

Chapter 4

Introduction to Reactor Design

4.1 GENERAL DISCUSSION

So far we have considered the mathematical expression called the *rate equation* which describes the progress of a homogeneous reaction. The rate equation for a reacting component i is an intensive measure, and it tells how rapidly component i forms or disappears in a given environment as a function of the conditions there, or

$$r_i = \frac{1}{V} \left(\frac{dN_i}{dt} \right)_{\text{by reaction}} = f(\text{conditions within the region of volume } V)$$

This is a differential expression.

In reactor design we want to know what size and type of reactor and method of operation are best for a given job. Because this may require that the conditions in the reactor vary with position as well as time, this question can only be answered by a proper integration of the rate equation for the operation. This may pose difficulties because the temperature and composition of the reacting fluid may vary from point to point within the reactor, depending on the endothermic or exothermic character of the reaction, the rate of heat addition or removal from the system, and the flow pattern of fluid through the vessel. In effect, then, many factors must be accounted for in predicting the performance of a reactor. How best to treat these factors is the main problem of reactor design.

Equipment in which homogeneous reactions are effected can be one of three general types; the *batch*, the *steady-state flow*, and the *unsteady-state flow* or *semibatch* reactor. The last classification includes all reactors that do not fall into the first two categories. These types are shown in Fig. 4.1.

Let us briefly indicate the particular features and the main areas of application of these reactor types. Naturally these remarks will be amplified further along in the text. The batch reactor is simple, needs little supporting equipment, and is therefore ideal for small-scale experimental studies on reaction kinetics. Industrially it is used when relatively small amounts of material are to be treated. The steady-state flow reactor is ideal for industrial purposes when large quantities of material are to be processed and when the rate of reaction is fairly high to extremely high. Supporting equipment needs are great; however, extremely good

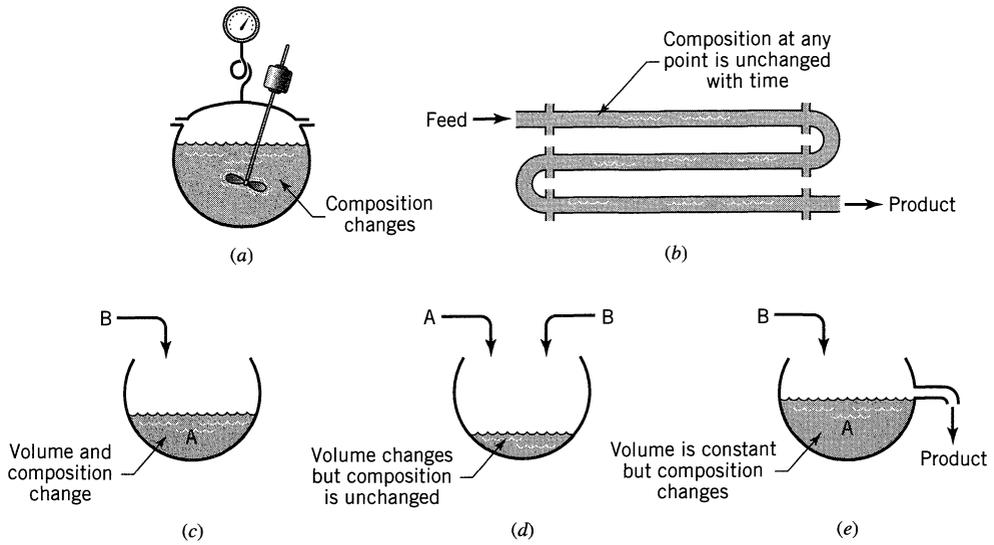


Figure 4.1 Broad classification of reactor types. (a) The batch reactor. (b) The steady-state flow reactor. (c), (d), and (e) Various forms of the semibatch reactor.

product quality control can be obtained. As may be expected, this is the reactor that is widely used in the oil industry. The semibatch reactor is a flexible system but is more difficult to analyze than the other reactor types. It offers good control of reaction speed because the reaction proceeds as reactants are added. Such reactors are used in a variety of applications from the calorimetric titrations in the laboratory to the large open hearth furnaces for steel production.

The starting point for all design is the *material balance* expressed for any reactant (or product). Thus, as illustrated in Fig. 4.2, we have

$$\left(\begin{array}{c} \text{rate of} \\ \text{reactant} \\ \text{flow into} \\ \text{element} \\ \text{of volume} \end{array} \right) = \left(\begin{array}{c} \text{rate of} \\ \text{reactant} \\ \text{flow out} \\ \text{of element} \\ \text{of volume} \end{array} \right) + \left(\begin{array}{c} \text{rate of reactant} \\ \text{loss due to} \\ \text{chemical reaction} \\ \text{within the element} \\ \text{of volume} \end{array} \right) + \left(\begin{array}{c} \text{rate of} \\ \text{accumulation} \\ \text{of reactant} \\ \text{in element} \\ \text{of volume} \end{array} \right) \quad (1)$$

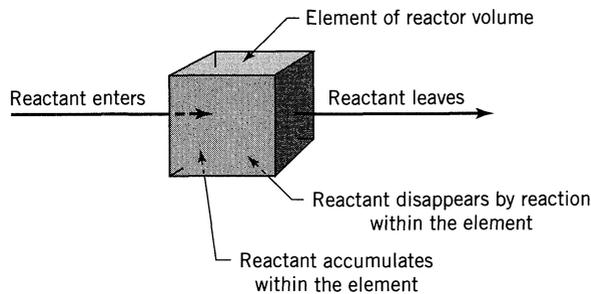


Figure 4.2 Material balance for an element of volume of the reactor.

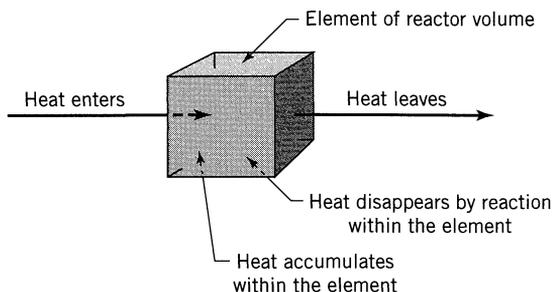


Figure 4.3 Energy balance for an element of volume of the reactor.

Where the composition within the reactor is uniform (independent of position), the accounting may be made over the whole reactor. Where the composition is not uniform, it must be made over a differential element of volume and then integrated across the whole reactor for the appropriate flow and concentration conditions. For the various reactor types this equation simplifies one way or another, and the resultant expression when integrated gives the basic *performance equation* for that type of unit. Thus, in the batch reactor the first two terms are zero; in the steady-state flow reactor the fourth term disappears; for the semibatch reactor all four terms may have to be considered.

In nonisothermal operations *energy balances* must be used in conjunction with material balances. Thus, as illustrated in Fig. 4.3, we have

$$\left(\begin{array}{c} \text{rate of heat} \\ \text{flow into} \\ \text{element of} \\ \text{volume} \end{array} \right) = \left(\begin{array}{c} \text{rate of heat} \\ \text{flow out of} \\ \text{element of} \\ \text{volume} \end{array} \right) + \left(\begin{array}{c} \text{rate of} \\ \text{disappearance} \\ \text{of heat by} \\ \text{reaction within} \\ \text{element of} \\ \text{volume} \end{array} \right) + \left(\begin{array}{c} \text{rate of} \\ \text{accumulation} \\ \text{of heat within} \\ \text{element of} \\ \text{volume} \end{array} \right) \quad (2)$$

Again, depending on circumstances, this accounting may be made either about a differential element of reactor or about the reactor as a whole.

The material balance of Eq. 1 and the energy balance of Eq. 2 are tied together by their third terms because the heat effect is produced by the reaction itself.

Since Eqs. 1 and 2 are the starting points for all design, we consider their integration for a variety of situations of increasing complexity in the chapters to follow.

When we can predict the response of the reacting system to changes in operating conditions (how rates and equilibrium conversion change with temperature and pressure), when we are able to compare yields for alternative designs (adiabatic versus isothermal operations, single versus multiple reactor units, flow versus batch system), and when we can estimate the economics of these various alternatives, then and only then will we feel sure that we can arrive at the design well fitted for the purpose at hand. Unfortunately, real situations are rarely simple.

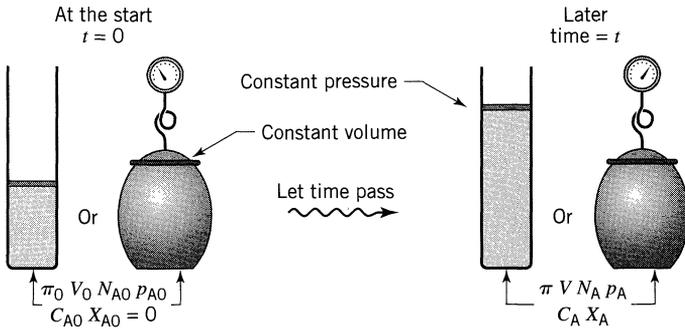


Figure 4.4 Symbols used for batch reactors.

Should we explore all reasonable design alternatives? How sophisticated should our analysis be? What simplifying assumptions should we make? What shortcuts should we take? Which factors should we ignore and which should we consider? And how should the reliability and completeness of the data at hand influence our decisions? Good engineering judgment, which only comes with experience, will suggest the appropriate course of action.

Symbols and Relationship between C_A and X_A

For the reaction $aA + bB \rightarrow rR$, with inerts iI , Figs. 4.4 and 4.5 show the symbols commonly used to tell what is happening in the batch and flow reactors. These figures show that there are two related measures of the extent of reaction, the concentration C_A and the conversion X_A . However, the relationship between C_A and X_A is often not obvious but depends on a number of factors. This leads to three special cases, as follows.

Special Case 1. Constant Density Batch and Flow Systems. This includes most liquid reactions and also those gas reactions run at constant temperature and density. Here C_A and X_A are related as follows:

$$\left. \begin{aligned} X_A &= 1 - \frac{C_A}{C_{A0}} \quad \text{and} \quad dX_A = -\frac{dC_A}{C_{A0}} \\ \frac{C_A}{C_{A0}} &= 1 - X_A \quad \text{and} \quad dC_A = -C_{A0}dX_A \end{aligned} \right\} \text{for } \varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} = 0 \quad (3)$$

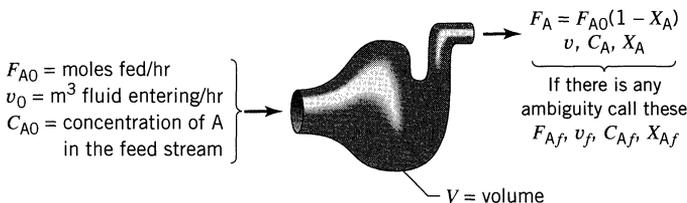


Figure 4.5 Symbols used for flow reactors.

To relate the changes in B and R to A we have

$$\frac{C_{A0} - C_A}{a} = \frac{C_{B0} - C_B}{b} = \frac{C_R - C_{R0}}{r} \quad \text{or} \quad \frac{C_{A0}X_A}{a} = \frac{C_{B0}X_B}{b} \quad (4)$$

Special Case 2. Batch and Flow Systems of Gases of Changing Density but with T and π Constant. Here the density changes because of the change in number of moles during reaction. In addition, we require that the volume of a fluid element changes linearly with conversion, or $V = V_0(1 + \varepsilon_A X_A)$.

$$\left. \begin{aligned} X_A &= \frac{C_{A0} - C_A}{C_{A0} + \varepsilon_A C_A} & \text{and} & \quad dX_A = -\frac{C_{A0}(1 + \varepsilon_A)}{(C_{A0} + \varepsilon_A C_A)^2} dC_A \\ \frac{C_A}{C_{A0}} &= \frac{1 - X_A}{1 + \varepsilon_A X_A} & \text{and} & \quad \frac{dC_A}{C_{A0}} = -\frac{1 + \varepsilon_A}{(1 + \varepsilon_A X_A)^2} dX_A \end{aligned} \right\} \text{for}$$

$$\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} \neq 0 \quad (5)$$

To follow changes in the other components we have

$$\text{between} \begin{cases} \varepsilon_A X_A = \varepsilon_B X_B \\ \frac{a\varepsilon_A}{C_{A0}} = \frac{b\varepsilon_B}{C_{B0}} \end{cases} \quad \text{for products} \begin{cases} \frac{C_R}{C_{A0}} = \frac{(r/a)X_A + C_{R0}/C_{A0}}{1 + \varepsilon_A X_A} \\ \frac{C_I}{C_{I0}} = \frac{1}{1 + \varepsilon_A X_A} \end{cases} \quad (6)$$

Special Case 3. Batch and Flow Systems for Gases in General (varying ρ , T , π) which react according to



Pick one reactant as the basis for determining the conversion. We call this the *key reactant*. Let A be the key. Then for *ideal gas* behavior,

$$X_A = \frac{1 - \frac{C_A}{C_{A0}} \left(\frac{T\pi_0}{T_0\pi} \right)}{1 + \varepsilon_A \frac{C_A}{C_{A0}} \left(\frac{T\pi_0}{T_0\pi} \right)} \quad \text{or} \quad \frac{C_A}{C_{A0}} = \frac{1 - X_A \left(\frac{T_0\pi}{T\pi_0} \right)}{1 + \varepsilon_A X_A \left(\frac{T_0\pi}{T\pi_0} \right)}$$

$$X_A = \frac{\frac{C_{B0}}{C_{A0}} - \frac{C_B}{C_{A0}} \left(\frac{T\pi_0}{T_0\pi} \right)}{\frac{b}{a} + \varepsilon_A \frac{C_B}{C_{A0}} \left(\frac{T\pi_0}{T_0\pi} \right)} \quad \text{or} \quad \frac{C_B}{C_{A0}} = \frac{\frac{C_{B0}}{C_{A0}} - \frac{b}{a} X_A \left(\frac{T_0\pi}{T\pi_0} \right)}{1 + \varepsilon_A X_A \left(\frac{T_0\pi}{T\pi_0} \right)}$$

$$\frac{C_R}{C_{A0}} = \frac{\frac{C_{R0}}{C_{A0}} + \frac{r}{a} X_A \left(\frac{T_0\pi}{T\pi_0} \right)}{1 + \varepsilon_A X_A \left(\frac{T_0\pi}{T\pi_0} \right)}$$

For high-pressure nonideal gas behavior replace $\left(\frac{T_0\pi}{\tau_0\pi_0}\right)$ by $\left(\frac{z_0T_0\pi}{zT\pi}\right)$, where z is the compressibility factor. To change to another key reactant, say B, note that

$$\frac{a\varepsilon_A}{C_{A0}} = \frac{b\varepsilon_B}{C_{B0}} \quad \text{and} \quad \frac{C_{A0}X_A}{a} = \frac{C_{B0}X_B}{b}$$

For liquids or isothermal gases with no change pressure and density

$$\varepsilon_A \rightarrow 0 \quad \text{and} \quad \left(\frac{T_0\pi}{T\pi_0}\right) \rightarrow 1$$

and the preceding expressions simplify greatly.

EXAMPLE 4.1 A BALANCE FROM STOICHIOMETRY

Consider a feed $C_{A0} = 100$, $C_{B0} = 200$, $C_{i0} = 100$ to a steady-flow reactor. The isothermal gas-phase reaction is



If $C_A = 40$ at the reactor exit, what is C_B , X_A , and X_B there?

SOLUTION

First sketch what is known (see Fig. E4.1).

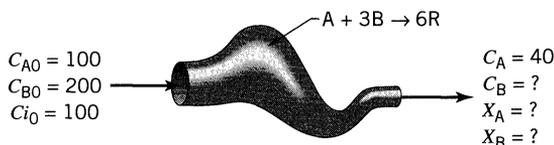


Figure E4.1

Next recognize that this problem concerns Special Case 2. So evaluate ε_A and ε_B . For this take 400 volumes of gas

$$\left. \begin{array}{l} \text{at } X_A = 0 \quad V = 100A + 200B + 100i = 400 \\ \text{at } X_A = 1 \quad V = 0A - 100B + 600R + 100i = 600 \end{array} \right\} \varepsilon_A = \frac{600 - 400}{400} = \frac{1}{2}$$

Then from the equations in the text

$$\varepsilon_B = \frac{\varepsilon_A C_{B0}}{b C_{A0}} = \frac{(1/2)(200)}{3(100)} = \frac{1}{3}$$

$$X_A = \frac{C_{A0} - C_A}{C_{A0} + \varepsilon_A C_A} = \frac{100 - 40}{100 + (1/2)40} = \frac{60}{120} = \underline{\underline{0.5}}$$

$$X_B = \frac{b C_{A0} X_A}{C_{B0}} = \frac{3(100)(0.5)}{200} = \underline{\underline{0.75}}$$

$$C_B = C_{B0} \left(\frac{1 - X_B}{1 + \varepsilon_B X_B} \right) = \frac{200(1 - 0.75)}{1 + (1/3)(0.75)} = \underline{\underline{40}}$$

PROBLEMS

The following four problems consider an isothermal single-phase flow reactor operating at steady-state and constant pressure.

- 4.1. Given a gaseous feed, $C_{A0} = 100$, $C_{B0} = 200$, $A + B \rightarrow R + S$, $X_A = 0.8$. Find X_B , C_A , C_B .
- 4.2. Given a dilute aqueous feed, $C_{A0} = C_{B0} = 100$, $A + 2B \rightarrow R + S$, $C_A = 20$. Find X_A , X_B , C_B .
- 4.3. Given a gaseous feed, $C_{A0} = 200$, $C_{B0} = 100$, $A + B \rightarrow R$, $C_A = 50$. Find X_A , X_B , C_B .
- 4.4. Given a gaseous feed, $C_{A0} = C_{B0} = 100$, $A + 2B \rightarrow R$, $C_B = 20$. Find X_A , X_B , C_A .

In the following two problems a continuous stream of fluid enters a vessel at temperature T_0 and pressure π_0 , reacts there, and leaves at T and π .

- 4.5. Given a gaseous feed, $T_0 = 400$ K, $\pi_0 = 4$ atm, $C_{A0} = 100$, $C_{B0} = 200$, $A + B \rightarrow 2R$, $T = 300$ K, $\pi = 3$ atm, $C_A = 20$. Find X_A , X_B , C_B .
- 4.6. Given a gaseous feed, $T_0 = 1000$ K, $\pi_0 = 5$ atm, $C_{A0} = 100$, $C_{B0} = 200$, $A + B \rightarrow 5R$, $T = 400$ K, $\pi = 4$ atm, $C_A = 20$. Find X_A , X_B , C_B .
- 4.7. *A Commercial Popcorn Popping Popcorn Popper.* We are constructing a 1-liter popcorn popper to be operated in steady flow. First tests in this unit show that 1 liter/min of raw corn feed stream produces 28 liter/min of mixed exit stream. Independent tests show that when raw corn pops its volume goes from 1 to 31. With this information determine what fraction of raw corn is popped in the unit.

Chapter 5

Ideal Reactors for a Single Reaction

In this chapter we develop the performance equations for a single fluid reacting in the three ideal reactors shown in Fig. 5.1. We call these *homogeneous reactions*. Applications and extensions of these equations to various isothermal and nonisothermal operations are considered in the following four chapters.

In the *batch reactor*, or BR, of Fig. 5.1a the reactants are initially charged into a container, are well mixed, and are left to react for a certain period. The resultant mixture is then discharged. This is an unsteady-state operation where composition changes with time; however, at any instant the composition throughout the reactor is uniform.

The first of the two ideal steady-state flow reactors is variously known as the plug flow, slug flow, piston flow, ideal tubular, and unmixed flow reactor, and it is shown in Fig. 5.1b. We refer to it as the *plug flow reactor*, or PFR, and to this pattern of flow as *plug flow*. It is characterized by the fact that the flow of fluid through the reactor is orderly with no element of fluid overtaking or mixing with any other element ahead or behind. Actually, there may be lateral mixing of fluid in a plug flow reactor; however, there must be no mixing or diffusion along

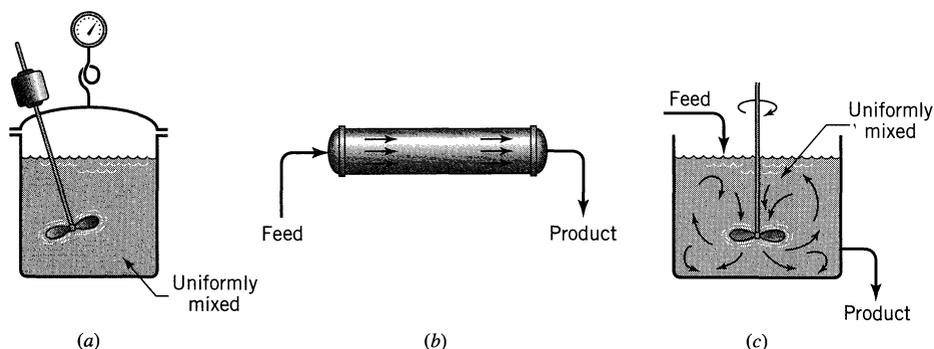


Figure 5.1 The three types of ideal reactors: (a) batch reactor, or BR; (b) plug flow reactor, or PFR; and (c) mixed flow reactor, or MFR.

the flow path. The necessary and sufficient condition for plug flow is for the residence time in the reactor to be the same for all elements of fluid.*

The other ideal steady-state flow reactor is called the mixed reactor, the backmix reactor, the ideal stirred tank reactor, the C* (meaning C-star), CSTR, or the CFSTR (constant flow stirred tank reactor), and, as its names suggest, it is a reactor in which the contents are well stirred and uniform throughout. Thus, the exit stream from this reactor has the same composition as the fluid within the reactor. We refer to this type of flow as *mixed flow*, and the corresponding reactor the *mixed flow reactor*, or MFR.

These three ideals are relatively easy to treat. In addition, one or other usually represents the best way of contacting the reactants—no matter what the operation. For these reasons, we often try to design real reactors so that their flows approach these ideals, and much of the development in this book centers about them.

In the treatment to follow it should be understood that the term V , called the reactor volume, really refers to the volume of fluid in the reactor. When this differs from the internal volume of reactor, then V_r designates the internal volume of reactor while V designates the volume of reacting fluid. For example, in solid catalyzed reactors with voidage ε we have

$$V = \varepsilon V_r$$

For homogeneous systems, however, we usually use the term V alone.

5.1 IDEAL BATCH REACTOR

Make a material balance for any component A. For such an accounting we usually select the limiting component. In a batch reactor, since the composition is uniform throughout at any instant of time, we may make the accounting about the whole reactor. Noting that no fluid enters or leaves the reaction mixture during reaction, Eq. 4.1, which was written for component A, becomes

$$\overset{=0}{\cancel{\text{input}}} = \overset{=0}{\cancel{\text{output}}} + \text{disappearance} + \text{accumulation}$$

or

$$+ \left(\begin{array}{c} \text{rate of loss of reactant A} \\ \text{within reactor due to} \\ \text{chemical reaction} \end{array} \right) = - \left(\begin{array}{c} \text{rate of accumulation} \\ \text{of reactant A} \\ \text{within the reactor} \end{array} \right) \quad (1)$$

Evaluating the terms of Eq. 1, we find

$$\begin{array}{l} \text{disappearance of A} \\ \text{by reaction,} \\ \text{moles/time} \end{array} = (-r_A)V = \left(\frac{\text{moles A reacting}}{(\text{time})(\text{volume of fluid})} \right) (\text{volume of fluid})$$

$$\begin{array}{l} \text{accumulation of A,} \\ \text{moles/time} \end{array} = \frac{dN_A}{dt} = \frac{d[N_{A0}(1 - X_A)]}{dt} = -N_{A0} \frac{dX_A}{dt}$$

* The necessary condition follows directly from the definition of plug flow. However, the sufficient condition—that the same residence times implies plug flow—can be established only from the second law of thermodynamics.

By replacing these two terms in Eq. 1, we obtain

$$(-r_A)V = N_{A0} \frac{dX_A}{dt} \quad (2)$$

Rearranging and integrating then gives

$$t = N_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)V} \quad (3)$$

This is the general equation showing the time required to achieve a conversion X_A for either isothermal or nonisothermal operation. The volume of reacting fluid and the reaction rate remain under the integral sign, for in general they both change as reaction proceeds.

This equation may be simplified for a number of situations. If the density of the fluid remains constant, we obtain

$$t = C_{A0} \int_0^{X_A} \frac{dX_A}{-r_A} = - \int_{C_{A0}}^{C_A} \frac{dC_A}{-r_A} \quad \text{for } \varepsilon_A = 0 \quad (4)$$

For all reactions in which the volume of reacting mixture changes proportionately with conversion, such as in single gas-phase reactions with significant density changes, Eq. 3 becomes

$$t = N_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)V_0(1 + \varepsilon_A X_A)} = C_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)(1 + \varepsilon_A X_A)} \quad (5)$$

In one form or another, Eqs. 2 to 5 have all been encountered in Chapter 3. They are applicable to both isothermal and nonisothermal operations. For the latter the variation of rate with temperature, and the variation of temperature with conversion, must be known before solution is possible. Figure 5.2 is a graphical representation of two of these equations.

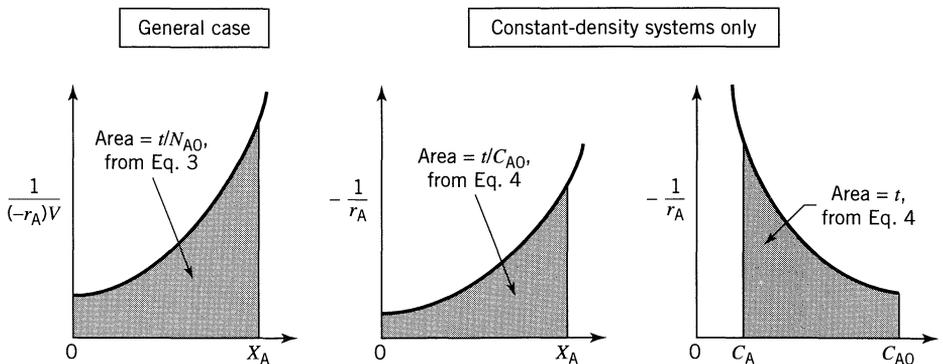


Figure 5.2 Graphical representation of the performance equations for batch reactors, isothermal or nonisothermal.

Space-Time and Space-Velocity

Just as the reaction time t is the natural performance measure for a batch reactor, so are the space-time and space-velocity the proper performance measures of flow reactors. These terms are defined as follows:

Space-time:

$$\tau = \frac{1}{s} = \left(\frac{\text{time required to process one reactor volume of feed measured at specified conditions}}{\text{reactor volume of feed measured at specified conditions}} \right) = [\text{time}] \quad (6)$$

Space-velocity:

$$s = \frac{1}{\tau} = \left(\frac{\text{number of reactor volumes of feed at specified conditions which can be treated in unit time}}{\text{reactor volume of feed measured at specified conditions}} \right) = [\text{time}^{-1}] \quad (7)$$

Thus, a space-velocity of 5 hr^{-1} means that five reactor volumes of feed at specified conditions are being fed into the reactor per hour. A space-time of 2 min means that every 2 min one reactor volume of feed at specified conditions is being treated by the reactor.

Now we may arbitrarily select the temperature, pressure, and state (gas, liquid, or solid) at which we choose to measure the volume of material being fed to the reactor. Certainly, then, the value for space-velocity or space-time depends on the conditions selected. If they are of the stream entering the reactor, the relation between s and τ and the other pertinent variables is

$$\begin{aligned} \tau &= \frac{1}{s} = \frac{C_{A0}V}{F_{A0}} = \frac{\left(\frac{\text{moles A entering}}{\text{volume of feed}} \right) (\text{volume of reactor})}{\left(\frac{\text{moles A entering}}{\text{time}} \right)} \\ &= \frac{V}{v_0} = \frac{(\text{reactor volume})}{(\text{volumetric feed rate})} \end{aligned} \quad (8)$$

It may be more convenient to measure the volumetric feed rate at some standard state, especially when the reactor is to operate at a number of temperatures. If, for example, the material is gaseous when fed to the reactor at high temperature but is liquid at the standard state, care must be taken to specify precisely what state has been chosen. The relation between the space-velocity and space-time for actual feed conditions (unprimed symbols) and at standard conditions (designated by primes) is given by

$$\tau' = \frac{1}{s'} = \frac{C'_{A0}V}{F_{A0}} = \tau \frac{C'_{A0}}{C_{A0}} = \frac{1}{s} \frac{C'_{A0}}{C_{A0}} \quad (9)$$

In most of what follows, we deal with the space-velocity and space-time based on feed at actual entering conditions; however, the change to any other basis is easily made.

5.2 STEADY-STATE MIXED FLOW REACTOR

The performance equation for the mixed flow reactor is obtained from Eq. 4.1, which makes an accounting of a given component within an element of volume of the system. But since the composition is uniform throughout, the accounting may be made about the reactor as a whole. By selecting reactant A for consideration, Eq. 4.1 becomes

$$\text{input} = \text{output} + \text{disappearance by reaction} + \text{accumulation} = 0 \quad (10)$$

As shown in Fig. 5.3, if $F_{A0} = v_0 C_{A0}$ is the molar feed rate of component A to the reactor, then considering the reactor as a whole we have

$$\text{input of A, moles/time} = F_{A0}(1 - X_{A0}) = F_{A0}$$

$$\text{output of A, moles/time} = F_A = F_{A0}(1 - X_A)$$

$$\begin{aligned} \text{disappearance of A} \\ \text{by reaction,} \\ \text{moles/time} \end{aligned} = (-r_A)V = \left(\frac{\text{moles A reacting}}{(\text{time})(\text{volume of fluid})} \right) \left(\text{volume of reactor} \right)$$

Introducing these three terms into Eq. 10, we obtain

$$F_{A0}X_A = (-r_A)V$$

which on rearrangement becomes

OR

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \frac{\Delta X_A}{-r_A} = \frac{X_A}{-r_A}$$

$$\tau = \frac{1}{s} = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = \frac{C_{A0}X_A}{-r_A}$$

any ε_A (11)

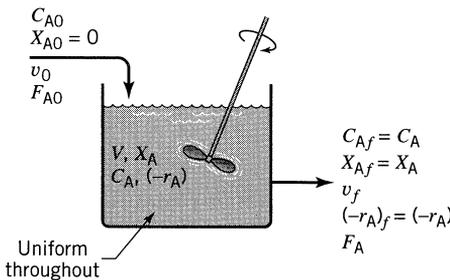


Figure 5.3 Notation for a mixed reactor.

where X_A and r_A are measured at exit stream conditions, which are the same as the conditions within the reactor.

More generally, if the feed on which conversion is based, subscript 0, enters the reactor partially converted, subscript i , and leaves at conditions given by subscript f , we have

$$\frac{V}{F_{A0}} = \frac{\Delta X_A}{(-r_A)_f} = \frac{X_{Af} - X_{Ai}}{(-r_A)_f}$$

or (12)

$$\tau = \frac{VC_{A0}}{F_{A0}} = \frac{C_{A0}(X_{Af} - X_{Ai})}{(-r_A)_f}$$

For the special case of constant-density systems $X_A = 1 - C_A/C_{A0}$, in which case the performance equation for mixed reactors can also be written in terms of concentrations or

or (13)

$$\frac{V}{F_{A0}} = \frac{X_A}{-r_A} = \frac{C_{A0} - C_A}{C_{A0}(-r_A)}$$

$$\tau = \frac{V}{v} = \frac{C_{A0}X_A}{-r_A} = \frac{C_{A0} - C_A}{-r_A} \quad \varepsilon_A = 0$$

These expressions relate in a simple way the four terms X_A , $-r_A$, V , F_{A0} ; thus, knowing any three allows the fourth to be found directly. In design, then, the size of reactor needed for a given duty or the extent of conversion in a reactor of given size is found directly. In kinetic studies each steady-state run gives, without integration, the reaction rate for the conditions within the reactor. The ease of interpretation of data from a mixed flow reactor makes its use very attractive in kinetic studies, in particular with messy reactions (e.g., multiple reactions and solid catalyzed reactions).

Figure 5.4 is a graphical representation of these mixed flow performance equations. For any specific kinetic form the equations can be written out directly.

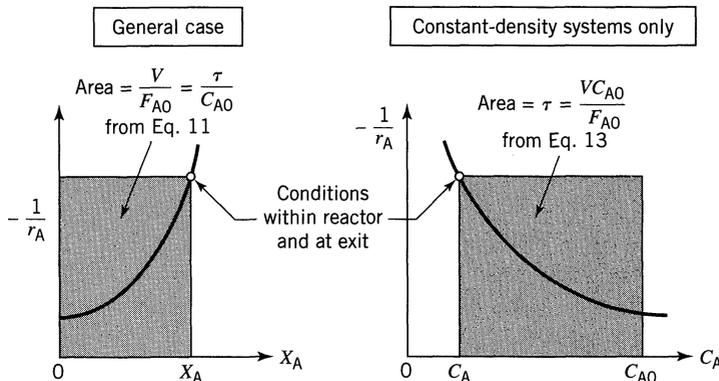


Figure 5.4 Graphical representation of the design equations for mixed flow reactor.

As an example, for constant density systems $C_A/C_{A0} = 1 - X_A$, thus the performance expression for first-order reaction becomes

$$k\tau = \frac{X_A}{1 - X_A} = \frac{C_{A0} - C_A}{C_A} \quad \text{for } \varepsilon_A = 0 \quad (14a)$$

On the other hand, for linear expansion

$$V = V_0(1 + \varepsilon_A X_A) \quad \text{and} \quad \frac{C_A}{C_{A0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A}$$

thus for first-order reaction the performance expression of Eq. 11 becomes

$$k\tau = \frac{X_A(1 + \varepsilon_A X_A)}{1 - X_A} \quad \text{for any } \varepsilon_A \quad (14b)$$

For second-order reaction, $A \rightarrow$ products, $-r_A = kC_A^2$, $\varepsilon_A = 0$, the performance equation of Eq. 11 becomes

$$k\tau = \frac{C_{A0} - C_A}{C_A^2} \quad \text{or} \quad C_A = \frac{-1 + \sqrt{1 + 4k\tau C_{A0}}}{2k\tau} \quad (15)$$

Similar expressions can be written for any other form of rate equation. These expressions can be written either in terms of concentrations or conversions. Using conversions is simpler for systems of changing density, while either form can be used for systems of constant density.

EXAMPLE 5.1 REACTION RATE IN A MIXED FLOW REACTOR

One liter per minute of liquid containing A and B ($C_{A0} = 0.10$ mol/liter, $C_{B0} = 0.01$ mol/liter) flow into a mixed reactor of volume $V = 1$ liter. The materials react in a complex manner for which the stoichiometry is unknown. The outlet stream from the reactor contains A, B, and C ($C_{Af} = 0.02$ mol/liter, $C_{Bf} = 0.03$ mol/liter, $C_{Cf} = 0.04$ mol/liter), as shown in Fig. E5.1. Find the rate of reaction of A, B, and C for the conditions within the reactor.

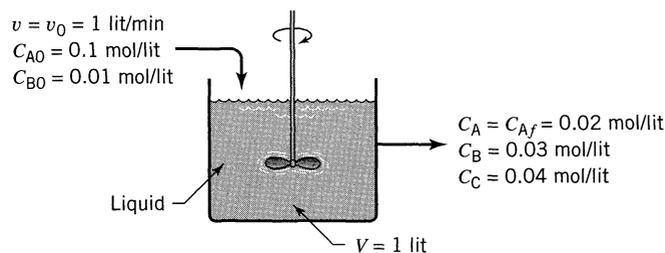


Figure E5.1

SOLUTION

For a liquid in a mixed flow reactor $\varepsilon_A = 0$ and Eq. 13 applies to each of the reacting components, giving for the rate of disappearance:

$$-r_A = \frac{C_{A0} - C_A}{\tau} = \frac{C_{A0} - C_A}{V/v} = \frac{0.10 - 0.02}{1/1} = \underline{\underline{0.08 \text{ mol/liter} \cdot \text{min}}}$$

$$-r_B = \frac{C_{B0} - C_B}{\tau} = \frac{0.01 - 0.03}{1} = \underline{\underline{-0.02 \text{ mol/liter} \cdot \text{min}}}$$

$$-r_C = \frac{C_{C0} - C_C}{\tau} = \frac{0 - 0.04}{1} = \underline{\underline{-0.04 \text{ mol/liter} \cdot \text{min}}}$$

Thus A is disappearing while B and C are being formed. ■

EXAMPLE 5.2 KINETICS FROM A MIXED FLOW REACTOR

Pure gaseous reactant A ($C_{A0} = 100$ millimol/liter) is fed at a steady rate into a mixed flow reactor ($V = 0.1$ liter) where it dimerizes ($2A \rightarrow R$). For different gas feed rates the following data are obtained:

| | | | | |
|---------------------------|------|------|-----|------|
| Run number | 1 | 2 | 3 | 4 |
| v_0 , liter/hr | 10.0 | 3.0 | 1.2 | 0.5 |
| C_{Af} , millimol/liter | 85.7 | 66.7 | 50 | 33.4 |

Find a rate equation for this reaction.

SOLUTION

For this stoichiometry, $2A \rightarrow R$, the expansion factor is

$$\varepsilon_A = \frac{1 - 2}{2} = -\frac{1}{2}$$

and the corresponding relation between concentration and conversion is

$$\frac{C_A}{C_{A0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A} = \frac{1 - X_A}{1 - \frac{1}{2} X_A}$$

or

$$X_A = \frac{1 - C_A/C_{A0}}{1 + \varepsilon_A C_A/C_{A0}} = \frac{1 - C_A/C_{A0}}{1 - C_A/2C_{A0}}$$

The conversion for each run is then calculated and tabulated in column 4 of Table E5.2.

Table E5.2

| Run | Given | | Calculated | | | |
|-----|-------|-------|------------|--------------------------------------|------------|---------------|
| | v_0 | C_A | X_A | $(-r_A) = \frac{v_0 C_{A0} X_A}{V}$ | $\log C_A$ | $\log (-r_A)$ |
| 1 | 10.0 | 85.7 | 0.25 | $\frac{(10)(100)(0.25)}{0.1} = 2500$ | 1.933 | 3.398 |
| 2 | 3.0 | 66.7 | 0.50 | 1500 | 1.824 | 3.176 |
| 3 | 1.2 | 50 | 0.667 | 800 | 1.699 | 2.903 |
| 4 | 0.5 | 33.3 | 0.80 | 400 | 1.522 | 2.602 |

From the performance equation, Eq. 11, the rate of reaction for each run is given by

$$(-r_A) = \frac{v_0 C_{A0} X_A}{V}, \quad \left[\frac{\text{millimol}}{\text{liter} \cdot \text{hr}} \right]$$

These values are tabulated in column 5 of Table E5.2.

Having paired values of r_A and C_A (see Table E5.2) we are ready to test various kinetic expressions. Instead of separately testing for first-order (plot r_A vs. C_A), second-order (plot r_A vs. C_A^2), etc., let us test directly for n th-order kinetics. For this take logarithms of $-r_A = kC_A^n$, giving

$$\log(-r_A) = \log k + n \log C_A$$

For n th-order kinetics this data should give a straight line on a $\log(-r_A)$ vs. $\log C_A$ plot. From columns 6 and 7 of Table E5.2 and as shown in Fig. E5.2, the

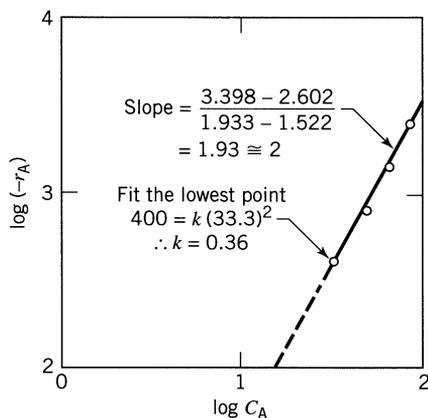


Figure E5.2

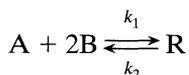
four data points are reasonably represented by a straight line of slope 2, so the rate equation for this dimerization is

$$\underline{-r_A = \left(0.36 \frac{\text{liter}}{\text{hr} \cdot \text{millimol}}\right) C_A^2, \quad \left[\frac{\text{millimol}}{\text{liter} \cdot \text{hr}}\right]}$$

Comment. If we ignore the density change in our analysis (or put $\varepsilon_A = 0$ and use $C_A/C_{A0} = 1 - X_A$) we end up with an incorrect rate equation (reaction order $n \cong 1.6$) which when used in design would give wrong performance predictions.

EXAMPLE 5.3 MIXED FLOW REACTOR PERFORMANCE

The elementary liquid-phase reaction



with rate equation

$$-r_A = -\frac{1}{2} r_B = (12.5 \text{ liter}^2/\text{mol}^2 \cdot \text{min}) C_A C_B^2 - (1.5 \text{ min}^{-1}) C_R, \quad \left[\frac{\text{mol}}{\text{liter} \cdot \text{min}}\right]$$

is to take place in a 6-liter steady-state mixed flow reactor. Two feed streams, one containing 2.8 mol A/liter and the other containing 1.6 mol B/liter, are to be introduced at equal volumetric flow rates into the reactor, and 75% conversion of limiting component is desired (see Fig. E5.3). What should be the flow rate of each stream? Assume a constant density throughout.

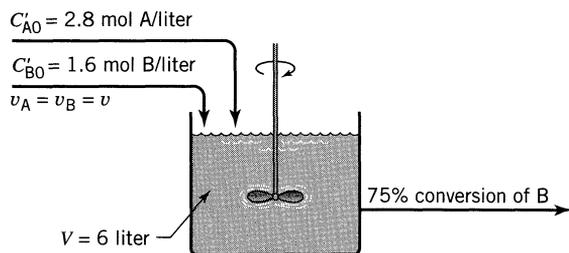


Figure E5.3

SOLUTION

The concentration of components in the mixed feed stream is

$$C_{A0} = 1.4 \text{ mol/liter}$$

$$C_{B0} = 0.8 \text{ mol/liter}$$

$$C_{R0} = 0$$

These numbers show that B is the limiting component, so for 75% conversion of B and $\varepsilon = 0$, the composition in the reactor and in the exit stream is

$$C_A = 1.4 - 0.6/2 = 1.1 \text{ mol/liter}$$

$$C_B = 0.8 - 0.6 = 0.2 \text{ mol/liter} \quad \text{or} \quad 75\% \text{ conversion}$$

$$C_R = 0.3 \text{ mol/liter}$$

Writing the rate and solving the problem in terms of B we have at the conditions within the reactor

$$\begin{aligned} -r_B &= 2(-r_A) = (2 \times 12.5)C_A C_B^2 - (2 \times 1.5)C_R \\ &= \left(25 \frac{\text{liter}^2}{\text{mol}^2 \cdot \text{min}}\right) \left(1.1 \frac{\text{mol}}{\text{liter}}\right) \left(0.2 \frac{\text{mol}}{\text{liter}}\right)^2 - (3 \text{ min}^{-1}) \left(0.3 \frac{\text{mol}}{\text{liter}}\right) \\ &= (1.1 - 0.9) \frac{\text{mol}}{\text{liter} \cdot \text{min}} = 0.2 \frac{\text{mol}}{\text{liter} \cdot \text{min}} \end{aligned}$$

For no density change, the performance equation of Eq. 13 gives

$$\tau = \frac{V}{v} = \frac{C_{B0} - C_B}{-r_B}$$

Hence the volumetric flow rate into and out of the reactor is

$$\begin{aligned} v &= \frac{V(-r_B)}{C_{B0} - C_B} \\ &= \frac{(6 \text{ liter})(0.2 \text{ mol/liter} \cdot \text{min})}{(0.8 - 0.6) \text{ mol/liter}} = \underline{\underline{6 \text{ liter/min}}} \end{aligned}$$

or

3 liter/min of each of the two feed streams

5.3 STEADY-STATE PLUG FLOW REACTOR

In a plug flow reactor the composition of the fluid varies from point to point along a flow path; consequently, the material balance for a reaction component must be made for a differential element of volume dV . Thus for reactant A, Eq. 4.1 becomes

$$\text{input} = \text{output} + \text{disappearance by reaction} + \overset{=0}{\text{accumulation}} \quad (10)$$

Referring to Fig. 5.5, we see for volume dV that

$$\text{input of A, moles/time} = F_A$$

$$\text{output of A, moles/time} = F_A + dF_A$$

disappearance of A by

$$\text{reaction, moles/time} = (-r_A)dV$$

$$= \left(\frac{\text{moles A reacting}}{(\text{time})(\text{volume of fluid})} \right) (\text{volume of element})$$

Introducing these three terms in Eq. 10, we obtain

$$F_A = (F_A + dF_A) + (-r_A)dV$$

Noting that

$$dF_A = d[F_{A0}(1 - X_A)] = -F_{A0}dX_A$$

We obtain on replacement

$$F_{A0}dX_A = (-r_A)dV \quad (16)$$

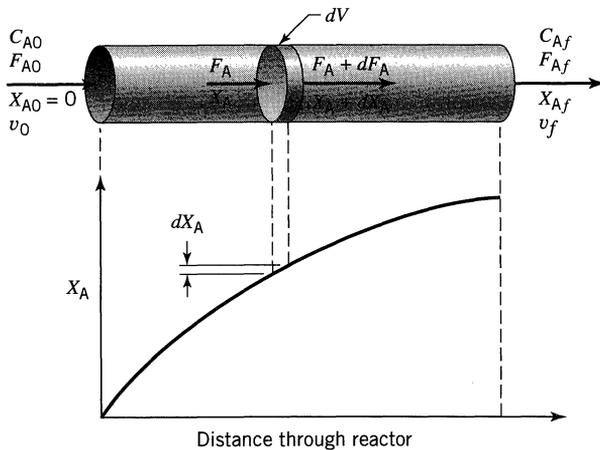


Figure 5.5 Notation for a plug flow reactor.

This, then, is the equation which accounts for A in the differential section of reactor of volume dV . For the reactor as a whole the expression must be integrated. Now F_{A0} , the feed rate, is constant, but r_A is certainly dependent on the concentration or conversion of materials. Grouping the terms accordingly, we obtain

$$\int_0^V \frac{dV}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

Thus

$$\begin{aligned} \frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} &= \int_0^{X_{Af}} \frac{dX_A}{-r_A} \\ \tau = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} &= C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A} \end{aligned} \quad \text{any } \varepsilon_A \quad (17)$$

Equation 17 allows the determination of reactor size for a given feed rate and required conversion. Compare Eqs. 11 and 17. The difference is that in plug flow r_A varies, whereas in mixed flow r_A is constant.

As a more general expression for plug flow reactors, if the feed on which conversion is based, subscript 0, enters the reactor partially converted, subscript i , and leaves at a conversion designated by subscript f , we have

$$\frac{V}{F_{A0}} = \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}$$

or

$$\tau = C_{A0} \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}$$

(18)

For the special case of *constant-density systems*

$$X_A = 1 - \frac{C_A}{C_{A0}} \quad \text{and} \quad dX_A = -\frac{dC_A}{C_{A0}}$$

in which case the performance equation can be expressed in terms of concentrations, or

$$\begin{aligned} \frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} &= \int_0^{X_{Af}} \frac{dX_A}{-r_A} = -\frac{1}{C_{A0}} \int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A} \\ \tau = \frac{V}{v_0} &= C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A} = -\int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A} \end{aligned} \quad \varepsilon_A = 0 \quad (19)$$

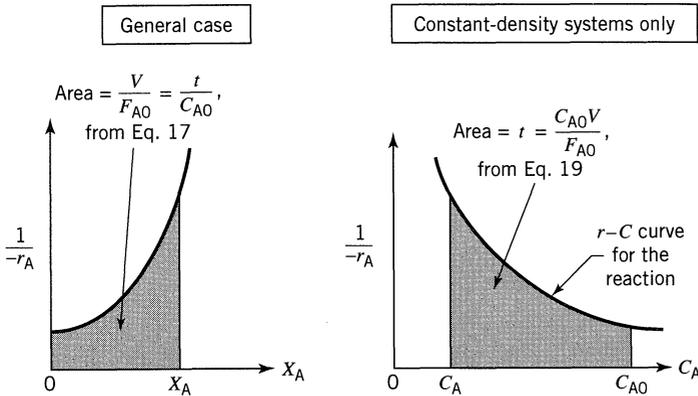


Figure 5.6 Graphical representation of the performance equations for plug flow reactors.

These performance equations, Eqs. 17 to 19, can be written either in terms of concentrations or conversions. For systems of changing density it is more convenient to use conversions; however, there is no particular preference for constant density systems. Whatever its form, the performance equations interrelate the *rate of reaction*, the *extent of reaction*, the *reactor volume*, and the *feed rate*, and if any one of these quantities is unknown it can be found from the other three.

Figure 5.6 displays these performance equations and shows that the space-time needed for any particular duty can always be found by numerical or graphical integration. However, for certain simple kinetic forms analytic integration is possible—and convenient. To do this, insert the kinetic expression for r_A in Eq. 17 and integrate. Some of the simpler integrated forms for plug flow are as follows: *Zero-order homogeneous reaction*, any constant ε_A

$$k\tau = \frac{kC_{A0}V}{F_{A0}} = C_{A0}X_A \quad (20)$$

First-order irreversible reaction, $A \rightarrow$ products, any constant ε_A ,

$$k\tau = -(1 + \varepsilon_A) \ln(1 - X_A) - \varepsilon_A X_A \quad (21)$$

First-order reversible reaction, $A \rightleftharpoons rR$, $C_{R0}/C_{A0} = M$, kinetics approximated or fitted by $-r_A = k_1C_A - k_2C_R$ with an observed equilibrium conversion X_{Ae} , any constant ε_A ,

$$k_1\tau = \frac{M + rX_{Ae}}{M + r} \left[-(1 + \varepsilon_A X_{Ae}) \ln\left(1 - \frac{X_A}{X_{Ae}}\right) - \varepsilon_A X_A \right] \quad (22)$$

Second-order irreversible reaction, $A + B \rightarrow$ products with equimolar feed or $2A \rightarrow$ products, any constant ε_A ,

$$C_{A0}k\tau = 2\varepsilon_A(1 + \varepsilon_A)\ln(1 - X_A) + \varepsilon_A^2 X_A + (\varepsilon_A + 1)^2 \frac{X_A}{1 - X_A} \quad (23)$$

Where the density is constant, put $\varepsilon_A = 0$ to obtain the simplified performance equation.

By comparing the batch expressions of Chapter 3 with these plug flow expressions we find:

- (1) For systems of constant density (constant-volume batch and constant-density plug flow) the performance equations are identical, τ for plug flow is equivalent to t for the batch reactor, and the equations can be used interchangeably.
- (2) For systems of changing density there is no direct correspondence between the batch and the plug flow equations and the correct equation must be used for each particular situation. In this case the performance equations cannot be used interchangeably.

The following illustrative examples show how to use these expressions.

EXAMPLE 5.4 PLUG FLOW REACTOR PERFORMANCE

A homogeneous gas reaction $A \rightarrow 3R$ has a reported rate at 215°C

$$-r_A = 10^{-2} C_A^{1/2}, \quad [\text{mol/liter} \cdot \text{sec}]$$

Find the space-time needed for 80% conversion of a 50% A–50% inert feed to a plug flow reactor operating at 215°C and 5 atm ($C_{A0} = 0.0625$ mol/liter).

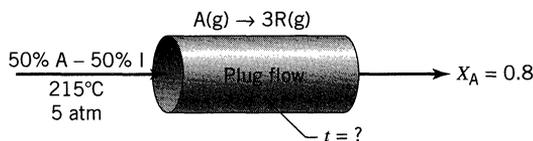


Figure E5.4a

SOLUTION

For this stoichiometry and with 50% inerts, two volumes of feed gas would give four volumes of completely converted product gas; thus

$$\varepsilon_A = \frac{4 - 2}{2} = 1$$

in which case the plug flow performance equation, Eq. 17, becomes

$$\tau = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A} = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{k C_{A0}^{1/2} \left(\frac{1 - X_A}{1 + \varepsilon_A X_A} \right)^{1/2}} = \frac{C_{A0}^{1/2}}{k} \int_0^{0.8} \left(\frac{1 + X_A}{1 - X_A} \right)^{1/2} dX_A \quad (i)$$

The integral can be evaluated in any one of three ways: graphically, numerically, or analytically. Let us illustrate these methods.

Table E5.4

| X_A | $\frac{1 + X_A}{1 - X_A}$ | $\left(\frac{1 + X_A}{1 - X_A}\right)^{1/2}$ |
|-------|---------------------------|--|
| 0 | 1 | 1 |
| 0.2 | $\frac{1.2}{0.8} = 1.5$ | 1.227 |
| 0.4 | 2.3 | 1.528 |
| 0.6 | 4 | 2 |
| 0.8 | 9 | 3 |

Graphical Integration. First evaluate the function to be integrated at selected values (see Table E5.4) and plot this function (see Fig. E5.4b).

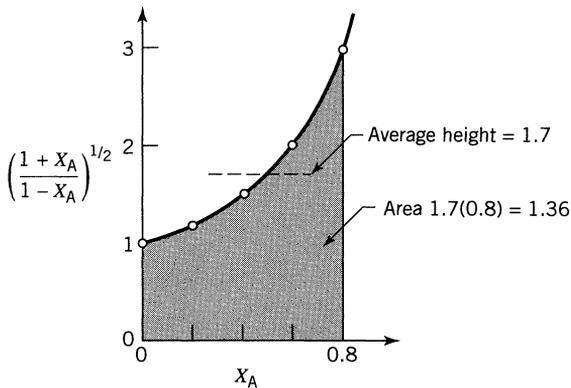


Figure E5.4b

Counting squares or estimating by eye we find

$$\text{Area} = \int_0^{0.8} \left(\frac{1 + X_A}{1 - X_A}\right)^{1/2} dX_A = (1.70)(0.8) = \underline{\underline{1.36}}$$

Numerical Integration. Using Simpson's rule, applicable to an even number of uniformly spaced intervals on the X_A axis, we find for the data of Table E5.4,

$$\begin{aligned} \int_0^{0.8} \left(\frac{1 + X_A}{1 - X_A}\right)^{1/2} dX_A &= (\text{average height})(\text{total width}) \\ &= \left[\frac{1(1) + 4(1.227) + 2(1.528) + 4(2) + 1(3)}{12} \right] (0.8) \\ &= \underline{\underline{1.331}} \end{aligned}$$

Analytical Integration. From a table of integrals

$$\int_0^{0.8} \left(\frac{1 + X_A}{1 - X_A} \right)^{1/2} dX_A = \int_0^{0.8} \frac{1 + X_A}{\sqrt{1 - X_A^2}} dX_A$$

$$= \left(\arcsin X_A - \sqrt{1 - X_A^2} \right) \Big|_0^{0.8} = \underline{\underline{1.328}}$$

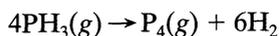
The method of integration recommended depends on the situation. In this problem probably the numerical method is the quickest and simplest and gives a good enough answer for most purposes.

So with the integral evaluated, Eq. (i) becomes

$$\tau = \frac{(0.0625 \text{ mol/liter})^{1/2}}{(10^{-2} \text{ mol}^{1/2}/\text{liter}^{1/2} \cdot \text{sec})} (1.33) = \underline{\underline{33.2 \text{ sec}}}$$

EXAMPLE 5.5 PLUG FLOW REACTOR VOLUME

The homogeneous gas decomposition of phosphine



proceeds at 649°C with the first-order rate

$$-r_{\text{PH}_3} = (10/\text{hr}) C_{\text{PH}_3}$$

What size of plug flow reactor operating at 649°C and 460 kPa can produce 80% conversion of a feed consisting of 40 mol of pure phosphine per hour?

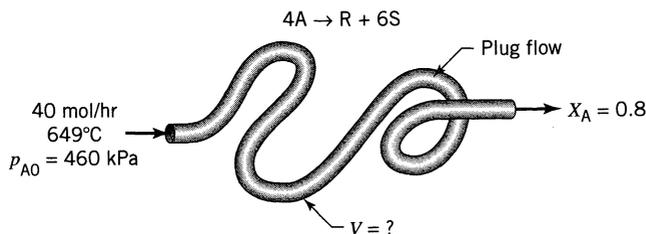


Figure E5.5

SOLUTION

Let $A = \text{PH}_3$, $R = \text{P}_4$, $S = \text{H}_2$. Then the reaction becomes



with

$$-r_A = (10/\text{hr}) C_A$$

The volume of plug flow reactor is given by Eq. 21

$$V = \frac{F_{A0}}{kC_{A0}} \left[(1 + \varepsilon_A) \ln \frac{1}{1 - X_A} - \varepsilon_A X_A \right]$$

Evaluating the individual terms in this expression gives

$$F_{A0} = 40 \text{ mol/hr}$$

$$k = 10/\text{hr}$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{460\,000 \text{ Pa}}{(8.314 \text{ Pa} \cdot \text{m}^3/\text{mol} \cdot \text{K})(922 \text{ K})} = 60 \text{ mol/m}^3$$

$$\varepsilon_A = \frac{7 - 4}{4} = 0.75$$

$$X_A = 0.8$$

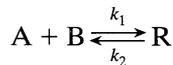
hence the volume of reactor

$$V = \frac{40 \text{ mol/hr}}{(10/\text{hr})(60 \text{ mol/m}^3)} \left[(1 + 0.75) \ln \frac{1}{0.2} - 0.75(0.8) \right] = 0.148 \text{ m}^3$$

$$= \underline{\underline{148 \text{ liters}}}$$

EXAMPLE 5.6 TEST OF A KINETIC EQUATION IN A PLUG FLOW REACTOR

We suspect that the gas reaction between A, B, and R is an elementary reversible reaction



and we plan to test this with experiments in an isothermal plug flow reactor.

- Develop the isothermal performance equation for these kinetics for a feed of A, B, R, and inerts.
- Show how to test this equation for an equimolar feed of A and B.

SOLUTION

(a) Feed of A, B, R, and inerts. For this elementary reaction the rate is

$$-r_A = k_1 C_A C_B - k_2 C_R = k_1 \frac{N_A N_B}{V} - k_2 \frac{N_R}{V}$$

At constant pressure, basing expansion and conversion on substance A,

$$-r_A = k_1 \frac{N_{A0} - N_{A0} X_A}{V_0(1 + \varepsilon_A X_A)} \frac{N_{B0} - N_{A0} X_A}{V_0(1 + \varepsilon_A X_A)} - k_2 \frac{N_{R0} + N_{A0} X_A}{V_0(1 + \varepsilon_A X_A)}$$

Letting $M = C_{B0}/C_{A0}$, $M' = C_{R0}/C_{A0}$, we obtain

$$-r_A = k_1 C_{A0}^2 \frac{(1 - X_A)(M - X_A)}{(1 + \varepsilon_A X_A)^2} - k_2 C_{A0} \frac{M' + X_A}{1 + \varepsilon_A X_A}$$

Hence, the design equation for plug flow, Eq. 17, becomes

$$\tau = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A} = \int_0^{X_{Af}} \frac{(1 + \varepsilon_A X_A)^2 dX_A}{k_1 C_{A0} (1 - X_A)(M - X_A) - k_2 (M' + X_A)(1 + \varepsilon_A X_A)}$$

In this expression ε_A accounts for the stoichiometry and for inerts present in the feed.

(b) Equimolar feed of A and B. For $C_{A0} = C_{B0}$, $C_{R0} = 0$, and no inerts, we have $M = 1$, $M' = 0$, $\varepsilon_A = -0.5$; hence the expression for part a reduces to

$$\tau = \int_0^{X_{Af}} \frac{(1 - 0.5X_A)^2 dX_A}{k_1 C_{A0} (1 - X_A)^2 - k_2 X_A (1 - 0.5X_A)} \quad \text{call this} \quad \int_0^{X_{Af}} f(X_A) dX_A \quad (i)$$

Having V , v_0 , and X_A data from a series of experiments, separately evaluate the left side and the right side of Eq. (i). For the right side, at various X_A

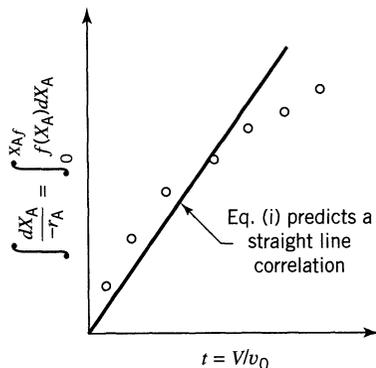


Figure E5.6

evaluate $f(X_A)$, then integrate graphically to give $\int f(X_A)dX_A$ and then make the plot of Fig. E5.6. If the data fall on a reasonably straight line, then the suggested kinetic scheme can be said to be satisfactory in that it fits the data.

Holding Time and Space Time for Flow Reactors

We should be clearly aware of the distinction between these two measures of time, \bar{t} and τ . They are defined as follows:

$$\tau = \left(\begin{array}{l} \text{time needed to} \\ \text{treat one reactor} \\ \text{volume of feed} \end{array} \right) = \frac{V}{v_0} = \frac{C_{A0}V}{F_{A0}}, \quad [\text{hr}] \quad (6) \text{ or } (8)$$

$$\bar{t} = \left(\begin{array}{l} \text{mean residence time} \\ \text{of flowing material} \\ \text{in the reactor} \end{array} \right) = C_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)(1 + \varepsilon_A X_A)}, \quad [\text{hr}] \quad (24)$$

For constant density systems (all liquids and constant density gases)

$$\tau = \bar{t} = \frac{V}{v}$$

For changing density systems $\bar{t} \neq \tau$ and $\bar{t} \neq V/v_0$ in which case it becomes difficult to find how these terms are related.

As a simple illustration of the difference between \bar{t} and τ , consider two cases of the steady-flow popcorn popper of Problem 4.7 which takes in 1 liter/min of raw corn and produces 28 liters/min of product popcorn.

Consider three cases, called X, Y, and Z, which are shown in Fig. 5.7. In the first case (case X) all the popping occurs at the back end of the reactor. In the

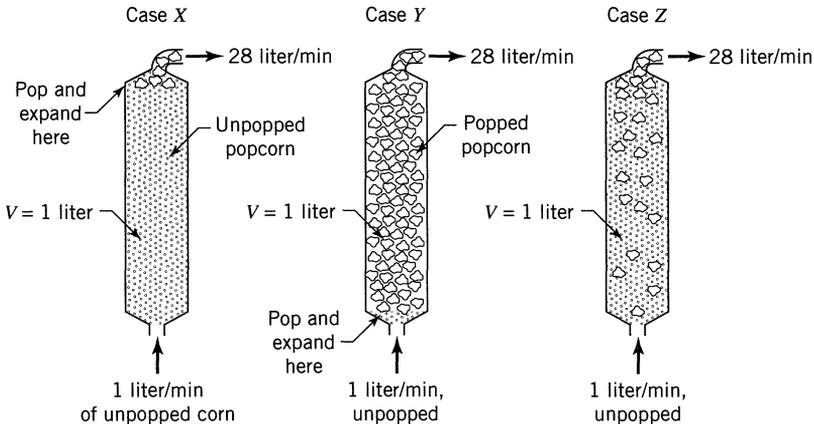


Figure 5.7 For the same τ value the \bar{t} values differ in these three cases.

second case (case Y) all the popping occurs at the front end of the reactor. In the third case (case Z) the popping occurs somewhere between entrance and exit. In all three cases

$$\tau_X = \tau_Y = \tau_Z = \frac{V}{v_0} = \frac{1 \text{ liter}}{1 \text{ liter/min}} = 1 \text{ min}$$

irrespective of where the popping occurs. However, we see that the residence time in the three cases is very different, or

$$\bar{t}_X = \frac{1 \text{ liter}}{1 \text{ liter/min}} = 1 \text{ min}$$

$$\bar{t}_Y = \frac{1 \text{ liter}}{28 \text{ liter/min}} \cong 2 \text{ sec}$$

\bar{t}_Z is somewhere between 2 and 60 s, depending on the kinetics

Note that the value of \bar{t} depends on what happens in the reactor, while the value of τ is independent of what happens in the reactor.

This example shows that \bar{t} and τ are not, in general, identical. Now which is the natural performance measure for reactors? For batch systems Chapter 3 shows that it is the time of reaction; however, holding time does not appear anywhere in the performance equations for flow systems developed in this chapter, Eqs. 13 to 19, while it is seen that space-time or V/F_{A0} does naturally appear. Hence, τ or V/F_{A0} is the proper performance measure for flow systems.

The above simple example shows that in the special case of constant fluid density the space-time is equivalent to the holding time; hence, these terms can be used interchangeably. This special case includes practically all liquid phase reactions. However, for fluids of changing density, e.g., nonisothermal gas reactions or gas reactions with changing number of moles, a distinction should be made between τ and \bar{t} and the correct measure should be used in each situation.

Summary of Performance Equations

Tables 5.1 and 5.2 present the integrated performance equations for single ideal reactors.

REFERENCES

- Corcoran, W. H., and Lacey, W. N., *Introduction to Chemical Engineering Problems*, McGraw Hill, New York, 1970, p. 103.
 Pease, R. N., *J. Am. Chem. Soc.*, **51**, 3470 (1929).

Table 5.1 Performance Equations for n th-order Kinetics and $\varepsilon_A = 0$

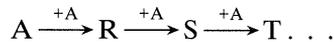
| | Plug Flow or Batch | Mixed Flow |
|--|--|--|
| $n = 0$ $-r_A = k$ | $\frac{k\tau}{C_{A0}} = \frac{C_{A0} - C_A}{C_{A0}} = X_A$ (20) | $\frac{k\tau}{C_{A0}} = \frac{C_{A0} - C_A}{C_{A0}} = X_A$ |
| $n = 1$ $-r_A = kC_A$ | $k\tau = \ln \frac{C_{A0}}{C_A} = \ln \frac{1}{1 - X_A}$ (3.12) | $k\tau = \frac{C_{A0} - C_A}{C_A} = \frac{X_A}{1 - X_A}$ (14a) |
| $n = 2$ $-r_A = kC_A^2$ | $k\tau C_{A0} = \frac{C_{A0} - C_A}{C_A} = \frac{X_A}{1 - X_A}$ (3.16) | $k\tau = \frac{(C_{A0} - C_A)}{C_A^2} = \frac{X_A}{C_{A0}(1 - X_A)^2}$ (15) |
| any n $-r_A = kC_A^n$ | $(n - 1)C_{A0}^{n-1}k\tau = \left(\frac{C_A}{C_{A0}}\right)^{1-n} - 1 = (1 - X_A)^{1-n} - 1$ (3.29) | $k\tau = \frac{C_{A0} - C_A}{C_A^n} = \frac{X_A}{C_{A0}^{n-1}(1 - X_A)^n}$ |
| $n = 1$ $A \xrightleftharpoons[R]{1} R$ $C_{R0} = 0$ | $k_1\tau = \left(1 - \frac{C_{Ae}}{C_{A0}}\right) \ln \left(\frac{C_{A0} - C_{Ae}}{C_A - C_{Ae}}\right) = X_{Ae} \ln \left(\frac{X_{Ae}}{X_{Ae} - X_A}\right)$ | $k_1\tau = \frac{(C_{A0} - C_A)(C_{A0} - C_{Ae})}{C_{A0}(C_A - C_{Ae})} = \frac{X_A X_{Ae}}{X_{Ae} - X_A}$ |
| General rate | $\tau = \int_{C_A}^{C_{A0}} \frac{dC_A}{-r_A} = C_{A0} \int_0^{X_{Ae}} \frac{dX_A}{-r_A}$ (19) | $\tau = \frac{C_{A0} - C_A}{-r_{Af}} = \frac{C_{A0} X_A}{-r_{Af}}$ (13) |

Table 5.2 Performance Equations for n th-order Kinetics and $\varepsilon_A \neq 0$

| | Plug Flow | Mixed Flow |
|--|--|--|
| $n = 0$ $-r_A = k$ | $\frac{k\tau}{C_{A0}} = X_A$ (20) | $\frac{k\tau}{C_{A0}} = X_A$ |
| $n = 1$ $-r_A = kC_A$ | $k\tau = (1 + \varepsilon_A) \ln \frac{1}{1 - X_A} - \varepsilon_A X_A$ (21) | $k\tau = \frac{X_A(1 + \varepsilon_A X_A)}{1 - X_A}$ (14b) |
| $n = 2$ $-r_A = kC_A^2$ | $k\tau C_{A0} = 2\varepsilon_A(1 + \varepsilon_A) \ln(1 - X_A) + \varepsilon_A^2 X_A + (\varepsilon_A + 1)^2 \cdot \frac{X_A}{1 - X_A}$ (23) | $k\tau C_{A0} = \frac{X_A(1 + \varepsilon_A X_A)^2}{(1 - X_A)^2}$ (15) |
| any n $-r_A = kC_A^n$ | | $k\tau C_{A0}^{n-1} = \frac{X_A(1 + \varepsilon_A X_A)^n}{(1 - X_A)^n}$ |
| $n = 1$ $A \xrightarrow[\frac{2}{r}]{1} rR$ $C_{R0} = 0$ | $\frac{k\tau}{X_{Ae}} = (1 + \varepsilon_A X_{Ae}) \ln \frac{X_{Ae}}{X_{Ae} - X_A} - \varepsilon_A X_A$ (22) | $\frac{k\tau}{X_{Ae}} = \frac{X_A(1 + \varepsilon_A X_A)}{X_{Ae} - X_A}$ |
| General expression | $\tau = C_{A0} \int_0^{X_A} \frac{dX_A}{-r_A}$ (17) | $\tau = \frac{C_{A0} X_A}{-r_A}$ (11) |

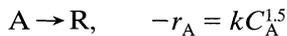
PROBLEMS

- 5.1. Consider a gas-phase reaction $2A \rightarrow R + 2S$ with unknown kinetics. If a space velocity of 1/min is needed for 90% conversion of A in a plug flow reactor, find the corresponding space-time and mean residence time or holding time of fluid in the plug flow reactor.
- 5.2. In an isothermal batch reactor 70% of a liquid reactant is converted in 13 min. What space-time and space-velocity are needed to effect this conversion in a plug flow reactor and in a mixed flow reactor?
- 5.3. A stream of aqueous monomer A (1 mol/liter, 4 liter/min) enters a 2-liter mixed flow reactor, is radiated therein, and polymerizes as follows:



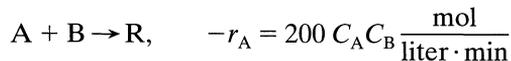
In the exit stream $C_A = 0.01$ mol/liter, and for a particular reaction product W, $C_W = 0.0002$ mol/liter. Find the rate of reaction of A and the rate of formation of W.

- 5.4. We plan to replace our present mixed flow reactor with one having double the volume. For the same aqueous feed (10 mol A/liter) and the same feed rate find the new conversion. The reaction kinetics are represented by



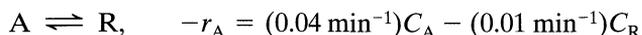
and present conversion is 70%.

- 5.5. An aqueous feed of A and B (400 liter/min, 100 mmol A/liter, 200 mmol B/liter) is to be converted to product in a plug flow reactor. The kinetics of the reaction is represented by



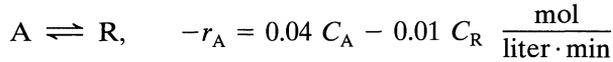
Find the volume of reactor needed for 99.9% conversion of A to product.

- 5.6. A plug flow reactor (2 m^3) processes an aqueous feed (100 liter/min) containing reactant A ($C_{A0} = 100$ mmol/liter). This reaction is reversible and represented by



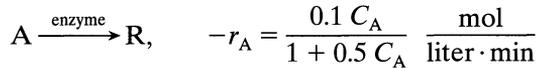
First find the equilibrium conversion and then find the actual conversion of A in the reactor.

- 5.7. The off gas from a boiling water nuclear power reactor contains a whole variety of radioactive trash, one of the most troublesome being Xe-133 (half life = 5.2 days). This off gas flows continuously through a large holdup tank in which its mean residence time is 30 days, and where we can assume that the contents are well mixed. Find the fraction of activity removed in the tank.
- 5.8. A mixed flow reactor (2 m^3) processes an aqueous feed (100 liter/min) containing reactant A ($C_{A0} = 100 \text{ mmol/liter}$). The reaction is reversible and represented by



What is the equilibrium conversion and the actual conversion in the reactor?

- 5.9. A specific enzyme acts as catalyst in the fermentation of reactant A. At a given enzyme concentration in the aqueous feed stream (25 liter/min) find the volume of plug flow reactor needed for 95% conversion of reactant A ($C_{A0} = 2 \text{ mol/liter}$). The kinetics of the fermentation at this enzyme concentration is given by

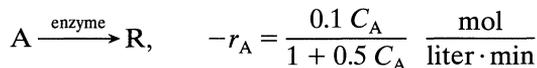


- 5.10. A gaseous feed of pure A (2 mol/liter, 100 mol/min) decomposes to give a variety of products in a plug flow reactor. The kinetics of the conversion is represented by



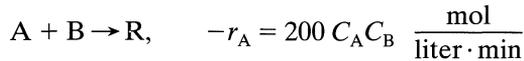
Find the expected conversion in a 22-liter reactor.

- 5.11. Enzyme E catalyses the fermentation of substrate A (the reactant) to product R. Find the size of mixed flow reactor needed for 95% conversion of reactant in a feed stream (25 liter/min) of reactant (2 mol/liter) and enzyme. The kinetics of the fermentation at this enzyme concentration are given by



- 5.12. An aqueous feed of A and B (400 liter/min, 100 mmol A/liter, 200 mmol B/liter) is to be converted to product in a mixed flow reactor. The kinetics

of the reaction are represented by



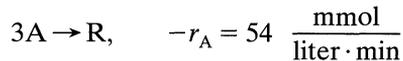
Find the volume of reactor needed for 99.9% conversion of A to product.

5.13. At 650°C phosphine vapor decomposes as follows:



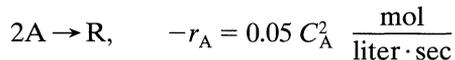
What size of plug flow reactor operating at 649°C and 11.4 atm is needed for 75% conversion of 10 mol/hr of phosphine in a 2/3 phosphine–1/3 inert feed?

5.14. A stream of pure gaseous reactant A ($C_{A0} = 660$ mmol/liter) enters a plug flow reactor at a flow rate of $F_{A0} = 540$ mmol/min and polymerizes there as follows



How large a reactor is needed to lower the concentration of A in the exit stream to $C_{Af} = 330$ mmol/liter?

5.15. A gaseous feed of pure A (1 mol/liter) enters a mixed flow reactor (2 liters) and reacts as follows:



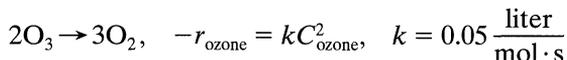
Find what feed rate (liter/min) will give an outlet concentration $C_A = 0.5$ mol/liter.

5.16. Gaseous reactant A decomposes as follows:



Find the conversion of A in a 50% A–50% inert feed ($v_0 = 180$ liter/min, $C_{A0} = 300$ mmol/liter) to a 1 m³ mixed flow reactor.

5.17. 1 liter/s of a 20% ozone–80% air mixture at 1.5 atm and 93°C passes through a plug flow reactor. Under these conditions ozone decomposes by homogeneous reaction



What size reactor is needed for 50% decomposition of ozone? This problem is a modification of a problem given by Corcoran and Lacey (1970).

- 5.18.** An aqueous feed containing A (1 mol/liter) enters a 2-liter plug flow reactor and reacts away ($2A \rightarrow R$, $-r_A = 0.05 C_A^2$ mol/liter \cdot s). Find the outlet concentration of A for a feed rate of 0.5 liter/min.
- 5.19.** Pure gaseous A at about 3 atm and 30°C (120 mmol/liter) is fed into a 1-liter mixed flow reactor at various flow rates. There it decomposes, and the exit concentration of A is measured for each flow rate. From the following data find a rate equation to represent the kinetics of the decomposition of A. Assume that reactant A alone affects the rate.

| | | | | | |
|--------------------|------|------|-----|-----|--------------------|
| v_0 , liter/min | 0.06 | 0.48 | 1.5 | 8.1 | $A \rightarrow 3R$ |
| C_A , mmol/liter | 30 | 60 | 80 | 105 | |

- 5.20.** A mixed flow reactor is being used to determine the kinetics of a reaction whose stoichiometry is $A \rightarrow R$. For this purpose various flow rates of an aqueous solution of 100 mmol A/liter are fed to a 1-liter reactor, and for each run the outlet concentration of A is measured. Find a rate equation to represent the following data. Also assume that reactant alone affects the rate.

| | | | |
|--------------------|---|----|----|
| v , liter/min | 1 | 6 | 24 |
| C_A , mmol/liter | 4 | 20 | 50 |

- 5.21.** We are planning to operate a batch reactor to convert A into R. This is a liquid reaction, the stoichiometry is $A \rightarrow R$, and the rate of reaction is given in Table P5.21. How long must we react each batch for the concentration to drop from $C_{A0} = 1.3$ mol/liter to $C_{Af} = 0.3$ mol/liter?

Table P5.21

| C_A , mol/liter | $-r_A$, mol/liter \cdot min |
|-------------------|--------------------------------|
| 0.1 | 0.1 |
| 0.2 | 0.3 |
| 0.3 | 0.5 |
| 0.4 | 0.6 |
| 0.5 | 0.5 |
| 0.6 | 0.25 |
| 0.7 | 0.10 |
| 0.8 | 0.06 |
| 1.0 | 0.05 |
| 1.3 | 0.045 |
| 2.0 | 0.042 |

- 5.22.** For the reaction of Problem 5.21, what size of plug flow reactor would be needed for 80% conversion of a feed stream of 1000 mol A/hr at $C_{A0} = 1.5$ mol/liter?

- 5.23. (a)** For the reaction of Problem 5.21, what size of mixed flow reactor is needed for 75% conversion of a feed stream of 1000 mol A/hr at $C_{A0} = 1.2$ mol/liter?
- (b)** Repeat part (a) with the modification that the feed rate is doubled, thus 2000 mol A/hr at $C_{A0} = 1.2$ mol/liter are to be treated.
- (c)** Repeat part (a) with the modification that $C_{A0} = 2.4$ mol/liter; however, 1000 mol A/hr are still to be treated down to $C_{Af} = 0.3$ mol/liter.
- 5.24.** A high molecular weight hydrocarbon gas A is fed continuously to a heated high temperature mixed flow reactor where it thermally cracks (homogeneous gas reaction) into lower molecular weight materials, collectively called R, by a stoichiometry approximated by $A \rightarrow 5R$. By changing the feed rate different extents of cracking are obtained as follows:

| | | | | |
|------------------------------|-----|------|------|------|
| F_{A0} , millimol/hr | 300 | 1000 | 3000 | 5000 |
| $C_{A,out}$, millimol/liter | 16 | 30 | 50 | 60 |

The internal void volume of the reactor is $V = 0.1$ liter, and at the temperature of the reactor the feed concentration is $C_{A0} = 100$ millimol/liter. Find a rate equation to represent the cracking reaction.

- 5.25.** The aqueous decomposition of A is studied in an experimental mixed flow reactor. The results in Table P5.25 are obtained in steady-state runs. To obtain 75% conversion of reactant in a feed, $C_{A0} = 0.8$ mol/liter, what holding time is needed in a plug flow reactor?

Table P5.25

| Concentration of A, mol/liter | | Holding Time, sec |
|-------------------------------|----------------|----------------------|
| In Feed | In Exit Stream | |
| 2.00 | 0.65 | 300 |
| 2.00 | 0.92 | 240 |
| 2.00 | 1.00 | 250 |
| 1.00 | 0.56 | 110 |
| 1.00 | 0.37 | 360 |
| 0.48 | 0.42 | 24 |
| 0.48 | 0.28 | 200 |
| 0.48 | 0.20 | 560 |

- 5.26.** Repeat the previous problem but for a mixed flow reactor.
- 5.27.** HOLMES: You say he was last seen tending this vat
 SIR BOSS: You mean "overflow stirred tank reactor," Mr. Holmes.
 HOLMES: You must excuse my ignorance of your particular technical jargon, Sir Boss.
 SIR BOSS: That's all right; however, you must find him, Mr. Holmes.

Imbibit was a queer chap; always staring into the reactor, taking deep breaths, and licking his lips, but he was our very best operator. Why, since he left, our conversion of googliox has dropped from 80% to 75%. HOLMES (*tapping the side of the vat idly*): By the way, what goes on in the vat?

SIR BOSS: Just an elementary second-order reaction, between ethanol and googliox, if you know what I mean. Of course, we maintain a large excess of alcohol, about 100 to 1 and . . .

HOLMES (*interrupting*): Intriguing, we checked every possible lead in town and found not a single clue.

SIR BOSS (*wiping away the tears*): We'll give the old chap a raise—about twopence per week—if only he'll come back.

DR. WATSON: Pardon me, but may I ask a question?

HOLMES: Why certainly, Watson.

WATSON: What is the capacity of this vat, Sir Boss?

SIR BOSS: A hundred Imperial gallons, and we always keep it filled to the brim. That is why we call it an overflow reactor. You see we are running at full capacity—profitable operation you know.

HOLMES: Well, my dear Watson, we must admit that we're stumped, for without clues deductive powers are of no avail.

WATSON: Ahh, but there is where you are wrong, Holmes. (*Then, turning to the manager*): Imbibit was a largish fellow—say about 18 stone—was he not?

SIR BOSS: Why yes, how did you know?

HOLMES (*with awe*): Amazing, my dear Watson!

WATSON (*modestly*): Why it's quite elementary, Holmes. We have all the clues necessary to deduce what happened to the happy fellow. But first of all, would someone fetch me some dill?

With Sherlock Holmes and Sir Boss impatiently waiting, Dr. Watson casually leaned against the vat, slowly and carefully filled his pipe, and—with the keen sense of the dramatic—lit it. There our story ends.

(a) What momentous revelation was Dr. Watson planning to make, and how did he arrive at this conclusion?

(b) Why did he never make it?

5.28. The data in Table P5.28 have been obtained on the decomposition of gaseous reactant A in a constant volume batch reactor at 100°C. The

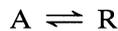
Table P5.28

| t , sec | p_A , atm | t , sec | p_A , atm |
|-----------|-------------|-----------|-------------|
| 0 | 1.00 | 140 | 0.25 |
| 20 | 0.80 | 200 | 0.14 |
| 40 | 0.68 | 260 | 0.08 |
| 60 | 0.56 | 330 | 0.04 |
| 80 | 0.45 | 420 | 0.02 |
| 100 | 0.37 | | |

stoichiometry of the reaction is $2A \rightarrow R + S$. What size plug flow reactor (in liters) operating at 100°C and 1 atm can treat 100 mol A/hr in a feed consisting of 20% inerts to obtain 95% conversion of A?

5.29. Repeat the previous problem for a mixed flow reactor.

5.30. The aqueous decomposition of A produces R as follows:



The following results are obtained in a series of steady state runs, all having no R in the feed stream.

| Space Time, τ , sec | C_{A0} , In Feed, mol/liter | C_{Af} , In Exit Stream, mol/liter |
|-----------------------------|----------------------------------|---|
| 50 | 2.0 | 1.00 |
| 16 | 1.2 | 0.80 |
| 60 | 2.0 | 0.65 |
| 22 | 1.0 | 0.56 |
| 4.8 | 0.48 | 0.42 |
| 72 | 1.00 | 0.37 |
| 40 | 0.48 | 0.28 |
| 112 | 0.48 | 0.20 |

From this kinetic information, find the size of reactor needed to achieve 75% conversion of a feed stream of $v = 1$ liter/sec and $C_{A0} = 0.8$ mol/liter. In the reactor the fluid follows

- (a) plug flow
- (b) mixed flow

Chapter 6

Design for Single Reactions

There are many ways of processing a fluid: in a single batch or flow reactor, in a chain of reactors possibly with interstage feed injection or heating, in a reactor with recycle of the product stream using various feed ratios and conditions, and so on. Which scheme should we use? Unfortunately, numerous factors may have to be considered in answering this question; for example, the reaction type, planned scale of production, cost of equipment and operations, safety, stability and flexibility of operation, equipment life expectancy, length of time that the product is expected to be manufactured, ease of convertibility of the equipment to modified operating conditions or to new and different processes. With the wide choice of systems available and with the many factors to be considered, no neat formula can be expected to give the optimum setup. Experience, engineering judgment, and a sound knowledge of the characteristics of the various reactor systems are all needed in selecting a reasonably good design and, needless to say, the choice in the last analysis will be dictated by the economics of the overall process.

The reactor system selected will influence the economics of the process by dictating the size of the units needed and by fixing the ratio of products formed. The first factor, reactor size, may well vary a hundredfold among competing designs while the second factor, product distribution, is usually of prime consideration where it can be varied and controlled.

In this chapter we deal with *single reactions*. These are reactions whose progress can be described and followed adequately by using one and only one rate expression coupled with the necessary stoichiometric and equilibrium expressions. For such reactions product distribution is fixed; hence, the important factor in comparing designs is the reactor size. We consider in turn the size comparison of various single and multiple ideal reactor systems. Then we introduce the recycle reactor and develop its performance equations. Finally, we treat a rather unique type of reaction, the autocatalytic reaction, and show how to apply our findings to it.

Design for multiple reactions, for which the primary consideration is product distribution, is treated in the next two chapters.

6.1 SIZE COMPARISON OF SINGLE REACTORS

Batch Reactor

First of all, before we compare flow reactors, let us mention the batch reactor briefly. The batch reactor has the advantage of small instrumentation cost and flexibility of operation (may be shut down easily and quickly). It has the disadvantage of high labor and handling cost, often considerable shutdown time to empty, clean out, and refill, and poorer quality control of the product. Hence we may generalize to state that the batch reactor is well suited to produce small amounts of material and to produce many different products from one piece of equipment. On the other hand, for the chemical treatment of materials in large amounts the continuous process is nearly always found to be more economical.

Regarding reactor sizes, a comparison of Eqs. 5.4 and 5.19 for a given duty and for $\varepsilon = 0$ shows that an element of fluid reacts for the same length of time in the batch and in the plug flow reactor. Thus, the same volume of these reactors is needed to do a given job. Of course, on a long-term production basis we must correct the size requirement estimate to account for the shutdown time between batches. Still, it is easy to relate the performance capabilities of the batch reactor with the plug flow reactor.

Mixed Versus Plug Flow Reactors, First- and Second-Order Reactions

For a given duty the ratio of sizes of mixed and plug flow reactors will depend on the extent of reaction, the stoichiometry, and the form of the rate equation. For the general case, a comparison of Eqs. 5.11 and 5.17 will give this size ratio. Let us make this comparison for the large class of reactions approximated by the simple n th-order rate law

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = kC_A^n$$

where n varies anywhere from zero to three. For mixed flow Eq. 5.11 gives

$$\tau_m = \left(\frac{C_{A0}V}{F_{A0}} \right)_m = \frac{C_{A0}X_A}{-r_A} = \frac{1}{kC_{A0}^{n-1}} \frac{X_A(1 + \varepsilon_A X_A)^n}{(1 - X_A)^n}$$

whereas for plug flow Eq. 5.17 gives

$$\tau_p = \left(\frac{C_{A0}V}{F_{A0}} \right)_p = C_{A0} \int_0^{X_A} \frac{dX_A}{-r_A} = \frac{1}{kC_{A0}^{n-1}} \int_0^{X_A} \frac{(1 + \varepsilon_A X_A)^n dX_A}{(1 - X_A)^n}$$

Dividing we find that

$$\frac{(\tau C_{A0}^{n-1})_m}{(\tau C_{A0}^{n-1})_p} = \frac{\left(\frac{C_{A0}^n V}{F_{A0}} \right)_m}{\left(\frac{C_{A0}^n V}{F_{A0}} \right)_p} = \frac{\left[X_A \left(\frac{1 + \varepsilon_A X_A}{1 - X_A} \right)^n \right]_m}{\left[\int_0^{X_A} \left(\frac{1 + \varepsilon_A X_A}{1 - X_A} \right)^n dX_A \right]_p} \quad (1)$$

With constant density, or $\varepsilon = 0$, this expression integrates to

$$\frac{(\tau C_{A0}^{n-1})_m}{(\tau C_{A0}^{n-1})_p} = \frac{\left[\frac{X_A}{(1 - X_A)^n} \right]_m}{\left[\frac{(1 - X_A)^{1-n} - 1}{n - 1} \right]_p}, \quad n \neq 1$$

or

$$\frac{(\tau C_{A0}^{n-1})_m}{(\tau C_{A0}^{n-1})_p} = \frac{\left(\frac{X_A}{1 - X_A} \right)_m}{-\ln(1 - X_A)_p}, \quad n = 1$$

(2)

Equations 1 and 2 are displayed in graphical form in Fig. 6.1 to provide a quick comparison of the performance of plug flow with mixed flow reactors. For

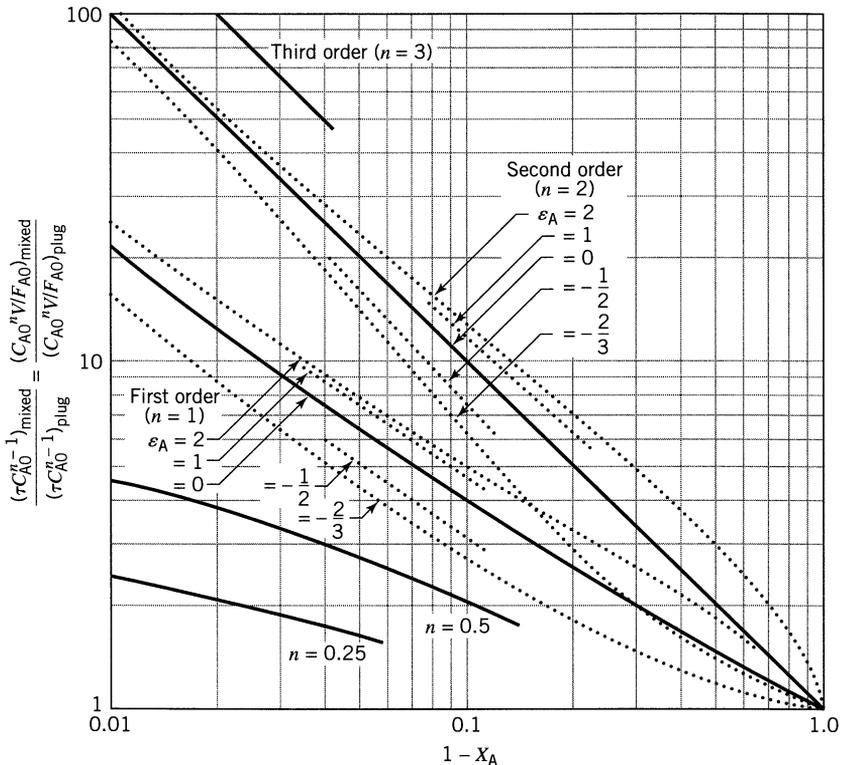


Figure 6.1 Comparison of performance of single mixed flow and plug flow reactors for the n th-order reactions



The ordinate becomes the volume ratio V_m/V_p or space-time ratio τ_m/τ_p if the same quantities of identical feed are used.

identical feed composition C_{A0} and flow rate F_{A0} the ordinate of this figure gives directly the volume ratio required for any specified conversion. Figure 6.1 shows the following.

1. For any particular duty and for all positive reaction orders the mixed reactor is always larger than the plug flow reactor. The ratio of volumes increases with reaction order.
2. When conversion is small, the reactor performance is only slightly affected by flow type. The performance ratio increases very rapidly at high conversion; consequently, a proper representation of the flow becomes very important in this range of conversion.
3. Density variation during reaction affects design; however, it is normally of secondary importance compared to the difference in flow type.

Figures 6.5 and 6.6 show the same first- and second-order curves for $\varepsilon = 0$ but also include dashed lines which represent fixed values of the dimensionless reaction rate group, defined as

$k\tau$ for first-order reaction

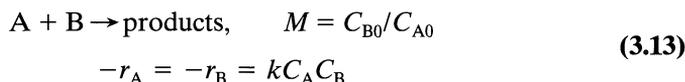
$kC_{A0}\tau$ for second-order reaction

With these lines we can compare different reactor types, reactor sizes, and conversion levels.

Example 6.1 illustrates the use of these charts.

Variation of Reactant Ratio for Second-Order Reactions

Second-order reactions of two components and of the type



behave as second-order reactions of one component when the reactant ratio is unity. Thus

$$-r_A = kC_A C_B = kC_A^2 \quad \text{when } M = 1 \quad (3)$$

On the other hand, when a large excess of reactant B is used then its concentration does not change appreciably ($C_B \cong C_{B0}$) and the reaction approaches first-order behavior with respect to the limiting component A, or

$$-r_A = kC_A C_B = (kC_{B0})C_A = k'C_A \quad \text{when } M \gg 1 \quad (4)$$

Thus in Fig. 6.1, and in terms of the limiting component A, the size ratio of mixed to plug flow reactors is represented by the region between the first-order and the second-order curves.

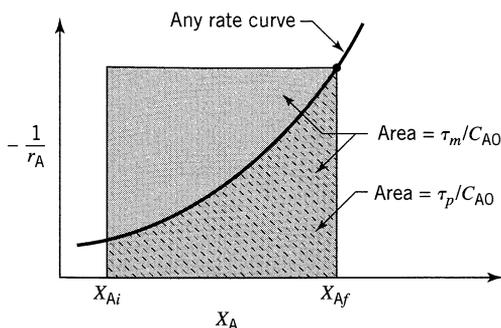


Figure 6.2 Comparison of performance of mixed flow and plug flow reactors for any reaction kinetics.

General Graphical Comparison

For reactions with arbitrary but known rate the performance capabilities of mixed and plug flow reactors are best illustrated in Fig. 6.2. The ratio of shaded and of hatched areas gives the ratio of space-times needed in these two reactors.

The rate curve drawn in Fig. 6.2 is typical of the large class of reactions whose rate decreases continually on approach to equilibrium (this includes all n th-order reactions, $n > 0$). For such reactions it can be seen that mixed flow always needs a larger volume than does plug flow for any given duty.

6.2 MULTIPLE-REACTOR SYSTEMS

Plug Flow Reactors in Series and/or in Parallel

Consider N plug flow reactors connected in series, and let X_1, X_2, \dots, X_N be the fractional conversion of component A leaving reactor 1, 2, \dots , N . Basing the material balance on the feed rate of A to the first reactor, we find for the i th reactor from Eq. 5.18

$$\frac{V_i}{F_0} = \int_{X_{i-1}}^{X_i} \frac{dX}{-r}$$

or for the N reactors in series

$$\begin{aligned} \frac{V}{F_0} &= \sum_{i=1}^N \frac{V_i}{F_0} = \frac{V_1 + V_2 + \dots + V_N}{F_0} \\ &= \int_{X_0=0}^{X_1} \frac{dX}{-r} + \int_{X_1}^{X_2} \frac{dX}{-r} + \dots + \int_{X_{N-1}}^{X_N} \frac{dX}{-r} = \int_0^{X_N} \frac{dX}{-r} \end{aligned}$$

Hence, N plug flow reactors in series with a total volume V gives the same conversion as a single plug flow reactor of volume V .

For the optimum hook up of plug flow reactors connected in parallel or in any parallel-series combination, we can treat the whole system as a single plug flow reactor of volume equal to the total volume of the individual units if the feed is distributed in such a manner that fluid streams that meet have the same composition. Thus, for reactors in parallel V/F or τ must be the same for each parallel line. Any other way of feeding is less efficient.

EXAMPLE 6.1 OPERATING A NUMBER OF PLUG FLOW REACTORS

The reactor setup shown in Fig. E6.1 consists of three plug flow reactors in two parallel branches. Branch D has a reactor of volume 50 liters followed by a reactor of volume 30 liters. Branch E has a reactor of volume 40 liters. What fraction of the feed should go to branch D?

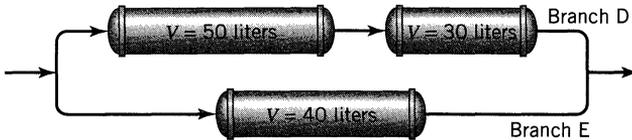


Figure E6.1

SOLUTION

Branch D consists of two reactors in series; hence, it may be considered to be a single reactor of volume

$$V_D = 50 + 30 = 80 \text{ liters}$$

Now for reactors in parallel V/F must be identical if the conversion is to be the same in each branch. Therefore,

$$\left(\frac{V}{F}\right)_D = \left(\frac{V}{F}\right)_E$$

or

$$\frac{F_D}{F_E} = \frac{V_D}{V_E} = \frac{80}{40} = 2$$

Therefore, two-thirds of the feed must be fed to branch D.

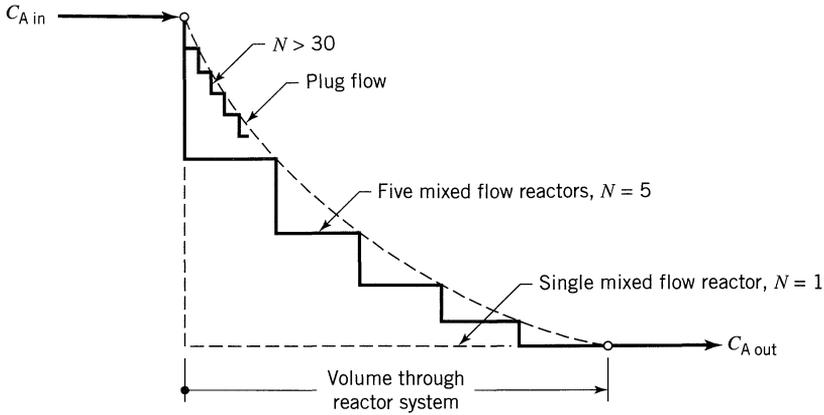


Figure 6.3 Concentration profile through an N -stage mixed flow reactor system compared with single flow reactors.

Equal-Size Mixed Flow Reactors in Series

In plug flow, the concentration of reactant decreases progressively through the system; in mixed flow, the concentration drops immediately to a low value. Because of this fact, a plug flow reactor is more efficient than a mixed flow reactor for reactions whose rates increase with reactant concentration, such as n th-order irreversible reactions, $n > 0$.

Consider a system of N mixed flow reactors connected in series. Though the concentration is uniform in each reactor, there is, nevertheless, a change in concentration as fluid moves from reactor to reactor. This stepwise drop in concentration, illustrated in Fig. 6.3, suggests that the larger the number of units in series, the closer should the behavior of the system approach plug flow. This will be shown to be so.

Let us now quantitatively evaluate the behavior of a series of N equal-size mixed flow reactors. Density changes will be assumed to be negligible; hence $\epsilon = 0$ and $t = \tau$. As a rule, with mixed flow reactors it is more convenient to develop the necessary equations in terms of concentrations rather than fractional conversions; therefore, we use this approach. The nomenclature used is shown in Fig. 6.4 with subscript i referring to the i th vessel.

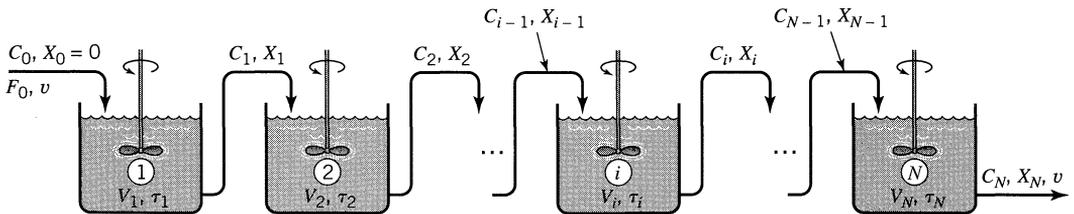


Figure 6.4 Notation for a system of N equal-size mixed reactors in series.

First-Order Reactions. From Eq. 5.12 a material balance for component A about vessel i gives

$$\tau_i = \frac{C_0 V_i}{F_0} = \frac{V_i}{v} = \frac{C_0(X_i - X_{i-1})}{-r_{Ai}}$$

Because $\varepsilon = 0$ this may be written in terms of concentrations. Hence

$$\tau_i = \frac{C_0[(1 - C_i/C_0) - (1 - C_{i-1}/C_0)]}{kC_i} = \frac{C_{i-1} - C_i}{kC_i}$$

or

$$\frac{C_{i-1}}{C_i} = 1 + k\tau_i \quad (5)$$

Now the space-time τ (or mean residence time t) is the same in all the equal-size reactors of volume V_i . Therefore,

$$\frac{C_0}{C_N} = \frac{1}{1 - X_N} = \frac{C_0 C_1}{C_1 C_2} \cdots \frac{C_{N-1}}{C_N} = (1 + k\tau_i)^N \quad (6a)$$

Rearranging, we find for the system as a whole

$$\tau_{N \text{ reactors}} = N\tau_i = \frac{N}{k} \left[\left(\frac{C_0}{C_N} \right)^{1/N} - 1 \right] \quad (6b)$$

In the limit, for $N \rightarrow \infty$, this equation reduces to the plug flow equation

$$\tau_p = \frac{1}{k} \ln \frac{C_0}{C} \quad (7)$$

With Eqs. 6b and 7 we can compare performance of N reactors in series with a plug flow reactor or with a single mixed flow reactor. This comparison is shown in Fig. 6.5 for first-order reactions in which density variations are negligible.

Second-Order Reactions. We may evaluate the performance of a series of mixed flow reactors for a second-order, bimolecular-type reaction, no excess of either reactant, by a procedure similar to that of a first-order reaction. Thus, for

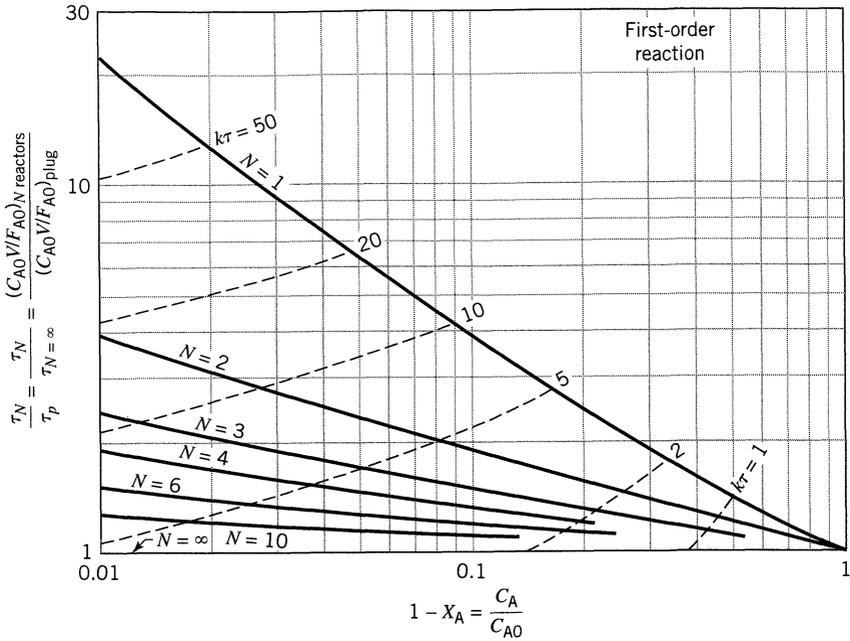
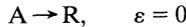


Figure 6.5 Comparison of performance of a series of N equal-size mixed flow reactors with a plug flow reactor for the first-order reaction



For the same processing rate of identical feed the ordinate measures the volume ratio V_N/V_p directly.

N reactors in series we find

$$C_N = \frac{1}{4k\tau_i} \left(-2 + 2 \sqrt{-1 \dots + 2 \sqrt{-1 + 2 \sqrt{1 + 4C_0k\tau_i}}} \right) \quad (8a)$$

whereas for plug flow

$$\frac{C_0}{C} = 1 + C_0k\tau_p \quad (8b)$$

A comparison of the performance of these reactors is shown in Fig. 6.6.

Figures 6.5 and 6.6 support our intuition by showing that the volume of system required for a given conversion decreases to plug flow volume as the number of reactors in series is increased, the greatest change taking place with the addition of a second vessel to a one-vessel system.

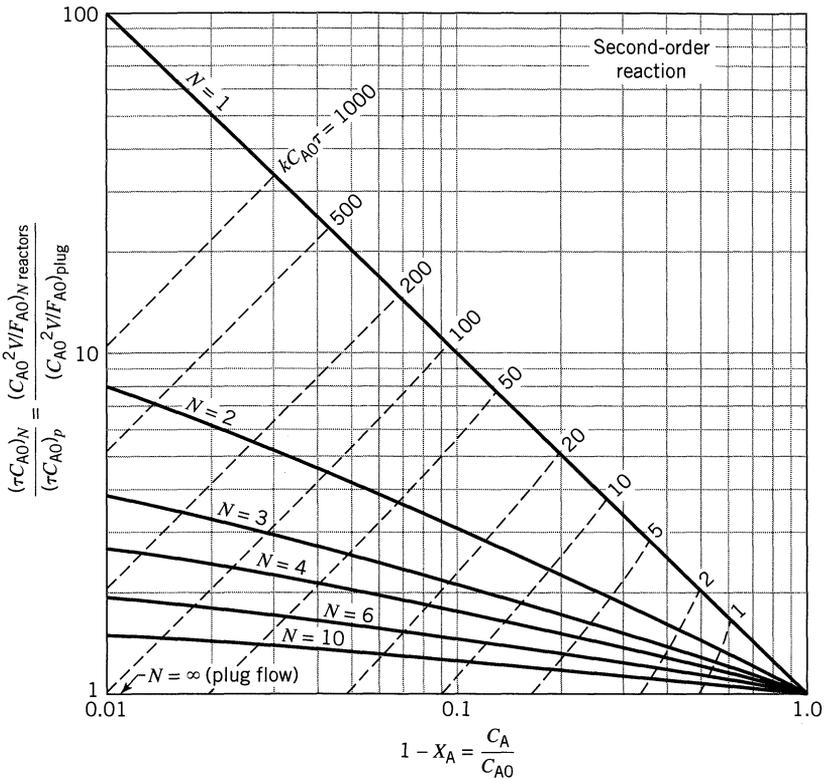
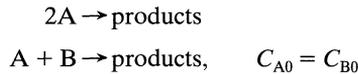


Figure 6.6 Comparison of performance of a series of N equal-size mixed flow reactors with a plug flow reactor for elementary second-order reactions



with negligible expansion. For the same processing rate of identical feed the ordinate measures the volume ratio V_N/V_p or space-time ratio τ_N/τ_p directly.

EXAMPLE 6.2 MIXED FLOW REACTORS IN SERIES

At present 90% of reactant A is converted into product by a second-order reaction in a single mixed flow reactor. We plan to place a second reactor similar to the one being used in series with it.

- For the same treatment rate as that used at present, how will this addition affect the conversion of reactant?
- For the same 90% conversion, by how much can the treatment rate be increased?

SOLUTION

The sketch of Fig. E6.2 shows how the performance chart of Fig. 6.6 can be used to help solve this problem.

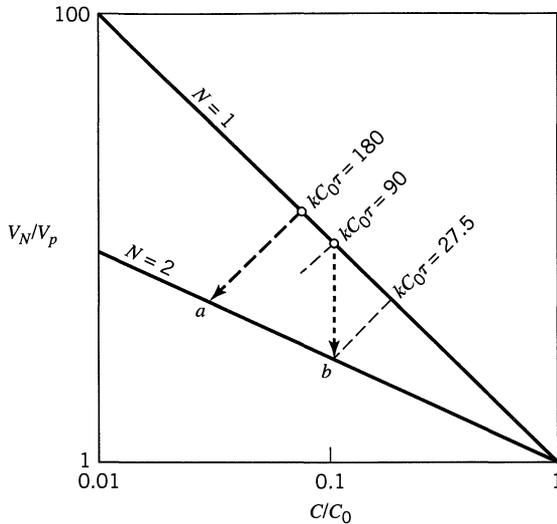


Figure E6.2

(a) Find the conversion for the same treatment rate. For the single reactor at 90% conversion we have from Fig. 6.6

$$kC_0\tau = 90$$

For the two reactors the space-time or holding time is doubled; hence, the operation will be represented by the dashed line of Fig. 6.6 where

$$kC_0\tau = 180$$

This line cuts the $N = 2$ line at a conversion $X = 97.4\%$, point *a*.

(b) Find the treatment rate for the same conversion. Staying on the 90% conversion line, we find for $N = 2$ that

$$kC_0\tau = 27.5, \quad \text{point } b$$

Comparing the value of the reaction rate group for $N = 1$ and $N = 2$, we find

$$\frac{(kC_0\tau)_{N=2}}{(kC_0\tau)_{N=1}} = \frac{\tau_{N=2}}{\tau_{N=1}} = \frac{(V/v)_{N=2}}{(V/v)_{N=1}} = \frac{27.5}{90}$$

Since $V_{N=2} = 2V_{N=1}$ the ratio of flow rates becomes

$$\frac{v_{N=1}}{v_{N=1}} = \frac{90}{27.5} (2) = 6.6$$

Thus, the treatment rate can be raised to 6.6 times the original.

Note. If the second reactor had been operated in parallel with the original unit then the treatment rate could only be doubled. Thus, there is a definite advantage in operating these two units in series. This advantage becomes more pronounced at higher conversions.

Mixed Flow Reactors of Different Sizes in Series

For arbitrary kinetics in mixed flow reactors of different size, two types of questions may be asked: how to find the outlet conversion from a given reactor system, and the inverse question, how to find the best setup to achieve a given conversion. Different procedures are used for these two problems. We treat them in turn.

Finding the Conversion in a Given System A graphical procedure for finding the outlet composition from a series of mixed flow reactors of various sizes for reactions with negligible density change has been presented by Jones (1951). All that is needed is an r versus C curve for component A to represent the reaction rate at various concentrations.

Let us illustrate the use of this method by considering three mixed flow reactors in series with volumes, feed rates, concentrations, space-times (equal to residence times because $\varepsilon = 0$), and volumetric flow rates as shown in Fig. 6.7. Now from Eq. 5.11, noting that $\varepsilon = 0$, we may write for component A in the first reactor

$$\tau_1 = \bar{t}_1 = \frac{V_1}{v} = \frac{C_0 - C_1}{(-r)_1}$$

or

$$-\frac{1}{\tau_1} = \frac{(-r)_1}{C_1 - C_0} \quad (9)$$

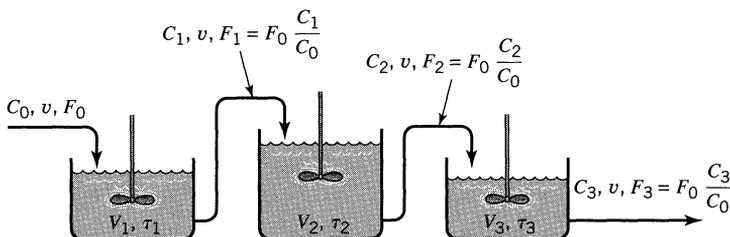


Figure 6.7 Notation for a series of unequal-size mixed flow reactors.

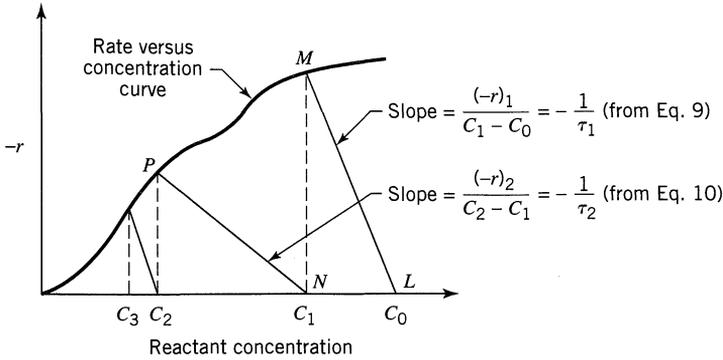


Figure 6.8 Graphical procedure for finding compositions in a series of mixed flow reactors.

Similarly, from Eq. 5.12 for the i th reactor we may write

$$-\frac{1}{\tau_i} = \frac{(-r)_i}{C_i - C_{i-1}} \quad (10)$$

Plot the C versus r curve for component A and suppose that it is as shown in Fig. 6.8. To find the conditions in the first reactor note that the inlet concentration C_0 is known (point L), that C_1 and $(-r)_1$ correspond to a point on the curve to be found (point M), and that the slope of the line $LM = MN/NL = (-r)_1 / (C_1 - C_0) = -(1/\tau_1)$ from Eq. 6.9. Hence, from C_0 draw a line of slope $-(1/\tau_1)$ until it cuts the rate curve; this gives C_1 . Similarly, we find from Eq. 6.10 that a line of slope $-(1/\tau_2)$ from point N cuts the curve at P , giving the concentration C_2 of material leaving the second reactor. This procedure is then repeated as many times as needed.

With slight modification this graphical method can be extended to reactions in which density changes are appreciable.

Determining the Best System for a Given Conversion. Suppose we want to find the minimum size of two mixed flow reactors in series to achieve a specified conversion of feed which reacts with arbitrary but known kinetics. The basic performance expressions, Eqs. 5.11 and 5.12, then give, in turn, for the first reactor

$$\tau_1 = \frac{X_1}{(-r)_1} \quad (11)$$

and for the second reactor

$$\tau_2 = \frac{X_2 - X_1}{(-r)_2} \quad (12)$$

These relationships are displayed in Fig. 6.9 for two alternative reactor arrangements, both giving the same final conversion X_2 . Note, as the intermediate

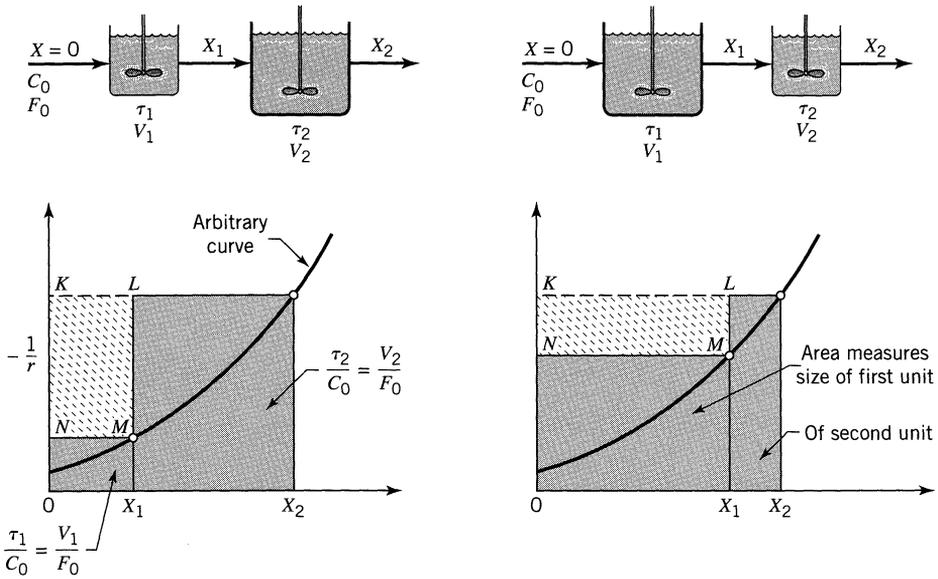


Figure 6.9 Graphical representation of the variables for two mixed flow reactors in series.

conversion X_1 changes, so does the size ratio of the units (represented by the two shaded areas) as well as the total volume of the two vessels required (the total area shaded).

Figure 6.9 shows that the total reactor volume is as small as possible (total shaded area is minimized) when the rectangle $KLMN$ is as large as possible. This brings us to the problem of choosing X_1 (or point M on the curve) so as to maximize the area of this rectangle. Consider this general problem.

Maximization of Rectangles. In Fig. 6.10, construct a rectangle between the x - y axes and touching the arbitrary curve at point $M(x, y)$. The area of the rectangle is then

$$A = xy \tag{13}$$

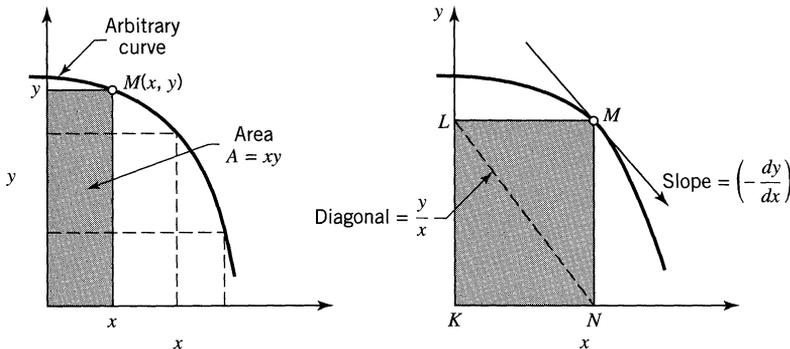


Figure 6.10 Graphical procedure for maximizing the area of a rectangle.

This area is maximized when

$$dA = 0 = y \, dx + x \, dy$$

or when

$$-\frac{dy}{dx} = \frac{y}{x} \quad (14)$$

In words, this condition means that the area is maximized when M is at that point where the slope of the curve equals the slope of the diagonal NL of the rectangle. Depending on the shape of the curve, there may be more than one or there may be no “best” point. However, for n th-order kinetics, $n > 0$, there always is just one “best” point.

We will use this method of maximizing a rectangle in later chapters. But let us return to our problem.

The optimum size ratio of the two reactors is achieved where the slope of the rate curve at M equals the diagonal NL . The best value of M is shown in Fig. 6.11, and this determines the intermediate conversion X_1 as well as the size of units needed.

The optimum size ratio for two mixed flow reactors in series is found in general to be dependent on the kinetics of the reaction and on the conversion level. For the special case of first-order reactions equal-size reactors are best; for reaction orders $n > 1$ the smaller reactor should come first; for $n < 1$ the larger should come first (see Problem 6.3). However, Szepe and Levenspiel (1964) show that the advantage of the minimum size system over the equal-size system is quite small, only a few percent at most. Hence, overall economic consideration would nearly always recommend using equal-size units.

The above procedure can be extended directly to multistage operations; however, here the argument for equal-size units is stronger still than for the two-stage system.

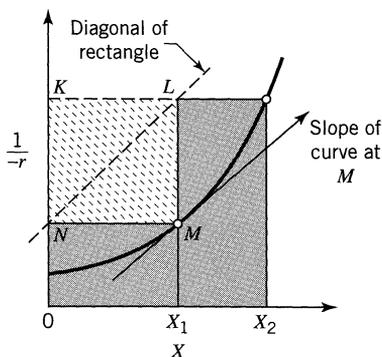


Figure 6.11 Maximization of rectangles applied to find the optimum intermediate conversion and optimum sizes of two mixed flow reactors in series.

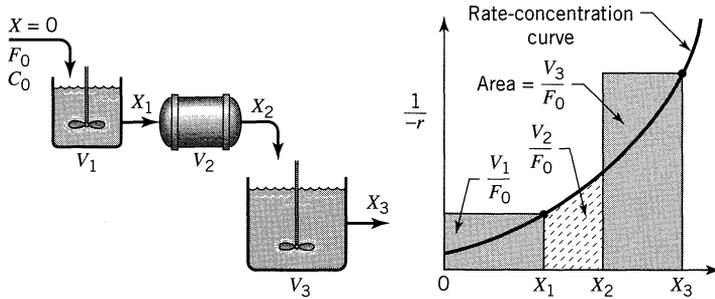


Figure 6.12 Graphical design procedure for reactors in series.

Reactors of Different Types in Series

If reactors of different types are put in series, such as a mixed flow reactor followed by a plug flow reactor which in turn is followed by another mixed flow reactor, we may write for the three reactors

$$\frac{V_1}{F_0} = \frac{X_1 - X_0}{(-r)_1}, \quad \frac{V_2}{F_0} = \int_{x_1}^{x_2} \frac{dX}{-r}, \quad \frac{V_3}{F_0} = \frac{X_3 - X_2}{(-r)_3}$$

These relationships are represented in graphical form in Fig. 6.12. This allows us to predict the overall conversions for such systems, or conversions at intermediate points between the individual reactors. These intermediate conversions may be needed to determine the duty of interstage heat exchangers.

Best Arrangement of a Set of Ideal Reactors. For the most effective use of a given set of ideal reactors we have the following general rules:

1. For a reaction whose rate-concentration curve rises monotonically (any n th-order reaction, $n > 0$) the reactors should be connected in series. They should be ordered so as to keep the concentration of reactant as high as possible if the rate-concentration curve is concave ($n > 1$), and as low as possible if the curve is convex ($n < 1$). As an example, for the case of Fig. 6.12 the ordering of units should be plug, small mixed, large mixed, for $n > 1$; the reverse order should be used when $n < 1$.
2. For reactions where the rate-concentration curve passes through a maximum or minimum the arrangement of units depends on the actual shape of curve, the conversion level desired, and the units available. No simple rules can be suggested.
3. Whatever may be the kinetics and the reactor system, an examination of the $1/(-r_A)$ vs. C_A curve is a good way to find the best arrangement of units.

The problems at the end of this chapter illustrate these findings.

6.3 RECYCLE REACTOR

In certain situations it is found to be advantageous to divide the product stream from a plug flow reactor and return a portion of it to the entrance of the reactor. Let the *recycle ratio* R be defined as

$$R = \frac{\text{volume of fluid returned to the reactor entrance}}{\text{volume leaving the system}} \quad (15)$$

This recycle ratio can be made to vary from zero to infinity. Reflection suggests that as the recycle ratio is raised the behavior shifts from plug flow ($R = 0$) to mixed flow ($R = \infty$). Thus, recycling provides a means for obtaining various degrees of backmixing with a plug flow reactor. Let us develop the performance equation for the recycle reactor.

Consider a recycle reactor with nomenclature as shown in Fig. 6.13. Across the reactor itself Eq. 5.18 for plug flow gives

$$\frac{V}{F'_{A0}} = \int_{X_{A1}}^{X_{A2}=X_{Af}} \frac{dX_A}{-r_A} \quad (16)$$

where F'_{A0} would be the feed rate of A if the stream entering the reactor (fresh feed plus recycle) were unconverted. Since F'_{A0} and X_{A1} are not known directly, they must be written in terms of known quantities before Eq. 16 can be used. Let us now do this.

The flow entering the reactor includes both fresh feed and the recycle stream. Measuring the flow split at point L (point K will not do if $\varepsilon \neq 0$) we then have

$$\begin{aligned} F'_{A0} &= \left(\begin{array}{l} \text{A which would enter in an} \\ \text{unconverted recycle stream} \end{array} \right) + \left(\begin{array}{l} \text{A entering in} \\ \text{fresh feed} \end{array} \right) \\ &= RF_{A0} + F_{A0} = (R + 1)F_{A0} \end{aligned} \quad (17)$$

Now to the evaluation of X_{A1} : from Eq. 4.5 we may write

$$X_{A1} = \frac{1 - C_{A1}/C_{A0}}{1 + \varepsilon_A C_{A1}/C_{A0}} \quad (18)$$

Because the pressure is taken to be constant, the streams meeting at point K may be added directly. This gives

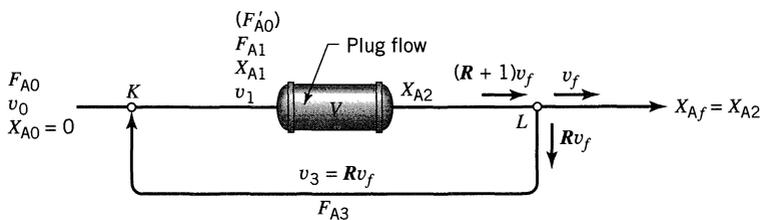


Figure 6.13 Nomenclature for the recycle reactor.

$$C_{A1} = \frac{F_{A1}}{v_1} = \frac{F_{A0} + F_{A3}}{v_0 + Rv_f} = \frac{F_{A0} + RF_{A0}(1 - X_{Af})}{v_0 + Rv_0(1 + \varepsilon_A X_{Af})} = C_{A0} \left(\frac{1 + R - RX_{Af}}{1 + R + R\varepsilon_A X_{Af}} \right) \quad (19)$$

Combining Eqs. 18 and 19 gives X_{A1} in terms of measured quantities, or

$$X_{A1} = \left(\frac{R}{R+1} \right) X_{Af} \quad (20)$$

Finally, on replacing Eqs. 17 and 20 in Eq. 16 we obtain the useful form for the performance equation for recycle reactors, good for any kinetics, any ε value and for $X_{A0} = 0$.

$$\frac{V}{F_{A0}} = (R+1) \int_{\left(\frac{R}{R+1}\right) X_{Af}}^{X_{Af}} \frac{dX_A}{-r_A} \quad \dots \text{any } \varepsilon_A \quad (21)$$

For the special case where density changes are negligible we may write this equation in terms of concentrations, or

$$\tau = \frac{C_{A0}V}{F_{A0}} = -(R+1) \int_{\frac{C_{A0} + RC_{Af}}{R+1}}^{C_{Af}} \frac{dC_A}{-r_A} \quad \dots \varepsilon_A = 0 \quad (22)$$

These expressions are represented graphically in Fig. 6.14.

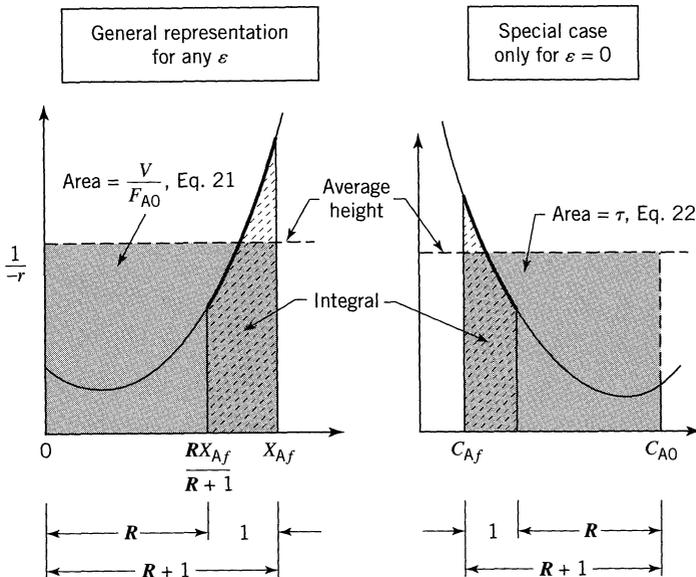


Figure 6.14 Representation of the performance equation for recycle reactors.

For the extremes of negligible and infinite recycle the system approaches plug flow and mixed flow, or

$$\frac{V}{F_{A0}} = (R + 1) \int_{\frac{R}{R+1} X_{Af}}^{X_{Af}} \frac{dX_A}{-r_A}$$

$R = 0$
 \downarrow
 $\frac{V}{F_{A0}} = \int_A^{X_{Af}} \frac{dX_A}{-r_A}$

 plug flow

$R = \infty$
 \downarrow
 $\frac{V}{F_{A0}} = \frac{X_{Af}}{-r_{Af}}$

 mixed flow

The approach to these extremes is shown in Fig. 6.15.

Integration of the recycle equation gives, for *first-order reaction*, $\varepsilon_A = 0$,

$$\frac{k\tau}{R + 1} = \ln \left[\frac{C_{A0} + RC_{Af}}{(R + 1)C_{Af}} \right] \quad (23)$$

and for *second-order reaction*, $2A \rightarrow$ products, $-r_A = kC_A^2$, $\varepsilon_A = 0$,

$$\frac{kC_{A0}\tau}{R + 1} = \frac{C_{A0}(C_{A0} - C_{Af})}{C_{Af}(C_{A0} + RC_{Af})} \quad (24)$$

The expressions for $\varepsilon_A \neq 0$ and for other reaction orders can be evaluated, but are more cumbersome.

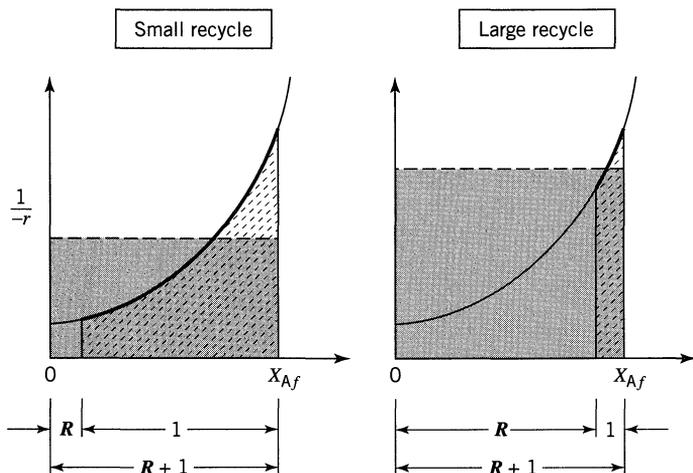


Figure 6.15 The recycle extremes approach plug flow ($R \rightarrow 0$) and mixed flow ($R \rightarrow \infty$).

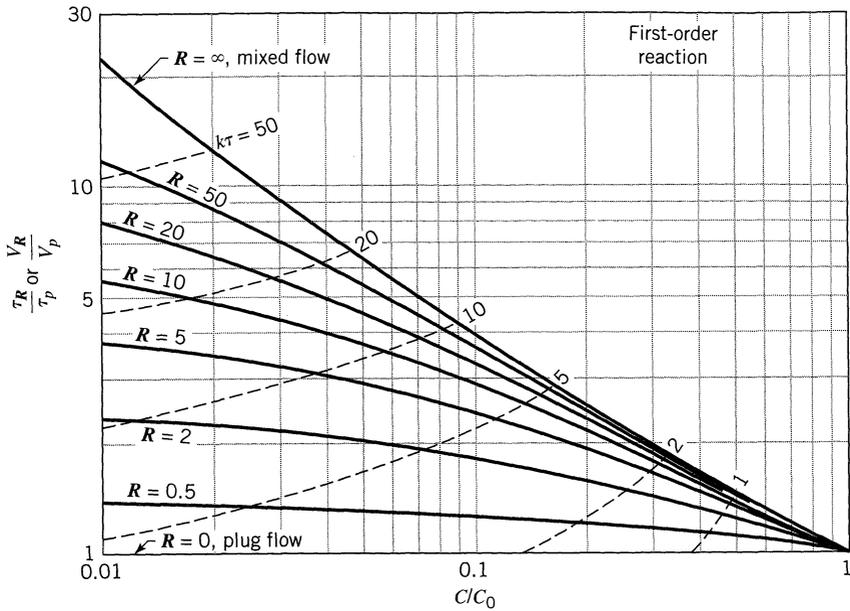
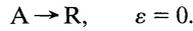


Figure 6.16 Comparison of performance of recycle and plug flow for first-order reactions



Figures 6.16 and 6.17 show the transition from plug to mixed flow as R increases, and a match of these curves with those for N tanks in series (Figs. 6.5 and 6.6) gives the following rough comparison for equal performance:

| No. of tanks | R for first-order reaction | | | R for second-order reaction | | |
|--------------|------------------------------|----------|----------|-------------------------------|----------|----------|
| | at $X_A = 0.5$ | 0.90 | 0.99 | at $X_A = 0.5$ | 0.90 | 0.99 |
| 1 | ∞ | ∞ | ∞ | ∞ | ∞ | ∞ |
| 2 | 1.0 | 2.2 | 5.4 | 1.0 | 2.8 | 7.5 |
| 3 | 0.5 | 1.1 | 2.1 | 0.5 | 1.4 | 2.9 |
| 4 | 0.33 | 0.68 | 1.3 | 0.33 | 0.90 | 1.7 |
| 10 | 0.11 | 0.22 | 0.36 | 0.11 | 0.29 | 0.5 |
| ∞ | 0 | 0 | 0 | 0 | 0 | 0 |

The recycle reactor is a convenient way for approaching mixed flow with what is essentially a plug flow device. Its particular usefulness is with solid catalyzed reactions with their fixed bed contactors. We meet this and other applications of recycle reactors in later chapters.

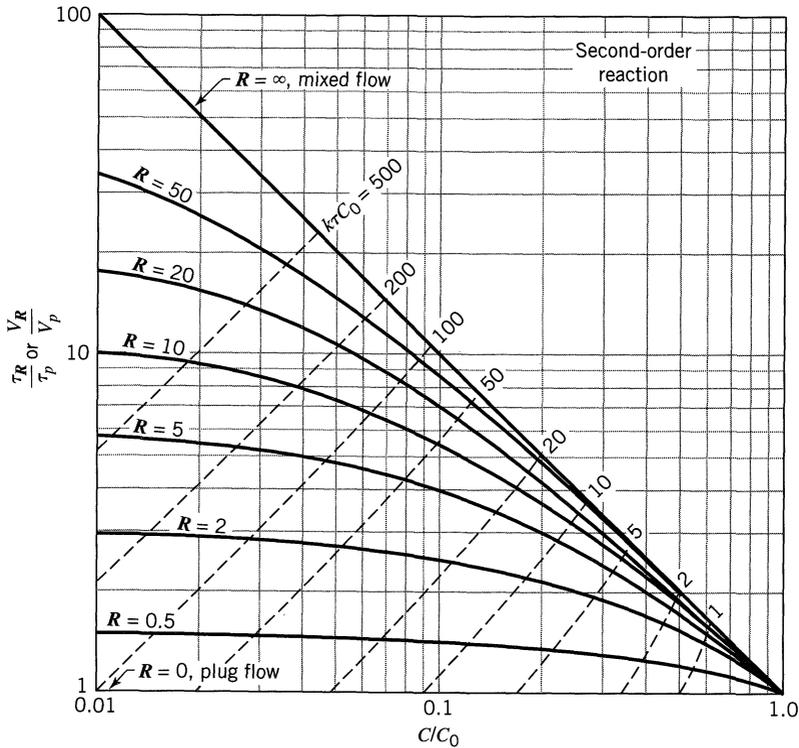
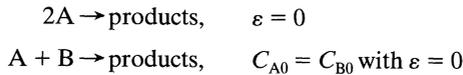


Figure 6.17 Comparison of performance of recycle reactors with plug flow reactors for elementary second-order reactions (Personal communication, from T. J. Fitzgerald and P. Filleli):



6.4 AUTOCATALYTIC REACTIONS

When a material reacts away by any n th order rate ($n > 0$) in a batch reactor, its rate of disappearance is rapid at the start when the concentration of reactant is high. This rate then slows progressively as reactant is consumed. In an autocatalytic reaction, however, the rate at the start is low because little product is present; it increases to a maximum as product is formed and then drops again to a low value as reactant is consumed. Figure 6.18 shows a typical situation.

Reactions with such rate-concentration curves lead to interesting optimization problems. In addition, they provide a good illustration of the general design method presented in this chapter. For these reasons let us examine these reactions in some detail. In our approach we deal exclusively with their $1/(-r_A)$ versus X_A curves with their characteristic minima, as shown in Fig. 6.18.

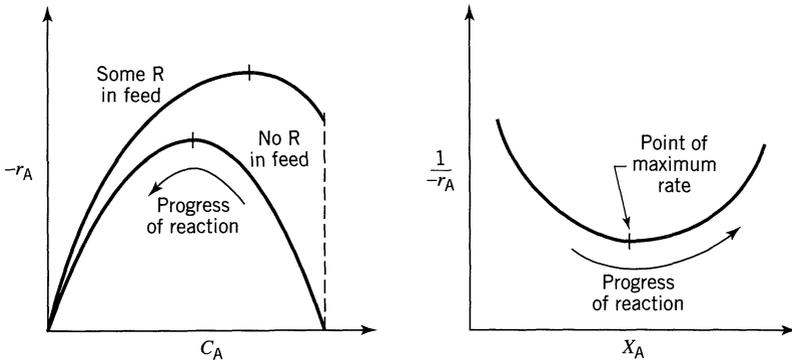
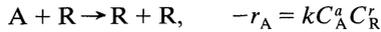


Figure 6.18 Typical rate-concentration curve for autocatalytic reactions, for example:



Plug Flow Versus Mixed Flow Reactor, No Recycle. For any particular rate-concentration curve a comparison of areas in Fig. 6.19 will show which reactor is superior (which requires a smaller volume) for a given job. We thus find

1. At low conversion the mixed reactor is superior to the plug flow reactor.
2. At high enough conversions the plug flow reactor is superior.

These findings differ from ordinary n th-order reactions ($n > 0$) where the plug flow reactor is always more efficient than the mixed flow reactor. In addition, we should note that a plug flow reactor will not operate at all with a feed of pure reactant. In such a situation the feed must be continually primed with product, an ideal opportunity for using a recycle reactor.

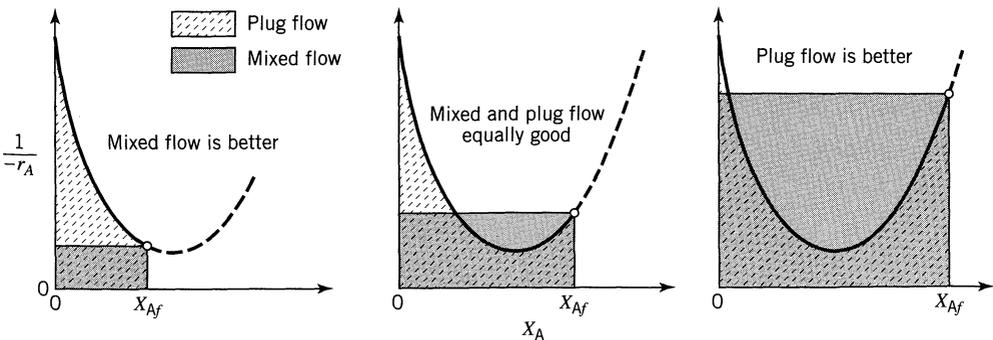


Figure 6.19 For autocatalytic reactions mixed flow is more efficient at low conversions, plug flow is more efficient at high conversions.

Optimum Recycle Operations. When material is to be processed to some fixed final conversion X_{Af} in a recycle reactor, reflection suggests that there must be a particular recycle ratio which is optimum in that it minimizes the reactor volume or space-time. Let us determine this value of R .

The *optimum recycle ratio* is found by differentiating Eq. 21 with respect to R and setting to zero, thus

$$\text{take } \frac{d(\tau/C_{A0})}{dR} = 0 \quad \text{for} \quad \frac{\tau}{C_{A0}} = \int_{X_{Ai} = \frac{RX_{Af}}{R+1}}^{X_{Af}} \frac{R+1}{(-r_A)} dX_A \quad (25)$$

This operation requires differentiating under an integral sign. From the theorems of calculus, if

$$F(R) = \int_{a(R)}^{b(R)} f(x, R) dx \quad (26)$$

then

$$\frac{dF}{dR} = \int_{a(R)}^{b(R)} \frac{\partial f(x, R)}{\partial R} dx + f(b, R) \frac{db}{dR} - f(a, R) \frac{da}{dR} \quad (27)$$

For our case, Eq. 25, we then find

$$\frac{d(\tau/C_{A0})}{dR} = 0 = \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-r_A)} + 0 - \frac{R+1}{(-r_A)} \Big|_{X_{Ai}} \frac{dX_{Ai}}{dR}$$

where

$$\frac{dX_{Ai}}{dR} = \frac{X_{Af}}{(R+1)^2}$$

Combining and rearranging then gives for the optimum

$$\boxed{\frac{1}{-r_A} \Big|_{X_{Ai}} = \frac{\int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}}{(X_{Af} - X_{Ai})}} \quad (28)$$

In words, the optimum recycle ratio introduces to the reactor a feed whose $1/(-r_A)$ value (KL in Fig. 6.20) equals the average $1/(-r_A)$ value in the reactor as a whole (PQ in Fig. 6.20). Figure 6.20 compares this optimum with conditions where the recycle is either too high or too low.

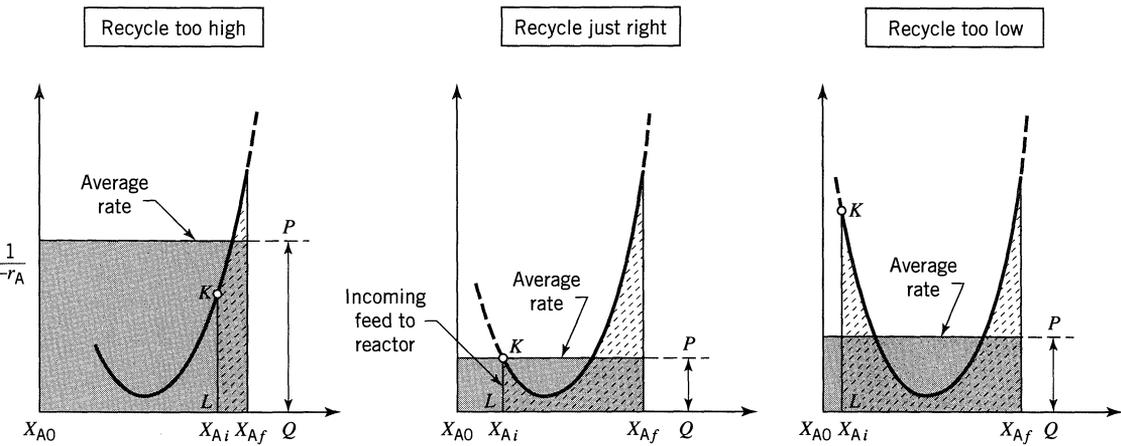


Figure 6.20 Correct recycle ratio for an autocatalytic reaction compared with recycle ratios which are too high and too low.

Occurrence of Autocatalytic Reactions. The most important examples of autocatalytic reactions are the broad class of fermentation reactions which result from the reaction of microorganism on an organic feed. When they can be treated as single reactions, the methods of this chapter can be applied directly. Another type of reaction which has autocatalytic behavior is the exothermic reaction (say, the combustion of fuel gas) proceeding in an adiabatic manner with cool reactants entering the system. In such a reaction, called *autothermal*, heat may be considered to be the product which sustains the reaction. Thus, with plug flow the reaction will die. With backmixing the reaction will be self-sustaining because the heat generated by the reaction can raise fresh reactants to a temperature at which they will react. Autothermal reactions are of great importance in solid catalyzed gas-phase systems and are treated later in the book.

Reactor Combinations

For autocatalytic reactions all sorts of reactor arrangements are to be considered if product recycle or product separation with recycle is allowable. In general, for a rate-concentration curve as shown in Fig. 6.21 one should always try to reach point *M* in one step (using mixed flow in a single reactor), then follow with plug flow or as close to plug flow as possible. This procedure is shown as the shaded area in Fig. 6.21a.

When separation and reuse of unconverted reactant is possible, operate at point *M* (see Fig. 6.21b).

The volume required is now the very minimum, less than any of the previous ways of operating. However, the overall economics, including the cost of separation and of recycle, will determine which scheme is the optimum overall.

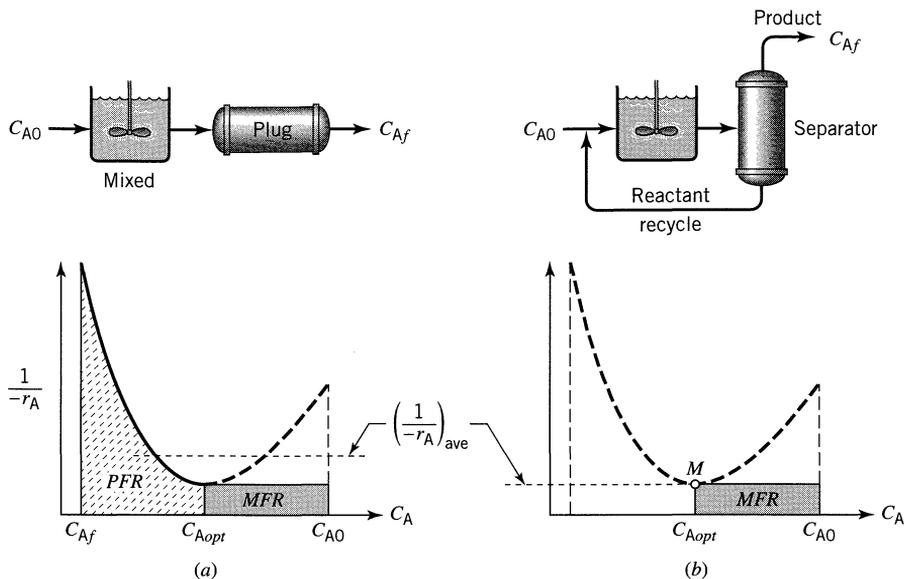


Figure 6.21 (a) The best multiple reactor scheme. (b) The best scheme when unconverted reactant can be separated and recycled.

EXAMPLE 6.3 FINDING THE BEST REACTOR SETUP

In the presence of a specific enzyme E, which acts as a homogeneous catalyst, a harmful organic A present in industrial waste water degrades into harmless chemicals. At a given enzyme concentration C_E tests in a laboratory mixed flow reactor give the following results:

| | | | | | | | | |
|--------------------------------|-----|---|----|---|----|----|----|----|
| C_{A0} , mmol/m ³ | 2 | 5 | 6 | 6 | 11 | 14 | 16 | 24 |
| C_A , mmol/m ³ | 0.5 | 3 | 1 | 2 | 6 | 10 | 8 | 4 |
| τ , min | 30 | 1 | 50 | 8 | 4 | 20 | 20 | 4 |

We wish to treat 0.1 m³/min of this waste water having $C_{A0} = 10$ mmol/m³ to 90% conversion with this enzyme at concentration C_E .

- One possibility is to use a long tubular reactor (assume plug flow) with possible recycle of exit fluid. What design do you recommend? Give the size of the reactor, tell if it should be used with recycle, and if so determine the recycle flow rate in cubic meters per minute (m³/min). Sketch your recommended design.
- Another possibility is to use one or two stirred tanks (assume ideal). What two-tank design do you recommend, and how much better is it than the one-tank arrangement?
- What arrangement of plug flow and mixed flow reactors would you use to minimize the total volume of reactors needed? Sketch your recommended design and show the size of units selected. We should mention that separation and recycle of part of the product stream is not allowed.

SOLUTION

First calculate and tabulate $1/-r_A$ at the measured C_A . This is shown as the last line of Table E6.3. Next, draw the $1/-r_A$ vs. C_A curve. This is seen to be U-shaped (see Figs. E6.3a, b, c) so we must prepare to deal with an autocatalytic type reacting system.

Table E6.3

| | | | | | | | | |
|---|-----|-----|----|---|-----|----|-----|-----|
| $C_{A0}, \text{mmol/m}^3$ | 2 | 5 | 6 | 6 | 11 | 14 | 16 | 24 |
| $C_A, \text{mmol/m}^3$ | 0.5 | 3 | 1 | 2 | 6 | 10 | 8 | 4 |
| τ, min | 30 | 1 | 50 | 8 | 4 | 20 | 20 | 4 |
| $\frac{1}{-r_A} = \frac{\tau}{C_{A0} - C_A}, \frac{\text{m}^3 \cdot \text{min}}{\text{mmol}}$ | 20 | 0.5 | 10 | 2 | 0.8 | 5 | 2.5 | 0.2 |

Part (a) Solution. From the $-1/r_A$ vs. C_A curve we see that we should use plug flow with recycle. From Fig. E6.3a we find

$$C_{Ain} = 6.6 \text{ mmol/m}^3$$

$$R = \frac{10 - 6.6}{6.6 - 1} = 0.607$$

$$V = \tau v_0 = \text{area}(v_0) = [(10 - 1)(1.2)](0.1) = \underline{\underline{1.08 \text{ m}^3}}$$

$$v_R = v_0 R = 0.1(0.607) = \underline{\underline{0.0607 \text{ m}^3/\text{min}}}$$

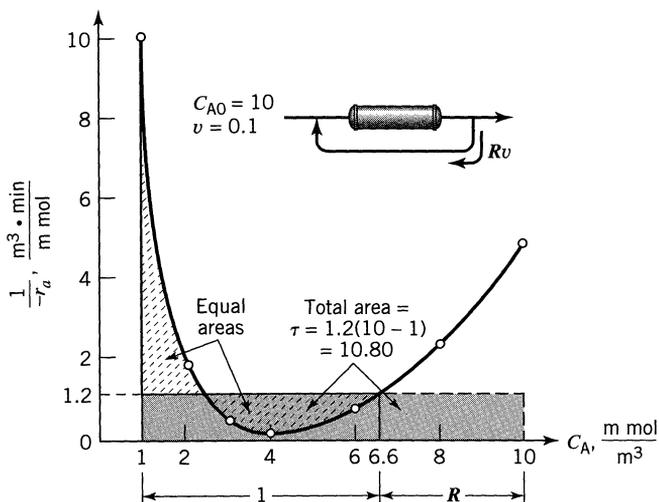


Figure E6.3a Plug flow with recycle.

Part (b) Solution. Drawing slopes and diagonals according to the method of maximization of rectangles we end up with Fig. E6.3b.

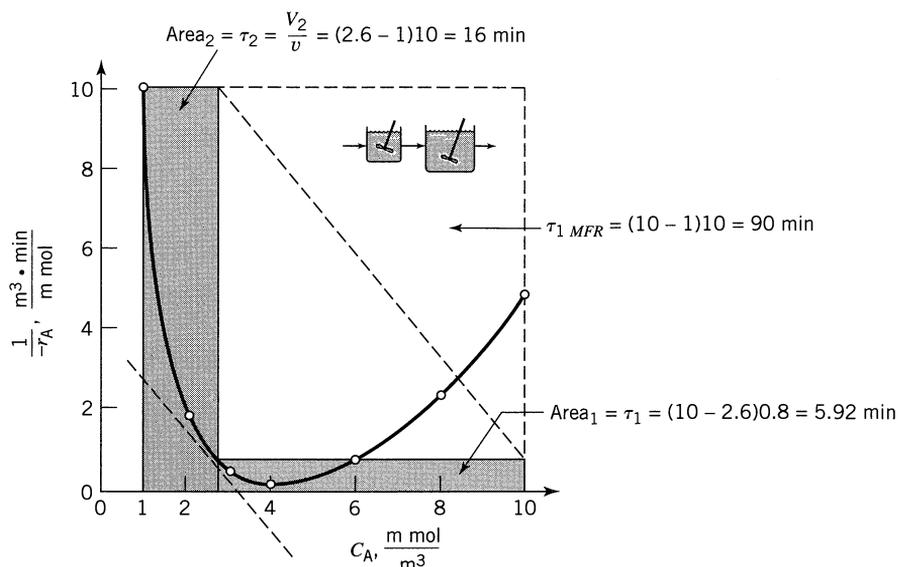


Figure E6.3b One and two mixed flow reactors in series.

For 1 tank $V = \tau v = 90(0.1) = \underline{\underline{9.0 \text{ m}^3}}$

For 2 tanks $\left. \begin{array}{l} V_1 = \tau_1 v = 5.92(0.1) = 0.59 \\ V_2 = \tau_2 v = 16(0.1) = 1.6 \end{array} \right\} V_{\text{total}} = \underline{\underline{2.19 \text{ m}^3}}$

Part (c) Solution. Following the reasoning in this chapter we should use a mixed flow reactor followed by a plug flow reactor. So with Fig. E6.3c we find

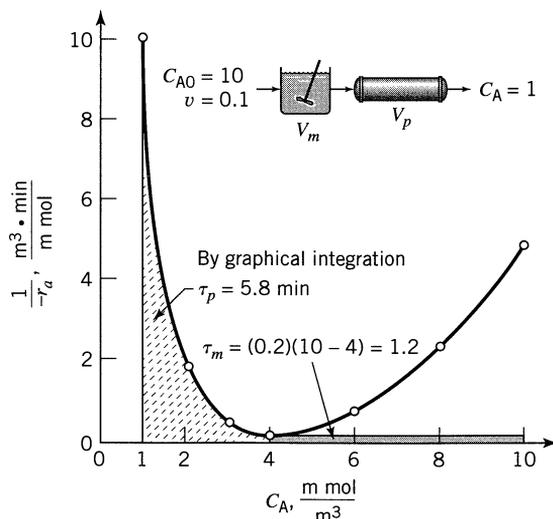


Figure E6.3c Arrangement with smallest volume.

$$\left. \begin{array}{l} \text{For the MFR } V_m = v\tau_m = 0.1(1.2) = 0.12 \text{ m}^3 \\ \text{For the PFR } V_p = v\tau_p = 0.1(5.8) = 0.58 \text{ m}^3 \end{array} \right\} V_{\text{total}} = \underline{\underline{0.7 \text{ m}^3}}$$

Note which scheme (a) or (b) or (c) gives the smallest size of reactors.

REFERENCES

- Jones, R. W., *Chem. Eng. Progr.*, **47**, 46 (1951).
 Szepe, S., and O. Levenspiel, *Ind. Eng. Chem. Process Design Develop.*, **3**, 214 (1964).

PROBLEMS

- 6.1.** A liquid reactant stream (1 mol/liter) passes through two mixed flow reactors in a series. The concentration of A in the exit of the first reactor is 0.5 mol/liter. Find the concentration in the exit stream of the second reactor. The reaction is second-order with respect to A and $V_2/V_1 = 2$.
- 6.2.** Water containing a short-lived radioactive species flows continuously through a well-mixed holdup tank. This gives time for the radioactive material to decay into harmless waste. As it now operates, the activity of the exit stream is 1/7 of the feed stream. This is not bad, but we'd like to lower it still more.
 One of our office secretaries suggests that we insert a baffle down the middle of the tank so that the holdup tank acts as two well-mixed tanks in series. Do you think this would help? If not, tell why; if so, calculate the expected activity of the exit stream compared to the entering stream.
- 6.3.** An aqueous reactant stream (4 mol A/liter) passes through a mixed flow reactor followed by a plug flow reactor. Find the concentration at the exit of the plug flow reactor if in the mixed flow reactor $C_A = 1$ mol/liter. The reaction is second-order with respect to A, and the volume of the plug flow unit is three times that of the mixed flow unit.
- 6.4.** Reactant A ($A \rightarrow R$, $C_{A0} = 26$ mol/m³) passes in steady flow through four equal-size mixed flow reactors in series ($\tau_{\text{total}} = 2$ min). When steady state is achieved the concentration of A is found to be 11, 5, 2, 1 mol/m³ in the four units. For this reaction, what must be τ_{plug} so as to reduce C_A from $C_{A0} = 26$ to $C_{Af} = 1$ mol/m³?
- 6.5.** Originally we had planned to lower the activity of a gas stream containing radioactive Xe-138 (half-life = 14 min) by having it pass through two holdup tanks in series, both well mixed and of such size that the mean residence time of gas is 2 weeks in each tank. It has been suggested that we replace the two tanks with a long tube (assume plug flow). What must be the size of this tube compared to the two original stirred tanks, and

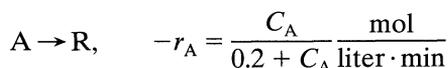
what should be the mean residence time of gas in this tube for the same extent of radioactive decay?

- 6.6.** At 100°C pure gaseous A reacts away with stoichiometry $2A \rightarrow R + S$ in a constant volume batch reactor as follows:

| | | | | | | | | | |
|--------------------|------|------|------|------|------|------|------|------|------|
| $t, \text{ sec}$ | 0 | 20 | 40 | 60 | 80 | 100 | 120 | 140 | 160 |
| $p_A, \text{ atm}$ | 1.00 | 0.96 | 0.80 | 0.56 | 0.32 | 0.18 | 0.08 | 0.04 | 0.02 |

What size of plug flow reactor operating at 100°C and 1 atm can treat 100 moles A/hr in a feed consisting of 20% inerts to obtain 95% conversion of A?

- 6.7.** We wish to treat 10 liters/min of liquid feed containing 1 mol A/liter to 99% conversion. The stoichiometry and kinetics of the reaction are given by



Suggest a good arrangement for doing this using two mixed flow reactors, and find the size of the two units needed. Sketch the final design chosen.

- 6.8.** From steady-state kinetics runs in a mixed flow reactor, we obtain the following data on the reaction $A \rightarrow R$.

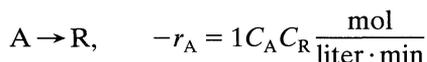
| $\tau, \text{ sec}$ | $C_{A0}, \text{ mmol/liter}$ | $C_A, \text{ mmol/liter}$ |
|---------------------|------------------------------|---------------------------|
| 60 | 50 | 20 |
| 35 | 100 | 40 |
| 11 | 100 | 60 |
| 20 | 200 | 80 |
| 11 | 200 | 100 |

Find the space time needed to treat a feed of $C_{A0} = 100$ mmol/liter to 80% conversion

- (a) in a plug flow reactor.
 (b) in a mixed flow reactor.

- 6.9.** At present we have 90% conversion of a liquid feed ($n = 1$, $C_{A0} = 10$ mol/liter) to our plug flow reactor with recycle of product ($R = 2$). If we shut off the recycle stream, by how much will this lower the processing rate of our feed to the same 90% conversion?

- 6.10.** Aqueous feed containing reactant A ($C_{A0} = 2$ mol/liter) enters a plug flow reactor (10 liter) which has a provision for recycling a portion of the flowing stream. The reaction kinetics and stoichiometry are

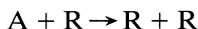


and we wish to get 96% conversion. Should we use the recycle stream? If so, at what value should we set the recycle flow rate so as to obtain the highest production rate, and what volumetric feed rate can we process to this conversion in the reactor?

- 6.11.** Consider the autocatalytic reaction $A \rightarrow R$, with $-r_A = 0.001 C_A C_R$ mol/liter \cdot s. We wish to process 1.5 liters/s of a $C_{A0} = 10$ mol/liter feed to the highest conversion possible in the reactor system consisting of four 100-liter mixed flow reactors connected as you wish and any feed arrangement. Sketch your recommended design and feed arrangement and determine C_{Af} from this system.
- 6.12.** A first-order liquid-phase reaction, 92% conversion, is taking place in a mixed flow reactor. It has been suggested that a fraction of the product stream, with no additional treatment, be recycled. If the feed rate remains unchanged, in what way would this affect conversion?
- 6.13.** 100 liters/hr of radioactive fluid having a half-life of 20 hr is to be treated by passing it through two ideal stirred tanks in series, $V = 40\,000$ liters each. In passing through this system, how much will the activity decay?
- 6.14.** At present the elementary liquid-phase reaction $A + B \rightarrow R + S$ takes place in a plug flow reactor using equimolar quantities of A and B. Conversion is 96%, $C_{A0} = C_{B0} = 1$ mol/liter. If a mixed flow reactor ten times as large as the plug flow reactor were hooked up in series with the existing unit, which unit should come first and by what fraction could production be increased for that setup?
- 6.15.** The kinetics of the aqueous-phase decomposition of A is investigated in two mixed flow reactors in series, the second having twice the volume of the first reactor. At steady state with a feed concentration of 1 mol A/liter and mean residence time of 96 sec in the first reactor, the concentration in the first reactor is 0.5 mol A/liter and in the second is 0.25 mol A/liter. Find the kinetic equation for the decomposition.
- 6.16.** Using a color indicator which shows when the concentration of A falls below 0.1 mol/liter, the following scheme is devised to explore the kinetics of the decomposition of A. A feed of 0.6 mol A/liter is introduced into the first of the two mixed flow reactors in series, each having a volume of 400 cm³. The color change occurs in the first reactor for a steady-state feed rate of 10 cm³/min, and in the second reactor for a steady-state feed rate of 50 cm³/min. Find the rate equation for the decomposition of A from this information.
- 6.17.** The elementary irreversible aqueous-phase reaction $A + B \rightarrow R + S$ is carried out isothermally as follows. Equal volumetric flow rates of two liquid streams are introduced into a 4-liter mixing tank. One stream contains 0.020 mol A/liter, the other 1.400 mol B/liter. The mixed stream is then

passed through a 16-liter plug flow reactor. We find that some R is formed in the mixing tank, its concentration being 0.002 mol/liter. Assuming that the mixing tank acts as a mixed flow reactor, find the concentration of R at the exit of the plug flow reactor as well as the fraction of initial A that has been converted in the system.

- 6.18.** At present conversion is $2/3$ for our elementary second-order liquid reaction $2A \rightarrow 2R$ when operating in an isothermal plug flow reactor with a recycle ratio of unity. What will be the conversion if the recycle stream is shut off?
- 6.19.** We wish to explore various reactor setups for the transformation of A into R. The feed contains 99% A, 1% R; the desired product is to consist of 10% A, 90% R. The transformation takes place by means of the elementary reaction



with rate constant $k = 1$ liter/mol \cdot min. The concentration of active materials is

$$C_{A0} + C_{R0} = C_A + C_R = C_0 = 1 \text{ mol/liter}$$

throughout.

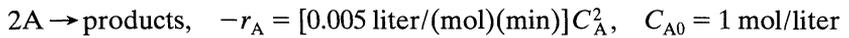
What reactor holding time will yield a product in which $C_R = 0.9$ mol/liter (a) in a plug flow reactor, (b) in a mixed flow reactor, and (c) in a minimum-size setup without recycle?

- 6.20.** Reactant A decomposes with stoichiometry $A \rightarrow R$ and with rate dependent only on C_A . The following data on this aqueous decomposition are obtained in a mixed flow reactor:

| τ , sec | C_{A0} | C_A |
|--------------|----------|-------|
| 14 | 200 | 100 |
| 25 | 190 | 90 |
| 29 | 180 | 80 |
| 30 | 170 | 70 |
| 29 | 160 | 60 |
| 27 | 150 | 50 |
| 24 | 140 | 40 |
| 19 | 130 | 30 |
| 15 | 120 | 20 |
| 12 | 110 | 10 |
| 20 | 101 | 1 |

Determine which setup, plug flow, mixed flow, or any two-reactor combination gives minimum τ for 90% conversion of a feed consisting of $C_{A0} = 100$. Also find this τ minimum. If a two-reactor scheme is found to be optimum, give C_A between stages and τ for each stage.

- 6.21.** For an irreversible first-order liquid-phase reaction ($C_{A0} = 10$ mol/liter) conversion is 90% in a plug flow reactor. If two-thirds of the stream leaving the reactor is recycled to the reactor entrance, and if the throughput to the whole reactor-recycle system is kept unchanged, what does this do to the concentration of reactant leaving the system?
- 6.22.** At room temperature the second-order irreversible liquid-phase reaction proceeds as follows:



A batch reactor takes 18 min to fill and empty. What percent conversion and reaction time should we use so as to maximize the daily output of product R?

Design for Parallel Reactions

Introduction to Multiple Reactions

The preceding chapter on single reactions showed that the performance (size) of a reactor was influenced by the pattern of flow within the vessel. In this and the next chapter, we extend the discussion to multiple reactions and show that for these, both the size requirement and the distribution of reaction products are affected by the pattern of flow within the vessel. We may recall at this point that the distinction between a *single* reaction and *multiple* reactions is that the single reaction requires only one rate expression to describe its kinetic behavior whereas multiple reactions require more than one rate expression.

Since multiple reactions are so varied in type and seem to have so little in common, we may despair of finding general guiding principles for design. Fortunately, this is not so because many multiple reactions can be considered to be combinations of two primary types: *parallel* reactions and *series* reactions.

In this chapter we treat parallel reactions. In the next chapter we treat series reactions as well as all sorts of series-parallel combinations.

Let us consider the general approach and nomenclature. First of all, we find it more convenient to deal with concentrations rather than conversions. Second, in examining product distribution the procedure is to eliminate the time variable by dividing one rate equation by another. We end up then with equations relating the rates of change of certain components with respect to other components of the systems. Such relationships are relatively easy to treat. Thus, we use two distinct analyses, one for determination of reactor size and the other for the study of product distribution.

The two requirements, small reactor size and maximization of desired product, may run counter to each other. In such a situation an economic analysis will yield the best compromise. In general, however, product distribution controls; consequently, this chapter concerns primarily optimization with respect to product distribution, a factor which plays no role in single reactions.

Finally, we ignore expansion effects in this chapter; thus, we take $\varepsilon = 0$ throughout. This means that we may use the terms mean residence time, reactor holding time, space time, and reciprocal space velocity interchangeably.

Qualitative Discussion About Product Distribution. Consider the decomposition of A by either one of two paths:



with corresponding rate equations

$$r_R = \frac{dC_R}{dt} = k_1 C_A^{a_1} \quad (2a)$$

$$r_S = \frac{dC_S}{dt} = k_2 C_A^{a_2} \quad (2b)$$

Dividing Eq. 2a by Eq. 2b gives a measure of the relative rates of formation of R and S. Thus

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_2}{k_1} C_A^{a_1 - a_2} \quad (3)$$

and we wish this ratio to be as large as possible.

Now C_A is the only factor in this equation which we can adjust and control (k_1 , k_2 , a_1 , and a_2 are all constant for a specific system at a given temperature) and we can keep C_A low throughout the reactor by any of the following means: by using a mixed flow reactor, maintaining high conversions, increasing inerts in the feed, or decreasing the pressure in gas-phase systems. On the other hand, we can keep C_A high by using a batch or plug flow reactor, maintaining low conversions, removing inerts from the feed, or increasing the pressure in gas-phase systems.

For the reactions of Eq. 1 let us see whether the concentration of A should be kept high or low.

If $a_1 > a_2$, or the desired reaction is of higher order than the unwanted reaction, Eq. 3 shows that a high reactant concentration is desirable since it increases the R/S ratio. As a result, a batch or plug flow reactor would favor formation of product R and would require a minimum reactor size.

If $a_1 < a_2$, or the desired reaction is of lower order than the unwanted reaction, we need a low reactant concentration to favor formation of R. But this would also require large mixed flow reactor.

If $a_1 = a_2$, or the two reactions are of the same order, Eq. 3 becomes

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2} = \text{constant}$$

Hence, product distribution is fixed by k_2/k_1 alone and is unaffected by type of reactor used.

We also may control product distribution by varying k_2/k_1 . This can be done in two ways:

1. By changing the temperature level of operation. If the activation energies of the two reactions are different, k_1/k_2 can be made to vary. Chapter 9 considers this problem.
2. By using a catalyst. One of the most important features of a catalyst is its selectivity in depressing or accelerating specific reactions. This may be a much more effective way of controlling product distribution than any of the methods discussed so far.

We summarize our qualitative findings as follows:

For reactions in parallel, the concentration level of reactants is the key to proper control of product distribution. A high reactant concentration favors the reaction of higher order, a low concentration favors the reaction of lower order, while the concentration level has no effect on the product distribution for reactions of the same order.

(4)

When you have two or more reactants, combinations of high and low reactant concentrations can be obtained by controlling the concentration of feed materials, by having certain components in excess, and by using the correct contacting pattern of reacting fluids. Figures 7.1 and 7.2 illustrate methods of contacting two reacting fluids in continuous and noncontinuous operations that keep the concentrations of these components both high, both low, or one high and the other low. In general, the number of reacting fluids involved, the possibility of recycle, and the cost of possible alternative setups must all be considered before the most desirable contacting pattern can be achieved.

In any case, the use of the proper contacting pattern is the critical factor in obtaining a favorable distribution of products for multiple reactions.

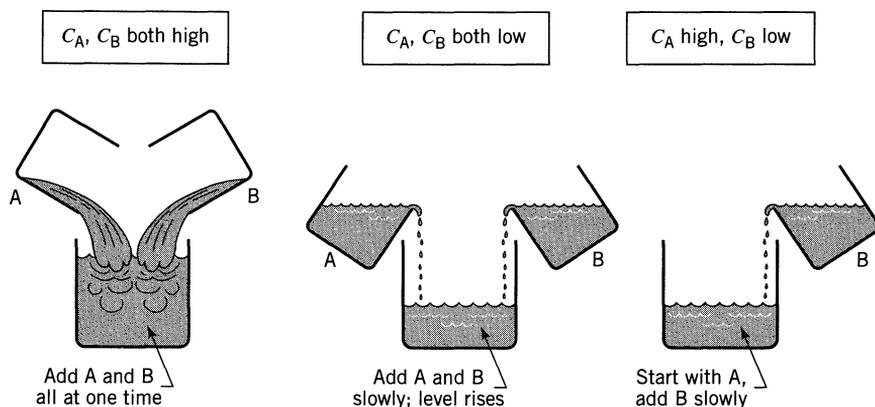


Figure 7.1 Contacting patterns for various combinations of high and low concentration of reactants in noncontinuous operations.

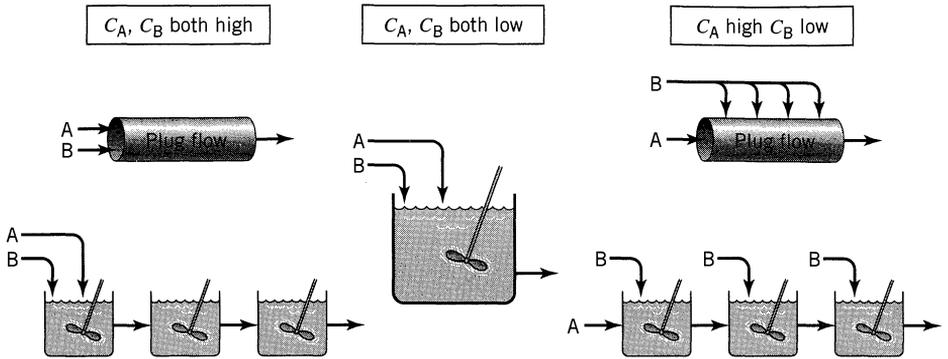
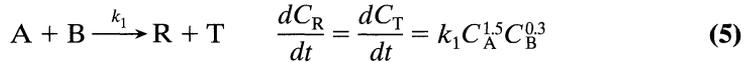


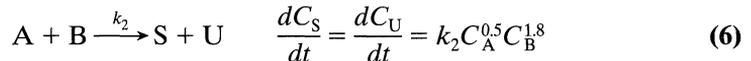
Figure 7.2 Contacting patterns for various combinations of high and low concentration of reactants in continuous flow operations.

EXAMPLE 7.1 CONTACTING PATTERNS FOR REACTIONS IN PARALLEL

The desired liquid-phase reaction



is accompanied by the unwanted side reaction



From the standpoint of favorable product distribution, order the contacting schemes of Fig. 7.2, from the most desirable to the least desirable.

SOLUTION

Dividing Eq. (5) by Eq. (6) gives the ratio

$$\frac{r_R}{r_S} = \frac{k_1}{k_2} C_A C_B^{-1.5}$$

which is to be kept as large as possible. According to the rule for reactions in parallel, we want to keep C_A high, C_B low, and since the concentration dependency of B is more pronounced than of A, it is more important to have low C_B than high C_A . The contacting schemes are therefore ordered as shown in Fig. E7.1.

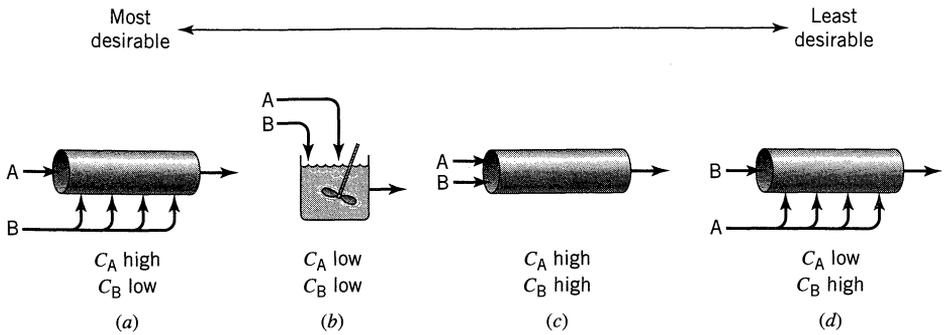


Figure E7.1

Comment. Example 7.2 verifies these qualitative findings. We should also note that there are still other contacting schemes which are superior to the best found in this example. For example, if we can use an excess of a reactant, or if it is practical to separate and recycle unconverted reactant, then vastly improved product distribution is possible.

Quantitative Treatment of Product Distribution and of Reactor Size. If rate equations are known for the individual reactions, we can quantitatively determine product distribution and reactor-size requirements. For convenience in evaluating product distribution we introduce two terms, φ and Φ . First, consider the decomposition of reactant A, and let φ be the fraction of A disappearing at any instant which is transformed into desired product R. We call this the *instantaneous fractional yield of R*. Thus at any C_A

$$\varphi = \left(\frac{\text{moles R formed}}{\text{moles A reacted}} \right) = \frac{dC_R}{-dC_A} \quad (7)$$

For any particular set of reactions and rate equations φ is a function of C_A , and since C_A in general varies through the reactor, φ will also change with position in the reactor. So let us define Φ as the fraction of all the reacted A that has been converted into R, and let us call this the *overall fractional yield of R*. The overall fractional yield is then the mean of the instantaneous fractional yields at all points within the reactor; thus we may write

$$\Phi = \left(\frac{\text{all R formed}}{\text{all A reacted}} \right) = \frac{C_{R_f}}{C_{A_0} - C_{A_f}} = \frac{C_{R_f}}{(-\Delta C_A)} = \bar{\varphi}_{\text{in reactor}} \quad (8)$$

It is the overall fractional yield that really concerns us for it represents the product distribution at the reactor outlet. Now the proper averaging for φ depends

on the type of flow within the reactor. Thus for *plug flow*, where C_A changes progressively through the reactor, we have from Eq. 7:

$$\text{For PFR: } \Phi_p = \frac{-1}{C_{A0} - C_{Af}} \int_{C_{A0}}^{C_{Af}} \varphi dC_A = \frac{1}{\Delta C_A} \int_{C_{A0}}^{C_{Af}} \varphi dC_A \quad (9)$$

For *mixed flow*, the composition is C_{Af} everywhere, so φ is likewise constant throughout the reactor, and we have

$$\text{For MFR: } \Phi_m = \varphi_{\text{evaluated at } C_{Af}} \quad (10)$$

The over-all fractional yields from mixed and plug flow reactors processing A from C_{A0} to C_{Af} are related by

$$\Phi_m = \left(\frac{d\Phi_p}{dC_A} \right)_{\text{at } C_{Af}} \quad \text{and} \quad \Phi_p = \frac{1}{\Delta C_A} \int_{C_{A0}}^{C_{Af}} \Phi_m dC_A \quad (11)$$

These expressions allow us to predict the yields from one type of reactor given the yields from the other.

For a series of 1, 2, ..., N mixed flow reactors in which the concentration of A is C_{A1} , C_{A2} , ..., C_{AN} , the overall fractional yield is obtained by summing the fractional yields in each of the N vessels and weighting these values by the amount of reaction occurring in each vessel. Thus

$$\varphi_1(C_{A0} - C_{A1}) + \cdots + \varphi_N(C_{A,N-1} - C_{AN}) = \Phi_{N \text{ mixed}} (C_{A0} - C_{AN})$$

from which

$$\Phi_{N \text{ mixed}} = \frac{\varphi_1(C_{A0} - C_{A1}) + \varphi_2(C_{A1} - C_{A2}) + \cdots + \varphi_N(C_{A,N-1} - C_{AN})}{C_{A0} - C_{AN}} \quad (12)$$

For any reactor type the exit concentration of R is obtained directly from Eq. 8. Thus

$$C_{Rf} = \Phi(C_{A0} - C_{Af}) \quad (13)$$

and Fig. 7.3 shows how C_R is found for different types of reactors. For mixed flow reactors, or mixed flow reactors in series, the best outlet concentration to use, that which maximizes C_R , may have to be found by maximization of rectangles (see Chapter 6).

Now the shape of the φ versus C_A curve determines which type of flow gives the best product distribution, and Fig. 7.4 shows typical shapes of these curves for which plug flow, mixed flow, and mixed followed by plug flow are best.

These fractional yield expressions allow us to relate the product distribution from different types of reactors and to search for the best contacting scheme. However, one condition must be satisfied before we can safely use these relationships: We must truly have parallel reactions in which no product influences the

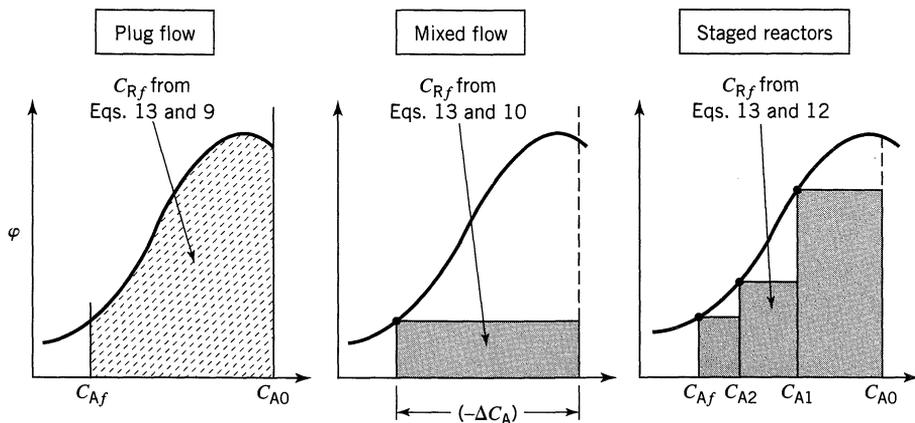


Figure 7.3 Shaded and dashed area gives total R formed.

rate to change the product distribution. The easiest way to test this is to add products to the feed and verify that the product distribution is in no way altered.

So far, the fractional yield of R has been taken as a function of C_A alone and has been defined on the basis of the amount of this component consumed. More generally, when there are two or more reactants involved, the fractional yield can be based on one of the reactants consumed, on all reactants consumed, or on products formed. It is simply a matter of convenience which definition is used. Thus, in general, we define $\varphi(M/N)$ as the instantaneous fractional yield of M, based on the disappearance or formation of N.

The use of fractional yields to determine the product distribution for parallel reactions was developed by Denbigh (1944, 1961).

The Selectivity. Another term, the selectivity, is often used in place of fractional yield. It is usually defined as follows:

$$\text{selectivity} = \left(\frac{\text{moles of desired product formed}}{\text{moles of undesired material formed}} \right)$$

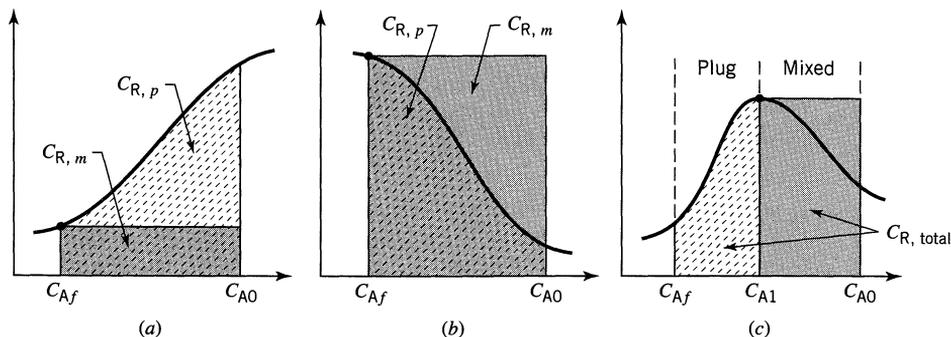
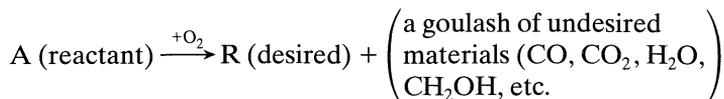


Figure 7.4 The contacting pattern with the largest area produces most R: (a) plug flow is best, (b) mixed flow is best, (c) mixed flow up to C_{A1} followed by plug flow is best.

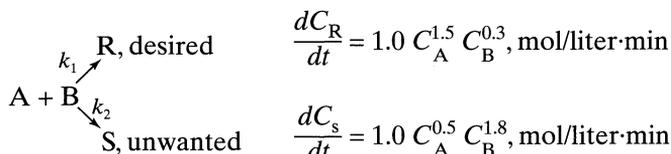
This definition may lead to difficulties. For example, if the reaction is the partial oxidation of a hydrocarbon, as follows:



Here the selectivity is hard to evaluate, and not very useful. Thus, we stay away from selectivity and use the clearly defined and useful fractional yield, $\varphi(R/A)$.

EXAMPLE 7.2. PRODUCT DISTRIBUTION FOR PARALLEL REACTIONS

Consider the aqueous reactions



For 90% conversion of A find the concentration of R in the product stream. Equal volumetric flow rates of the A and of B streams are fed to the reactor, and each stream has a concentration of 20 mol/liter of reactant.

The flow in the reactor follows.

- Plug flow
- Mixed flow
- The best of the four plug-mixed contacting schemes of Example 7.1.

SOLUTION

As a warning, be careful to get the concentrations right when you mix streams. We show this in the three sketches for this problem. Also, the instantaneous fractional yield of the desired compound is

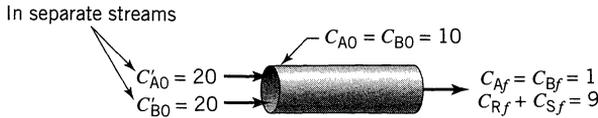
$$\varphi \left(\frac{R}{A} \right) = \frac{dC_R}{dC_R + dC_S} = \frac{k_1 C_A^{1.5} C_B^{0.3}}{k_1 C_A^{1.5} C_B^{0.3} + k_2 C_A^{0.5} C_B^{1.8}} = \frac{C_A}{C_A + C_B^{1.5}}$$

Now let us proceed.

(a) Plug Flow

Referring to Fig. E7.2a, noting that the starting concentration of each reactant in the combined feed is $C_{A0} = C_{B0} = 10$ mol/liter and that $C_A = C_B$ everywhere, we find from Eq. 9 that

$$\Phi_p = \frac{-1}{C_{A0} - C_{Af}} \int \varphi dC_A = \frac{-1}{10 - 1} \int_{10}^1 \frac{C_A dC_A}{C_A + C_A^{1.5}} = \frac{1}{9} \int_1^{10} \frac{dC_A}{1 + C_A^{0.5}}$$


Figure E7.2a

Let $C_A^{0.5} = x$, then $C_A = x^2$ and $dC_A = 2xdx$. Replacing C_A by x in the above expression gives

$$\Phi_p = \frac{1}{9} \int_1^{\sqrt{10}} \frac{2xdx}{1+x} = \frac{2}{9} \left[\int_1^{\sqrt{10}} dx - \int_1^{\sqrt{10}} \frac{dx}{1+x} \right]$$

$$= 0.32$$

$$\therefore C_{Rf} = 9(0.32) = \underline{\underline{2.86}}$$

$$C_{Sf} = 9(1 - 0.32) = \underline{\underline{6.14}}$$

(b) Mixed Flow

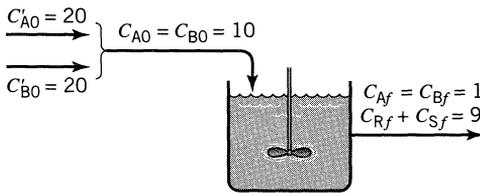
Referring to Fig. E7.2b, we have from Eq. 10, for $C_A = C_B$

$$\Phi_m \left(\frac{R}{A} \right) = \varphi_{\text{at exit}} = \frac{1}{1 + C_A^{0.5}} = 0.5$$

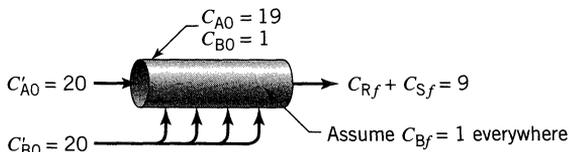
Therefore Eq. 13 gives

$$C_{Rf} = 9(0.5) = \underline{\underline{4.5 \text{ mol/liter}}}$$

$$C_{Sf} = 9(1 - 0.5) = \underline{\underline{4.5 \text{ mol/liter}}}$$


Figure E7.2b
(c) Plug Flow A—Mixed Flow B

Assuming that B is introduced into the reactor in such a way that $C_B = 1$ mol/liter throughout, we find concentrations as shown in Fig. E7.2c. Then accounting


Figure E7.2c

for the changing C_A in the reactor, we find

$$\begin{aligned}\Phi\left(\frac{R}{A}\right) &= \frac{-1}{C_{A0} - C_{Af}} \int_{C_{A0}}^{C_{Af}} \varphi dC_A = \frac{-1}{19 - 1} \int_{19}^1 \frac{C_A dC_A}{C_A + (1)^{1.5}} \\ &= \frac{1}{18} \left[\int_1^{19} dC_A - \int_1^{19} \frac{dC_A}{C_A + 1} \right] = \frac{1}{18} \left[(19 - 1) - \ln \frac{20}{2} \right] = 0.87\end{aligned}$$

Therefore

$$C_{Rf} = 9(0.87) = \underline{\underline{7.85 \text{ mol/liter}}}$$

$$C_{Sf} = 9(1 - 0.87) = \underline{\underline{1.15 \text{ mol/liter}}}$$

To summarize

For plug flow: $\Phi\left(\frac{R}{A}\right) = 0.32$ and $C_{Rf} = 2.86 \text{ mol/liter}$

For mixed flow: $\Phi\left(\frac{R}{A}\right) = 0.50$ and $C_{Rf} = 4.5 \text{ mol/liter}$

For the optimum: $\Phi\left(\frac{R}{A}\right) = 0.87$ and $C_{Rf} = 7.85 \text{ mol/liter}$

Note. These results verify the qualitative findings of Example 7.1.

The Side Entry Reactor

To evaluate how best to distribute the side entry feed and how to calculate the corresponding conversion equation is a rather complex problem. For this type of contacting in general see Westerterp et al. (1984).

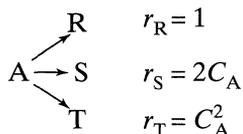
To actually build a commercial-sized side entry reactor is another problem. *Chem. Eng. News* (1997) reports on how this was cleverly done by using a reactor somewhat like a shell-and-tube heat exchanger which used porous walled tubes.

Reactant A flowed through the tubes which contained baffles to encourage lateral mixing of fluid and approach to plug flow. Reactant B, to be kept at a close-to-constant low concentration in the tubes, enters the exchanger through the shell side at a somewhat higher pressure than that in the tubes. Thus, B diffused into the tubes along the whole length of the tubes.

EXAMPLE 7.3 GOOD OPERATING CONDITIONS FOR PARALLEL REACTIONS

Often a desired reaction is accompanied by a variety of undesired side reactions, some of higher order, some of lower order. To see which type of single reactor gives the best product distribution, consider the simplest typical case, the parallel

decompositions of A, $C_{A0} = 2$,



Find the maximum expected C_{S} for isothermal operations

- in a mixed flow reactor
- in a plug flow reactor
- in a reactor of your choice if unreacted A can be separated from the product stream and returned to the feed at $C_{A0} = 2$.

SOLUTION

Since S is the desired product, let us write fractional yields in terms of S. Thus

$$\varphi(\text{S/A}) = \frac{dC_{\text{S}}}{dC_{\text{R}} + dC_{\text{S}} + dC_{\text{T}}} = \frac{2C_{\text{A}}}{1 + 2C_{\text{A}} + C_{\text{A}}^2} = \frac{2C_{\text{A}}}{(1 + C_{\text{A}})^2}$$

Plotting this function we find the curve of Fig. E7.3 whose maximum occurs where

$$\frac{d\varphi}{dC_{\text{A}}} = \frac{d}{dC_{\text{A}}} \left[\frac{2C_{\text{A}}}{(1 + C_{\text{A}})^2} \right] = 0$$

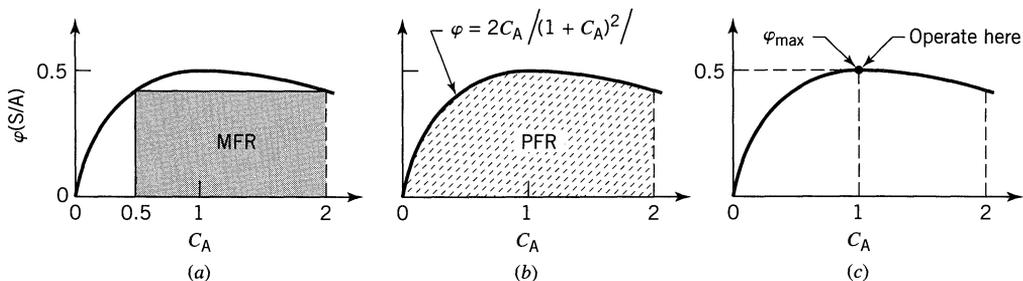


Figure E7.3a, b, c

Solving we find

$$\varphi = 0.5 \quad \text{at} \quad C_{\text{A}} = 1.0$$

(a) Mixed Reactor. Most S is formed when the rectangle under the φ versus C_{A} curve has the largest area. The required conditions can be found either by graphical maximization of rectangles or analytically. Since simple explicit expressions are available in this problem, let us use the latter approach. Then from Eqs. 10 and 13 we find for the area of the rectangle

$$C_{\text{Sf}} = \varphi(\text{S/A}) \cdot (-\Delta C_{\text{A}}) = \frac{2C_{\text{A}}}{(1 + C_{\text{A}})^2} (C_{\text{A}0} - C_{\text{A}})$$

Differentiating and setting to zero to find the conditions at which most S is formed

$$\frac{dC_{Sf}}{dC_A} = \frac{d}{dC_A} \left[\frac{2C_A}{(1 + C_A)^2} (2 - C_A) \right] = 0$$

Evaluating this quantity gives the optimum operating conditions of a mixed reactor as

$$\underline{\underline{C_{Sf} = \frac{2}{3}}} \quad \text{at} \quad C_{Af} = \frac{1}{2}$$

(b) Plug Flow Reactor. The production of S is maximum when the area under the φ versus C_A curve is maximum. This occurs at 100% conversion of A, as seen in Fig. E7.3b. Thus, from Eqs. 9 and 13

$$C_{Sf} = - \int_{C_{A0}}^{C_{Af}} \varphi(S/A) dC_A = \int_0^2 \frac{2C_A}{(1 + C_A)^2} dC_A$$

Evaluating this integral gives, for the plug flow optimum,

$$\underline{\underline{C_{Sf} = 0.867}} \quad \text{at} \quad C_{Af} = 0$$

(c) Any Reactor with Separation and Recycle of Unused Reactant. Since no reactant leaves the system unconverted, what is important is to operate at conditions of highest fractional yield. This is at $C_A = 1$, where $\varphi(S/A) = 0.5$, as shown in Fig. E7.3c. Thus, we should use a mixed flow reactor operating at $C_A = 1$. We would then have 50% of reactant A forming product S.

Comment. Summarizing, we find

$$\begin{aligned} \left(\frac{\text{moles S formed}}{\text{moles A fed}} \right) &= 0.33 \text{ for MFR} \\ &= 0.43 \text{ for a PFR} \\ &= 0.50 \text{ for an MFR with separation and recycle} \end{aligned}$$

Thus, a mixed flow reactor operating at conditions of highest φ with separation and recycle of unused reactant gives the best product distribution. This result is quite general for a set of parallel reactions of different order. ■

EXAMPLE 7.4 BEST OPERATING CONDITIONS FOR PARALLEL REACTIONS

For the reaction of Example 7.3 determine the arrangement of reactors which would produce most S in a flow system where recycle and reconcentration of unreacted feed is not possible. Find $C_{S,\text{total}}$ for this arrangement of reactors.

SOLUTION

From Fig. E7.4 we see that mixed flow followed by plug flow would be best.

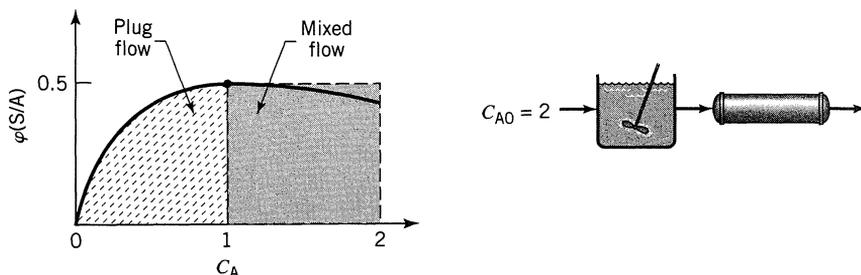


Figure E7.4

Thus, for mixed flow, from Example 7.3

$$C_A = 1, \varphi = 0.5, \quad \text{thus} \quad C_S = \varphi(\Delta C_A) = 0.5(2 - 1) = 0.5 \text{ mol/liter}$$

For plug flow, from Example 7.3

$$C_S = - \int_1^0 \varphi dC_A = \int_0^1 \frac{2C_A}{(1 + C_A)^2} dC_A = 0.386 \text{ mol/liter}$$

Therefore, the total amount of C_S formed is

$$C_{S, \text{total}} = 0.5 + 0.386 = \underline{\underline{0.886 \text{ mol/liter}}}$$

This is only slightly better than for plug flow alone, calculated in Example 7.3.

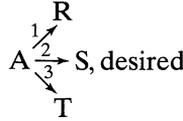
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 Denbigh, K. G., *Trans. Faraday Soc.*, **40**, 352 (1944).
 Denbigh, K. G., *Chem. Eng. Sci.*, **14**, 25 (1961).
 Westerterp, K. R., van Swaaij, W. P. M., and Beenackers, A. A. C. M., *Chemical Reactor Design and Operation*, Wiley, New York, 1984.

PROBLEMS

- 7.1.** For a given feed stream having C_{A0} should we use a PFR or a MFR and should we use a high or low or some intermediate conversion level for the

exit stream if we wish to maximize $\phi(S/A)$? The reaction system is



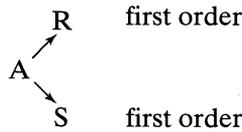
where $n_1, n_2,$ and n_3 are the reaction orders of reactions 1, 2, and 3.

- (a) $n_1 = 1, n_2 = 2, n_3 = 3$
- (b) $n_1 = 2, n_2 = 3, n_3 = 1$
- (c) $n_1 = 3, n_2 = 1, n_3 = 2$

Using separate feeds of A and B sketch the contacting pattern and reactor conditions which would best promote the formation of product R for the following systems of elementary reactions.

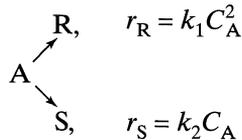
- | | |
|---|--|
| 7.2. $\left. \begin{array}{l} \text{A} + \text{B} \rightarrow \text{R} \\ \text{A} \rightarrow \text{S} \end{array} \right\}$ Flow system | 7.3. $\left. \begin{array}{l} \text{A} + \text{B} \rightarrow \text{R} \\ 2\text{A} \rightarrow \text{S} \\ 2\text{B} \rightarrow \text{T} \end{array} \right\}$ Batch system |
| 7.4. $\left. \begin{array}{l} \text{A} + \text{B} \rightarrow \text{R} \\ \text{A} \rightarrow \text{S} \end{array} \right\}$ Batch system | 7.5. $\left. \begin{array}{l} \text{A} + \text{B} \rightarrow \text{R} \\ 2\text{A} \rightarrow \text{S} \end{array} \right\}$ Flow system |

7.6. Substance A in a liquid reacts to produce R and S as follows:



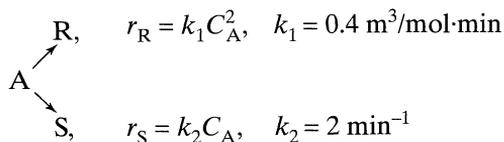
A feed ($C_{A0} = 1, C_{R0} = 0, C_{S0} = 0$) enters two mixed flow reactors in series, ($\tau_1 = 2.5$ min, $\tau_2 = 5$ min). Knowing the composition in the first reactor ($C_{A1} = 0.4, C_{R1} = 0.4, C_{S1} = 0.2$), find the composition leaving the second reactor.

7.7. Substance A in the liquid phase produces R and S by the following reactions:



The feed ($C_{A0} = 1.0, C_{R0} = 0, C_{S0} = 0.3$) enters two mixed flow reactors in series ($\tau_1 = 2.5$ min, $\tau_2 = 10$ min). Knowing the composition in the first reactor ($C_{A1} = 0.4, C_{R1} = 0.2, C_{S1} = 0.7$), find the composition leaving the second reactor.

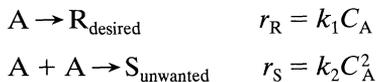
Liquid reactant A decomposes as follows:



A feed of aqueous A ($C_{\text{A}0} = 40 \text{ mol/m}^3$) enters a reactor, decomposes, and a mixture of A, R, and S leaves.

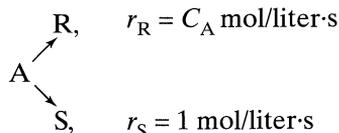
- 7.8.** Find C_{R} , and C_{S} and τ for $X_{\text{A}} = 0.9$ in a mixed flow reactor.
- 7.9.** Find C_{R} , and C_{S} and τ for $X_{\text{A}} = 0.9$ in a plug flow reactor.
- 7.10.** Find the operating condition (X_{A} , τ , and C_{S}) which maximizes C_{S} in a mixed flow reactor.
- 7.11.** Find the operating condition (X_{A} , τ , and C_{R}) which maximizes C_{R} in a mixed flow reactor.

7.12. Reactant A in a liquid either isomerizes or dimerizes as follows:



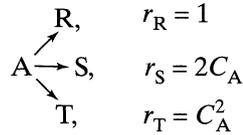
- (a) Write $\varphi(\text{R}/\text{A})$ and $\varphi[\text{R}/(\text{R} + \text{S})]$.
 With a feed stream of concentration $C_{\text{A}0}$ find $C_{\text{R,max}}$ which can be formed
- (b) in a plug flow reactor,
 (c) in a mixed flow reactor.
- A quantity of A of initial concentration $C_{\text{A}0} = 1 \text{ mol/liter}$ is dumped into a batch reactor and is reacted to completion.
- (d) If $C_{\text{S}} = 0.18 \text{ mol/liter}$ in the resultant mixture, what does this tell of the kinetics of the reaction?

7.13. In a reactive environment, chemical A decomposes as follows



For a feed stream $C_{\text{A}0} = 4 \text{ mol/liter}$ what size ratio of two mixed flow reactors will maximize the production rate of R? Also give the composition of A and R leaving these two reactors.

Consider the parallel decomposition of A of different orders



Determine the maximum concentration of desired product obtainable in

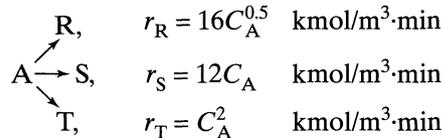
- (a) plug flow,
 (b) mixed flow.

7.14. R is the desired product and $C_{A0} = 2$.

7.15. S is the desired product and $C_{A0} = 4$.

7.16. T is the desired product and $C_{A0} = 5$.

Under ultraviolet radiation, reactant A of $C_{A0} = 10 \text{ kmol/m}^3$ in a process stream ($v = 1 \text{ m}^3/\text{min}$) decomposes as follows.



We wish to design a reactor setup for a specific duty. Sketch the scheme selected, and calculate the fraction of feed transformed into desired product as well as the volume of reactor needed.

7.17. Product R is the desired material.

7.18. Product S is the desired material.

7.19. Product T is the desired material.

The stoichiometry of a liquid-phase decomposition is known to be



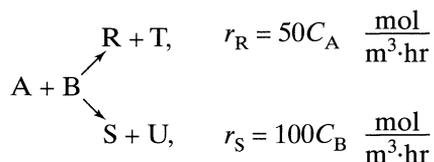
In a series of steady-state flow experiments ($C_{A0} = 100$, $C_{R0} = C_{S0} = 0$) in a laboratory mixed flow reactor the following results are obtained:

| | | | | | | | | | | |
|-------|----|----|----|----|----|----|----|----|----|----|
| C_A | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |
| C_R | 7 | 13 | 18 | 22 | 25 | 27 | 28 | 28 | 27 | 25 |

Further experiments indicate that the level of C_R and C_S have no effect on the progress of the reaction.

- 7.20.** With a feed $C_{A0} = 100$ and exit concentration $C_{Af} = 20$, find C_R at the exit from a plug flow reactor.
- 7.21.** With $C_{A0} = 200$ and $C_{Af} = 20$, find C_R at the exit from a mixed flow reactor.
- 7.22.** How should we operate a mixed flow reactor so as to maximize the production of R? Separation and recycle of unused reactant is not practical.

When aqueous A and aqueous B ($C_{A0} = C_{B0}$) are brought together they react in two possible ways:



to give a mixture whose concentration of active components (A, B, R, S, T, U) is $C_{\text{total}} = C_{A0} + C_{B0} = 60 \text{ mol/m}^3$. Find the size of reactor needed and the R/S ratio produced for 90% conversion of an equimolar feed of $F_{A0} = F_{B0} = 300 \text{ mol/hr}$:

- 7.23.** in a mixed flow reactor;
- 7.24.** in a plug flow reactor;
- 7.25.** in a reactor that gives highest C_R . Chapter 6 tells that this should be plug flow for A and side entry for B. In such a reactor introduce B in such a way that C_B is constant throughout the reactor.

- 7.26.** Reactant A decomposes in an isothermal batch reactor ($C_{A0} = 100$) to produce wanted R and unwanted S, and the following progressive concentration readings are recorded:

| | | | | | | | | | | | |
|-------|-------|----|----|----|----|----|----|----|----|----|------|
| C_A | (100) | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | (0) |
| C_R | (0) | 1 | 4 | 9 | 16 | 25 | 35 | 45 | 55 | 64 | (71) |

Additional runs show that adding R or S does not affect the distribution of products formed and that only A does. Also, it is noted that the total number of moles of A, R, and S is constant.

- (a) Find the φ versus C_A curve for this reaction.
 With a feed of $C_{A0} = 100$ and $C_{Af} = 10$, find C_R
- (b) from a mixed flow reactor,
 (c) from a plug flow reactor,
 (d) and (e): Repeat parts (b) and (c) with the modification that $C_{A0} = 70$.

- 7.27.** The great naval battle, to be known to history as the Battle of Trafalgar (1805), was soon to be joined. Admiral Villeneuve proudly surveyed his powerful fleet of 33 ships stately sailing in single file in the light breeze.

The British fleet under Lord Nelson was now in sight, 27 ships strong. Estimating that it would still be 2 hours before battle, Villeneuve popped open another bottle of burgundy and point by point reviewed his carefully thought-out battle strategy. As was the custom of naval battles at that time, the two fleets would sail in single file parallel to each other and in the same direction, firing their cannons madly. Now, by long experience in battles of this kind, it was a well-known fact that the rate of destruction of a fleet is proportional to the fire power of the opposing fleet. Considering his ships to be on a par, one for one, with the British, Villeneuve was confident of victory. Looking at his sundial, Villeneuve sighed and cursed the light wind—he'd never get it over with in time for his afternoon snooze. "Oh well," he sighed, "c'est la vie." He could see the headlines next morning: "British fleet annihilated, Villeneuve's losses are . . ." Villeneuve stopped short. How many ships would he lose? Villeneuve called over his chief bottle-cork popper, Monsieur Dubois, and asked this question. What answer does he get?

At this very moment, Nelson, who was enjoying the air on the poop deck of the *Victory*, was stuck with the realization that all was ready except for one detail—he had forgotten to formulate his battle plan. Commodore Archibald Forsythe-Smythe, his trusty trusty, was hurriedly called over for a conference. Being familiar with the firepower law, Nelson was loathe to fight the whole French fleet (he could see the headlines too). Now certainly it was no disgrace for Nelson to be defeated in battle by superior forces, so long as he did his best and played the game; however, he had a sneaking suspicion that maybe he could pull a fast one. With a nagging conscience as to whether it was cricket or not, he proceeded to investigate this possibility.

It was possible to "break the line"—that is, to start parallel to the French fleet, and then cut in and divide the enemy fleet into two sections. The rear section could be engaged and disposed of before the front section could turn around and rejoin the fray. Now to the question. Should he split the French fleet and if so, then where? Commodore Forsythe-Smythe, who was so rudely taken from his grog, grumpily agreed to consider this question and to advise Nelson at what point to split the French fleet so as to maximize their chance for success. He also agreed to predict the outcome of the battle using this strategy. What did he come up with?

- 7.28** Find the size of the two reactors needed in Example 7.4 (see Figure E7.4) for a feed flow rate of 100 liter/s, and for reaction rates given in units of mol/liter · s.