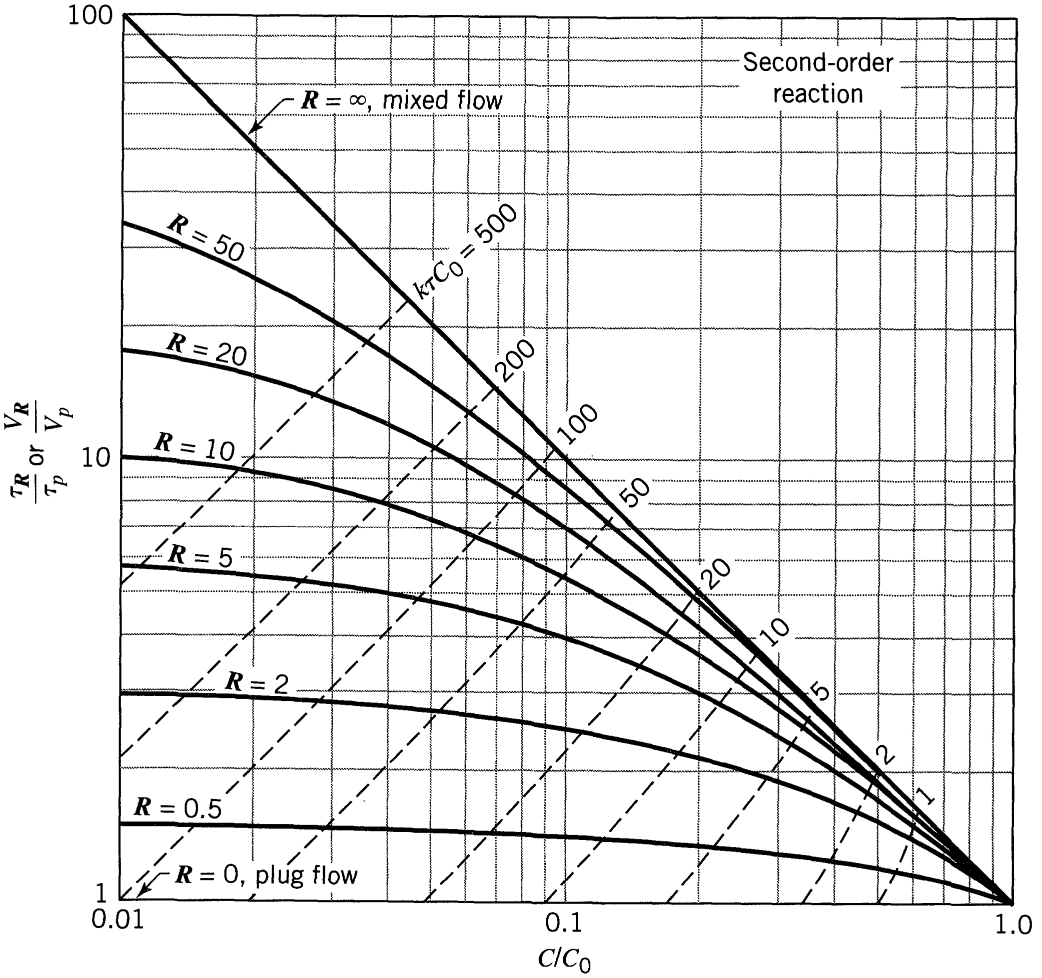


Figure 6.17 Comparison of performance of recycle reactors with plug flow reactors for elementary second-order reactions (Personal communication, from T. J. Fitzgerald and P. Fillesi):

$$2A \rightarrow \text{products}, \qquad \varepsilon = 0$$

$$A + B \rightarrow \text{products}, \qquad C_{A0} = C_{B0} \text{ with } \varepsilon = 0$$

6.4 AUTOCATALYTIC REACTIONS

When a material reacts away by any nth 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.

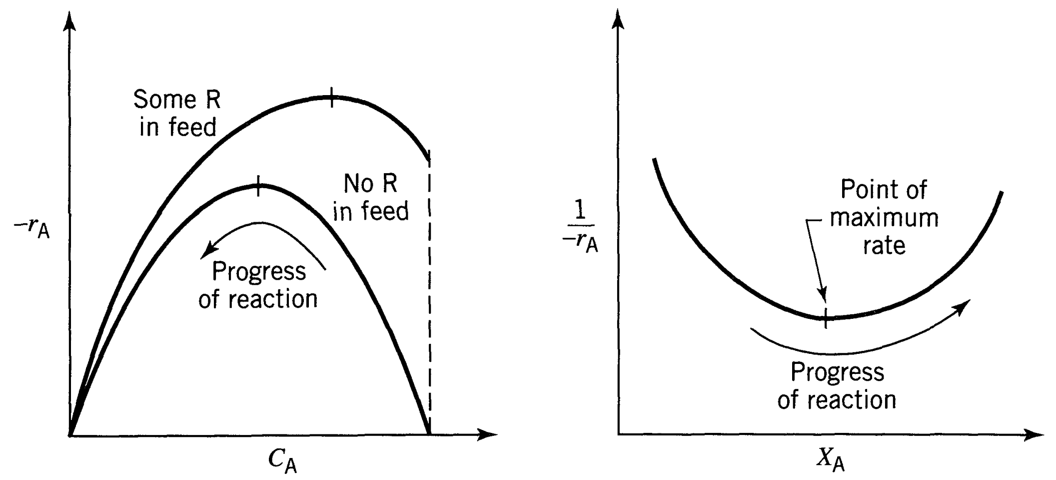


Figure 6.18 Typical rate-concentration curve for autocatalytic reactions, for example:

$$A + R \rightarrow R + R, \qquad -r_A = kC_A^a C_R^r$$

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 nth-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.

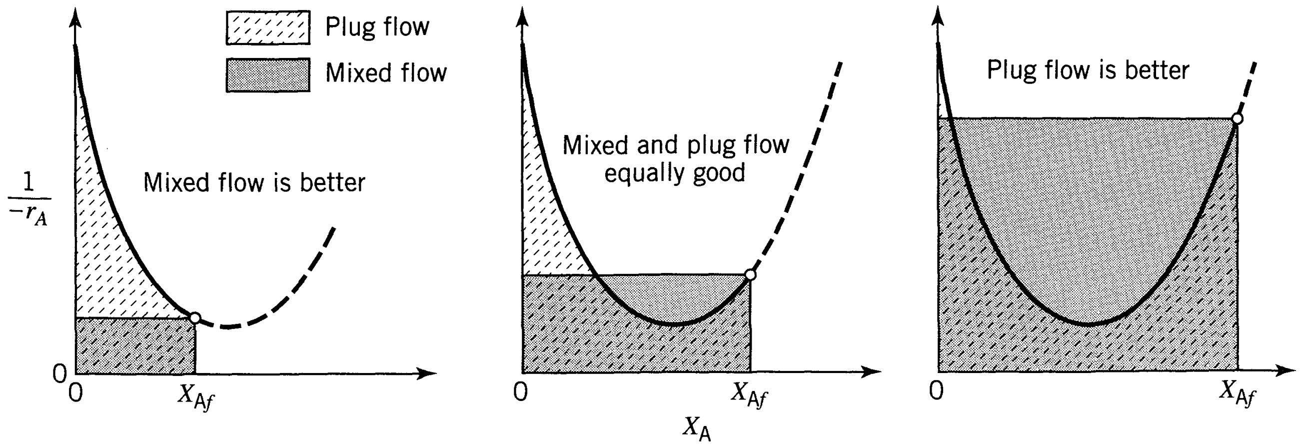


Figure 6.19 For autocatalytic reactions mixed flow is more efficient at low conversions, plug flow is more efficient at high conversions.

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 $\boldsymbol{R}$.

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

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

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

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

then

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

For our case, Eq. 25, we then find

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

where

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

Combining and rearranging then gives for the optimum

$$\boxed{\left.\frac{1}{-r_A}\right|_{X_{Ai}} = \frac{\displaystyle\int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}}{(X_{Af} - X_{Ai})}} \tag{28}$$

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.

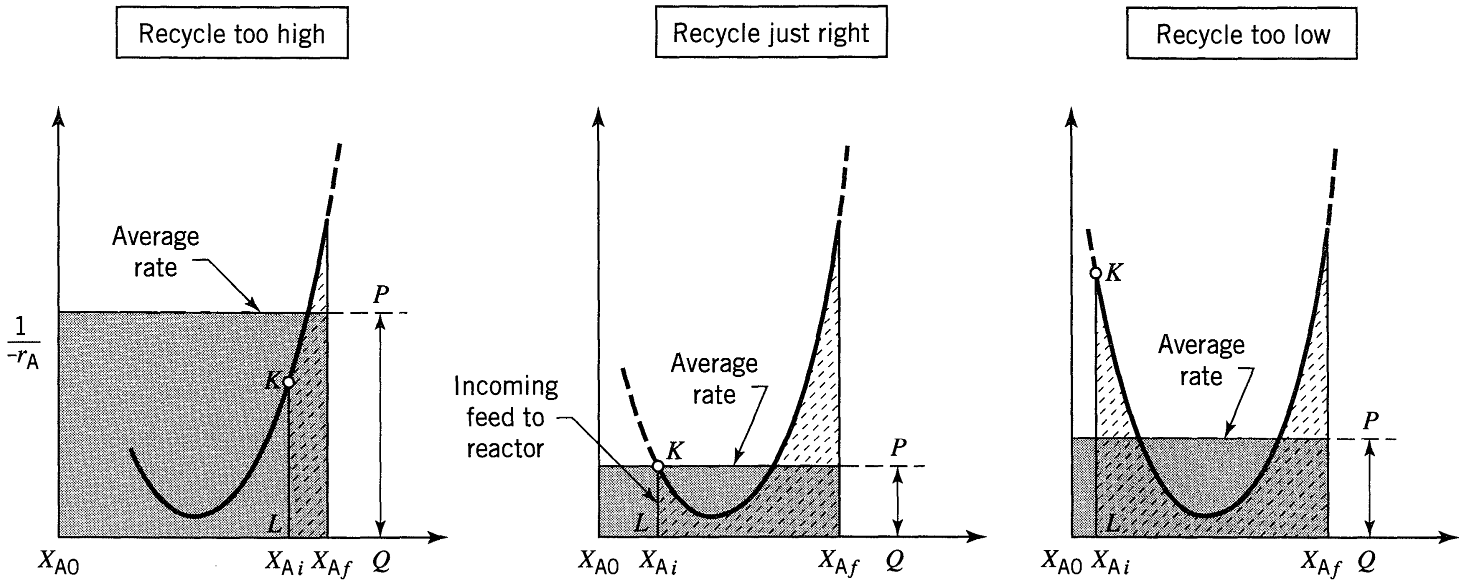


Figure 6.20 Correct recycle ratio for an autocatalytic reaction compared with recycle ratios which are too high and too low.

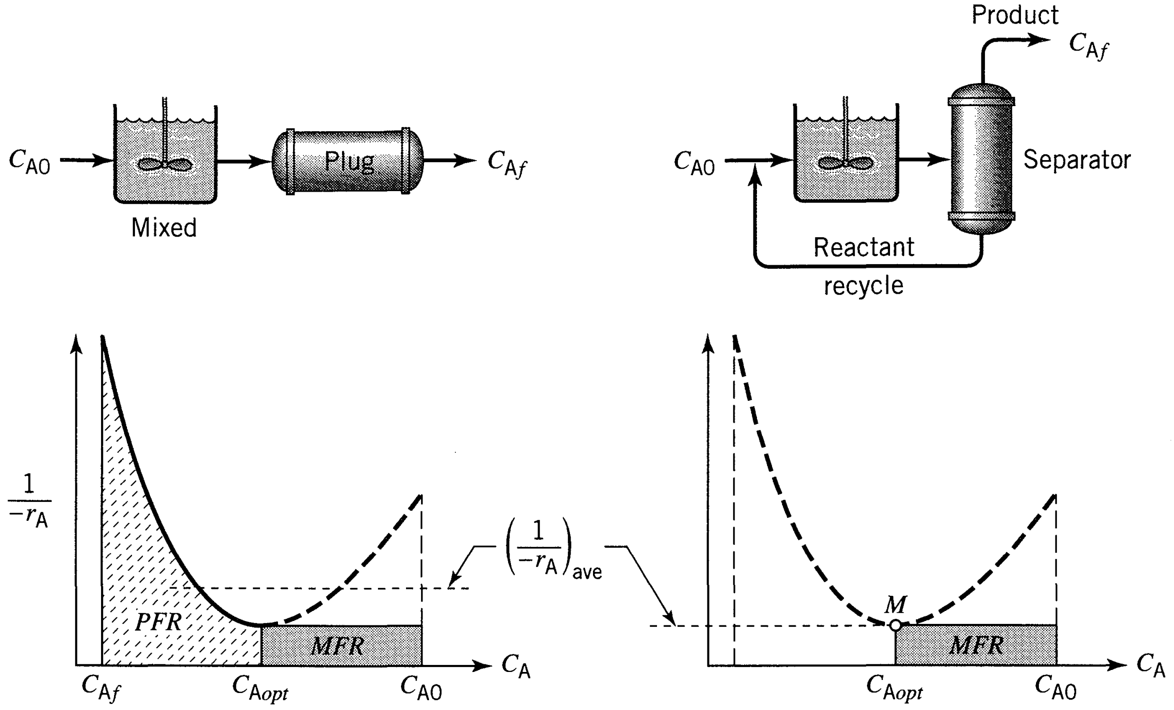
Occurrence of Autocatalytic Reactions. The most important examples of autocatalytic reactions are the broad class of fermentation reactions which result from the reaction of microorganism on an organic feed. When they can be treated as single reactions, the methods of this chapter can be applied directly. 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. 6.21*b*).

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.



(*a*) (*b*)

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 m^3/min of this waste water having C_{A0} = 10 mmol/m^3 to 90% conversion with this enzyme at concentration C_E.

(a) 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 (m^3/min). Sketch your recommended design.

(b) 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?

(c) 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. E6.3*a*, *b*, *c*) so we must prepare to deal with an autocatalytic type reacting system.

Table E6.3

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
$\dfrac{1}{-r_A} = \dfrac{\tau}{C_{A0} - C_A}, \dfrac{\text{m}^3 \cdot \text{min}}{\text{mmol}}$	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. E6.3*a* we find

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

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

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

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

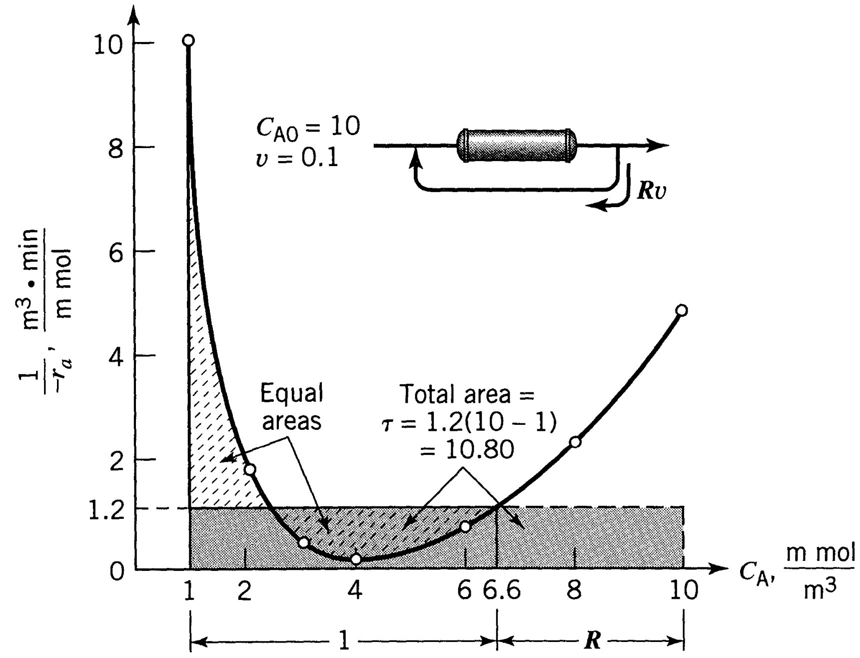


Figure E6.3*a* Plug flow with recycle.

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

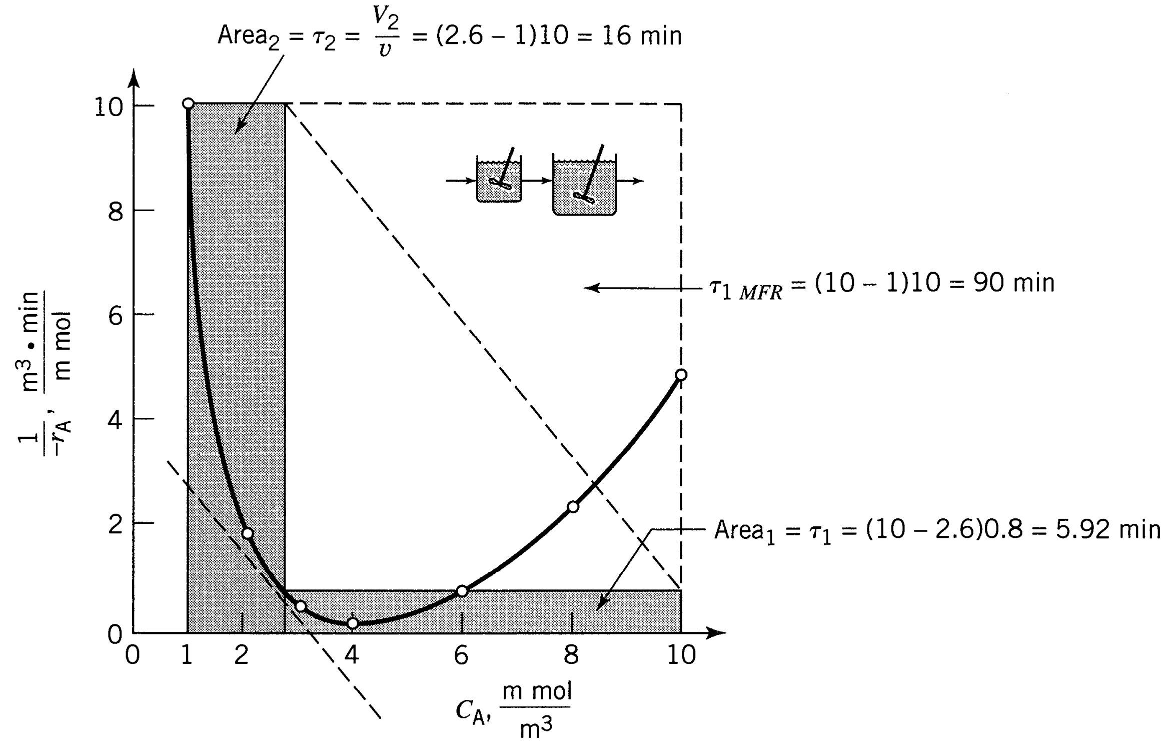


Figure E6.3*b* One and two mixed flow reactors in series.

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

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

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. E6.3*c* we find

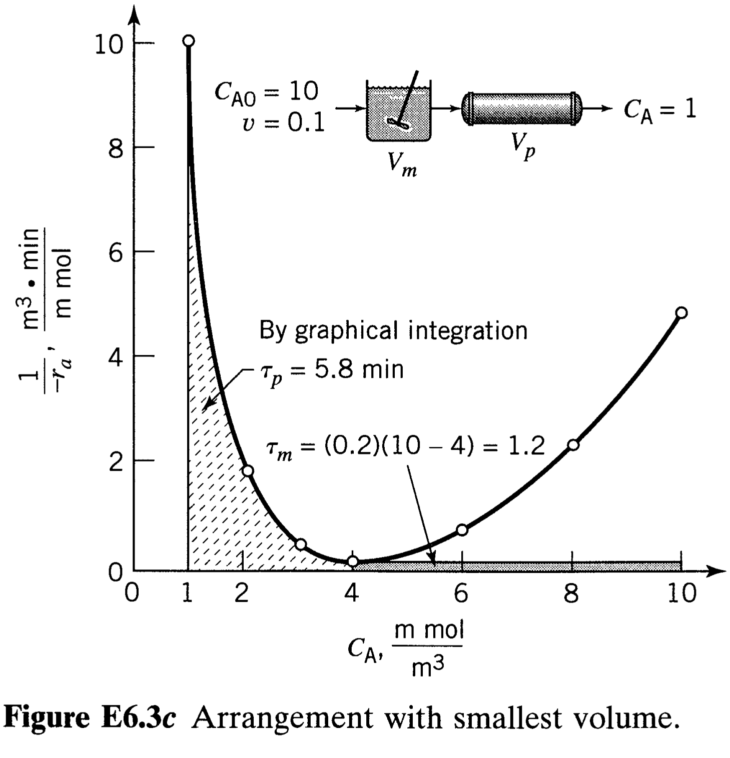


Figure E6.3*c* Arrangement with smallest volume.

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

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

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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 ($A \rightarrow R$, $C_{A0} = 26\ \text{mol/m}^3$) 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 $C_{Af} = 1\ \text{mol/m}^3$?

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, sec	0	20	40	60	80	100	120	140	160
p_A, 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

$$A \rightarrow R, \qquad -r_A = \frac{C_A}{0.2 + C_A} \frac{\text{mol}}{\text{liter} \cdot \text{min}}$$

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 $A \rightarrow R$.

τ, sec	C_{A0}, mmol/liter	C_A, 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 ($\boldsymbol{R} = 2$). 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

$$A \rightarrow R, \qquad -r_A = 1 C_A C_R \frac{\text{mol}}{\text{liter} \cdot \text{min}}$$

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 → R, with $-r_A = 0.001\ C_A C_R$ mol/liter·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 → 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 cm^3. The color change occurs in the first reactor for a steady-state feed rate of 10 cm^3/min, and in the second reactor for a steady-state feed rate of 50 cm^3/min. Find the rate equation for the decomposition of A from this information.

6.17. The elementary irreversible aqueous-phase reaction A + B → 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

$$A + R \rightarrow R + R$$

with rate constant $k = 1$ liter/mol·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:

$$2\mathrm{A} \rightarrow \text{products}, \quad -r_A = [0.005\ \text{liter}/(\text{mol})(\text{min})]C_A^2, \quad C_{A0} = 1\ \text{mol/liter}$$

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?