CHEN 416: CHEMICAL REACTION ENGINEERING II

DESIGN FOR MULTIPLE REACTIONS

LEARNING OBJECTIVES

- At the end of this lecture, students should be able to:
  - Explain what multiple reactions are citing different examples
  - Define different terms used in multiple reaction analysis
  - Carry-out qualitative and quantitative treatment of product distribution in parallel reactions.
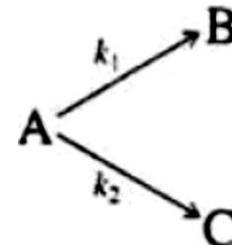
MULTIPLE REACTIONS

- In single reactions, the performance (size) of a reactor was influenced by the pattern of flow within the vessel.

- In multiple reactions, both the size requirement and the distribution of reaction products are affected by the pattern of flow within the vessel.

- 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.

- In multiple reactions,
  - it is more convenient to deal with concentrations rather than conversions.
  - product distribution are examined by eliminating the time variable by dividing one rate equation by another.
  - equations relating the rates of change of certain components with respect to other components of the systems are involved in the analysis
  - two analyses, one for determination of reactor size and the other for the study of product distribution are used.
  - minimization of reactor size and maximization of desired product, may run counter to each other, thus, economic analysis will yield the best option. However, product distribution is often preferred.

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MULTIPLE REACTIONS

❑ Types of Multiple Reactions
- series,
- parallel,
- complex, and
- independent.

▪ They can occur by themselves, in pairs, or all together.

▪ A combination of parallel and series reactions is often referred to as complex reactions.

❑ *Parallel* reactions (also called **competing** reactions) are reactions where the reactant is consumed by two different reaction pathways to form different products:

$$A \xrightarrow{k_1} B$$
$$A \xrightarrow{k_2} C$$

❑ *Series* reactions (also called **consecutive** *reactions*) are reactions where the reactant forms an intermediate product, which reacts further to form another product:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

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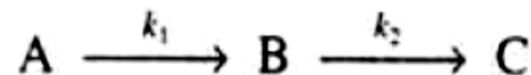
MULTIPLE REACTIONS

- *Complex* reactions are multiple reactions that involve a combination of both series and parallel reactions, such as

$$A + B \longrightarrow C + D$$
$$A + C \longrightarrow E$$

- *Independent* reactions are reactions that occur at the same time but neither the products nor reactants react with themselves or one another.

$$A \longrightarrow B + C$$
$$D \longrightarrow E + F$$

- **Desired and Undesired Reactions**,

- In the parallel reaction sequence

$$A \xrightarrow{k_D} D$$
$$A \xrightarrow{k_U} U$$

- or in the series sequence

$$A \xrightarrow{k_D} D \xrightarrow{k_U} U$$

- the minimization of the formation of U and maximization of *the* formation of D is the objective:
  - because the greater the amount of undesired product formed, the greater the cost of separating product U from the desired product D

MULTIPLE REACTIONS

- **Selectivity** tells us how one product is favored over another in multiple reactions.

- The formation of D with respect to U can be quantified by defining the selectivity and yield of the system.

- The **instantaneous selectivity** $(S_{D/U})$ of D with respect to U is defined as the ratio of the rate of formation of D to the rate of formation of U.

  -
  $$S_{D/U} = \frac{r_D}{r_U} = \frac{\text{rate of formation of D}}{\text{rate of formation of U}}$$
  8-1

- Also **the overall selectivity** $\tilde{S}_{D/U}$ is defined in terms of the flow rates leaving the reactor as

  -
  $$\tilde{S}_{D/U} = \frac{F_D}{F_U} = \frac{\text{Exit molar flow rate of desired product}}{\text{Exit molar flow rate of undesired product}}$$
  8-2

- For a batch reactor, the overall selectivity is given in terms of the number of moles of D and U *at* the end of the reaction time

  -
  $$\tilde{S}_{D/U} = \frac{N_D}{N_U}$$
  8-3

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MULTIPLE REACTIONS

- Reaction **yield**, like the selectivity, has two definitions: one based on the reaction rates and the other based on the ratio of molar flow rates.

- In the first case, the yield at a point can be defined as the ratio of the reaction rate of a given product to the reaction rate of the key reactant A. This is sometimes referred to as the **instantaneous yield**.

$$Y_D = \frac{r_D}{-r_A}$$

8-4

- In the case of reaction yield based on molar flow rates. **the overall yield**, $\tilde{Y}_D$, is defined as the ratio of moles of product formed *at* the end of the reaction to the number *of* moles of the key reactant A, that have been consumed.

- For a batch system:
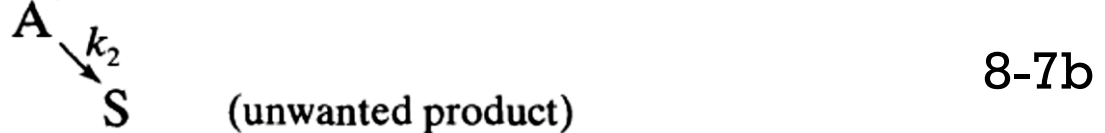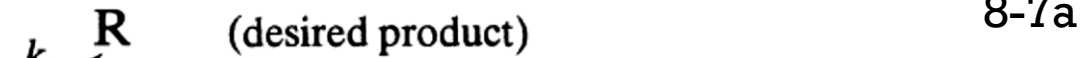
$$\tilde{Y}_D = \frac{N_D}{N_{A0} - N_A}$$

8-5

- For a flow system:

$$\tilde{Y}_D = \frac{F_D}{F_{A0} - F_A}$$

8-6

PRODUCT DISTRIBUTION: QUALITATIVE DISCUSSION

- Consider the decomposition of A by either one of two paths:

  -   8-7a

$$A \begin{array}{c} \nearrow^{k_1} R \quad \text{(desired product)} \\ \searrow_{k_2} S \quad \text{(unwanted product)} \end{array}$$

  -   8-7b

- with corresponding rate equations

  -   8-8a

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

  -   8-8b

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

- Dividing Eq. 8-8*a* by Eq. 8-8*b* gives a measure of the relative rates of formation of R and S (synonymous to instantaneous selectivity).

- Thus,

  -   8-9

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

- this ratio should be as large as possible to maximize desired prod.

- From Eq.8-9, C_A is the only factor that can adjusted and controlled *(since k_1, k_2, a_1 and a_2 are all constant for a specific system at a given temperature)*

PRODUCT DISTRIBUTION: QUALITATIVE DISCUSSION

- C_A can be kept low throughout the reactor by any of the following means:
  - by using a MFR,
  - maintaining high conversions,
  - increasing inerts in the feed, or
  - decreasing the pressure in gas-phase systems.

- Or C_A can be kept high by
  - using a batch or PFR,
  - maintaining low conversions,
  - removing inerts from the feed, or
  - increasing the pressure in gas phase systems.

- From Eq.8-7, If $a_1 > a_2$ or the desired reaction is of higher order than the unwanted reaction, Eq. 8-9 shows that a high reactant concentration is desirable since it increases the selectivity (R/S ratio).
  - So a batch or PFR would favor formation of product R and would require a minimum reactor size.

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PRODUCT DISTRIBUTION: QUALITATIVE DISCUSSION

- 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.
  - Hence a large MFR would be required.

- If $a_1 = a_2$ or the two reactions are of the same order, Eq.8-9 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.

- Product distribution can also be controlled by varying k_2/k_1.

- This can be done in two ways:
  - By changing the temperature level of the operation. If the activation energies of the two reactions are different, k_1/k_2 can be made to vary.
  - 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.

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PRODUCT DISTRIBUTION: QUALITATIVE DISCUSSION

- Qualitative product distribution can therefore be summarize 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.*

- With two or more reactants, combinations of high and low reactant concentrations can be obtained by
  - controlling the concentration of feed materials,
  - having certain components in excess, and
  - using the correct contacting pattern of reacting fluids.

- Figures 8-1 and 8-2 illustrate methods of contacting two reacting fluids in non-continuous and continuous operations that keep the concentrations of these components both high, both low, or one high and the other low.
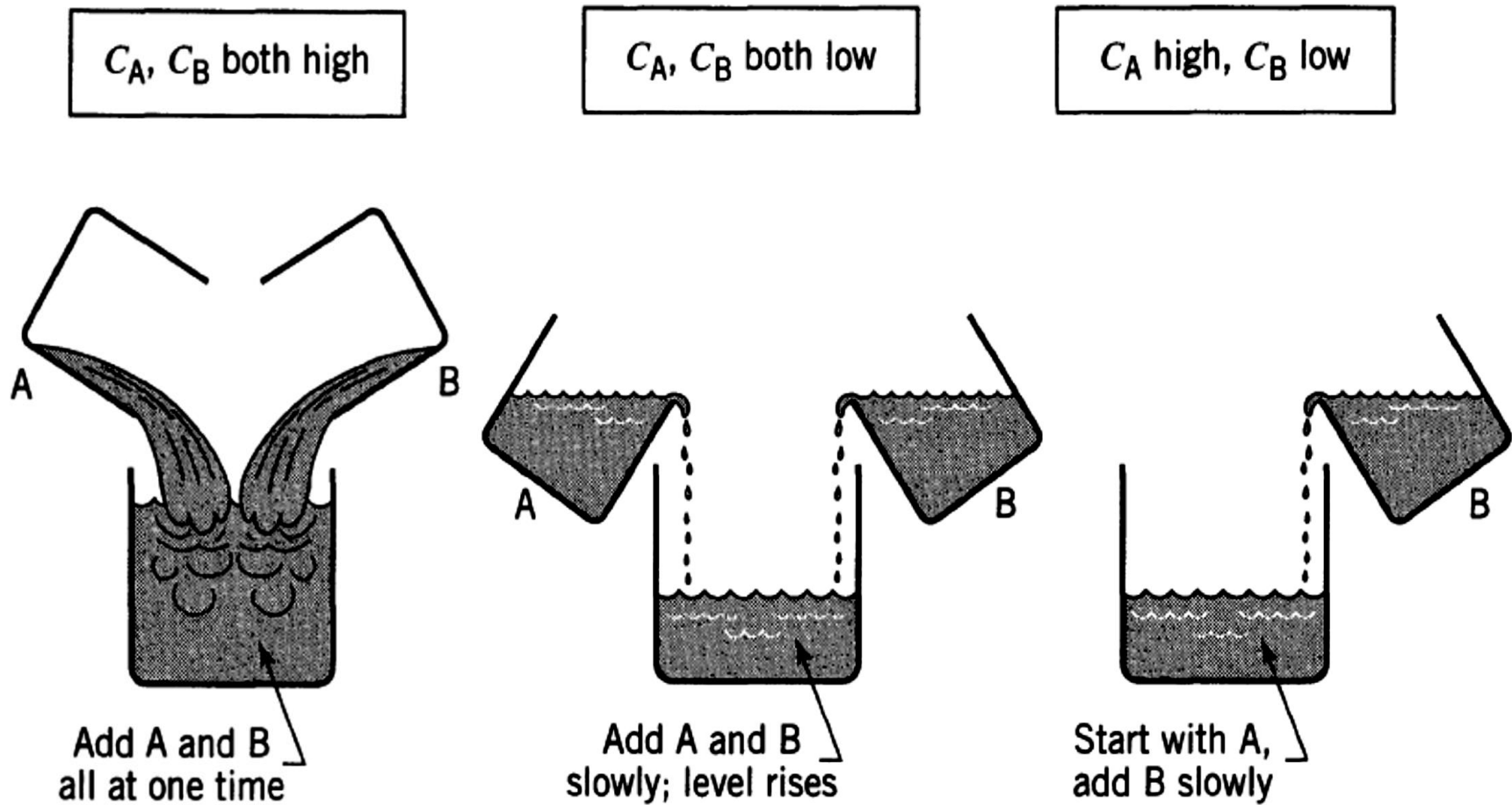
Figure 8-1 Contacting patterns for various combinations of high and low concentration of reactants in non-continuous operations
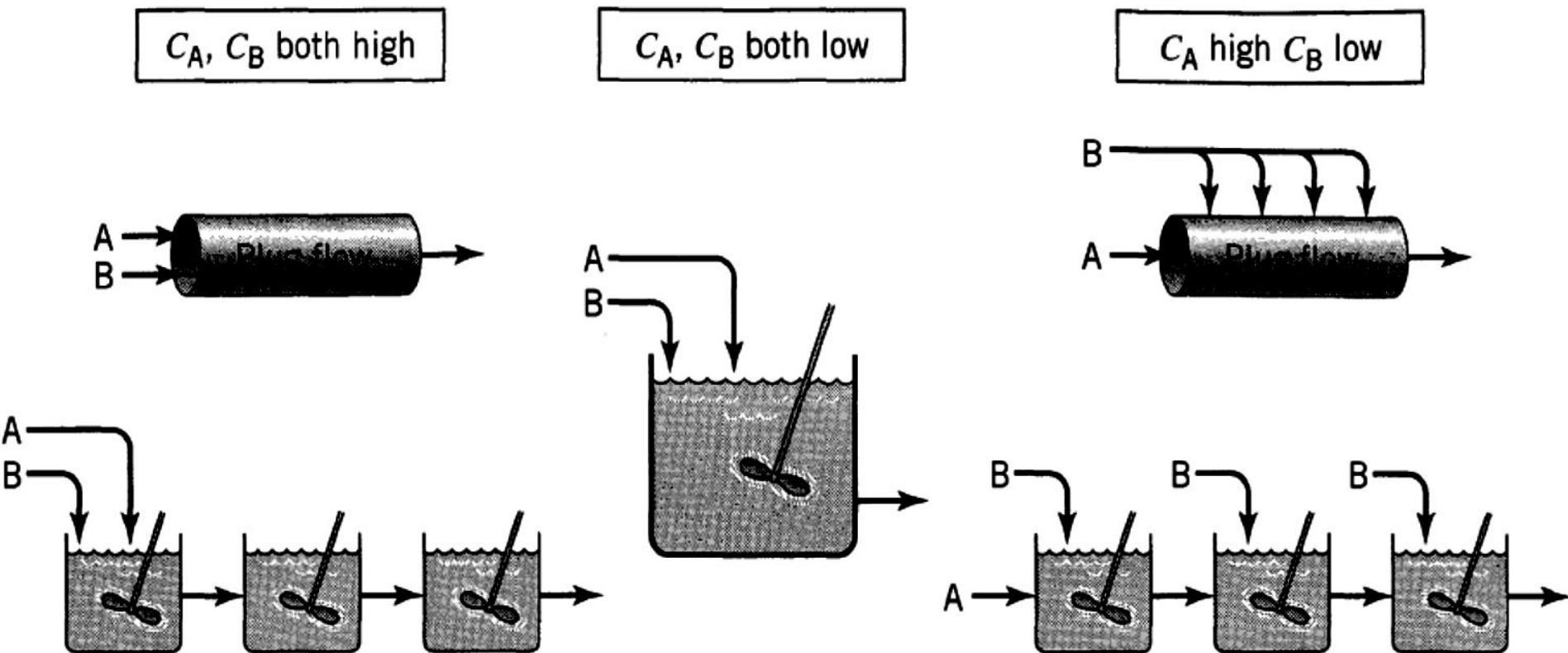
Figure 8-2 Contacting patterns for various combinations of high and low concentration of reactants in continuous operations

PRODUCT DISTRIBUTION: QUALITATIVE DISCUSSION

- In general the following must be considered before the most desirable contacting pattern can be achieved,
  - the number of reacting fluids involved,
  - the possibility of recycle, and
  - the cost of possible alternative setups.
- In any case, the use of the proper contacting pattern is the critical factor in obtaining a favorable distribution of products for multiple reactions.

PRODUCT DISTRIBUTION AND REACTOR SIZE: QUANTITATIVE TREATMENT

- For product distribution and reactor-size requirements to be quantitatively determined in multiple reactions, the rate equations for individual reactions in the multiple reaction must be known.

- For convenience in evaluating product distribution we introduce two terms, φ and Φ.

- Considering the decomposition of reactant A, let φ be the fraction of A disappearing at any instant which is transformed into desired product R. This is the *instantaneous fractional yield of* R.

- Thus at any C_A

$$\varphi = \left(\frac{\text{moles R formed}}{\text{moles A reacted}} \right) = \frac{dC_R}{-dC_A} \qquad \text{8-10}$$

- 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.

- NB: this is the same as the instantaneous yield earlier defined.

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PRODUCT DISTRIBUTION AND REACTOR SIZE: QUANTITATIVE TREATMENT

- Also Φ is defined as the fraction of all the reacted A that has been converted into R, and this is called **the *overall fractional yield of* R**.

- The overall fractional yield is the mean of the instantaneous fractional yields at all points within the reactor; thus we may write

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

8-11

  - The overall fractional yield is of primary concerns, since it represents the product distribution at the reactor outlet.

- The proper averaging for φ depends on the type of flow within the reactor.

  - for PFR, where C_A, changes progressively through the reactor, we have from Eqn.8-10:

$$\Phi_p = \frac{-1}{C_{A0} - C_{Af}} \int_{C_{A0}}^{C_{Af}} \varphi dC_A = \frac{1}{\Delta C_A} \int_{C_{A0}}^{C_{Af}} \varphi dC_A$$

8-12

  - for MFR, the composition is C_{Af} everywhere, so φ is likewise constant throughout the reactor, and we have

$$\Phi_m = \varphi_{\text{evaluated at } C_{Af}} \cdot$$

8-13

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PRODUCT DISTRIBUTION AND REACTOR SIZE: QUANTITATIVE TREATMENT

- The overall fractional yields from MFR and PFRs processing A from C_{A0} to C_{Af} are related by

$$\Phi_m = \left(\frac{d\Phi_p}{dC_A}\right)_{\text{at } C_{Af}} \qquad 8\text{-}14a$$

- and

$$\Phi_p = \frac{1}{\Delta C_A}\int_{C_{A0}}^{C_{Af}} \Phi_m \, dC_A \qquad 8\text{-}14b$$

- Eqn.8-14 allows the prediction of yields from one type of reactor given the yields from the other.

- For a series of $1, 2, \ldots, N$ MFRs in which the concentration of A is C_{AI}, $C_{A2}, \ldots, C_{AN,}$ 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

$$\varphi_1(C_{A0} - C_{A1}) + \cdots + \varphi_N(C_{A,N-1} - C_{AN}) = \Phi_{N\text{ mixed}}(C_{A0} - C_{AN}) \qquad 8\text{-}15$$

- from which

$$\Phi_{N\text{ mixed}} = \frac{\varphi_1(C_{A0} - C_{A1}) + \varphi_2(C_{A1} - C_{A2}) + \cdots + \varphi_N(C_{A,N-1} - C_{AN})}{C_{A0} - C_{AN}} \qquad 8\text{-}16$$

PRODUCT DISTRIBUTION AND REACTOR SIZE: QUANTITATIVE TREATMENT

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

$$C_{Rf} = \Phi(C_{A0} - C_{Af}) \qquad \text{8-17}$$

- and Fig. 8-3 shows how C_R is found for different types of reactors.
  - For MFR, or MFRs in series, the best outlet concentration to use, that which maximizes C_R, may have to be found by maximization of rectangles
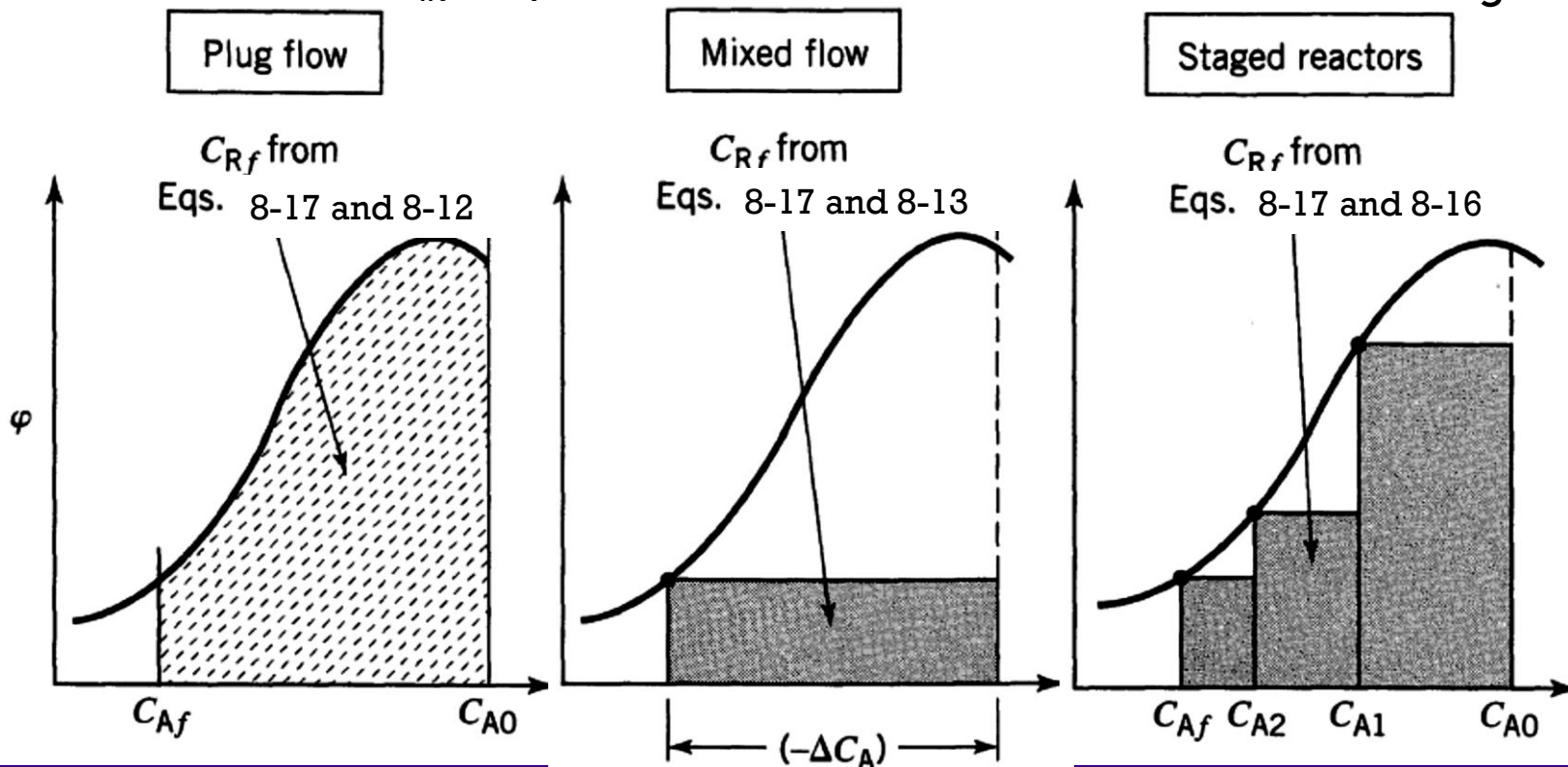

Figure 8.3 Shaded and dashed area gives total R formed.

PRODUCT DISTRIBUTION AND REACTOR SIZE: QUANTITATIVE TREATMENT

- The shape of the φ vs C_A curve determines which type of flow gives the best product distribution, and Fig. 8-4 shows typical shapes of these curves for which PFR, MFR, and MFR followed by PFR are best.
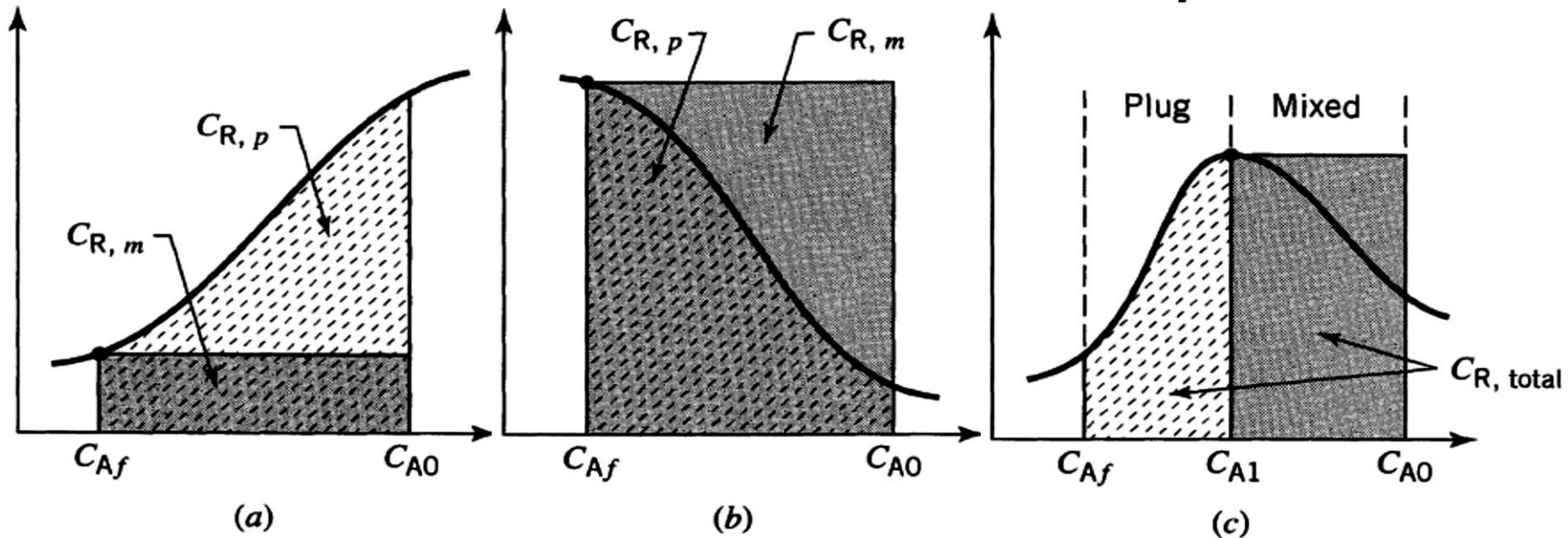

Figure 8-4 The contacting pattern with the largest area produces most R: (a) plug flow is best, (b) mixed flow is best, *(c)* mixed flow up to *CAI* followed by plug flow is best.

- These fractional yield expressions allow us to relate the product distribution from different types of reactors and to search for the best contacting scheme.
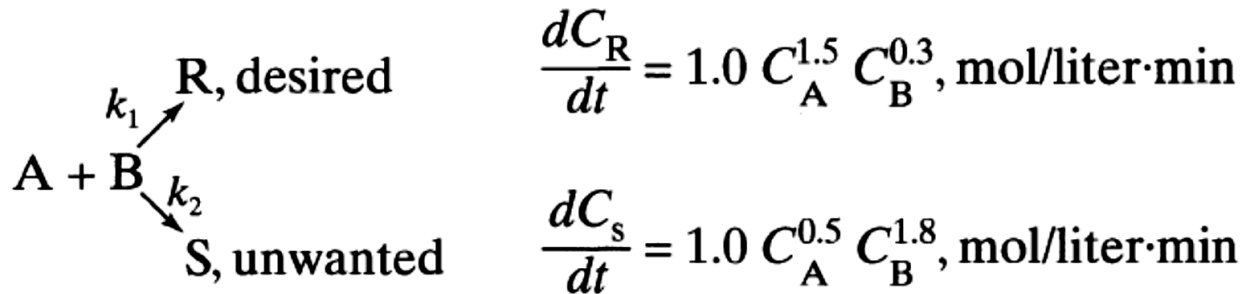
PRODUCT DISTRIBUTION AND REACTOR SIZE: QUANTITATIVE TREATMENT

- However, one condition must be satisfied before these relationships can be safely used:
  - the reaction must be parallel reactions in which no product influences the 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.

- 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.

- Generally, for two or more reactants, 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.

EXAMPLE

Consider the aqueous reactions

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

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

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

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.
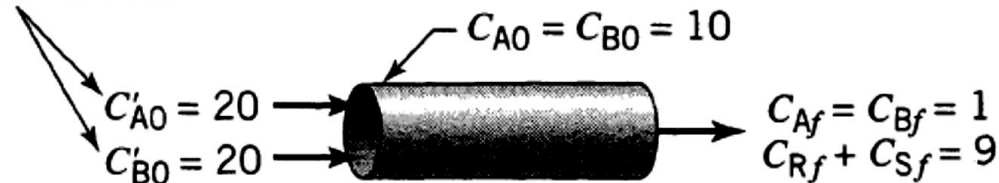
SOLUTION

- The instantaneous fractional yield of the desired compound is

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

- **(a) Plug Flow**

- Referring to Fig. E8.5a, 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. 8-12 that

In separate streams

$C_{A0} = C_{B0} = 10$

$C'_{A0} = 20$
$C'_{B0} = 20$

$C_{Af} = C_{Bf} = 1$
$C_{Rf} + C_{Sf} = 9$

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

- Let $C_A^{0.5} = x$, then $C_A = x^2$ and $dC_A = 2x\,dx$.

- Replacing C_A by x in the above expression gives

SOLUTION

$$\Phi_p = \frac{1}{9} \int_1^{\sqrt{10}} \frac{2x\,dx}{1+x} = \frac{2}{9}\left[\int_1^{\sqrt{10}} dx - \int_1^{\sqrt{10}} \frac{dx}{1+x}\right]$$
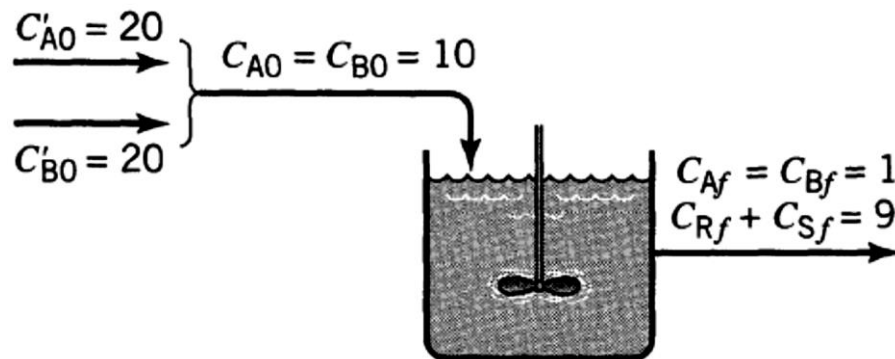
$$= 0.32$$

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

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

(b) Mixed Flow

Referring to Fig. E8-5b, we have from Eq. 8-13, for $C_A = C_B$.

$C'_{A0} = 20$

$C_{A0} = C_{B0} = 10$

$C'_{B0} = 20$

$C_{Af} = C_{Bf} = 1$
$C_{Rf} + C_{Sf} = 9$

$$\Phi_m \left(\frac{R}{A}\right) = \varphi_{\text{at exit}} = \frac{1}{1 + C_A^{0.5}} = 0.5$$
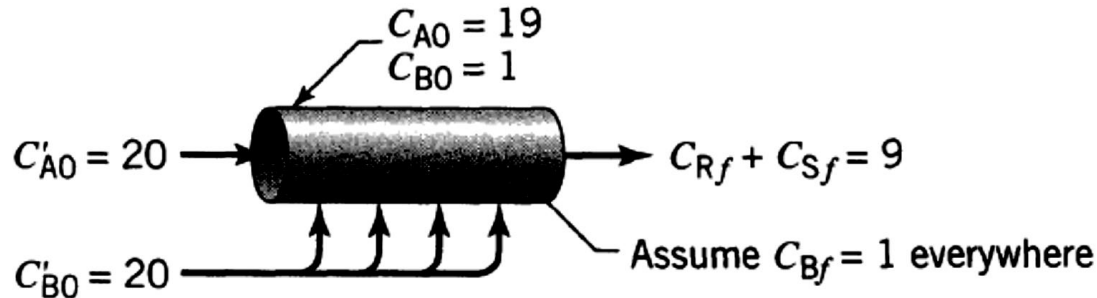
Therefore Eq. 8-16 gives

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

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SOLUTION

- **(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. E8-5c

$$C_{A0} = 19$$
$$C_{B0} = 1$$
$$C'_{A0} = 20 \longrightarrow$$
$$\longrightarrow C_{Rf} + C_{Sf} = 9$$
$$C'_{B0} = 20 \longrightarrow$$
Assume $C_{Bf} = 1$ everywhere

- Then accounting 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,

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

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

PRODUCT DISTRIBUTION: QUALITATIVE DISCUSSION FOR SERIES REACTION

- The rule governing product distribution for reactions in series suggest that:
  - *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.*

- As the intermediate is the desired reaction product, the rule allows the evaluation of the effectiveness of various reactor systems.
  - PFR and batch operations will both give a maximum R yield because there is no mixing of fluid streams of different compositions.
  - the MFR 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.

PRODUCT DISTRIBUTION: QUANTITATIVE DISCUSSION FOR SERIES REACTION IN PFR OR BATCH REACTORS

▪ For unimolecular-type reactions in batch reactors.

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$
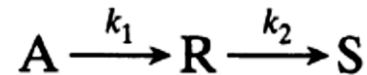
▪ The derivations assumed that the feed contained no reaction products R or S.

▪ The rate equations are:

$$r_A = -k_1 C_A$$

$$r_R = k_1 C_A - k_2 C_R$$

$$r_S = k_2 C_R$$

▪ If the reaction time is replaced by the space time, then,

$$\frac{C_A}{C_{A0}} = e^{-k_1 \tau}$$

▪ and

$$\frac{C_R}{C_{A0}} = \frac{k_1}{k_2 - k_1}\left(e^{-k_1 \tau} - e^{-k_2 \tau}\right)$$

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

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PRODUCT DISTRIBUTION: QUANTITATIVE DISCUSSION FOR SERIES REACTION IN PFR OR BATCH REACTORS

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

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

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

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

- Figure 8-6*a,* prepared for various k_2/k_1 values, illustrates how this ratio governs the concentration-time curves of the intermediate R. Figure 8-6b, a time-independent plot, relates the concentration of all reaction components.
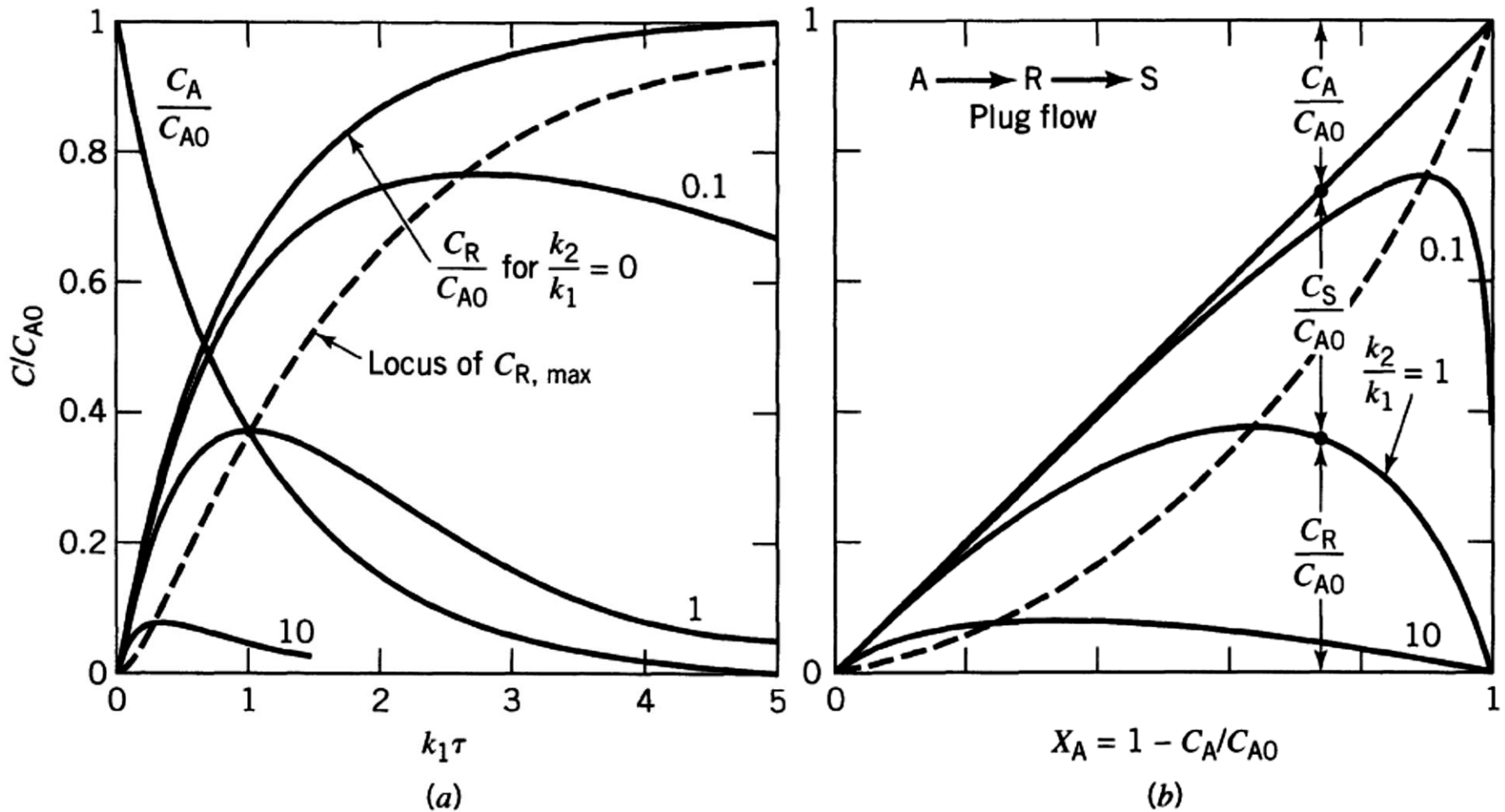
Figure *8.3a,* b Behavior of unimolecular-type reactions in a PFR: (a) concentration-time curves, and (b) relative concentration of the reaction components