Chapter 7

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:

$$k_1 \nearrow R \quad \text{(desired product)} \tag{1a}$$
$$A$$
$$k_2 \searrow S \quad \text{(unwanted product)} \tag{1b}$$
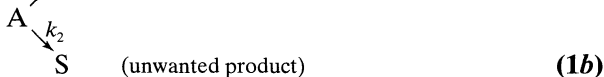
with corresponding rate equations

$$r_R = \frac{dC_R}{dt} = k_1 C_A^{a_1} \tag{2a}$$

$$r_S = \frac{dC_S}{dt} = k_2 C_A^{a_2} \tag{2b}$$

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

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

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.
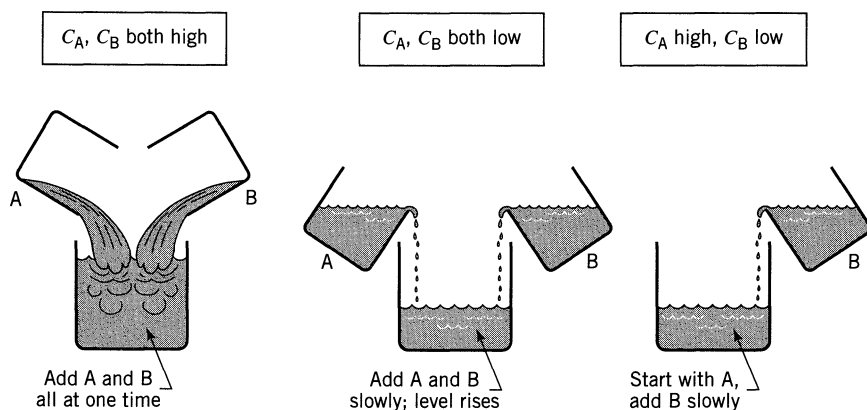

Figure 7.1 Contacting patterns for various combinations of high and low concentration of reactants in noncontinuous operations.
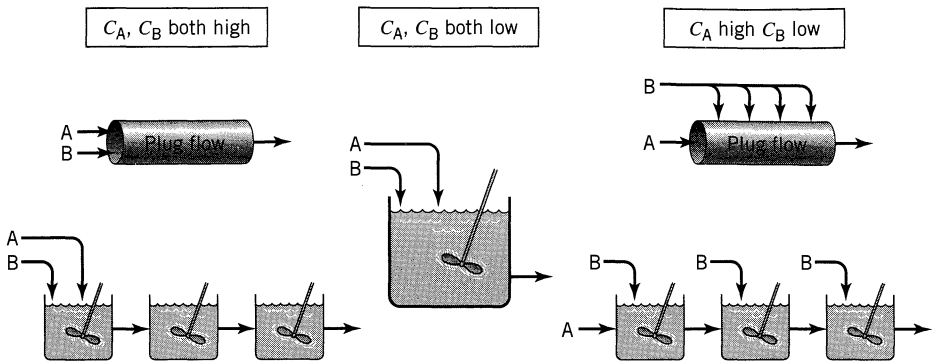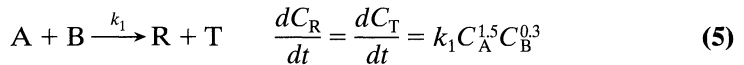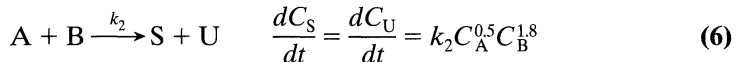
Figure 7.2 Contacting patterns for various combinations of high and low concentration of reactants in continuous flow operations.

EXAMPLE 7.1 **CONTACTING PATTERNS FOR REACTIONS IN PARALLEL**

The desired liquid-phase reaction

$$A + B \xrightarrow{k_1} R + T \qquad \frac{dC_R}{dt} = \frac{dC_T}{dt} = k_1 C_A^{1.5} C_B^{0.3} \qquad (5)$$

is accompanied by the unwanted side reaction

$$A + B \xrightarrow{k_2} S + U \qquad \frac{dC_S}{dt} = \frac{dC_U}{dt} = k_2 C_A^{0.5} C_B^{1.8} \qquad (6)$$

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.
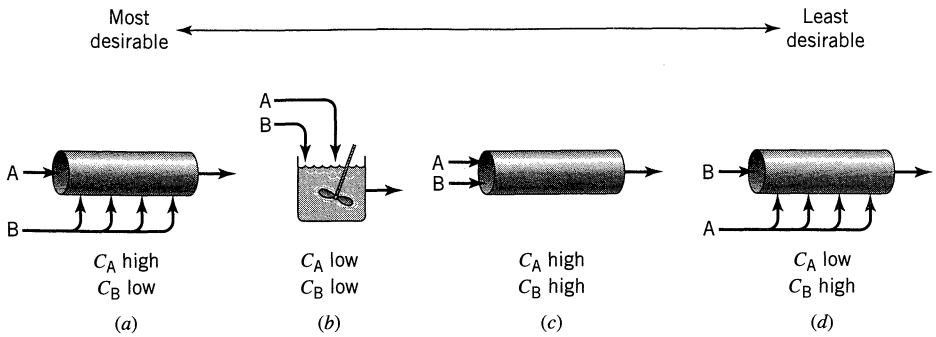
Figure E7.1

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

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

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

$$\Phi = \left(\frac{\text{all R formed}}{\text{all A reacted}}\right) = \frac{C_{R_f}}{C_{A0} - C_{Af}} = \frac{C_{R_f}}{(-\Delta C_A)} = \overline{\varphi}_{\text{in reactor}} \tag{8}$$

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:

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

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

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

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

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

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 $C_{A1}, C_{A2}, \ldots , C_{AN}$, 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

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

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

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

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
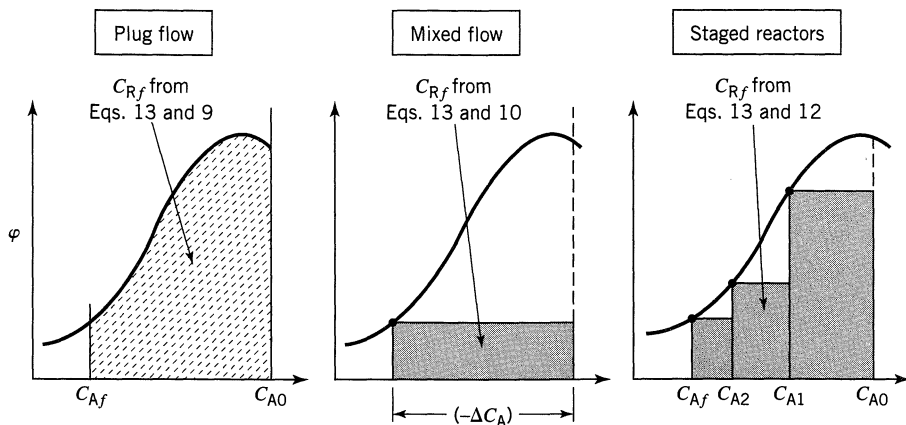
Figure 7.3 Shaded and dashed area gives total R formed.

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:

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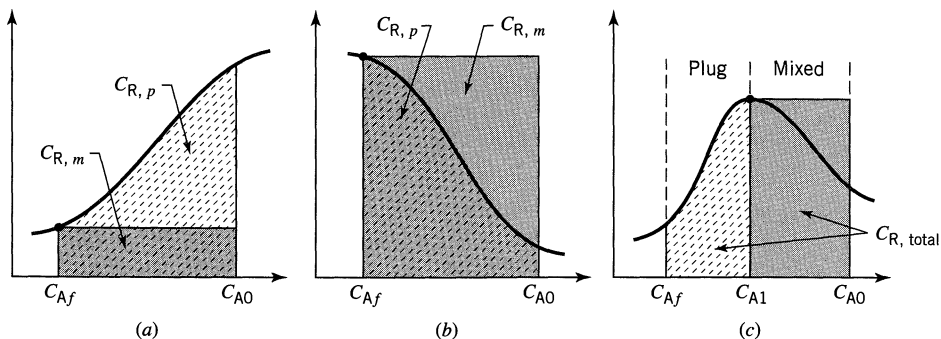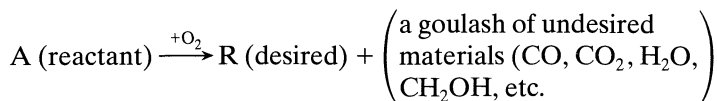

Figure 7.4 The contacting pattern with the largest area produces most R: (*a*) plug flow is best, (*b*) mixed flow is best, (*c*) mixed flow up to C_{A1} followed by plug flow is best.
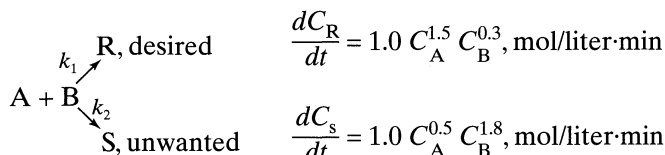
This definition may lead to difficulties. For example, if the reaction is the partial oxidation of a hydrocarbon, as follows:

$$A \text{ (reactant)} \xrightarrow{+O_2} R \text{ (desired)} + \begin{pmatrix} \text{a goulash of undesired} \\ \text{materials } (CO, CO_2, H_2O, \\ CH_2OH, \text{etc.} \end{pmatrix}$$

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

$$A + B \begin{array}{c} \overset{k_1}{\nearrow} R, \text{desired} \\ \underset{k_2}{\searrow} S, \text{unwanted} \end{array}$$

$$\frac{dC_R}{dt} = 1.0 \, C_A^{1.5} C_B^{0.3}, \text{mol/liter·min}$$

$$\frac{dC_s}{dt} = 1.0 \, C_A^{0.5} C_B^{1.8}, \text{mol/liter·min}$$

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.

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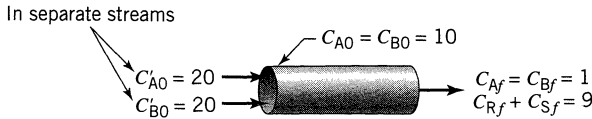
$$\varphi\left(\frac{R}{A}\right) = \frac{dC_R}{dC_R + dC_S} = \frac{k_1 C_A^{1.5} C_B^{0.3}}{k_1 C_A^{1.5} C_B^{0.3} + k_2 C_A^{0.5} C_B^{1.8}} = \frac{C_A}{C_A + C_B^{1.5}}$$

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

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

$$= 0.32$$

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

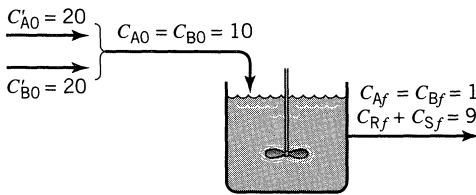$$C_{Sf} = 9(1 - 0.32) = \underline{\underline{6.14}}$$

(b) Mixed Flow

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

$$\Phi_m \left(\frac{R}{A} \right) = \varphi_{\text{at exit}} = \frac{1}{1 + C_A^{0.5}} = 0.5$$
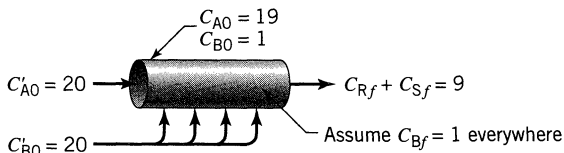
Therefore Eq. 13 gives

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

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

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

$$\Phi\left(\frac{R}{A}\right) = \frac{-1}{C_{A0} - C_{Af}} \int_{C_{A0}}^{C_{Af}} \varphi dC_A = \frac{-1}{19 - 1} \int_{19}^{1} \frac{C_A dC_A}{C_A + (1)^{1.5}}$$

$$= \frac{1}{18}\left[\int_{1}^{19} dC_A - \int_{1}^{19} \frac{dC_A}{C_A + 1}\right] = \frac{1}{18}\left[(19 - 1) - \ln\frac{20}{2}\right] = 0.87$$

Therefore

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

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

To summarize

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

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

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

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, $C_{A0} = 2$,

$$A \begin{array}{l} \nearrow R \qquad r_R = 1 \\ \rightarrow S \qquad r_S = 2C_A \\ \searrow T \qquad r_T = C_A^2 \end{array}$$
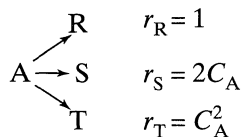
Find the maximum expected C_S for isothermal operations

(a) in a mixed flow reactor
(b) in a plug flow reactor
(c) 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

$$\varphi \, (S/A) = \frac{dC_S}{dC_R + dC_S + dC_T} = \frac{2C_A}{1 + 2C_A + C_A^2} = \frac{2C_A}{(1 + C_A)^2}$$

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

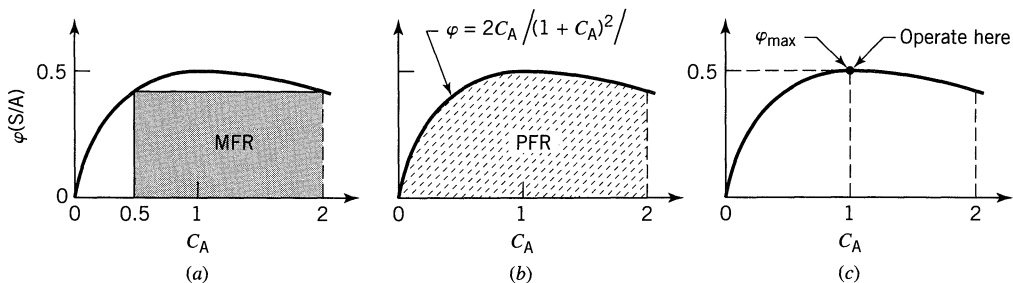$$\frac{d\varphi}{dC_A} = \frac{d}{dC_A} \left[\frac{2C_A}{(1 + C_A)^2} \right] = 0$$

Figure E7.3*a, b, c*

Solving we find

$$\varphi = 0.5 \quad \text{at} \quad C_A = 1.0$$

(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

$$C_{Sf} = \varphi \, (S/A) \cdot (-\Delta C_A) = \frac{2C_A}{(1 + C_A)^2} (C_{A0} - C_A)$$

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

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

(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,

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

(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 φ (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

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

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 $C_{S,total}$ for this arrangement of reactors.

SOLUTION

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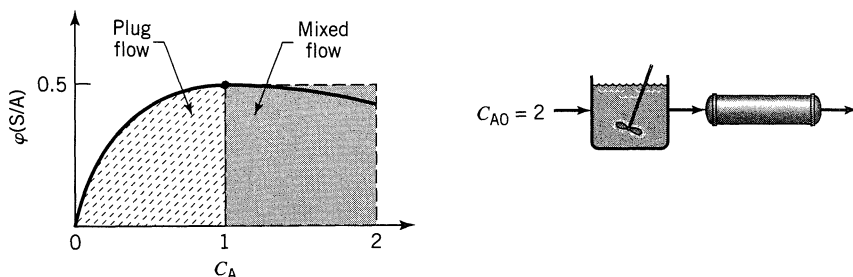

Figure E7.4

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. ∎

REFERENCES

Chem. and Eng. News, 51, April 7, 1997.
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 $\varphi(S/A)$? The reaction system is

$$A \overset{1}{\underset{3}{\overset{2}{\longrightarrow}}} \begin{matrix} R \\ S, \text{desired} \\ T \end{matrix}$$
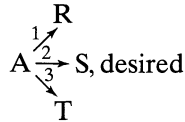
where n_1, n_2, and n_3 are the reaction orders of reactions 1, 2, and 3.
(a) $n_1 = 1$, $n_2 = 2$, $n_3 = 3$
(b) $n_1 = 2$, $n_2 = 3$, $n_3 = 1$
(c) $n_1 = 3$, $n_2 = 1$, $n_3 = 2$

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. $\left.\begin{matrix} A + B \rightarrow R \\ A \rightarrow S \end{matrix}\right\}$ Flow system

7.3. $\left.\begin{matrix} A + B \rightarrow R \\ 2A \rightarrow S \\ 2B \rightarrow T \end{matrix}\right\}$ Batch system

7.4. $\left.\begin{matrix} A + B \rightarrow R \\ A \rightarrow S \end{matrix}\right\}$ Batch system

7.5. $\left.\begin{matrix} A + B \rightarrow R \\ 2A \rightarrow S \end{matrix}\right\}$ Flow system

---

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

$$A \overset{\nearrow}{\underset{\searrow}{}} \begin{matrix} R \quad \text{first order} \\ \\ S \quad \text{first order} \end{matrix}$$
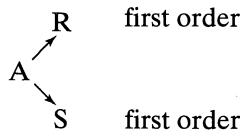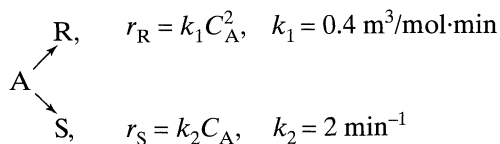
A feed ($C_{A0} = 1$, $C_{R0} = 0$, $C_{S0} = 0$) enters two mixed flow reactors in series, ($\tau_1 = 2.5$ min, $\tau_2 = 5$ min). Knowing the composition in the first reactor ($C_{A1} = 0.4$, $C_{R1} = 0.4$, $C_{S1} = 0.2$), find the composition leaving the second reactor.

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

$$A \overset{\nearrow}{\underset{\searrow}{}} \begin{matrix} R, \quad r_R = k_1 C_A^2 \\ \\ S, \quad r_S = k_2 C_A \end{matrix}$$
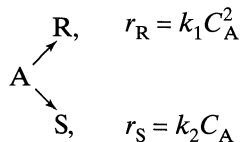
The feed ($C_{A0} = 1.0$, $C_{R0} = 0$, $C_{S0} = 0.3$) enters two mixed flow reactors in series ($\tau_1 = 2.5$ min, $\tau_2 = 10$ min). Knowing the composition in the first reactor ($C_{A1} = 0.4$, $C_{R1} = 0.2$, $C_{S1} = 0.7$), find the composition leaving the second reactor.

Liquid reactant A decomposes as follows:

$$A \nearrow^{R,} \quad r_R = k_1 C_A^2, \quad k_1 = 0.4 \text{ m}^3/\text{mol·min}$$
$$\searrow_{S,} \quad r_S = k_2 C_A, \quad k_2 = 2 \text{ min}^{-1}$$

A feed of aqueous A ($C_{A0} = 40 \text{ mol/m}^3$) enters a reactor, decomposes, and a mixture of A, R, and S leaves.

7.8. Find C_R, and C_S and τ for $X_A = 0.9$ in a mixed flow reactor.

7.9. Find C_R, and C_S and τ for $X_A = 0.9$ 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:

$$A \rightarrow R_{\text{desired}} \qquad r_R = k_1 C_A$$
$$A + A \rightarrow S_{\text{unwanted}} \qquad r_S = k_2 C_A^2$$
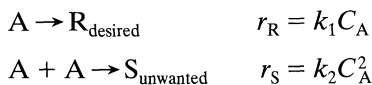
    (a) Write $\varphi(R/A)$ and $\varphi[R/(R + S)]$.
With a feed stream of concentration C_{A0} find $C_{R,\text{max}}$ which can be formed
    (b) in a plug flow reactor,
    (c) in a mixed flow reactor.
A quantity of A of initial concentration $C_{A0} = 1$ mol/liter is dumped into a batch reactor and is reacted to completion.
    (d) If $C_S = 0.18$ 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

$$A \nearrow^{R,} \quad r_R = C_A \text{ mol/liter·s}$$
$$\searrow_{S,} \quad r_S = 1 \text{ mol/liter·s}$$
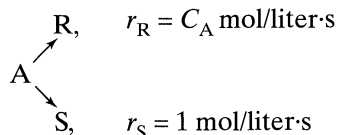
For a feed stream $C_{A0} = 4$ mol/liter what size ratio of two mixed flow reactors will maximize the production rate of R? Also give the composition of A and R leaving these two reactors.

Consider the parallel decomposition of A of different orders

$$A \begin{array}{l} \nearrow \text{R,} \quad r_R = 1 \\ \rightarrow \text{S,} \quad r_S = 2C_A \\ \searrow \text{T,} \quad r_T = C_A^2 \end{array}$$
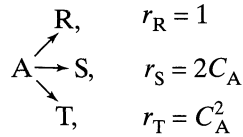
Determine the maximum concentration of desired product obtainable in
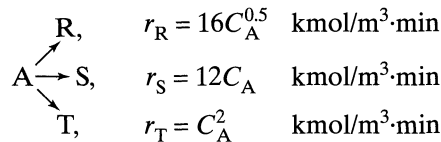 **(a)** plug flow,
  (b) mixed flow.

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 $C_{A0} = 10$ kmol/m³ in a process stream ($v = 1$m³/min) decomposes as follows.

$$A \begin{array}{l} \nearrow \text{R,} \quad r_R = 16C_A^{0.5} \quad \text{kmol/m}^3\text{·min} \\ \rightarrow \text{S,} \quad r_S = 12C_A \quad \text{kmol/m}^3\text{·min} \\ \searrow \text{T,} \quad r_T = C_A^2 \quad \text{kmol/m}^3\text{·min} \end{array}$$

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

$$A \begin{array}{l} \nearrow \text{R} \\ \searrow \text{S} \end{array}$$
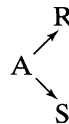
In a series of steady-state flow experiments ($C_{A0} = 100$, $C_{R0} = C_{S0} = 0$) in a laboratory mixed flow reactor the following results are obtained:

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:

$$A + B \begin{array}{c} \nearrow \\ \\ \searrow \end{array} \begin{array}{l} R + T, \qquad r_R = 50C_A \quad \dfrac{\text{mol}}{\text{m}^3 \cdot \text{hr}} \\ \\ S + U, \qquad r_S = 100C_B \quad \dfrac{\text{mol}}{\text{m}^3 \cdot \text{hr}} \end{array}$$
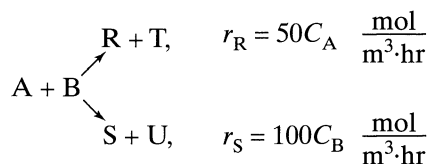
to give a mixture whose concentration of active components (A, B, R, S, T, U) is $C_{\text{total}} = C_{A0} + C_{B0} = 60$ mol/m³. Find the size of reactor needed and the R/S ratio produced for 90% conversion of an equimolar feed of $F_{A0} = F_{B0} = 300$ mol/hr:

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.
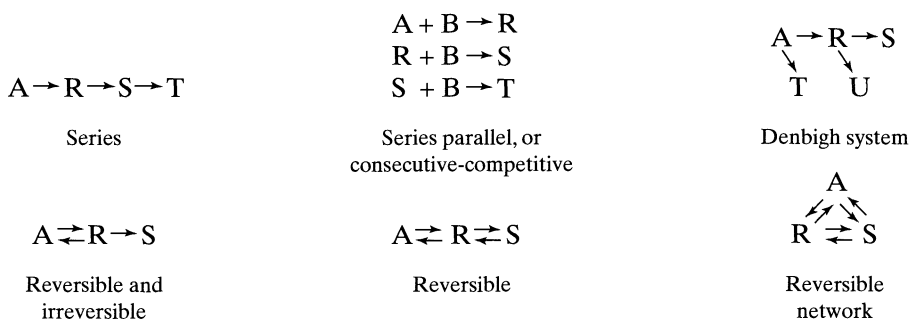
It was possible to "break the line"—that is, to start parallel to the French fleet, and then cut in and divide the enemy fleet into two sections. The rear section could be engaged and disposed of before the front section could turn around and rejoin the fray. Now to the question. Should he split the 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.

Chapter 8

Potpourri of Multiple Reactions

Chapter 7 considered reactions in parallel. These are reactions where the product does not react further. This chapter considers all sorts of reactions where the product formed may react further. Here are some examples:

$$A + B \rightarrow R$$
$$R + B \rightarrow S$$
$$A \rightarrow R \rightarrow S \rightarrow T \qquad S + B \rightarrow T$$

$$A \rightarrow R \rightarrow S$$
$$\searrow \quad \searrow$$
$$T \qquad U$$

<div style="text-align:center">

Series   Series parallel, or consecutive-competitive   Denbigh system

</div>

$$A \rightleftarrows R \rightarrow S \qquad\qquad A \rightleftarrows R \rightleftarrows S$$

$$A$$
$$\nearrow \searrow$$
$$R \rightleftarrows S$$

<div style="text-align:center">

Reversible and irreversible   Reversible   Reversible network

</div>

We develop or present the performance equations of some of the simpler systems and point out their special features such as maxima of intermediates.

8.1 IRREVERSIBLE FIRST-ORDER REACTIONS IN SERIES

For easy visualization consider that the reactions

$$A \xrightarrow{\ k_1\ } R \xrightarrow{\ k_2\ } S \tag{1}$$

proceed only in the presence of light, that they stop the instant the light is turned off, and that for a given intensity of radiation, the rate equations are

$$r_A = -k_1 C_A \tag{2}$$

$$r_R = k_1 C_A - k_2 C_R \tag{3}$$

$$r_S = k_2 C_R \tag{4}$$

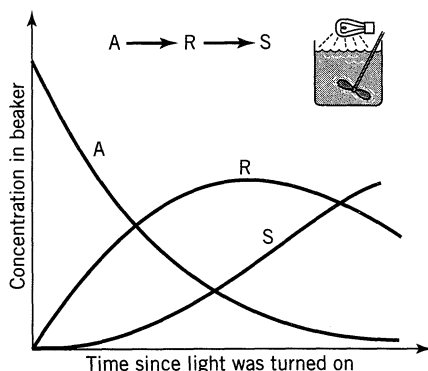Our discussion centers about these reactions.

Figure 8.1 Concentration-time curves if the contents of the beaker are irradiated uniformly.

Qualitative Discussion About Product Distribution.   Consider the following two ways of treating a beaker containing A: First, the contents are uniformly irradiated; second, a small stream is continuously withdrawn from the beaker, irradiated, and returned to the beaker; the rate of absorption of radiant energy is the same in the two cases. The two schemes are shown in Figs. 8.1 and 8.2. During this process A disappears and products are formed. Is the product distribution of R and S different in the two beakers? Let us see whether we can answer this question qualitatively for all values of the rate constants.

In the first beaker, when the contents are being irradiated all at the same time, the first bit of light will attack A alone because only A is present at the start. The result is that R is formed. With the next bit of light both A and R will compete; however, A is in very large excess so it will preferentially absorb the radiant energy to decompose and form more R. Thus, the concentration of R will rise while the concentration of A will fall. This process will continue until R is present in high enough concentration so that it can compete favorably with A for the radiant energy. When this happens, a maximum R concentration is reached. After this the decomposition of R becomes more rapid than its rate of
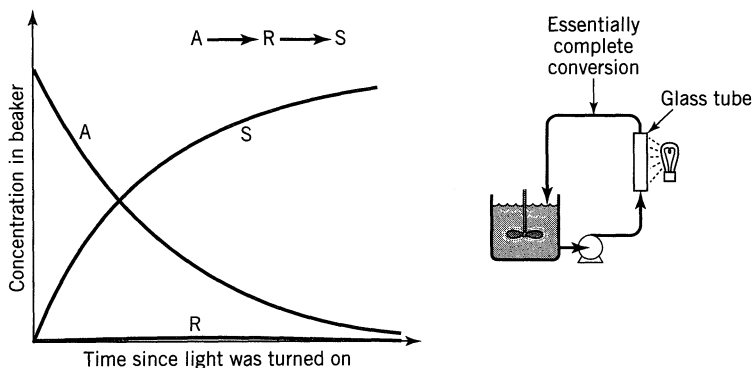

Figure 8.2 Concentration-time curves for the contents of the beaker if only a small portion of the fluid is irradiated at any instant.

formation and its concentration drops. A typical concentration time curve is shown in Fig. 8.1.

In the alternative way of treating A, a small fraction of the beaker's contents is continuously removed, irradiated, and returned to the beaker. Although the total absorption rate is the same in the two cases, the intensity of radiation received by the removed fluid is greater, and it could well be, if the flow rate is not too high, that the fluid being irradiated reacts essentially to completion. In this case, then, A is removed and S is returned to the beaker. So, as time passes the concentration of A slowly decreases in the beaker, S rises, while R is absent. This progressive change is shown in Fig. 8.2.

These two methods of reacting the contents of the beaker yield different product distributions and represent the two extremes in possible operations, one with a maximum possible formation of R and the other with a minimum, or no formation, of R. How can we best characterize this behavior? We note in the first method that the contents of the beaker remain homogeneous throughout, all changing slowly with time, whereas in the second a stream of highly reacted fluid is continually being mixed with fresh fluid. In other words, we are mixing two streams of different compositions. This discussion suggests the following rule governing product distribution for reactions in series.

> *For irreversible reactions in series the mixing of fluid of different composition is the key to the formation of intermediate. The maximum possible amount of any and all intermediates is obtained if fluids of different compositions and at different stages of conversion are not allowed to mix.*   **(5)**

As the intermediate is frequently the desired reaction product, this rule allows us to evaluate the effectiveness of various reactor systems. For example, plug flow and batch operations should both give a maximum R yield because here there is no mixing of fluid streams of different compositions. On the other hand, the mixed reactor should not give as high a yield of R as possible because a fresh stream of pure A is being mixed continually with an already reacted fluid in the reactor.

The following examples illustrate the point just made. We then give a quantitative treatment which will verify these qualitative findings.

EXAMPLE 8.1   ***FAVORABLE CONTACTING PATTERNS FOR ANY SET OF IRREVERSIBLE REACTIONS IN SERIES, NOT JUST*** $A \rightarrow R \rightarrow S$

Which contacting pattern of Figs. E8.1, when properly operated, can give a higher concentration of any intermediate, the contacting pattern on the left or the one on the right?
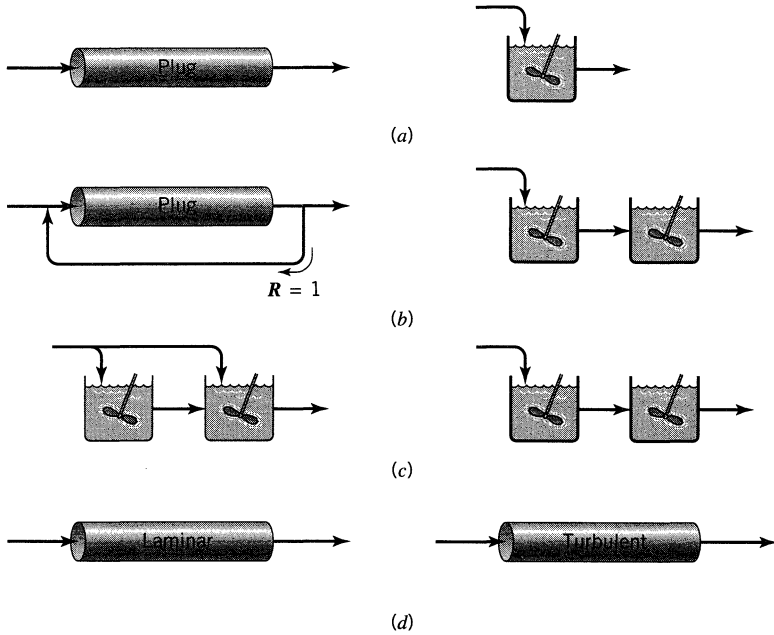
(a)

(b)

$R = 1$

(c)

(d)

**Figure E8.1*a*, *b*, *c*, *d***

SOLUTION

Focusing on the mixing rule for reactions in series, that the extent of mixing of streams of different composition should be minimized, we reason

for part (a): The left pattern is better; in fact it is the best possible flow scheme.

for part (b): Looking at Figs. 6.5, 6.6, and 6.16, 6.17 of Chapter 6 we see that the left is closer to plug flow for both first- and for second-order reactions. So we generalize this to any positive order reaction.

for part (c): The right pattern is better because it is closer to plug flow.

for part (d): Turbulent flow has less intermixing of fluids of different ages, less bypassing; hence, the right scheme is better.

Note. In the quantitative analysis that follows we verify this general and important rule.

Quantitative Treatment, Plug Flow or Batch Reactor. In Chapter 3 we developed the equations relating concentration with time for all components of the unimolecular-type reactions

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$
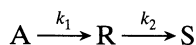
in batch reactors. The derivations assumed that the feed contained no reaction products R or S. If we replace reaction time by the space time, these equations apply equally well for plug flow reactors, thus

$$\frac{C_A}{C_{A0}} = e^{-k_1 \tau} \qquad \text{(3.47) or (6)}$$

$$\frac{C_R}{C_{A0}} = \frac{k_1}{k_2 - k_1} (e^{-k_1 \tau} - e^{-k_2 \tau}) \qquad \text{(3.49) or (7)}$$

$$C_S = C_{A0} - C_A - C_R$$

The maximum concentration of intermediate and the time at which it occurs is given by

$$\frac{C_{R,max}}{C_{A0}} = \left(\frac{k_1}{k_2}\right)^{k_2/(k_2 - k_1)} \qquad \text{(3.52) or (8)}$$

$$\tau_{p,opt} = \frac{1}{k_{\log mean}} = \frac{\ln(k_2/k_1)}{k_2 - k_1} \qquad \text{(3.51) or (9)}$$

This is also the point at which the rate of formation of S is most rapid.

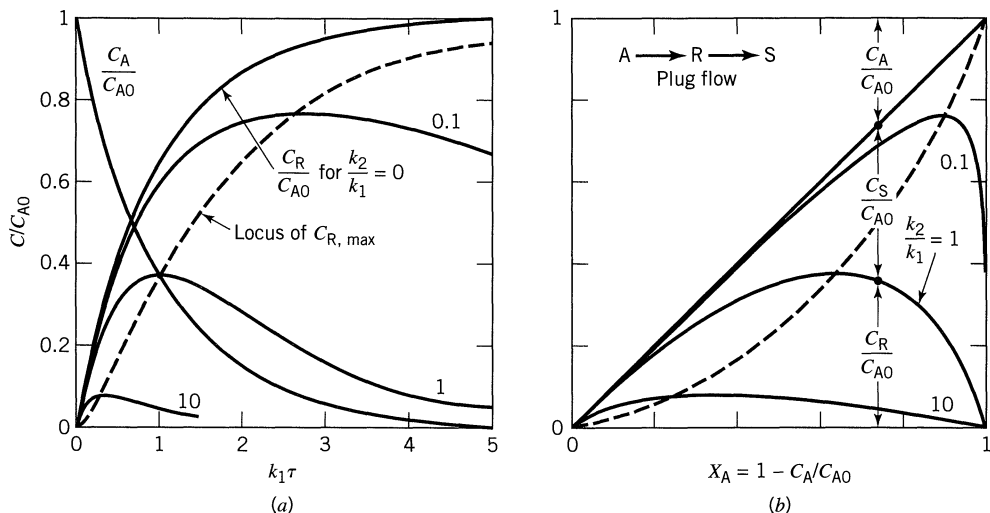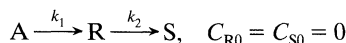Figure 8.3a, prepared for various k_2/k_1 values, illustrates how this ratio governs

Figure 8.3a, b Behavior of unimolecular-type reactions

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S, \quad C_{R0} = C_{S0} = 0$$

in a plug flow reactor: (a) concentration-time curves, and (b) relative concentration of the reaction components. See Fig. 8.13 for a more detailed figure.
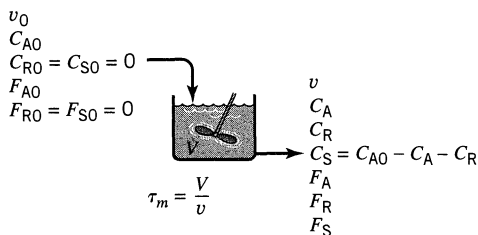
v_0
C_{A0}
$C_{R0} = C_{S0} = 0$
F_{A0}
$F_{R0} = F_{S0} = 0$

$\tau_m = \dfrac{V}{v}$

v
C_A
C_R
$C_S = C_{A0} - C_A - C_R$
F_A
F_R
F_S

Figure 8.4 Variables for reactions in series (no R or S in the feed) occurring in a mixed flow reactor.

the concentration-time curves of the intermediate R. Figure 8.3*b*, a time-independent plot, relates the concentration of all reaction components; also see Eq. 37.

Quantitative Treatment, Mixed Flow Reactor.   Let us develop the concentration-time curves for this reaction when it takes place in a mixed flow reactor. This may be done by referring to Fig. 8.4. Again, the derivation will be limited to a feed which contains no reaction product R or S.

By the steady-state material balance we obtain for any component

$$\text{input} = \text{output} + \text{disappearance by reaction} \qquad \textbf{(4.1)} \text{ or } \textbf{(10)}$$

which for reactant A becomes

$$F_{A0} = F_A + (-r_A)V$$

or

$$vC_{A0} = vC_A + k_1C_AV$$

Noting that

$$\frac{V}{v} = \tau_m = \bar{t} \tag{11}$$

we obtain for A, on rearranging,

$$\frac{C_A}{C_{A0}} = \frac{1}{1 + k_1\tau_m} \tag{12}$$

For component R the material balance, Eq. 10, becomes

$$vC_{R0} = vC_R + (-r_R)V$$

or

$$0 = vC_R + (-k_1C_A + k_2C_R)V$$

With Eqs. 11 and 12 we obtain, on rearranging,

$$\frac{C_R}{C_{A0}} = \frac{k_1 \tau_m}{(1 + k_1 \tau_m)(1 + k_2 \tau_m)} \tag{13}$$

C_S is found by simply noting that at any time

$$C_A + C_R + C_S = C_{A0} = \text{constant}$$

hence

$$\frac{C_S}{C_{A0}} = \frac{k_1 k_2 \tau_m^2}{(1 + k_1 \tau_m)(1 + k_2 \tau_m)} \tag{14}$$

The location and maximum concentration of R are found by determining $dC_R/d\tau_m = 0$. Thus

$$\frac{dC_R}{d\tau_m} = 0 = \frac{C_{A0} k_1 (1 + k_1 \tau_m)(1 + k_2 \tau_m) - C_{A0} k_1 \tau_m [k_1 (1 + k_2 \tau_m) + (1 + k_1 \tau_m) k_2]}{(1 + k_1 \tau_m)^2 (1 + k_2 \tau_m)^2}$$

which simplifies neatly to give

$$\boxed{\tau_{m,\text{opt}} = \frac{1}{\sqrt{k_1 k_2}}} \tag{15}$$

The corresponding concentration of R is given by replacing Eq. 15 in Eq. 13. On rearranging, this becomes

$$\boxed{\frac{C_{R,\text{max}}}{C_{A0}} = \frac{1}{[(k_2/k_1)^{1/2} + 1]^2}} \tag{16}$$

Typical concentration-time curves for various k_2/k_1 values are shown in Fig. 8.5*a*. A time-independent plot, Fig. 8.5*b*, relates the concentrations of reactant and products.

Remarks on Performance Characteristics, Kinetic Studies, and Design. Figures 8.3*a* and 8.5*a* show the general time-concentration behavior for plug and mixed flow reactors and are an aid in visualizing the actual progress of the reaction. Comparison of these figures shows that except when $k_1 = k_2$ the plug flow reactor always requires a smaller time than does the mixed reactor to achieve the maximum concentration of R, the difference in times becoming progressively
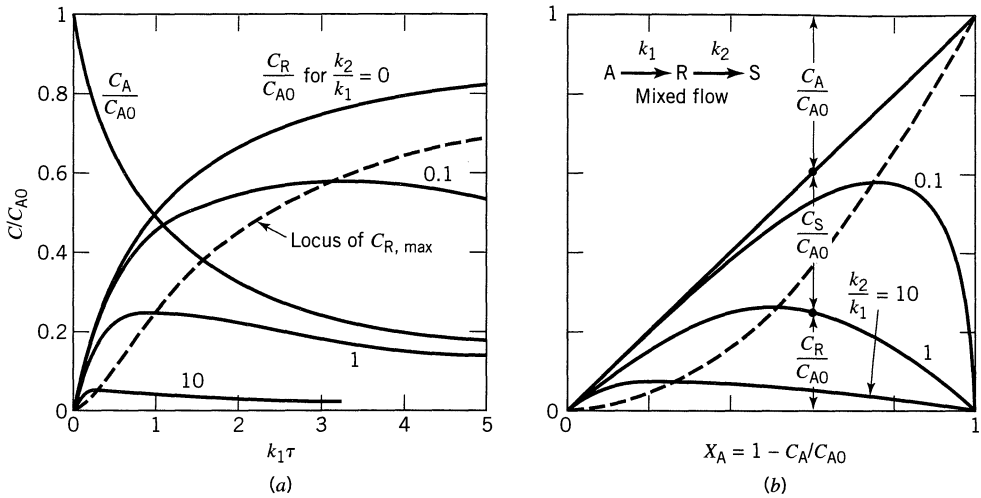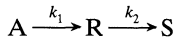
Figure 8.5a, b Behavior of unimolecular-type reactions

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

in a mixed flow reactor: (a) concentration-time curves, and (b) relative concentration of the reaction components. See Fig. 8.14 for a more detailed figure.

larger as k_2/k_1 departs from unity (see Eqs. 15 and 9). In addition, for any reaction the maximum obtainable concentration of R in a plug flow reactor is always higher than the maximum obtainable in a mixed reactor (see Eqs. 16 and 8). This verifies the conclusions arrived at by qualitative reasoning.

Figures 8.3b and 8.5b, time-independent plots, show the distribution of materials during reaction. Such plots find most use in kinetic studies because they allow the determination of k_2/k_1 by matching the experimental points with one of the family of curves on the appropriate graph. Figures 8.13 and 8.14 are more detailed representations of these two figures. Though not shown in the figures, C_S can be found by difference between C_{A0} and $C_A + C_R$.

Figure 8.6 presents the fractional yield curves for intermediate R as a function of the conversion level and the rate constant ratio. These curves clearly show that the fractional yield of R is always higher for plug flow than for mixed flow for any conversion level. A second important observation in this figure concerns the extent of conversion of A we should plan for. If for the reaction considered k_2/k_1 is much smaller than unity, we should design for a high conversion of A and probably dispense with recycle of unused reactant. However, if k_2/k_1 is greater than unity, the fractional yield drops very sharply even at low conversion. Hence, to avoid obtaining unwanted S instead of R we must design for a very small conversion of A per pass, separation of R, and recycle of unused reactant. In such a case large quantities of material will have to be treated in the A-R separator and recycled, and this part of the process will figure prominently in cost considerations.
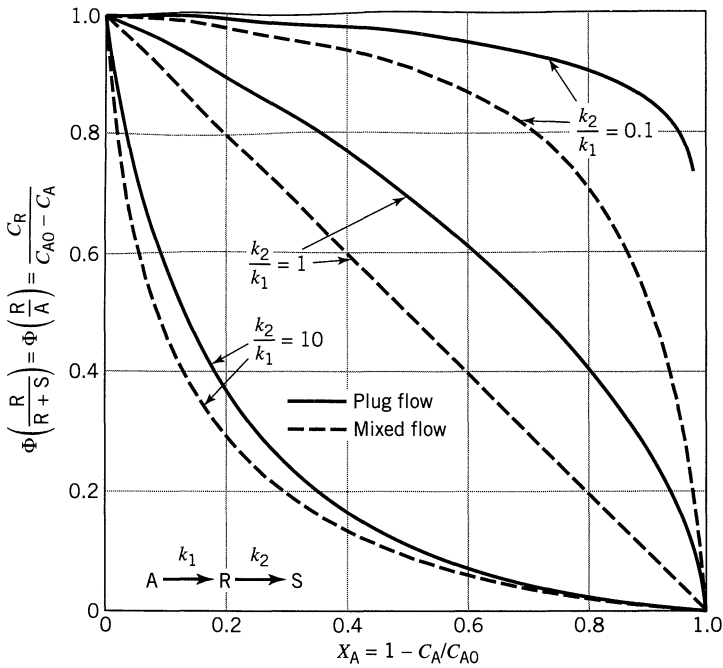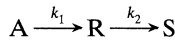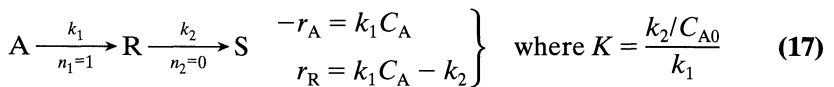
Figure 8.6 Comparison of the fractional yields of R in mixed flow and plug flow reactors for the unimolecular-type reactions

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

8.2 FIRST-ORDER FOLLOWED BY ZERO-ORDER REACTION

Let the reactions be

$$A \underset{n_1=1}{\xrightarrow{k_1}} R \underset{n_2=0}{\xrightarrow{k_2}} S \qquad \left. \begin{array}{l} -r_A = k_1 C_A \\[4pt] r_R = k_1 C_A - k_2 \end{array} \right\} \quad \text{where } K = \frac{k_2/C_{A0}}{k_1} \qquad (17)$$

For *batch or plug flow* with $C_{R0} = C_{S0} = 0$ integration gives

$$\boxed{\frac{C_A}{C_{A0}} = e^{-k_1 t}} \qquad (18)$$

and

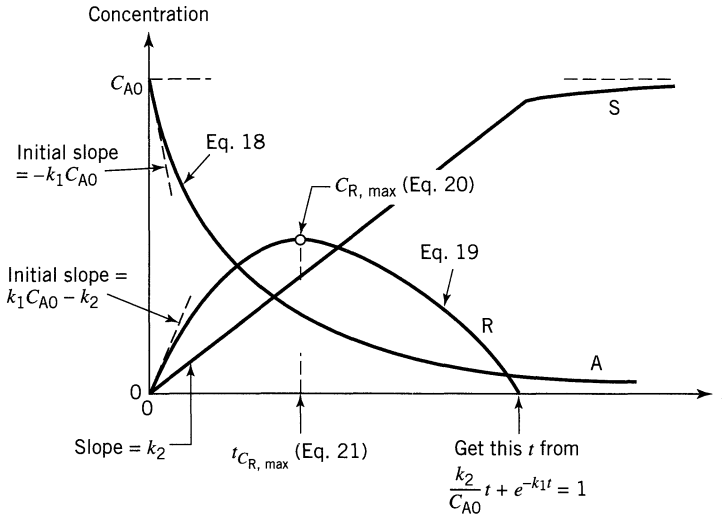$$\boxed{\frac{C_R}{C_{A0}} = 1 - e^{-k_1 t} - \frac{k_2}{C_{A0}} t} \qquad (19)$$

Figure 8.7 Product distribution for the reactions $A \xrightarrow{n=1} R \xrightarrow{n=0} S$

The maximum concentration of intermediate, $C_{R,max}$, and the time when this occurs is found to be

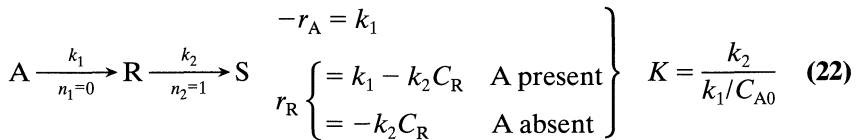$$\boxed{\frac{C_{R,max}}{C_{A0}} = 1 - K(1 - \ln K)} \qquad (20)$$

and

$$\boxed{t_{R,max} = \frac{1}{k_1} \ln \frac{1}{K}} \qquad (21)$$

Graphically we show these findings in Fig. 8.7.

8.3   ZERO-ORDER FOLLOWED BY FIRST-ORDER REACTION

Let the reactions be

$$A \xrightarrow[n_1=0]{k_1} R \xrightarrow[n_2=1]{k_2} S \qquad \left. \begin{array}{l} -r_A = k_1 \\ r_R \begin{cases} = k_1 - k_2 C_R \quad \text{A present} \\ = -k_2 C_R \qquad \text{A absent} \end{cases} \end{array} \right\} \quad K = \frac{k_2}{k_1/C_{A0}} \qquad (22)$$

for *batch or plug flow with* $C_{R0} = C_{S0} = 0$ integration gives

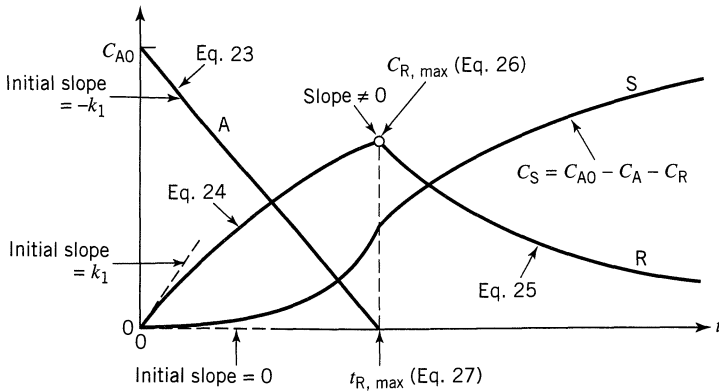$$\boxed{\frac{C_A}{C_{A0}} = 1 - \frac{k_1 t}{C_{A0}}} \qquad (23)$$

Figure 8.8 Product distribution for the reactions $A \xrightarrow{n=0} R \xrightarrow{n=1} S$

and

$$\frac{C_R}{C_{A0}} \begin{cases} = \dfrac{1}{K}(1 - e^{-k_2 t}) & t < \dfrac{C_{A0}}{k_1} \qquad (24) \\[2ex] = \dfrac{1}{K}(e^{K - k_2 t} - e^{-k_2 t}) & t > \dfrac{C_{A0}}{k_1} \qquad (25) \end{cases}$$

The maximum concentration of intermediate, $C_{R,max}$, and the time when this occurs is found to be

$$\frac{C_{R,max}}{C_{A0}} = \frac{1 - e^{-K}}{K} \qquad (26)$$

and

$$t_{R,max} = \frac{C_{A0}}{k_1} \qquad (27)$$

Graphically we show these findings in Fig. 8.8.

8.4 SUCCESSIVE IRREVERSIBLE REACTIONS OF DIFFERENT ORDERS

In principle, concentration-time curves can be constructed for successive reactions of different orders. For the plug flow or batch reactor and for the mixed reactor explicit solutions are difficult to obtain; thus, numerical methods provide the best tool for treating such reactions.

For these reactions the concentration-time curves are of little generality for they are dependent on the concentration of reactant in the feed. As with reactions in parallel, a rise in reactant concentration favors the higher-order reaction; a lower concentration favors the lower-order reaction. This causes a shift in $C_{R,max}$, and this property can be used to improve the product distribution.

8.5   REVERSIBLE REACTIONS

Solution of the equations for successive reversible reactions is quite formidable even for the first-order case; thus, we illustrate only the general characteristics for a few typical cases. Consider the reversible first-order reactions

$$A \rightleftharpoons R \rightleftharpoons S \qquad (28)$$

and

$$B \underset{\searrow U}{\overset{\nearrow T}{}} \qquad (29)$$

Figures 8.9 and 8.10 display the concentration time curves for the components in batch or plug flow for different values of the rate constants.

Figure 8.9 shows that the concentration of intermediate in reversible series reactions need not pass through a maximum, while Fig. 8.10 shows that a product may pass through a maximum concentration typical of an intermediate in the irreversible series reaction; however, the reactions may be of a different kind. A comparison of these figures shows that many of the curves are similar in shape, making it difficult to select a mechanism of reaction by experiment, especially if the kinetic data are somewhat scattered. Probably the best clue to distinguishing between parallel and series reactions is to examine initial rate data—data obtained for very small conversion of reactant. For series reactions the time-concentration curve for S has a zero initial slope, whereas for parallel reactions this is not so.

8.6   IRREVERSIBLE SERIES-PARALLEL REACTIONS

Multiple reactions that consist of steps in series and steps in parallel are called series-parallel reactions. From the point of view of proper contacting, these reactions are more interesting than the simpler types already considered because a larger choice of contacting is usually possible, leading to much wider differences in product distribution. Thus, design engineers are dealing with a more flexible system and this affords them the opportunity to display their talents in devising the best of the wide variety of possible contacting patterns. Let us develop our ideas with a reaction type that represents a broad class of industrially important reactions. We will then generalize our findings to other series-parallel reactions.
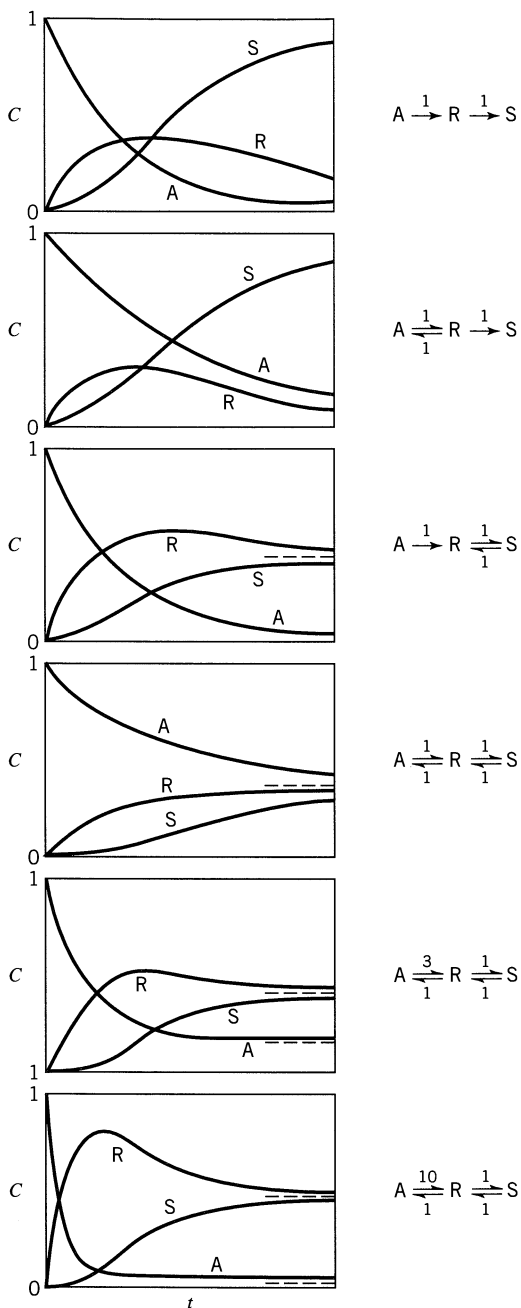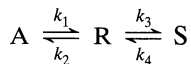
Figure 8.9 Concentration-time curves for the elementary reversible reactions

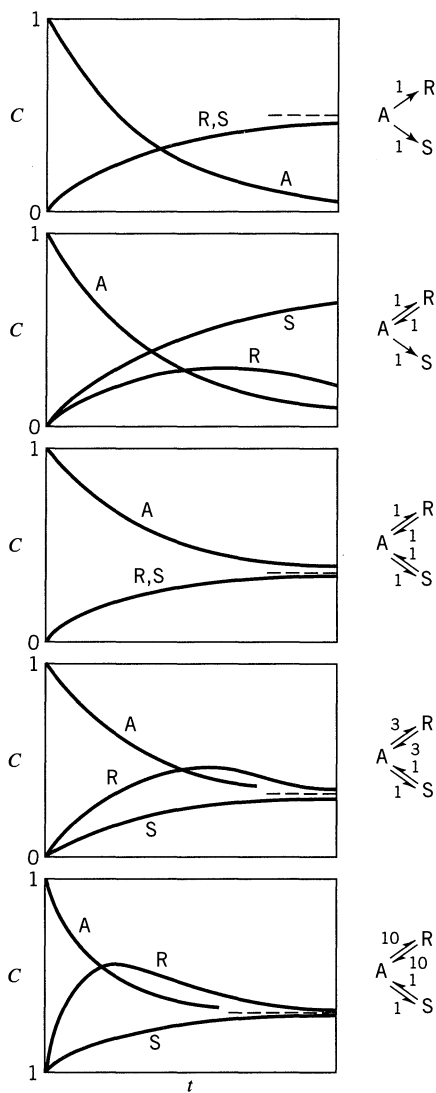$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R \underset{k_4}{\overset{k_3}{\rightleftharpoons}} S$$

From Jungers et al. (1958), p. 207.

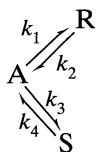**Figure 8.10** Concentration-time curves for the elementary reversible parallel reactions

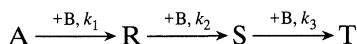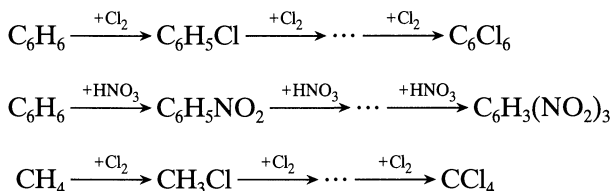For the reaction set consider the successive attack of a compound by a reactive material. The general representation of these reactions is

$$
\left.
\begin{aligned}
A + B &\xrightarrow{k_1} R \\
R + B &\xrightarrow{k_2} S \\
S + B &\xrightarrow{k_3} T \\
&\text{etc.}
\end{aligned}
\right\} \tag{30}
$$

or

$$
A \xrightarrow{+B,\, k_1} R \xrightarrow{+B,\, k_2} S \xrightarrow{+B,\, k_3} T
$$

where A is the compound to be attacked, B is the reactive material, and R, S, T, etc., are the polysubstituted materials formed during reaction. Examples of such reactions may be found in the successive substitutive halogenation (or nitration) of hydrocarbons, say benzene or methane, to form monohalo, dihalo, trihalo, etc., derivatives as shown below:

$$
C_6H_6 \xrightarrow{+Cl_2} C_6H_5Cl \xrightarrow{+Cl_2} \cdots \xrightarrow{+Cl_2} C_6Cl_6
$$

$$
C_6H_6 \xrightarrow{+HNO_3} C_6H_5NO_2 \xrightarrow{+HNO_3} \cdots \xrightarrow{+HNO_3} C_6H_3(NO_2)_3
$$

$$
CH_4 \xrightarrow{+Cl_2} CH_3Cl \xrightarrow{+Cl_2} \cdots \xrightarrow{+Cl_2} CCl_4
$$

Another important example is the addition of alkene oxides, say ethylene oxide, to compounds of the proton donor class such as amines, alcohols, water, and hydrazine to form monoalkoxy, dialkoxy, trialkoxy, etc., derivatives, some examples of which are shown below:

monoethanolamine, MEA   triethanolamine, TEA

ethylene glycol   diethylene glycol
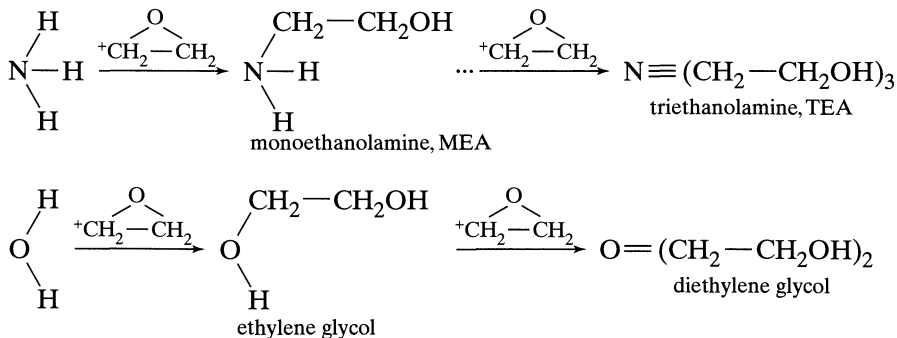
Such processes are frequently bimolecular, irreversible, hence second-order kinetically. When occurring in the liquid phase they are also essentially constant-density reactions.

Two-Step Irreversible Series-Parallel Reactions

We first consider the two-step reaction where the first substitution product is desired. Actually for an *n*-step reaction the third and succeeding reactions do not occur to any appreciable extent and may be ignored if the mole ratio of A to B is high (see qualitative treatment given next). The reaction set considered is thus

$$
\left.
\begin{aligned}
A + B &\xrightarrow{k_1} R \\
R + B &\xrightarrow{k_2} S
\end{aligned}
\right\}
\tag{31}
$$

With the assumption that the reaction is irreversible, bimolecular, and of constant density, the rate expressions are given by

$$
r_A = \frac{dC_A}{dt} = -k_1 C_A C_B
\tag{32}
$$

$$
r_B = \frac{dC_B}{dt} = -k_1 C_A C_B - k_2 C_R C_B
\tag{33}
$$

$$
r_R = \frac{dC_R}{dt} = k_1 C_A C_B - k_2 C_R C_B
\tag{34}
$$

$$
r_S = \frac{dC_S}{dt} = k_2 C_R C_B
\tag{35}
$$

Qualitative Discussion About Product Distribution. To get the "feel" for what takes place when A and B react according to Eq. 31, imagine that we have two beakers, one containing A and the other containing B. Should it make any difference in the product distribution how we mix A and B? To find out, consider the following ways of mixing the reactants: (a) add A slowly to B, (b) add B slowly to A, and finally (c) mix A and B together rapidly.

(a) Add A Slowly to B. For the first alternative pour A a little at a time into the beaker containing B, stirring thoroughly and making sure that all the A is used up and that the reaction stops before the next bit is added. With each addition a bit of R is produced in the beaker. But this R finds itself in an excess of B so it will react further to form S. The result is that at no time during the slow addition will A and R be present in any appreciable amount. The mixture becomes progressively richer in S and poorer in B. This continues until the beaker contains only S. Figure 8.11 shows this progressive change.

(b) Add B Slowly to A. Now pour B a little at a time into the beaker containing A, again stirring thoroughly. The first bit of B will be used up, reacting with A to form R. This R cannot react further for there is now no B present in the
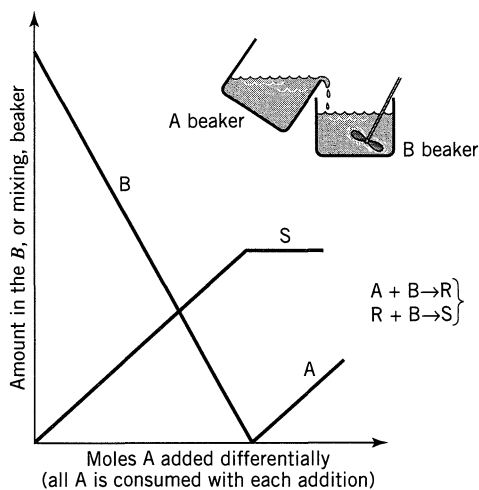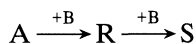
Figure 8.11 Distribution of materials in the B beaker for the method of mixing shown.

mixture. With the next addition of B, both A and R will compete with each other for the B added, and since A is in very large excess it will react with most of the B, producing even more R. This process will be repeated with progressive buildup of R and depletion of A until the concentration of R is high enough so that it can compete favorably with A for the B added. When this happens, the concentration of R reaches a maximum, then decreases. Finally, after addition of 2 moles of B for each mole of A, we end up with a solution containing only S. This progressive change is shown in Fig. 8.12.

(c) Mix A and B Rapidly. Now consider the third alternative where the contents of the two beakers are rapidly mixed together, the reaction being slow enough so that it does not proceed to any appreciable extent before the mixture becomes uniform. During the first few reaction increments R finds itself competing with a large excess of A for B and hence it is at a disadvantage. Carrying through this line of reasoning, we find the same type of distribution curve as for the mixture in which B is added slowly to A. This situation is shown in Fig. 8.12.

The product distribution of Figs. 8.11 and 8.12 are completely different. Thus, when A is kept uniform in composition as it reacts, as in Fig. 8.12, then R is formed. However, when fresh A is mixed with partly reacted mixture, as in Fig. 8.11, then no intermediate R forms. But this is precisely the behavior of reactions in series. Thus, as far as A, R, and S are concerned, we may view the reactions of Eq. 31 as

$$A \xrightarrow{\;+B\;} R \xrightarrow{\;+B\;} S$$

A second observation of Fig. 8.12 is that the concentration level of B, whether high or low, has no effect on the path of the reaction and on the distribution of
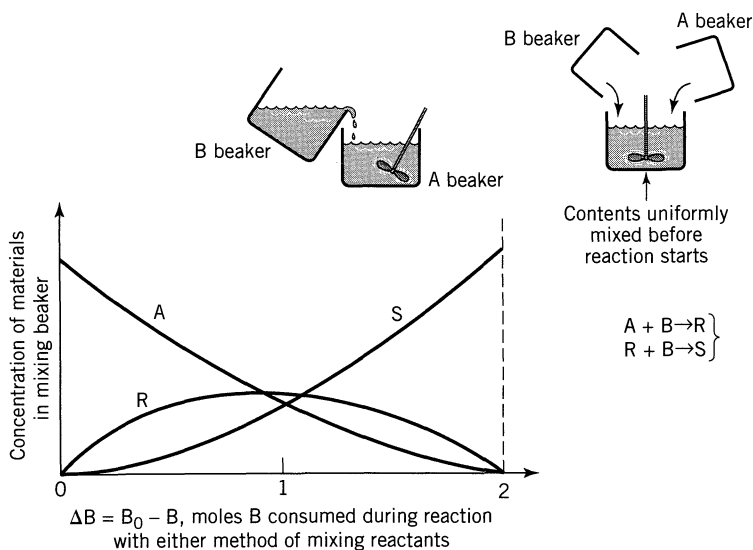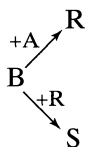
Figure 8.12 Distribution of materials in the mixing beaker for either of the methods of mixing shown.

products. But this is precisely the behavior of parallel reactions of the same order. So with respect to B, Eq. 31 can be looked at as

$$
\begin{array}{c}
\ \ ^{+A}\nearrow^{R} \\
B \\
\ \ _{+R}\searrow_{S}
\end{array}
$$

From this discussion we propose the general rule:

> *Irreversible series-parallel reactions can be analyzed in terms of their constituent series reactions and parallel reactions in that optimum contacting for favorable product distribution is the same as for the constituent reactions.*

For the reactions of Eq. 31 where R is desired this rule shows that the best way of contacting A and B is to react A uniformly, while adding B in any convenient way.

This is a powerful generalization which, without needing specific values for the rate constants, can already show in many cases which are the favorable contacting patterns. It is essential, however, to have the proper representation of the stoichiometry and form of rate equation. Example 8.6 and many of the problems of Chapter 10 apply these generalizations.

Quantitative Treatment, Plug Flow or Batch Reactor. Here we quantitatively treat the reactions of Eq. 31 with the understanding that R, the intermediate, is the desired product, and that the reaction is slow enough so that we may ignore the problems of partial reaction during the mixing of reactants.

In general, taking the ratio of two rate equations eliminates the time variable and gives information on the product distribution. So dividing Eq. 34 by Eq. 32 we obtain the first-order linear differential equation

$$\frac{r_R}{r_A} = \frac{dC_R}{dC_A} = -1 + \frac{k_2 C_R}{k_1 C_A} \tag{36}$$

whose method of solution is shown in Chapter 3. With no R present in the feed the limits of integration are C_{A0} to C_A for A and $C_{R0} = 0$ for R, and the solution of this differential equation is

$$\begin{aligned}
\frac{C_R}{C_{A0}} &= \frac{1}{1 - k_2/k_1}\left[\left(\frac{C_A}{C_{A0}}\right)^{k_2/k_1} - \frac{C_A}{C_{A0}}\right], & \frac{k_2}{k_1} &\neq 1 \\
\frac{C_R}{C_{A0}} &= \frac{C_A}{C_{A0}}\ln\frac{C_{A0}}{C_A}, & \frac{k_2}{k_1} &= 1
\end{aligned} \tag{37}$$

with maximum C_R at

$$\begin{aligned}
\frac{C_{R,max}}{C_{A0}} &= \left(\frac{k_1}{k_2}\right)^{k_2/(k_2-k_1)}, & \frac{k_2}{k_1} &\neq 1 \\
\frac{C_{R,max}}{C_{A0}} &= \frac{1}{e} = 0.368 & \frac{k_2}{k_1} &= 1
\end{aligned} \tag{38}$$

This gives the relationship between C_R and C_A in a batch or in a plug flow reactor. To find the concentrations of the other components, simply make a material balance. An A balance gives

$$C_{A0} + C_{R0} + C_{S0} = C_A + C_R + C_S \tag{39}$$

or

$$\Delta C_A + \Delta C_R + \Delta C_S = 0$$

from which C_S can be found as a function of C_A and C_R. Finally, a balance about B gives

$$\Delta C_B + \Delta C_R + 2\Delta C_S = 0 \tag{40}$$

from which C_B can be found.

Quantitative Treatment, Mixed Flow. Writing the design equation for mixed flow in terms of A and R gives

$$\tau_m = \frac{C_{A0} - C_A}{-r_A} = \frac{-C_R}{-r_R}$$

or

$$\tau_m = \frac{C_{A0} - C_A}{k_1 C_A C_B} = \frac{-C_R}{k_2 C_R C_B - k_1 C_A C_B}$$

Rearranging, we obtain

$$\frac{-C_R}{C_{A0} - C_A} = -1 + \frac{k_2 C_R}{k_1 C_A}$$

which is the difference equation corresponding to the differential equation, Eq. 36. Writing C_R in terms of C_A then gives

with

$$\boxed{\begin{aligned} C_R &= \frac{C_A(C_{A0} - C_A)}{C_A + (k_2/k_1)(C_{A0} - C_A)} \\[2mm] \frac{C_{R,max}}{C_{A0}} &= \frac{1}{[1 + (k_2/k_1)^{1/2}]^2} \end{aligned}}$$

(41)

Equations 39 and 40, material balances about A and B in plug flow, hold equally well for mixed flow and serve to complete the set of equations giving complete product distribution in this reactor.

Graphical Representation. Figures 8.13 and 8.14, time-independent plots, show the distribution of materials in plug and mixed flow and are prepared from Eqs. 37 to 41. As mentioned earlier, A, R, and S behave like the components in first-order reactions in series. Comparing Figs. 8.13 and 8.14 with Figs. 8.3b and 8.5b, we see that the distribution of these materials is the same in both cases, plug flow again giving a higher concentration of intermediate than mixed flow. The lines of slope 2 on these charts show the amount of B consumed to reach any particular point on the curve. It makes no difference whether B is added all at one time as in a batch reactor or a little at a time as in a semibatch reactor; in either case the same point on the chart will be reached when the same total amount of B is consumed.

   These figures indicate that no matter what reactor system is selected, when the fractional conversion of A is low the fractional yield of R is high. Thus, if it is possible to separate R cheaply from a product stream, the optimum setup for producing R is to have small conversions per pass coupled with a separation of R and recycle of unused A. The actual mode of operation will, as usual, depend on the economics of the system under study.
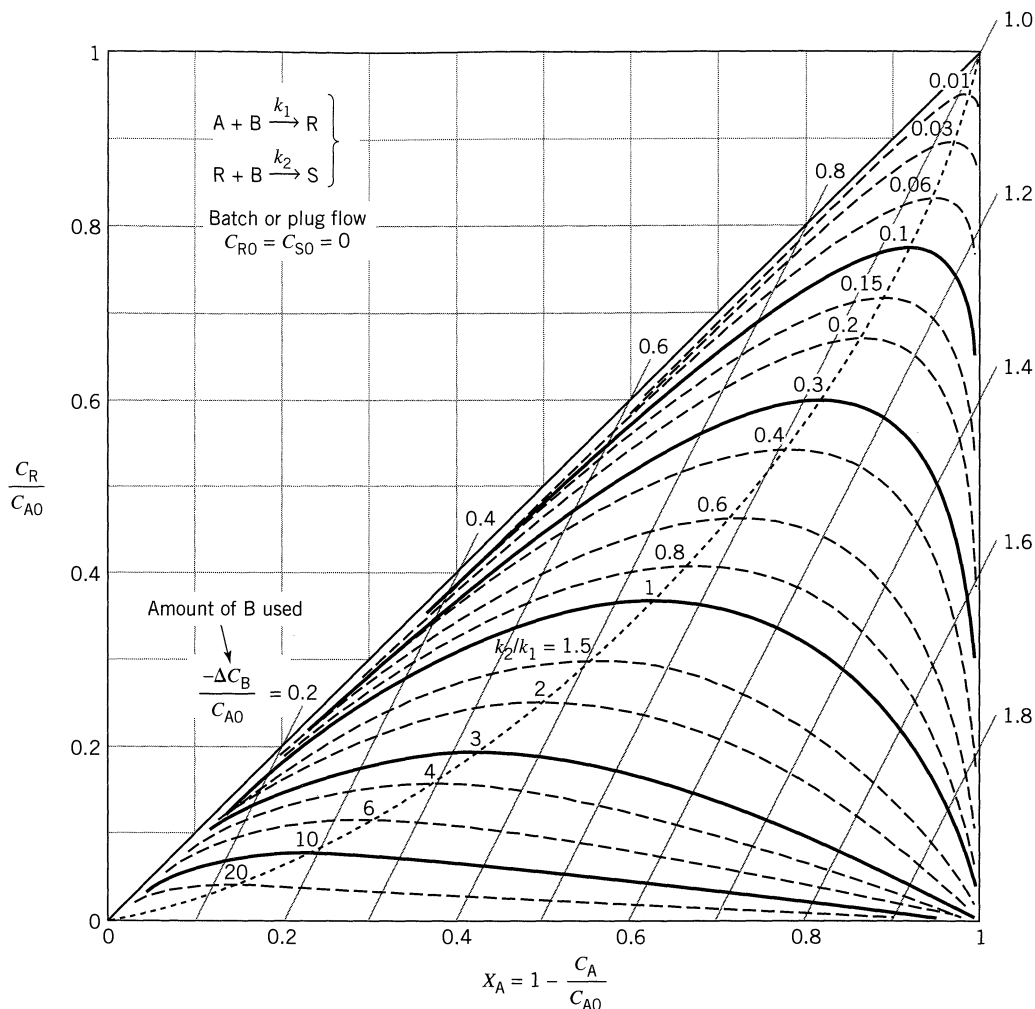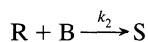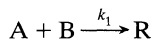
Figure 8.13 Distribution of materials in a batch or plug flow reactor for the elementary series-parallel reactions

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

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

Experimental Determination of the Kinetics of Reaction. The ratio k_2/k_1 may be found by analyzing the products of reaction from an experiment, and locating the corresponding point on the appropriate design chart. The simplest way to do this is to use different ratios of B to A in a batch reactor, allowing the reaction to go to completion each time. For each run a value of k_2/k_1 can be determined.
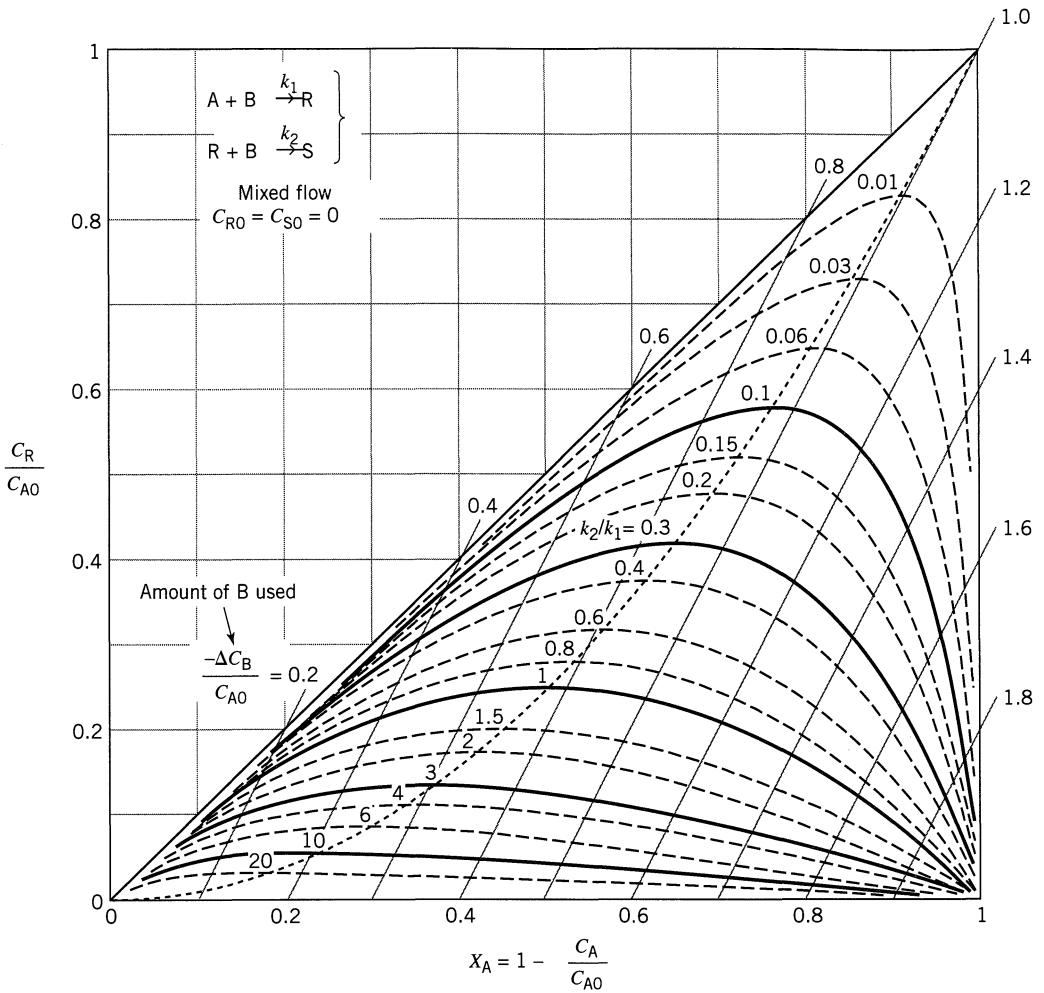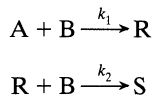
Figure 8.14 Distribution of materials in a mixed flow reactor for the elementary series-parallel reactions

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

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

The best mole ratios to use are those where the lines of constant k_2/k_1 are furthest apart, or when $-(\Delta B/A_0) \approx 1.0$, or close to equimolar ratios.

With k_2/k_1 known, all that is needed is k_1 which must be found by kinetic experiments. The simplest procedure is to use a large excess of B in which case the disappearance of A follows first-order kinetics.

EXAMPLE 8.2 **KINETICS OF SERIES-PARALLEL REACTION**

From each of the following experiments, what can we say about the rate constants of the multiple reactions

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

$$R + B \xrightarrow{k_2} S$$
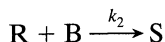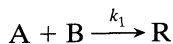
(a) Half a mole of B is poured bit by bit, with stirring, into a flask containing a mole of A. The reaction proceeds slowly, and when B is entirely consumed 0.67 mole of A remains unreacted.

(b) One mole of A and 1.25 moles of B are rapidly mixed, and the reaction is slow enough so that it does not proceed to any appreciable extent before homogeneity in composition is achieved. On completion of the reaction, 0.5 mole of R is found to be present in the mixture.

(c) One mole of A and 1.25 moles of B are rapidly brought together. The reaction is slow enough so that it does not proceed to any appreciable extent before homogeneity in A and B is achieved. At the time when 0.9 mole of B is consumed, 0.3 mole of S is present in the mixture.

SOLUTION

The sketches in Fig. E8.2 show how Fig. 8.13 is used to find the desired information. Thus we find:

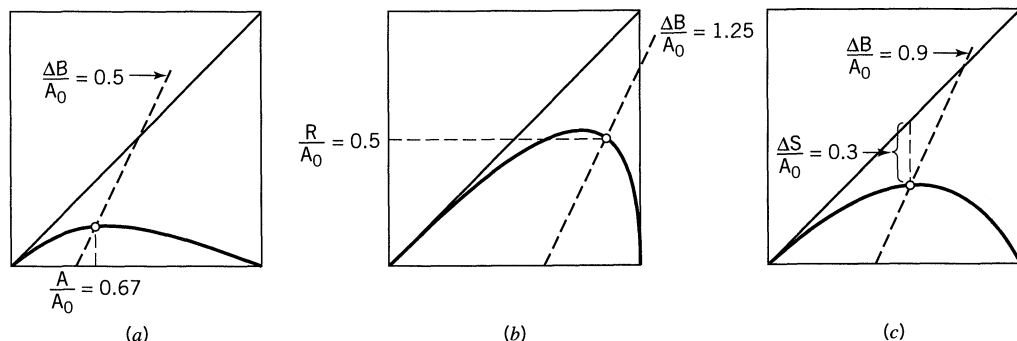**(a)** $k_2/k_1 = 4$,   **(b)** $k_2/k_1 = 0.4$,   **(c)** $k_2/k_1 = 1.45$

Figure E8.2

Extensions and Applications

Three or More Reactions. Analysis of three or more reactions can be made by procedures analogous to those presented. Of course, the mathematics becomes more involved; however, much of the extra labor can be avoided by selecting experimental conditions in which only two reactions need be considered at any time. Figure 8.15 shows product distribution curves for one such reaction set, the progressive chlorination of benzene.

Catipovic and Levenspiel (1979) have developed charts to represent the first three steps of an *n*-step reaction sequence. Beyond three steps, simple performance charts cannot be prepared.

Again, as with the two-reaction set, we find that a plug flow reactor yields a higher maximum concentration of any intermediate than does a mixed flow reactor.

Polymerization. The field of polymerization affords an opportunity for a fruitful application of these ideas. Often hundreds or even thousands of reactions in series occur in the formation of polymers, and the type of crosslinking and molecular weight distribution of these products are what gives these materials their particular physical properties of solubility, density, flexibility, etc.

Since the mode of mixing of monomers with their catalysts profoundly affects product distribution, great importance must be paid to this factor if the product is to have the desired physical and chemical properties. Denbigh (1947, 1951) considered some of the many aspects of this problem, and Fig. 8.16 shows for various kinetics how reactor type influences the molecular weight distribution of products.
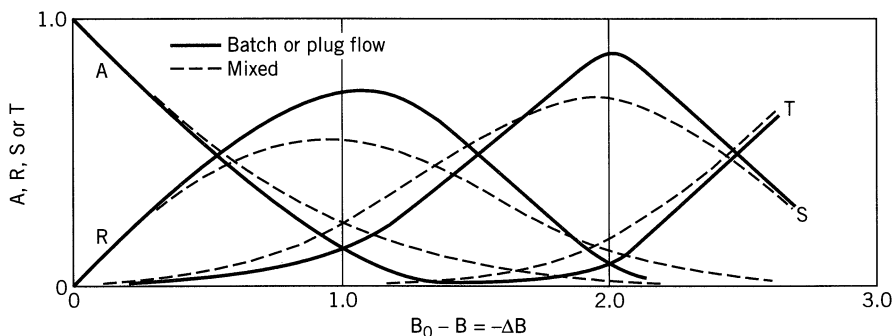
Figure 8.15 Product distribution in the progressive chlorination of benzene:

$$A + B \xrightarrow{k_1} R + U \qquad C_6H_6 + Cl_2 \xrightarrow{k_1} C_6H_5Cl + HCl$$

$$R + B \xrightarrow{k_2} S + U \quad \text{or} \quad C_6H_5Cl + Cl_2 \xrightarrow{k_2} C_6H_4Cl_2 + HCl$$

$$S + B \xrightarrow{k_3} T + U \qquad C_6H_4Cl_2 \xrightarrow{k_3} C_6H_3Cl_3 + HCl$$
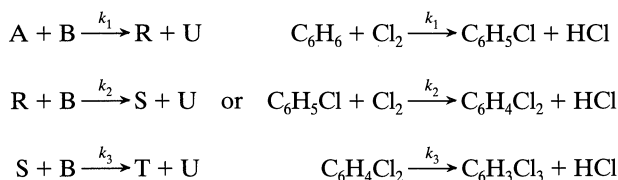
With $k_2/k_1 = 1/8$ and $k_3/k_1 = 1/240$; from R. B. MacMullin (1948).

Figure 8.16 Type of flow and kinetics influence the molecular weight distribution of polymer: (*a*) duration of polymerization reaction (life of active polymer) is short compared to the reactor holding time; (*b*) duration of polymerization reaction is long compared to the reactor holding time, or where polymerization has no termination reaction. Adapted from Denbigh (1947).

8.7 THE DENBIGH REACTIONS AND THEIR SPECIAL CASES
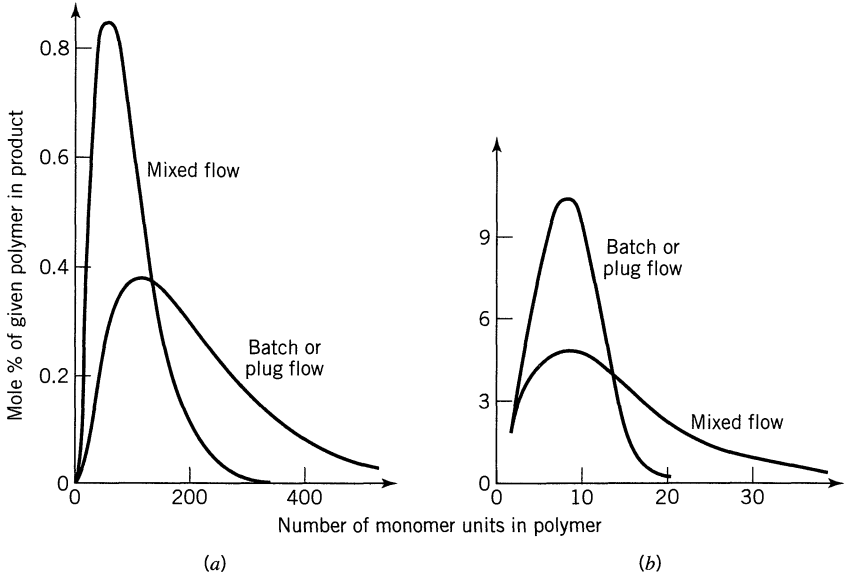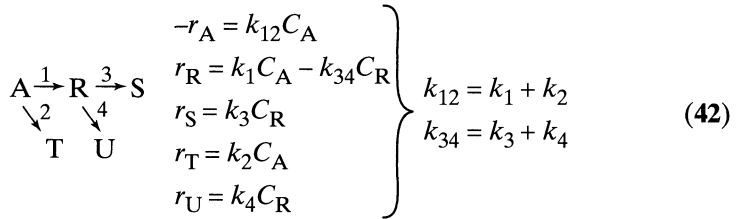
Denbigh (1958) was the first to treat the following rather general reaction scheme

$$\left.\begin{array}{l} -r_A = k_{12}C_A \\ r_R = k_1C_A - k_{34}C_R \\ r_S = k_3C_R \\ r_T = k_2C_A \\ r_U = k_4C_R \end{array}\right\} \quad \begin{array}{l} k_{12} = k_1 + k_2 \\ k_{34} = k_3 + k_4 \end{array} \qquad (42)$$

$$A \xrightarrow{1} R \xrightarrow{3} S$$
$$\quad \downarrow 2 \quad \downarrow 4$$
$$\quad T \quad U$$

with

$$C_{A0} + C_{R0} + C_{S0} + C_{T0} + C_{U0} = C_A + C_R + C_S + C_T + C_U \qquad (43)$$

The performance equations for this reaction scheme reduce directly to all the special cases, for example

$$A \to R \to S, \quad A \to R \mathop{\mathrm{\scriptstyle <}}\limits^{S}_{U}, \quad A \to R \to S, \quad A \mathop{\to}\limits^{R}\mathop{\searrow}\limits_{T} S, \quad A \mathop{\mathrm{\scriptstyle <}}\limits^{R}_{T}$$
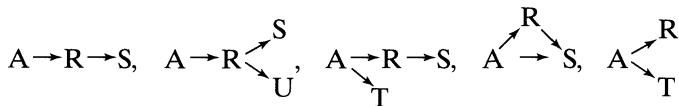
This scheme has wide application to a whole host of real reacting systems.

These rate equations are all of first order and so to develop the performance expressions does not involve complex mathematics, although it may be a tedious task. In our treatment we will not present the detailed calculation steps, but will just present the final results.

Batch or Plug Flow Reactors. Integration gives the performance equations for this system

$$\frac{C_A}{C_{A0}} = \exp(-k_{12}t) \tag{44}$$

$$\frac{C_R}{C_{A0}} = \frac{k_1}{k_{34} - k_{12}}[\exp(-k_{12}t) - \exp(-k_{34}t)] + \frac{C_{R0}}{C_{A0}}\exp(-k_{34}t) \tag{45}$$

$$\frac{C_S}{C_{A0}} = \frac{k_1 k_3}{k_{34} - k_{12}}\left[\frac{\exp(-k_{34}t)}{k_{34}} - \frac{\exp(-k_{12}t)}{k_{12}}\right] + \frac{k_1 k_3}{k_{12} k_{34}}$$

$$+ \frac{C_{R0}}{C_{A0}}\frac{k_3}{k_{34}}[1 - \exp(-k_{34}t)] + \frac{C_{S0}}{C_{A0}} \tag{46}$$

$$\frac{C_T}{C_{A0}} = \frac{k_2}{k_{12}}[1 - \exp(-k_{12}t)] + \frac{C_{T0}}{C_{A0}} \tag{47}$$

$$\frac{C_U}{C_{A0}} \ldots \text{same as } \frac{C_S}{C_{A0}} \text{ but with } k_3 \leftrightarrow k_4 \text{ and } C_{S0} \leftrightarrow C_{U0}$$

For the special case where $C_{R0} = C_{S0} = C_{T0} = C_{U0} = 0$ the above expressions simplify. We also can find $C_R = f(C_A)$, thus

$$\frac{C_R}{C_{A0}} = \frac{k_1}{k_{12} - k_{34}}\left[\left(\frac{C_A}{C_{A0}}\right)^{k_{34}/k_{12}} - \frac{C_A}{C_{A0}}\right] \tag{48}$$

and

$$\frac{C_{R,\max}}{C_{A0}} = \frac{k_1}{k_{12}}\left(\frac{k_{12}}{k_{34}}\right)^{k_{34}/(k_{34}-k_{12})} \tag{49}$$

at

$$t_{\max} = \frac{\ln(k_{34}/k_{12})}{k_{34} - k_{12}} \tag{50}$$

For $C_{R0} = C_{S0} = C_{T0} = C_{U0} = 0$ the behavior of the system is displayed as shown in Fig. 8.17. This figure also shows $C_{R,\max}$ and the time when this occurs in terms of the rate constants.
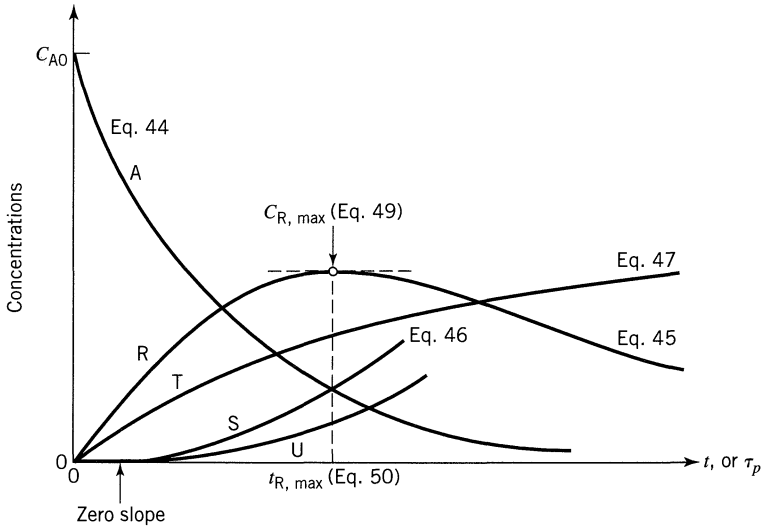
Figure 8.17 Progress of the Denbigh reaction scheme in a plug flow reactor for $C_{R0} = C_{S0} = C_{T0} = C_{U0} = 0$.

Mixed Flow Reactors. Using the mixed flow performance equation with these rates gives

$$\frac{C_A}{C_{A0}} = \frac{1}{(1 + k_{12}\tau_m)} \tag{51}$$

$$\frac{C_R}{C_{A0}} = \frac{k_1\tau_m}{(1 + k_{12}\tau_m)(1 + k_{34}\tau_m)} + \frac{C_{R0}}{C_{A0}}\frac{1}{(1 + k_{34}\tau_m)} \tag{52}$$

$$\frac{C_S}{C_{A0}} = \frac{k_1k_3\tau_m^2}{(1 + k_{12}\tau_m)(1 + k_{34}\tau_m)} + \frac{C_{R0}}{C_{A0}}\frac{k_3\tau_m}{(1 + k_{34}\tau_m)} + \frac{C_{S0}}{C_{A0}} \tag{53}$$

$$\frac{C_T}{C_{A0}} = \frac{k_2\tau_m}{(1 + k_{12}\tau_m)} + \frac{C_{T0}}{C_{A0}} \tag{54}$$

$$\frac{C_U}{C_{A0}} \cdots \text{same as } \frac{C_S}{C_{A0}} \text{ but with } k_3 \leftrightarrow k_4 \text{ and } C_{S0} \leftrightarrow C_{U0} \tag{55}$$

At the optimum

$$\frac{C_{Rmax}}{C_{A0}} = \left(\frac{k_1}{k_{12}}\right) \cdot \frac{1}{[(k_{34}/k_{12})^{1/2} + 1]^2} \tag{56}$$

at

$$\tau_{m,Rmax} = \frac{1}{(k_{12}/k_{34})^{1/2}} \tag{57}$$

Graphically, for $C_{R0} = C_{S0} = C_{T0} = C_{U0} = 0$, Fig. 8.18 shows the behavior of this system.
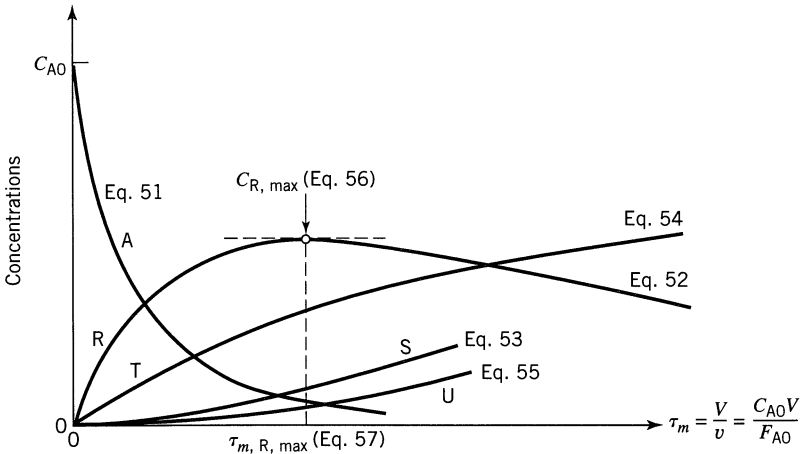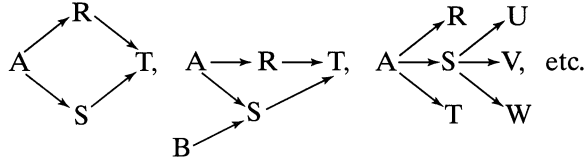
Figure 8.18 Progress of the Denbigh reaction scheme in a mixed flow reactor for $C_{R0} = C_{S0} = C_{T0} = C_{U0} = 0$.

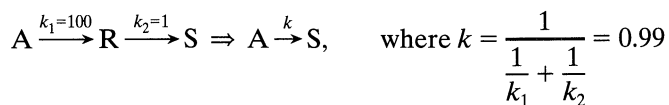## Comments, Suggestions, and Extensions

The equations of this chapter can be extended and applied directly to many other reaction schemes, for example

Some problems at the end of this chapter consider these extensions.

A careful examination of the shape of the C versus τ curves gives much useful information on the rate constants. Here are some clues:

- Look at the initial slope of the curves; measure the slopes. Are the initial slopes of produced materials zero or not?
- Measure the final concentration of all the reaction components.
- Find when an intermediate reaches its maximum concentration and measure this concentration.
- In searching for a model or mechanism for the reaction scheme make runs at different C_{A0} and different C_{B0}/C_{A0}.
- If possible, also make runs starting with intermediate. For example, for the reaction $A \rightarrow R \rightarrow S$ start with R alone and follow its disappearance.
- If the two steps of first-order reactions in series have very different values for their rate constants, we can approximate the overall behavior as follows:

$$A \xrightarrow{k_1=100} R \xrightarrow{k_2=1} S \Rightarrow A \xrightarrow{k} S, \qquad \text{where } k = \frac{1}{\dfrac{1}{k_1} + \dfrac{1}{k_2}} = 0.99$$

- For schemes involving different reaction orders, for reversible reactions, and for a very-many-step scheme typical of polymerizations, analysis becomes complicated.
- The key to optimum design for multiple reactions is proper contacting and proper flow pattern of fluids within the reactor. These requirements are determined by the stoichiometry and observed kinetics. Usually qualitative reasoning alone can already determine the correct contacting scheme. This is discussed further in Chapter 10. However, to determine the actual equipment size requires quantitative considerations.

EXAMPLE 8.3   *EVALUATE THE KINETICS FROM A BATCH EXPERIMENT*

Japanese researchers very carefully followed the oxidation of sodium sulfide Na_2S (A) to sodium thiosulfate $Na_2S_2O_3$ (R) in a batch reactor. Intermediates were measured and the results found were sketched in Fig. E8.3.

(a) Think up a simple network of reactions, all of first-order, to represent this oxidation.

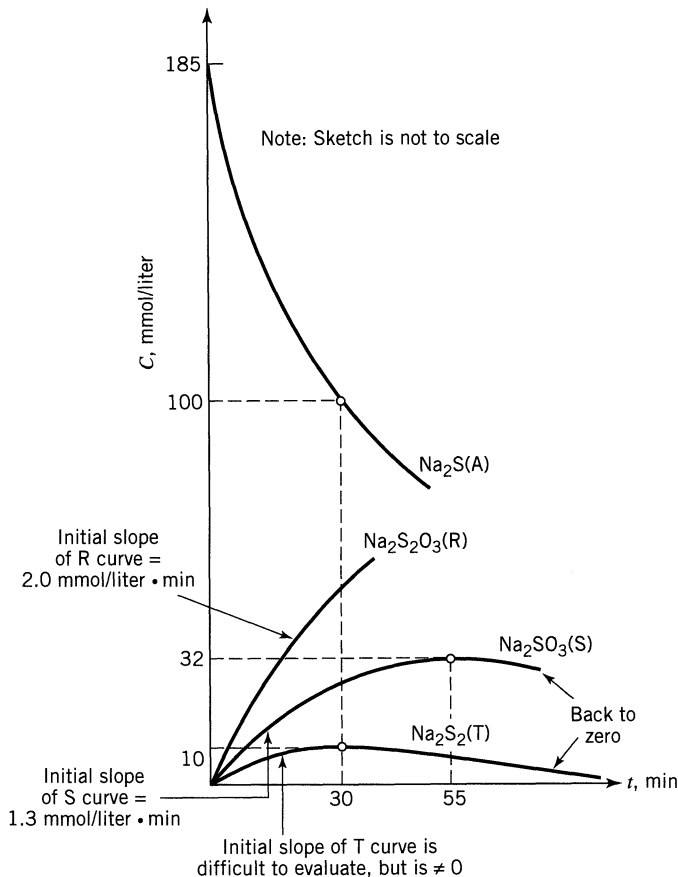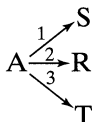**(b)** Evaluate the rate constants of this network.

Figure E8.3

SOLUTION

This problem draws on a number of techniques.

(a) First, Look for Clues in the Graph. We first note that the initial slopes of the R, S, and T curves are all nonzero, suggesting that these compounds are formed directly from A, or

$$A \overset{1}{\underset{3}{\overset{2}{\longrightarrow}}} \begin{matrix} S \\ R \\ T \end{matrix}$$

Next, since there is no S and T in the final product, our suggested reaction scheme is

$$A \overset{1}{\underset{3}{\overset{2}{\longrightarrow}}} \begin{matrix} S \\ \\ T \end{matrix} \overset{4}{\underset{5}{\longrightarrow}} R \tag{a}$$

(b) Evaluate the Rate Constants. Noting that A disappears by first-order kinetics, we have

$$\ln \frac{C_{A0}}{C_A} = \ln \frac{185}{100} = (k_1 + k_2 + k_3)t = k_{123}t = k_{123}(30)$$

from which

$$k_{123} = \underline{\underline{0.0205 \text{ min}^{-1}}}$$

From the initial rate for formation of R

$$\frac{dC_R}{dt} = k_2 C_{A0}$$

or

$$k_2 = \frac{dC_R/dt}{C_{A0}} = \frac{2.0}{185} = \underline{\underline{0.0108 \text{ min}^{-1}}}$$

Similarly for S

$$k_1 = \frac{dC_S/dt}{C_{A0}} = \frac{1.3}{185} = \underline{\underline{0.0070 \text{ min}^{-1}}}$$

So by difference

$$k_3 = k_{123} - k_1 - k_2 = 0.0205 - 0.0108 - 0.0070 = \underline{\underline{0.0027 \text{ min}^{-1}}}$$

Next, let us look at the maxima of the S and T curves. For S, by an extension of Eq. 49, we can write

$$\frac{C_{\text{Smax}}}{C_{\text{A0}}} = \frac{k_1}{k_{123}} \left(\frac{k_{123}}{k_4}\right)^{k_4/(k_4-k_{123})}$$

or

$$\frac{32}{185} = \frac{0.0070}{0.0205} \left(\frac{0.0205}{k_4}\right)^{k_4/(k_4-0.0205)}$$
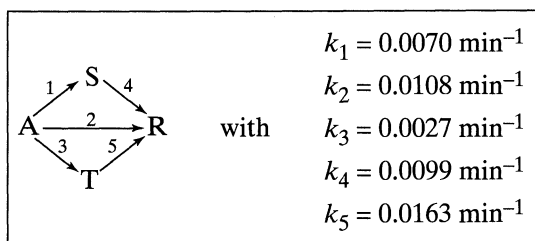
Solving for k_4 by trial and error gives

$$\underline{\underline{k_4 = 0.0099 \text{ min}^{-1}}}$$

Similarly for T

$$\frac{10}{185} = \frac{0.0027}{0.0205} \left(\frac{0.0205}{k_5}\right)^{k_5/(k_5-0.0205)}$$

$$\underline{\underline{k_5 = 0.0163 \text{ min}^{-1}}}$$

So we end up with the following kinetic scheme

$$k_1 = 0.0070 \text{ min}^{-1}$$
$$k_2 = 0.0108 \text{ min}^{-1}$$
with $\quad k_3 = 0.0027 \text{ min}^{-1}$ \hfill (b)
$$k_4 = 0.0099 \text{ min}^{-1}$$
$$k_5 = 0.0163 \text{ min}^{-1}$$

This problem was prepared by David L. Cates (1988).

REFERENCES

Catipovic, N., and Levenspiel, O., *Ind. Eng. Chem. Process Des. Dev.*, **18,** 558 (1979).
Denbigh, K. G., *Trans. Faraday Soc.*, **43,** 648 (1947).
Denbigh, K. G., *J. Appl. Chem.*, **1,** 227 (1951).
Denbigh, K. G., *Chem. Eng. Sci.*, **8,** 125 (1958).
Jungers, J. C., et al., *Cinétique Chimique Appliquée*, Technip, Paris, 1958.
MacMullin, R. B., *Chem. Eng. Prog.*, **44,** 183 (1948).

PROBLEMS

8.1. Starting with separate feeds of reactant A and B of given concentration (no dilution with inerts permitted), for the competitive-consecutive reactions with stoichiometry and rate as shown

$$A + B \rightarrow R_{\text{desired}} \cdots r_1$$
$$R + B \rightarrow S_{\text{unwanted}} \cdots r_2$$
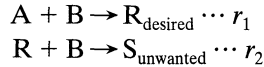
sketch the best contacting patterns for both continuous and noncontinuous operations:

(a) $r_1 = k_1 C_A C_B^2$
   $r_2 = k_2 C_R C_B$

(b) $r_1 = k_1 C_A C_B$
   $r_2 = k_2 C_R C_B^2$

(c) $r_1 = k_1 C_A C_B$
   $r_2 = k_2 C_R^2 C_B$

(d) $r_1 = k_1 C_A^2 C_B$
   $r_2 = k_2 C_R C_B$

8.2. Under appropriate conditions A decomposes as follows:

$$A \xrightarrow{k_1 = 0.1/\text{min}} R \xrightarrow{k_2 = 0.1/\text{min}} S$$
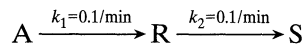
R is to be produced from 1000 liter/hr of feed in which $C_{A0} = 1$ mol/liter, $C_{R0} = C_{S0} = 0$.
(a) What size of plug flow reactor will maximize the concentration of R, and what is that concentration in the effluent stream from this reactor?
(b) What size of mixed flow reactor will maximize the concentration of R, and what is $C_{R,\text{max}}$ in the effluent stream from this reactor?

Pure A ($C_{A0} = 100$) is fed to a mixed flow reactor, R and S are formed, and the following outlet concentrations are recorded. Find a kinetic scheme to fit this data.

8.3.

Run	C_A	C_R	C_S
1	75	15	10
2	25	45	30

8.4.

Run	C_A	C_R	C_S
1	50	$33\frac{1}{3}$	$16\frac{2}{3}$
2	25	30	45

8.5.

| Run	C_A	C_R	C_S	t, min
1	50	40	10	5
2	20	40	40	20

8.6. In grinding a continuous flow of pigments for paint, our company finds that too many too-small and too many too-large particles exit from our well-mixed grinder. A multistage grinder, approximating plug flow, could also have been used, but wasn't. Anyway, in either type of grinder the pigments are progressively ground into smaller and smaller particles.

At present, the exit stream from our well-mixed grinder contains 10% too-large ($d_p > 147 \mu m$); 32% just-right ($d_p = 38 - 147 \mu m$); and 58% too-small ($d_p < 38 \mu m$) particles.

(a) Can you suggest a better grinding scheme for our present unit, and what would it give?

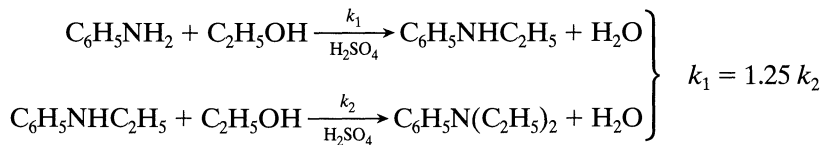**(b)** How about the multistage grinder? How would it do?

By "better" we mean giving more just right-sized pigment in the product stream. Also, separation and recycle of the size cuts is not practical.

8.7. Consider the following elementary reactions:

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

$$R + B \xrightarrow{k_2} S$$
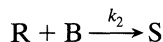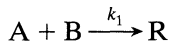
(a) One mole A and 3 moles B are rapidly mixed together. The reaction is very slow, allowing analysis of compositions at various times. When 2.2 moles B remain unreacted, 0.2 mole S is present in the mixture. What should be the composition of the mixture (A, B, R, and S) when the amount of S present is 0.6 mole?

(b) One mole A is added bit by bit with constant stirring to 1 mole B. Left overnight and then analyzed, 0.5 mole S is found. What can we say about k_2/k_1?

(c) One mole A and 1 mole B are thrown together and mixed in a flask. The reaction is very rapid and goes to completion before any rate measurements can be made. On analysis of the products of reaction 0.25 mole S is found to be present. What can we say about k_2/k_1?

8.8. The liquid phase reaction of aniline with ethanol produces wanted mono-ethylaniline and unwanted diethylaniline

$$C_6H_5NH_2 + C_2H_5OH \xrightarrow[H_2SO_4]{k_1} C_6H_5NHC_2H_5 + H_2O$$

$$C_6H_5NHC_2H_5 + C_2H_5OH \xrightarrow[H_2SO_4]{k_2} C_6H_5N(C_2H_5)_2 + H_2O$$

$$\left.\right\} \quad k_1 = 1.25 \, k_2$$

(a) An equimolar feed is introduced into a batch reactor, and reaction is allowed to proceed to completion. Find the concentration of reactants and products at the end of the run.

(b) Find the ratio of mono- to diethylaniline produced in a mixed flow

reactor for an alcohol-to-aniline feed ratio of 2 to 1 for 70% conversion of alcohol.

(c) For an equimolar feed to a plug flow reactor, what will be the conversion of the two reactants when the concentration of monoethylaniline is at its highest?

8.9. Monoethylaniline can also be produced in the vapor phase in a fluidized bed using natural bauxite as the solid catalyst. The elementary reactions are shown in the previous problem. Using an equimolar feed of aniline and ethanol, the fluidized bed produces 3 parts monoethylaniline to 2 parts diethylaniline for a 40% conversion of aniline. Assuming mixed flow of gas in the fluidized bed, find k_2/k_1 and the concentration ratio of reactants and products at the exit of the reactor.

Under the action of mixed enzymes reactant A is converted to products as follows:

$$A \xrightarrow[k_1]{+ \text{ enzyme}} R \xrightarrow[k_2]{+ \text{ enzyme}} S, \qquad n_1 = n_2 = 1$$
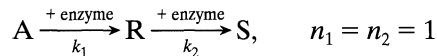
where the rate constants are dependent on the pH of the system.

(a) What reactor set-up (plug flow, mixed flow, or staged mixed flow units) and what uniform pH level would you use?

(b) If it were possible to change the pH level along the plug flow reactor, or from stage to stage in mixed flow units, in what direction would you change the pH level?

8.10. $k_1 = \text{pH}^2 - 8\,\text{pH} + 23$ with $2 < \text{pH} < 6$, and R the desired product
$k_2 = \text{pH} + 1$

8.11. $k_1 = \text{pH} + 1$ with $2 < \text{pH} < 6$, and S the desired product
$k_2 = \text{pH}^2 - 8\,\text{pH} + 23$

8.12. The progressive chlorination of *o*- and *p*-dichlorobenzene proceed with second-order rate, as shown in Fig. P8.12.
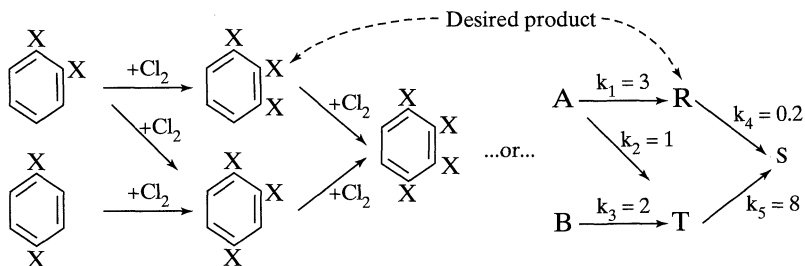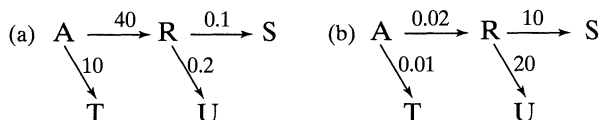

Figure P8.12

For a single-feed stream having $C_{A0} = 2$, $C_{B0} = 1$, and $1, 2, 3$-trichloroben-zene as the desired product

(a) Tell which kind of flow reactor is best.

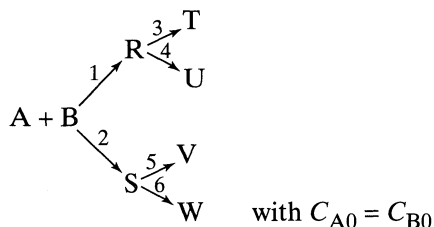**(b)** In this reactor find $C_{R,max}$.

See T. E. Corrigan, *Chem. Eng.*, **201**, March 1956, for discussion of this process.

8.13. Consider the following first order decompositions with rate constants as shown

$$\text{(a)} \quad A \xrightarrow{40} R \xrightarrow{0.1} S \qquad \text{(b)} \quad A \xrightarrow{0.02} R \xrightarrow{10} S$$
$$\qquad \downarrow 10 \quad \downarrow 0.2 \qquad\qquad \downarrow 0.01 \quad \downarrow 20$$
$$\qquad T \qquad U \qquad\qquad\quad T \qquad U$$

If a colleague reports that $C_S = 0.2\, C_{A0}$ in the exit stream of a plug flow reactor, what can you say about the concentration of the other reactor components, A, R, T, and U in the exit stream?

8.14. Chemicals A and B are thrown into a vat and react away according to the following elementary reactions:

$$A + B \begin{array}{c} \nearrow^{1} R \overset{3}{\underset{4}{<}} \begin{array}{c} T \\ U \end{array} \\ \searrow_{2} S \overset{5}{\underset{6}{<}} \begin{array}{c} V \\ W \end{array} \end{array} \quad \text{with } C_{A0} = C_{B0}$$

What can you say about these six rate constants if an analysis of the mixture shows that

$$C_T = 5 \text{ mol/liter} \qquad C_U = 1 \text{ mol/liter}$$
$$C_V = 9 \text{ mol/liter} \qquad C_W = 3 \text{ mol/liter}$$

at the time

(a) when reaction is incomplete?

(b) when reaction is complete?

8.15. With a particular catalyst and at a given temperature, the oxidation of naphthalene to phthalic anhydride proceeds as follows:

$$\begin{array}{c} R \\ {}^{1}\nearrow \searrow^{3} \\ A \xrightarrow{2} S \xrightarrow{4} T \end{array}$$

A = naphthalene	$k_1 = 0.21 \text{ s}^{-1}$
R = naphthaquinone	$k_2 = 0.20 \text{ s}^{-1}$
S = phthalic anhydride	$k_3 = 4.2 \text{ s}^{-1}$
T = oxidation products	$k_4 = 0.004 \text{ s}^{-1}$
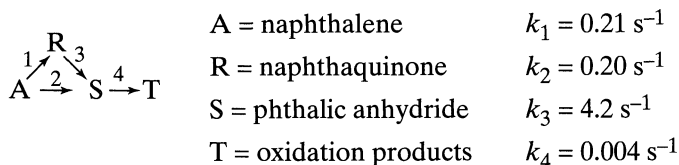
What reactor type gives the maximum yield of phthalic anhydride? Roughly estimate this yield and the fractional conversion of naphthalene which will give this yield. Note the word "roughly".

8.16. Sandy's Rock and Gravel Company wants to shift a mountain of gravel, estimated at about 20 000 tons, from one side of their yard to the other. For this they intend to use a power shovel to fill a hopper, which in turn feeds a belt conveyor. The latter then transports the gravel to the new location.

The shovel scoops up large amounts of gravel at first; however, as the gravel supply decreases, the handling capacity of the shovel also decreases because of the increased time required to move away from the hopper for a load and then return and dump. Roughly, then, we may estimate that the shovel's gravel handling rate is proportional to the size of the pile still to be moved, its initial rate being 10 ton/min. The conveyor, on the other hand, transports the gravel at a uniform 5 ton/min. At first the shovel will work faster than the conveyor, then slower. Hence, the storage bin will first accumulate material, then empty.

(a) What will be the largest amount of gravel in the bin?
(b) When will this occur?
(c) When will the rates of bin input and output be equal?
(d) When will the bin become empty?

8.17. A large fully automated municipal incinerator is being designed. A survey estimates the garbage load to be 1440 tons/day. This will be harvested by a fleet of compaction trucks which will disgorge their loads into an underground storage bin. A conveyor will then feed the garbage to the incinerator.

The proposed daily collection route is such that at the beginning of the working day (6 A.M. sharp!) relatively large quantities of garbage (average of 6 tons/min) are returned from nearby commercial areas. Subsequently, the supply will diminish as more remote suburban areas are serviced. It is assumed that the collection rate is proportional to the amount of garbage still to be collected, the initial rate being one truckload/min. The conveyor, on the other hand, will transport garbage at a uniform 1 ton/min to the incinerator. At the beginning of the working day, the trucks will work faster than the conveyor; later in the day, slower. Thus, each day the bin will accumulate material, then lose material.

To evaluate this operation, we need information. Please help us with this.

(a) At what time of day will the trucks have collected 95% of the day's garbage?
(b) How much garbage whould the storage bin be designed for?
(c) At what time of day will the bin be fullest?
(d) At what time of day will the bin be empty?

8.18. Upper Slobbovians and Lower Slobbovians are always at it . . . , crushing skulls, slitting throats, and so on. . . . At any gathering the rate at which Upper Slobs are killed is directly proportional to the number of Lower

Slobs around, and vice versa. And at the end of any meeting of these friendly people, either Upper Slobs leave or Lower Slobs, but never both.

Last week ten Upper Slobs happened upon three Lower Slobs, and when it was over eight Upper Slobs lived to tell of their exciting victory.

(a) From this encounter, how would you rate Upper and Lower Slobs as fighters? For example, would you say that they were equally good or that one Upper Slob is as good as 2.3 Lower Slobs, or what?

(b) What would be the outcome of a friendly meeting of ten Upper Slobs with ten Lower Slobs?

8.19. Chemical X, a powdered solid, is slowly and continuously fed for half an hour into a well-stirred vat of water. The solid quickly dissolves and hydrolyses to Y, which then slowly decomposes to Z as follows

$$Y \rightarrow Z, \quad -r_Y = kC_Y, \quad k = 1.5 \text{ hr}^{-1}$$

The volume of liquid in the vat stays close to 3 m³ throughout this operation, and if no reaction of Y to Z occurred, the concentration of Y in the vat would be 100 mol/m³ at the end of the half-hour addition of X.

(a) What is the maximum concentration of Y in the vat and at what time is this maximum reached?

(b) What is the concentration of product Z in the vat after 1 hour?

Problem prepared by Bhaskar Chandan (1990).

8.20. When oxygen is bubbled through a high-temperature batch of A-containing liquid material, A oxidizes slowly to give a slowly decomposing intermediate X and final product R. Here are the results of an experiment:

t, min	C_A, mol/m³	C_R, mol/m³
0	100	0
0.1	95.8	1.4
2.5	35	26
5	12	41
7.5	4.0	52
10	1.5	60
20	negligible	80
∞	0	100

We have no way of analyzing for X; however, we are safe in assuming that at any time $C_A + C_R + C_X = C_{A0}$. What can we say about the mechanism and kinetics of this oxidation? Hint: plot the data and examine the plot.

8.21. Chemical A reacts to form R ($k_1 = 6$ hr⁻¹) and R reacts away to form S ($k_2 = 3$ hr⁻¹). In addition R slowly decomposes to form T ($k_3 = 1$ hr⁻¹). If a solution containing 1.0 mol/liter of A is introduced into a batch reactor, how long would it take to reach $C_{R,max}$, and what would be $C_{R,max}$?