactor diameter
$\mathcal{D}$ = molecular-diffusion coefficient
$E$ = axial-mixing coefficient, expressed as a diffusion coefficient, area/unit time
$F_A$, $F_B$ = flux concentrations of compounds A and B; sometimes called *mixing-cup concentrations*
$k_1, k_2$ = reaction-rate constants
$L$ = length of the reactor
$L_B$ = length of the reactor required to reach maximum concentration of $B$
$L_{\min}$ = minimum allowable reactor length
$m, m', n, n'$ = exponents expressing dependence of reaction rates on concentrations of reactants; defined in Equations (1), (2), (3)
$N$ = number of well-mixed stages used to approximate a continuous flow reactor
$N_{Pe}$ = Peclet number, $= \frac{LV}{E}$
$N_{Re}$ = Reynolds number, $= \frac{DV}{\nu}$
$N_{Sc}$ = Schmidt number, $= \frac{\nu}{\mathcal{D}}$
$Q$ = flow rate of reaction mixture, vol./unit time
$R$ = concentration of reactant $R$
$R_o$ = concentration of $R$ in the reactor feed
$r$ = reduced radial coordinate: $r = 0$ at center, $r = 1$ at wall
$u$ = axial velocity at a point
$V$ = averge flow velocity in the reactor
$x$ = axial coordinate of the reactor
$y$ = a mathematical variable
$\delta$ = loss of selectivity; the fractional reduction in the maximum attainable amount of the product of interest
$\theta$ = parameter defined in Equation (30) has units of the reciprocal reaction-rate constant
$\nu$ = kinematic viscosity, area/unit time
$\tau$ = residence time

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*Manuscript received November 20, 1959; revision received November 9, 1962; paper accepted November 12, 1962. Paper presented at A.I.Ch.E. Atlanta meeting.*