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MULTIPLE REACTIONS

Chapter 6

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Introduction

After this chapter you will be able to focus on reactor selection and mole balances for multiple reactions

- ❑ Seldom does 1 reaction occur in a reactor
- ❑ Multiple reactions will occur (some desired / some undesired)
- ❑ Economic success of a plant depends on minimizing undesired side reactions

How we will go about it?

- ❑ Describe basic types of multiple reactions
- ❑ Define Selectivity and how it can be used to minimize unwanted side reactions
- ❑ Choice of operating conditions and reactor type
- ❑ Develop an algorithm to solve reaction engineering problems when multiple reactions are involved

Types of reactions

SERIES REACTIONS (CONSECUTIVE REACTIONS)



Intermediate product

Reaction of ethylene oxide with ammonia to form mono, di and tri-ethanol amine

PARALLEL REACTIONS (COMPETING REACTIONS)

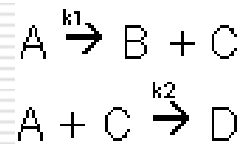


Two different pathways to form different products

Oxidation of ethylene to ethylene oxide and CO_2 / H_2O

Types of reactions

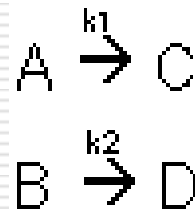
COMPLEX REACTIONS (CONSECUTIVE REACTIONS)



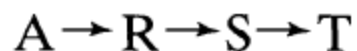
Butadiene (C_4H_6) from ethanol (ethylene, acetaldehyde, butadiene)

INDEPENDENT REACTIONS

Crude oil to Gasoline



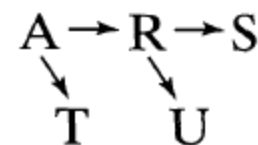
Potpourri of Reactions



Series



Series parallel, or
consecutive-competitive



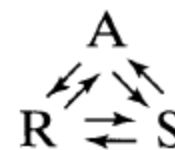
Denbigh system



Reversible and
irreversible



Reversible



Reversible
network

Desired and Undesired Reactions



Minimize the formation of U and maximize U (objective)



ECONOMIC INCENTIVE

Selectivity and Yield

Selectivity: Indication of preference of one product over another

INSTANTANEOUS
(rate of formation)

$$S_{DU} = \frac{r_D}{r_U}$$

OVERALL
(based on exit molar flowrate)

$$\bar{S}_{DU} = \frac{F_D}{F_U}$$

For batch reactor it will be in terms of number of moles
(Can we compare it for a CSTR?)

Selectivity and Yield

Yield: Ratio of the reaction rate of a given product to the reaction rate of the key reactant A

INSTANTANEOUS

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

OVERALL

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

For batch reactor it will be in terms of number of moles
(Can we compare it for a CSTR)

SELECTIVITY & CONVERSION NOT THE BEST OF FRIENDS!!

Selectivity and Yield

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

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

For PFR: $\Phi_p = \frac{-1}{C_{A0} - C_{A_f}} \int_{C_{A0}}^{C_{A_f}} \varphi dC_A = \frac{1}{\Delta C_A} \int_{C_{A0}}^{C_{A_f}} \varphi dC_A$ $\Phi_m = \varphi_{\text{evaluated at } C_{A_f}}$

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

Selectivity and Yield

φ be the fraction of A disappearing at any instant which is transformed into desired product R.

For any particular set of reactions and rate equations φ is a function of C_A .

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

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

Selectivity and Yield

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

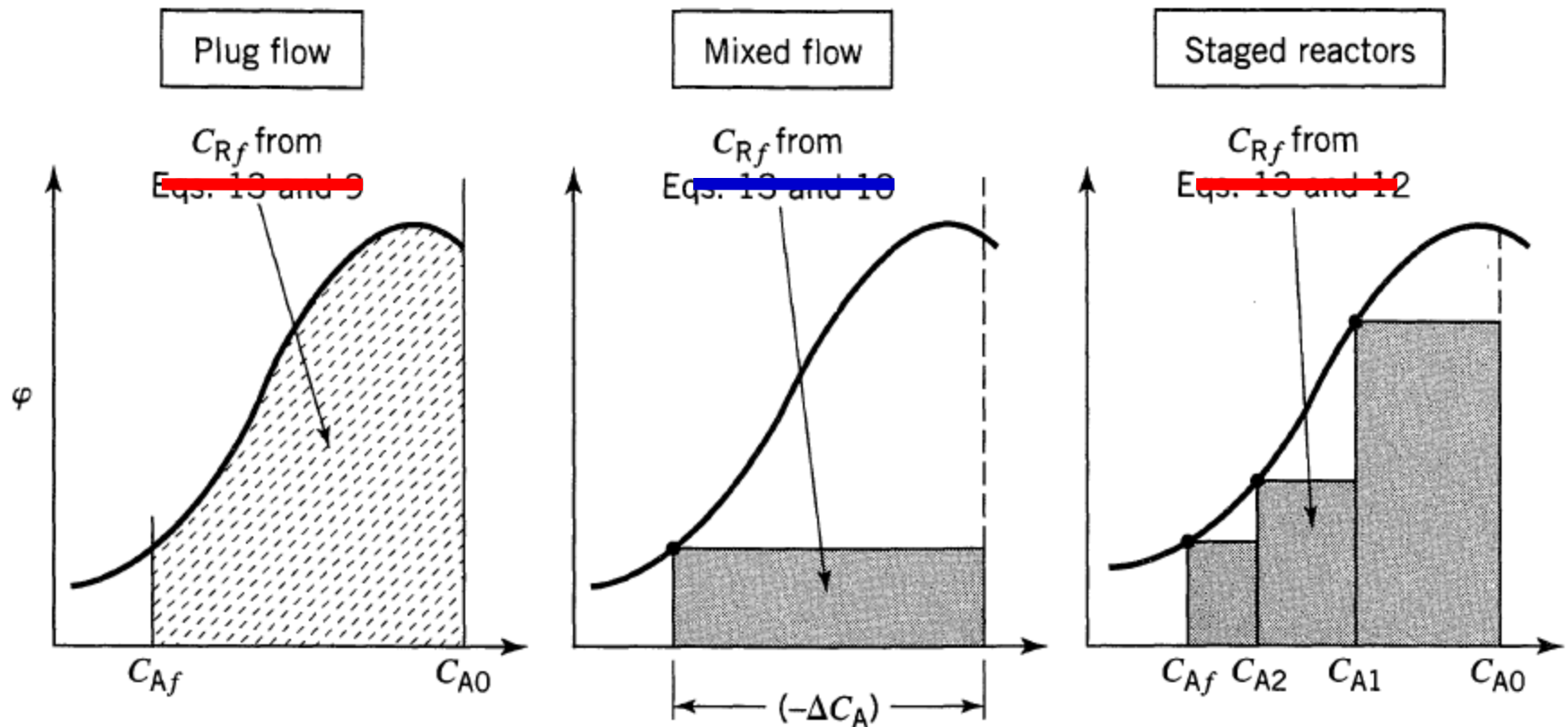
the exit concentration of R

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

C_R can be found for different reactors

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.

Selectivity and Yield



Selectivity and Yield

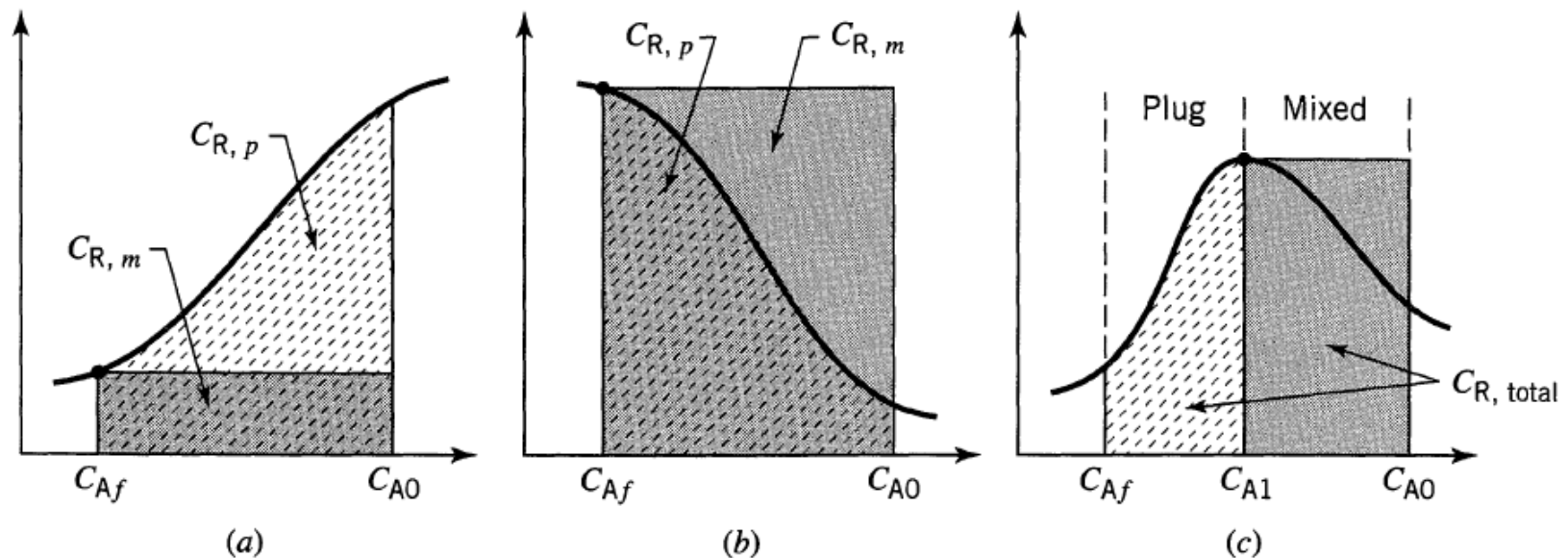
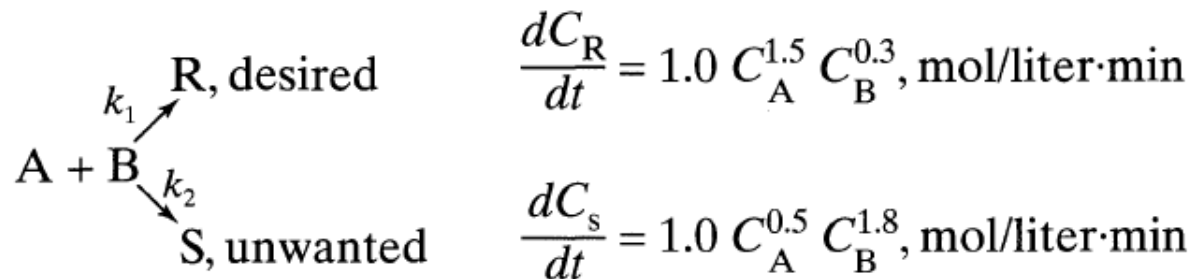


Figure 7.4 The contacting pattern with the largest area produces most R: (a) plug flow is best, (b) mixed flow is best, (c) mixed flow up to C_{A1} followed by plug flow is best.

Problem (Product Distribution)

Consider the aqueous reactions



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

The flow in the reactor follows.

- (a) Plug flow
- (b) Mixed flow
- (c) The best of the four plug-mixed contacting schemes of Example 7.1.

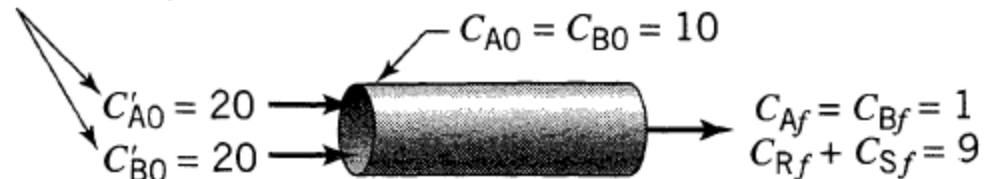
Solution

be careful to get the concentrations right when you mix streams

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

Plug Flow

In separate streams



Solution

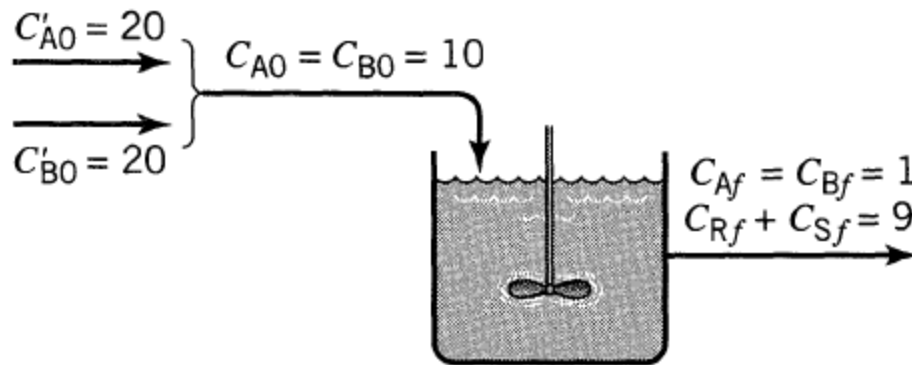
Let $C_A^{0.5} = x$, then $C_A = x^2$ and $dC_A = 2xdx$. Replacing C_A by x in the above expression gives

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

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

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

Solution



Mixed Flow

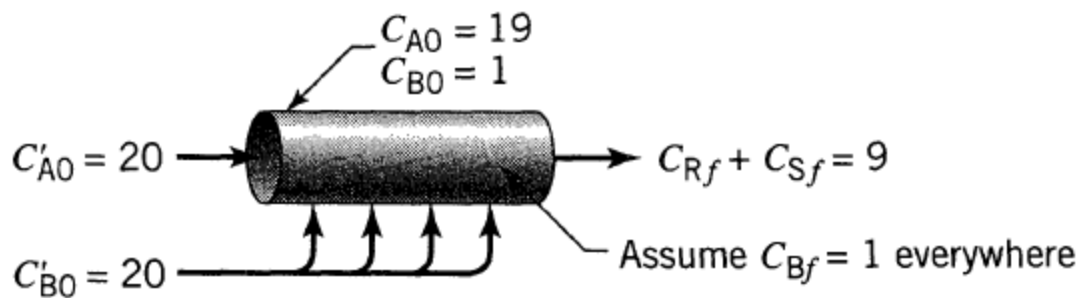
for $C_A = C_B$

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

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

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

Solution



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

Summarizing

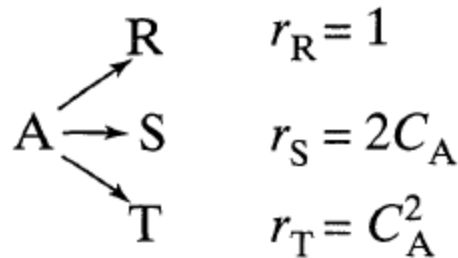
To summarize

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

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

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

Problem (Good operating conditions)



$$C_{\text{A}0} = 2,$$

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 $C_{\text{A}0} = 2$.

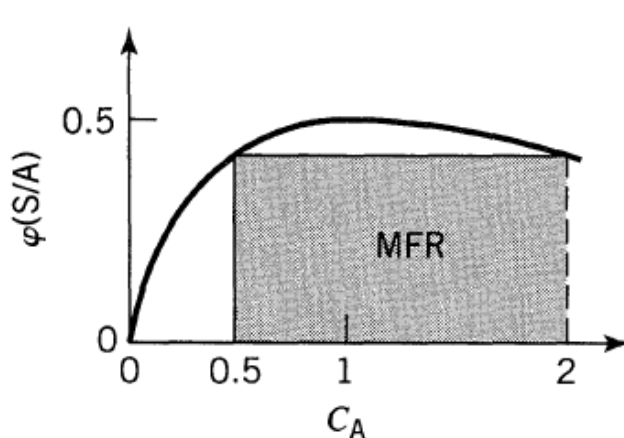
Solution

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

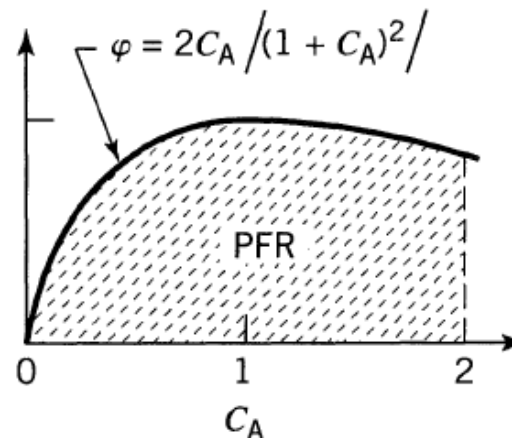
maximum occurs

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

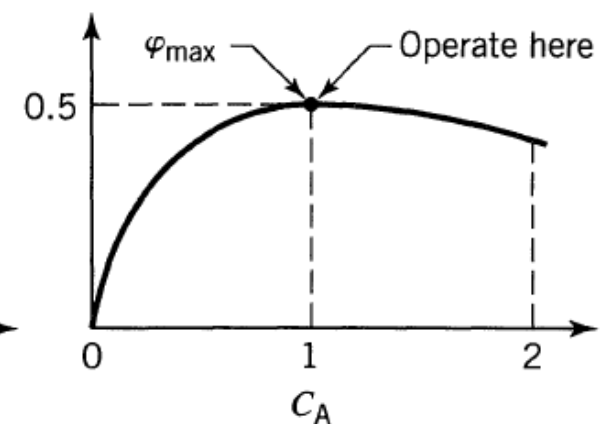
$$\varphi = 0.5 \quad \text{at} \quad C_A = 1.0$$



(a)



(b)



(c)

Solution

Mixed Reactor

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

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

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

Plug Flow Reactor

$$C_{Sf} = - \int_{C_{A0}}^{C_{Af}} \varphi(S/A) dC_A$$

$$= \int_0^2 \frac{2C_A}{(1 + C_A)^2} dC_A$$

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

Solution

Any Reactor with Separation and Recycle of Unused Reactant.

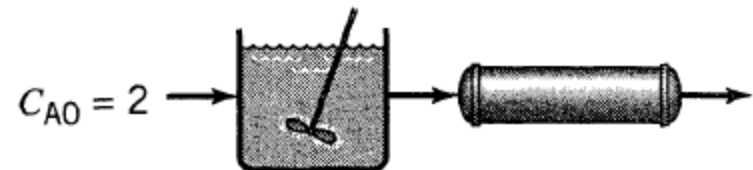
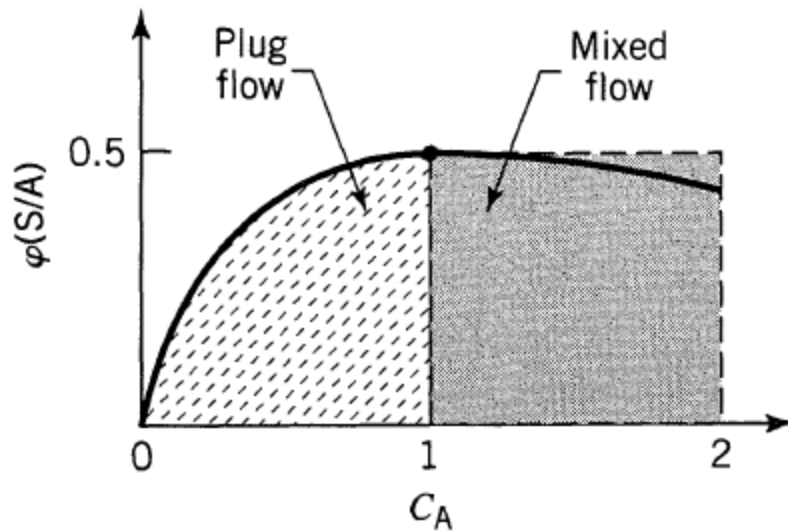
No

reactant leaves the system unconverted, what is important is to operate at conditions of highest fractional yield. This is at $C_A = 1$, where $\varphi(S/A) = 0.5$, as shown in ~~Fig. E7.2c~~. Thus, we should use a mixed flow reactor operating at $C_A = 1$. We would then have 50% of reactant A forming product S.

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

Problem (Best operating conditions)

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



Solution

for mixed flow

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

For plug flow

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

Therefore, the total amount of C_S formed is

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

Selectivity and Yield



**Selectivity
parameter**

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1 C_A^2 C_B}{k_2 C_A C_B} = \frac{k_1}{k_2} C_A$$

Run at high concentration of A. Use PFR.

Note

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.

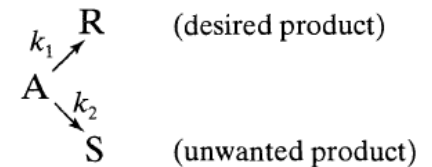
Parallel reactions



$-r_A = r_D + r_U$ (α_1 and α_2 are positive reaction orders)

Objective: $r_D \uparrow$ and $r_U \downarrow$

$$S_{DU} = \frac{r_D}{r_U} = (k_D/k_U) C_A^{\alpha_1 - \alpha_2}$$



Parallel reactions

□ Case 1: $\alpha_1 > \alpha_2$

□ Case 1: $\alpha_1 < \alpha_2$

Should the reaction be run at high or low temperatures?

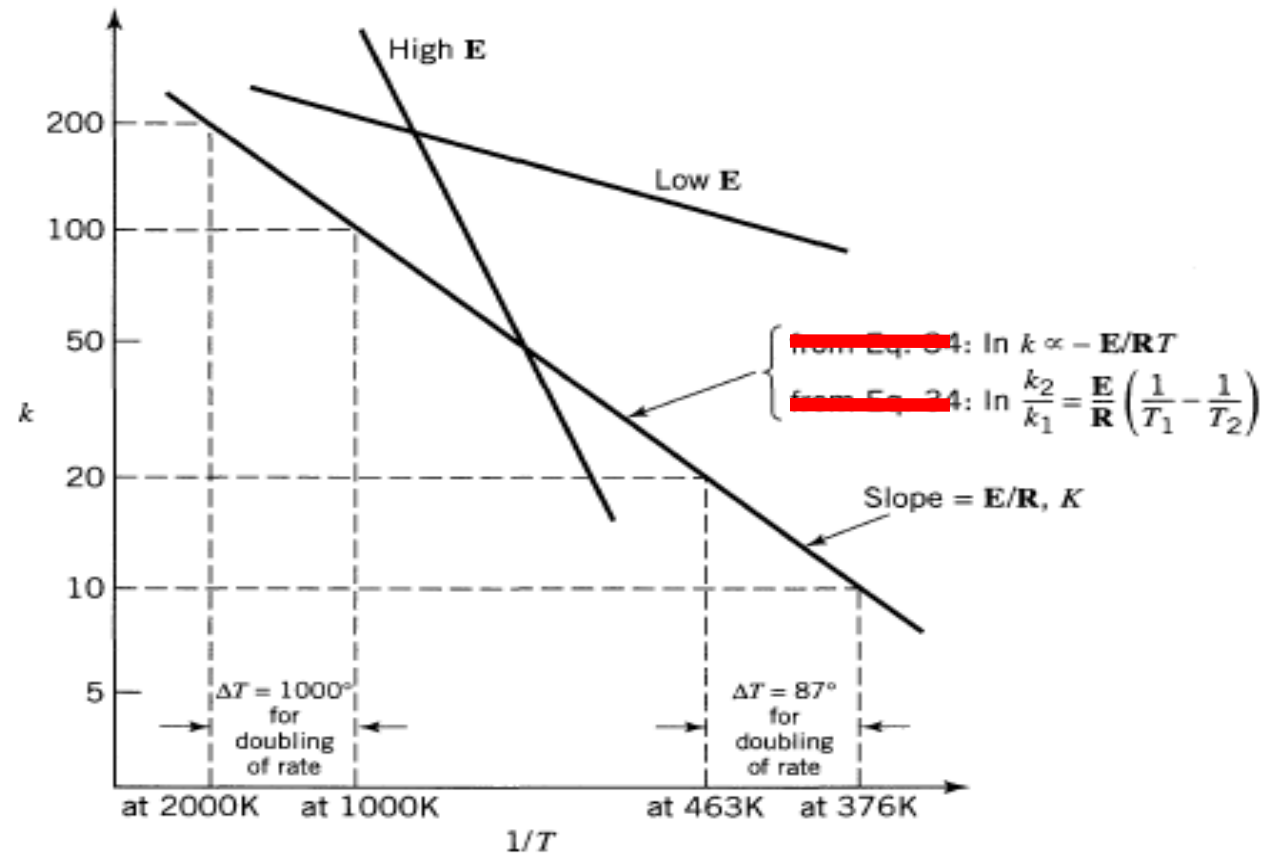
$$S_{D/U} \sim k_D / k_U = (A_D / A_U) e^{-[(E_D - E_U) / RT]}$$

□ Case 1: $E_D > E_U$

□ Case 1: $E_D < E_U$

The Activation Energy conundrum

E is the minimum energy required to start a reaction. That is all.



Note

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.

Summary

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.

Parallel reactions



desired product , $r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1}$



undesired product , $r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2}$

$$S_{DU} = \frac{r_D}{r_U} = (k_1/k_2) C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2}$$

Depends on whether $\alpha_1 - \alpha_2$ & $\beta_1 - \beta_2$ are positive and negative

Contacting patterns (PR)

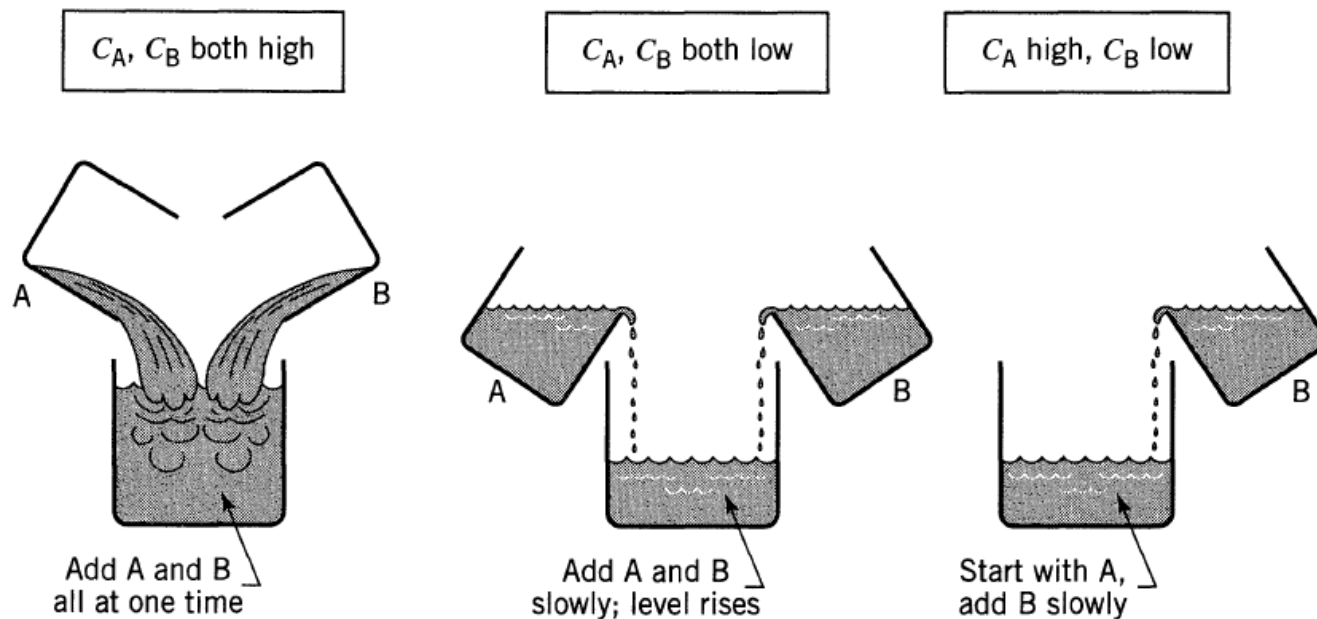


Figure 7.1 Contacting patterns for various combinations of high and low concentration of reactants in noncontinuous operations.

Contacting patterns (PR)

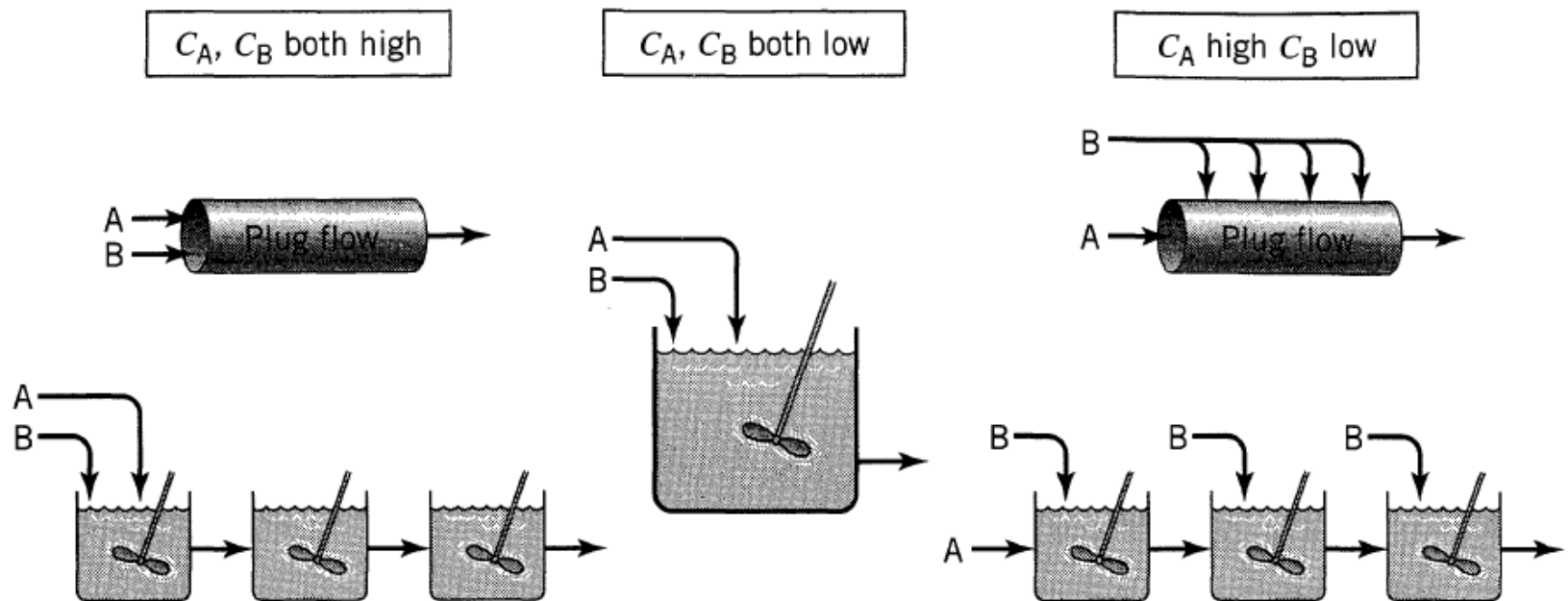
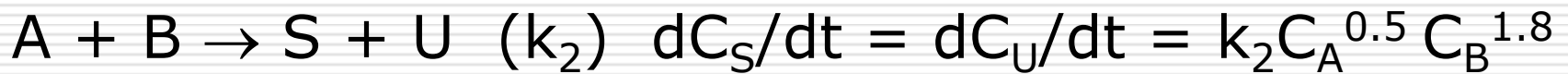


Figure 7.2 Contacting patterns for various combinations of high and low concentration of reactants in continuous flow operations.

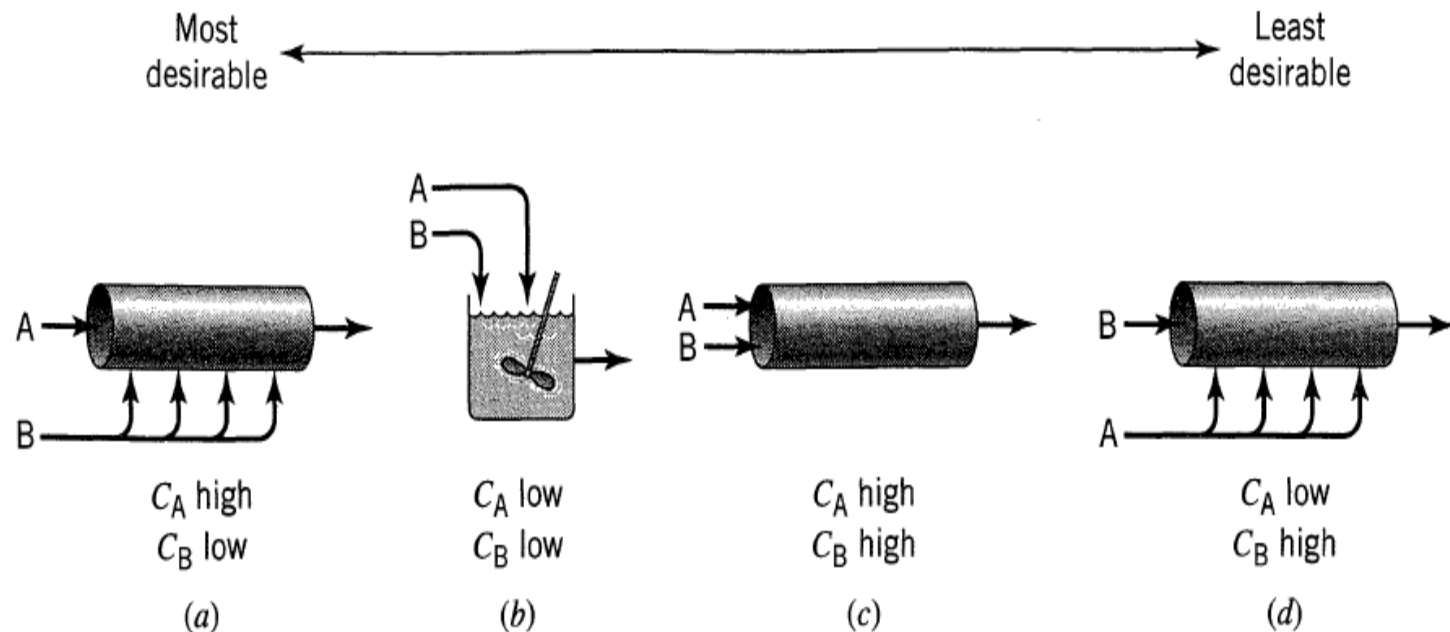
DIY (Contacting Schemes)

The desired liquid phase reaction



From the standpoint of favourable product distribution, order the contacting schemes from most desirable to least desirable

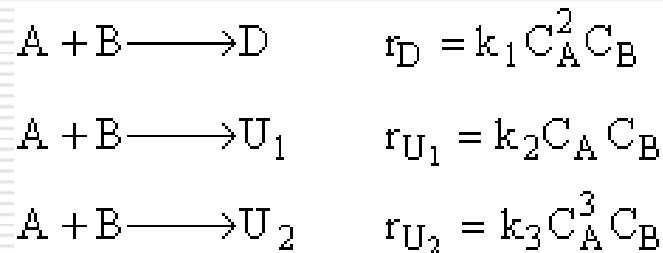
DIY (Contacting Schemes)



Better contacting schemes possible

Parallel reactions (Problem)

Determine the instantaneous selectivity, $S_{D/U}$, for the liquid phase reactions



Sketch the selectivity as a function of the concentration of A. Is there an optimum and if so what is it?

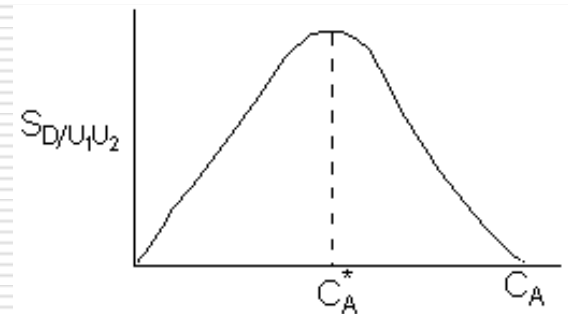
Parallel reactions (Solution)

Write the equation for selectivity

$$S_{D/U_1U_2} = \frac{r_D}{r_{U_1} + r_{U_2}} = \frac{k_1 C_A^2 C_B}{k_2 C_A C_B + k_3 C_A^3 C_B} = \frac{k_1 C_A}{k_2 + k_3 C_A^2} \quad \mathbf{1}$$

$$\frac{dS}{dC_A} = 0 = k_1 [k_2 + k_3 C_A^{*2}] - k_1 C_A^* [2k_3 C_A^*]$$

$$C_A^* = \sqrt{\frac{k_2}{k_3}} \quad \mathbf{2}$$



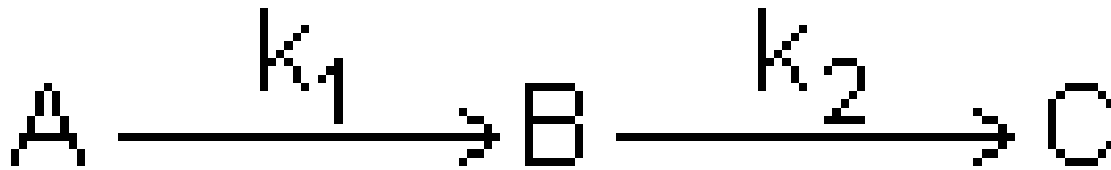
We can find C_A which will maximize selectivity

Parallel reactions (What else?)

- ❑ Selectivity can be calculated **Subs. Eq. 2 in 1**
- ❑ We can now calculate reactor volume to maximize selectivity ($V = (F_{a0} - F_A) / -r_A$)
- ❑ We can estimate the temperature at which we can operate the CSTR
- ❑ We can estimate conversion [$X = (C_{A0} - C_A^*) / C_{A0}$]
- ❑ Can we increase conversion of desired product?

$$V = v_0 C / r_A; dC/d\tau = r_A$$

Series reactions



Here the important variable is space time for a flow reactor and real time for a batch reactor

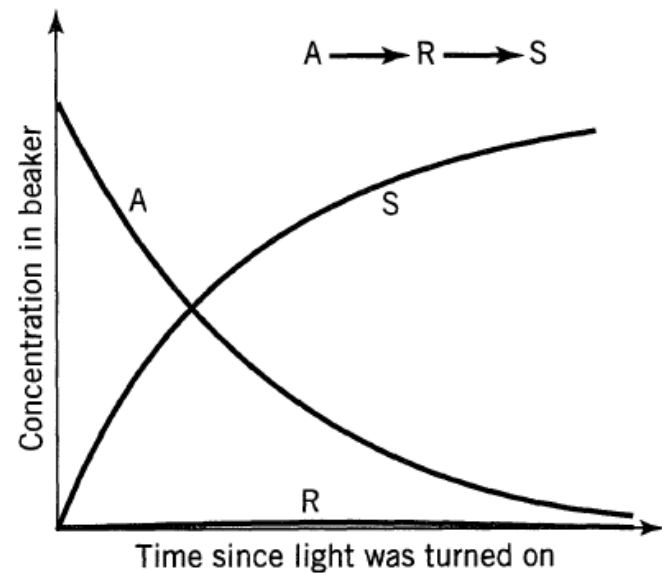
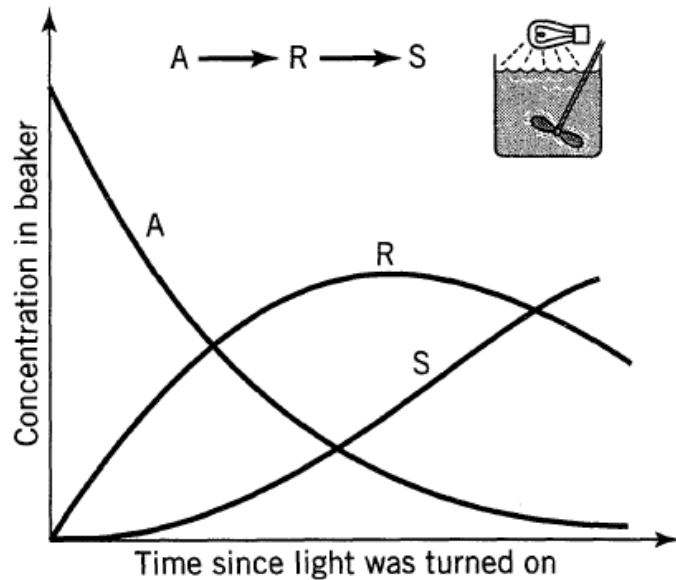
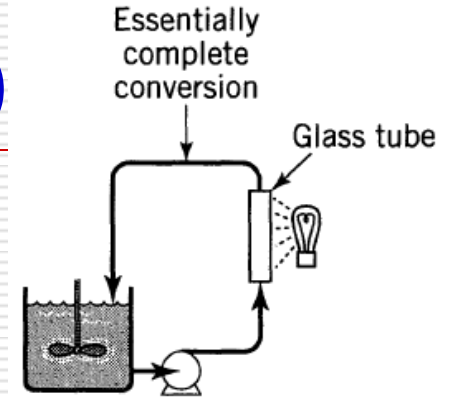
- Case 1: R1 faster than R2
- Case 1: R1 slower than R2

$$r_A = -k_1 C_A$$

$$r_R = k_1 C_A - k_2 C_R$$

$$r_S = k_2 C_R$$

Series reactions (Qualitative)

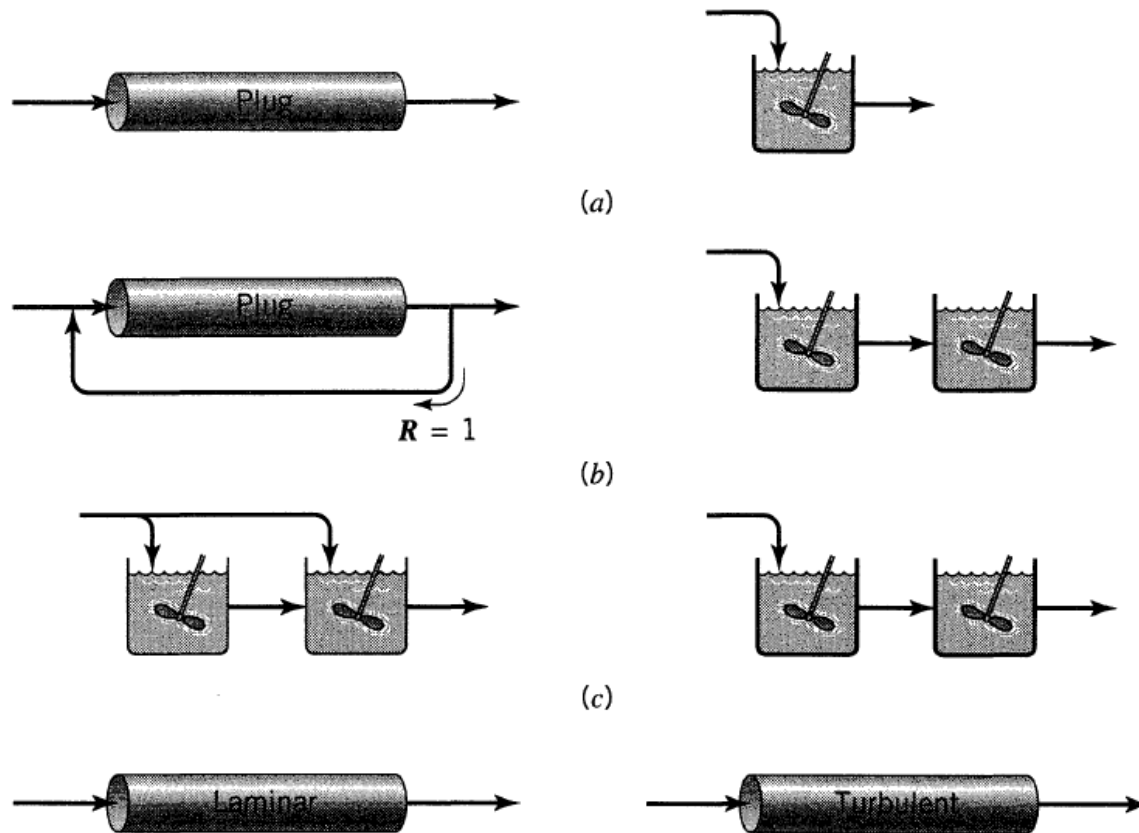


Series reactions (Qualitative)

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 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.

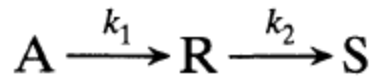
FAVORABLE CONTACTING PATTERNS FOR ANY SET OF IRREVERSIBLE REACTIONS IN SERIES, NOT JUST $A \rightarrow R \rightarrow S$



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

- 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.

Irreversible reaction in series (Plug flow)



Starting with A

$$-\ln \frac{C_A}{C_{A0}} = k_1 t \quad \text{or} \quad C_A = C_{A0} e^{-k_1 t}$$

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

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

$$r_S = \frac{dC_S}{dt} = k_2 C_R$$

Substituting in r_R

$$\frac{dC_R}{dt} + k_2 C_R = k_1 C_{A0} e^{-k_1 t}$$

$$\frac{dy}{dx} + Py = Q \quad \longrightarrow \quad ye^{\int P dx} = \int Qe^{\int P dx} dx + \text{constant}$$

Irreversible reaction in series

integrating factor is $e^{k_2 t}$. The constant of integration is found to be $-k_1 C_{A0}/(k_2 - k_1)$ from the initial conditions $C_{R0} = 0$ at $t = 0$, and the final expression for the changing concentration of R is

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

Noting that there is no change in total number of moles, the stoichiometry relates the concentrations of reacting components by

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

Irreversible reaction in series

$$C_S = C_{A0} \left(1 + \frac{k_2}{k_1 - k_2} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right)$$

if k_2 is much larger than k_1 , $C_S = C_{A0} (1 - e^{-k_1 t})$, $k_2 \gg k_1$

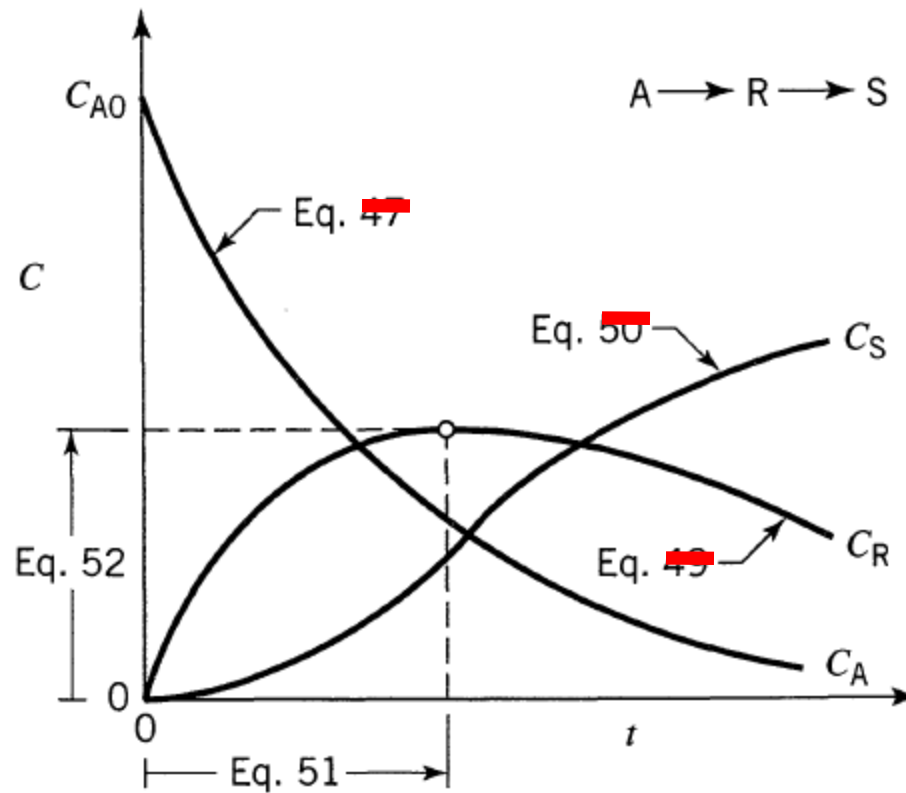
k_1 is much larger than k_2 , $C_S = C_{A0} (1 - e^{-k_2 t})$, $k_1 \gg k_2$

$$dC_R/dt = 0$$

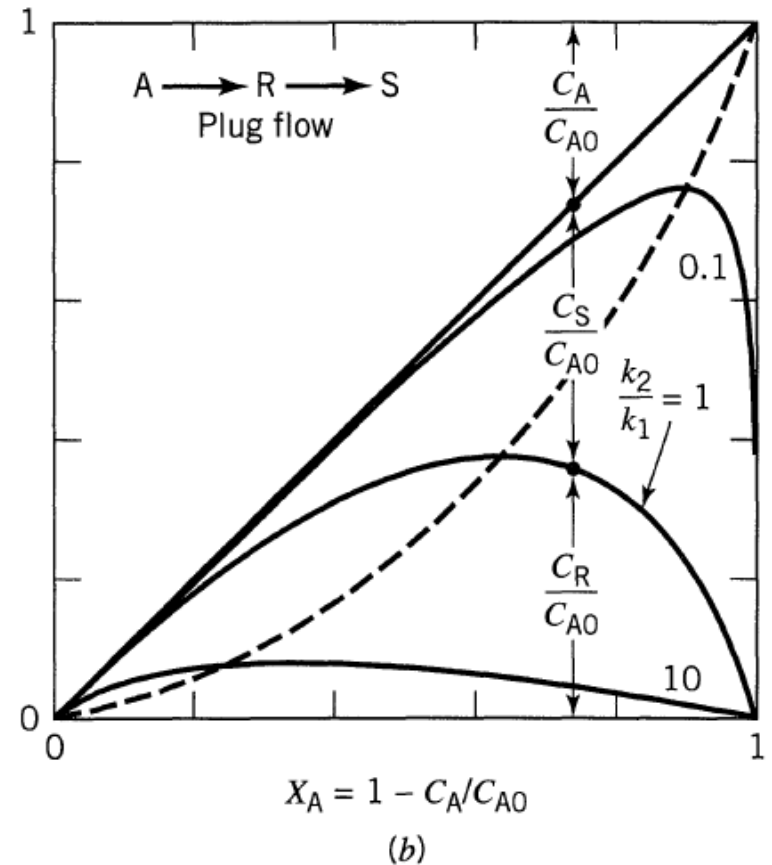
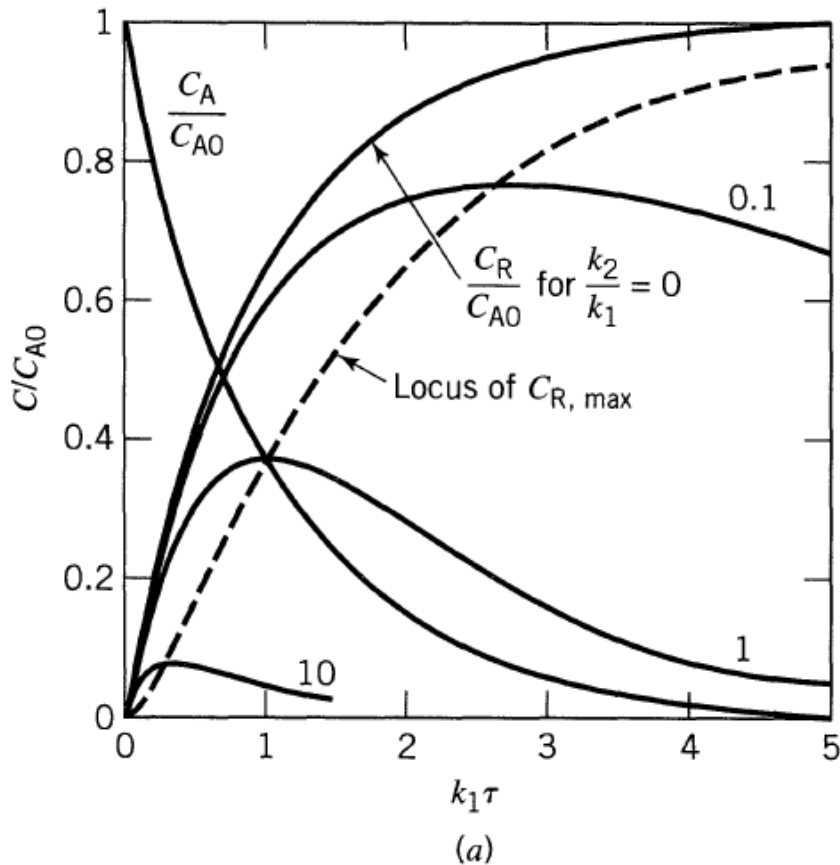
$$t_{\max} = \frac{1}{k_{\log \text{ mean}}} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$$

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

Irreversible reaction in series



Irreversible reaction in series



Series reactions



Species A: $-\frac{dC_A}{dt} = -r_A = k_1 C_A \quad \longrightarrow \quad C_A = C_{A0} \exp(-k_1 t)$

Species B: $\frac{dC_B}{dt} = r_B \quad \longrightarrow \quad r_B = r_{B\text{NET}} = r_{1B} + r_{2B}$

$r_B = k_1 C_A - k_2 C_B \quad \longrightarrow \quad \frac{dC_B}{dt} = k_1 C_{A0} \exp(-k_1 t) - k_2 C_B \quad \frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} \exp(-k_1 t)$

$$y'(x) + P(x)y(x) + Q(x) = 0$$

$$\exp(\int P(x)dx) = \text{IF}$$

Series reactions

$$e^{k_2 t}$$

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} \exp(-k_1 t)$$



Dividing by IF. we see we arrive back at Equation 1

$$\text{if.} = \exp(k_2 t)$$



$$\frac{d[C_B \exp(k_2 t)]}{dt} = k_1 C_{A0} \exp(k_2 - k_1)t$$

Differentiating the RHS of Equation (2)

Now integrating Equation (2)



$$C_B k_2 e^{k_2 t} = \frac{k_1 C_{A0}}{k_2 - k_1} e^{-k_1 t} + K_1 e^{-k_2 t}$$

Evaluating the constant of integration K_1

$$\text{when } t = 0 \text{ then } C_B = 0 \therefore K_1 = -\frac{k_1 C_{A0}}{k_2 - k_1}$$

$$e^{k_2 t} \frac{dC_B}{dt} + C_B k_2 e^{k_2 t} = k_1 C_{A0} e^{-k_1 t} e^{k_2 t}$$

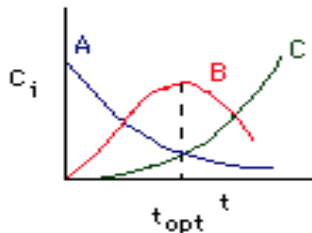
$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1} \left[e^{-k_1 t} - e^{-k_2 t} \right]$$

Series reactions

When do we stop the reaction to maximize B?

$$t = t_{\text{opt}} \text{ at } \frac{dC_B}{dt} = 0 \quad \longrightarrow \quad C_B = \frac{k_1 C_{A0}}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)]$$

$$\frac{dC_B}{dt} = 0 = \frac{k_1 C_{A0}}{k_2 - k_1} (-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}) \quad \longrightarrow \quad t_{\text{opt}} = \left(\frac{1}{k_2 - k_1} \right) \ln \frac{k_2}{k_1}$$

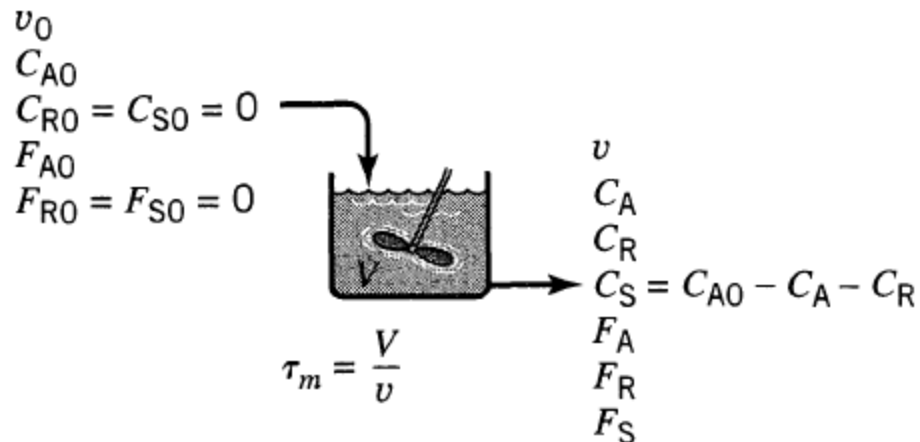


$$C_C = \frac{C_{A0}}{k_2 - k_1} \left[k_2 (1 - e^{-k_1 t}) - k_1 (1 - e^{-k_2 t}) \right]$$

What is X_{opt} ?

Series reactions (MFR)

feed which contains no reaction product R or S.



steady-state material balance

input = output + disappearance by reaction

Series reactions (MFR)

for reactant A

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

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

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


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

Series reactions (MFR)

For component R the material balance,

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

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


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

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

$$\frac{C_S}{C_{A0}} = \frac{k_1k_2\tau_m^2}{(1 + k_1\tau_m)(1 + k_2\tau_m)}$$

C_S is found by simply noting that at any time

Series reactions (MFR)

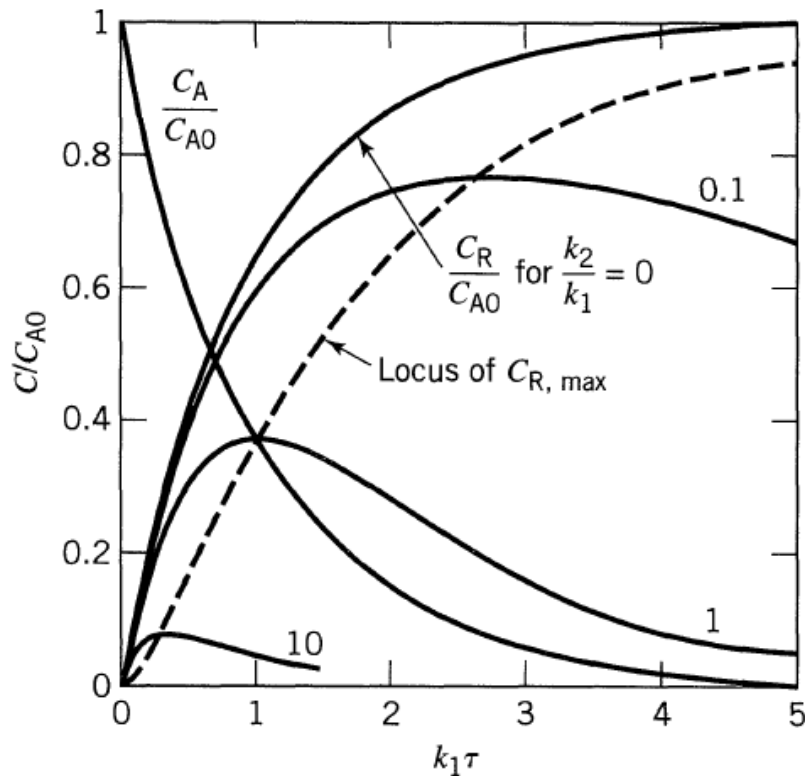
The location and maximum concentration of R are found by determining $dC_R/d\tau_m = 0$. Thus

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

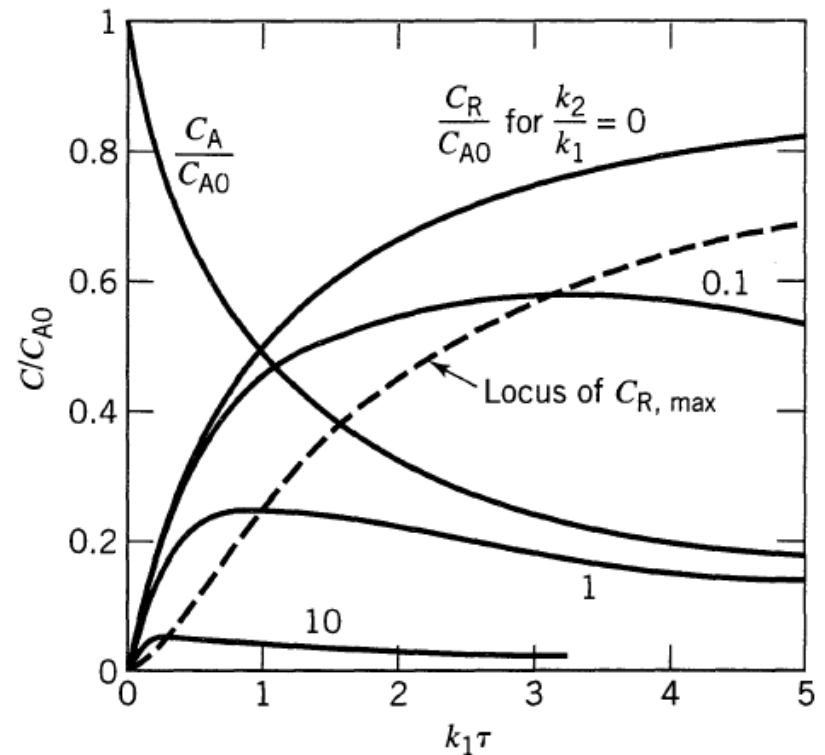
$$\tau_{m,\text{opt}} = \frac{1}{\sqrt{k_1k_2}}$$

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

Performance characteristics



PFR



MFR

Performance characteristics

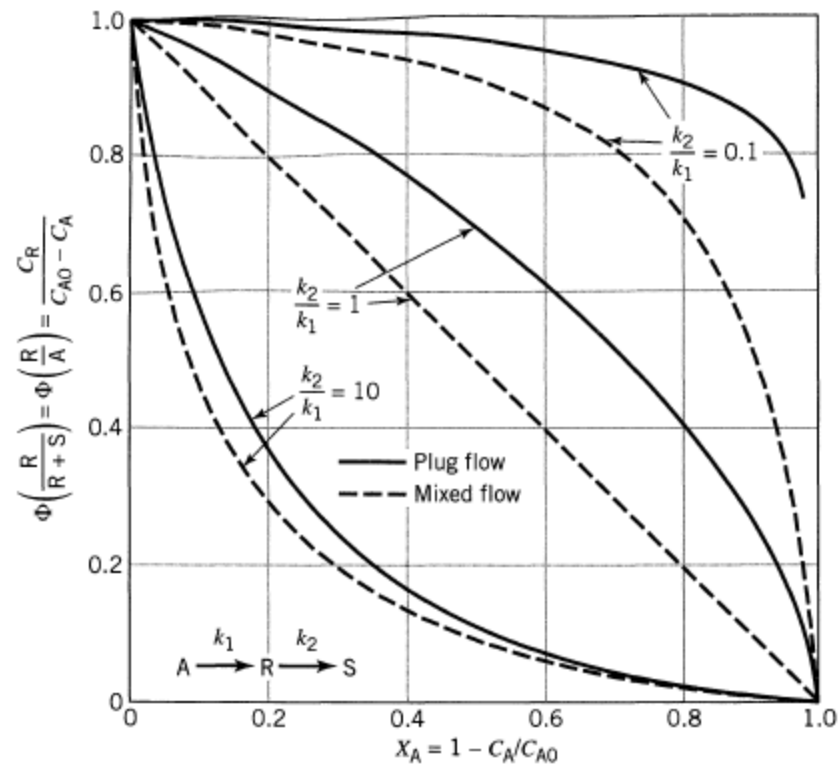


Figure 8.6 Comparison of the fractional yields of R in mixed flow and plug flow reactors for the unimolecular-type reactions

Reaction Selection criteria

- ☐ Selectivity
- ☐ Yield
- ☐ Temperature Control
- ☐ Safety
- ☐ Cost

Finding the Selectivity

For the elementary reaction,



with $k_1=0.1 \text{ s}^{-1}$ and $k_2=0.2 \text{ s}^{-1}$ with $C_{A0}= 2 \text{ mol/dm}^3$. Plot the concentration of B and selectivity of B to C as a function of space time in a CSTR.

$$\tilde{S}_{BC} = \frac{F_B}{F_C} = \frac{v_0 C_B}{v_0 C_C} = \frac{C_B}{C_C}$$

Finding the Selectivity

Species Balance on A & B

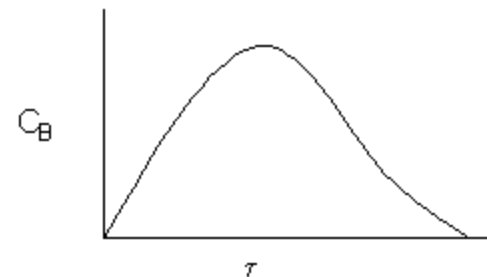
$$V = \frac{F_{A0} - F_A}{-r_A} = \frac{v_0 [C_{A0} - C_A]}{k_1 C_A}$$
$$\tau = \frac{C_{A0} - C_A}{k_1 C_A}$$

$$C_A = \frac{C_{A0}}{1 + \tau k_1}$$

$$V = \frac{0 - F_B}{r_B} = \frac{F_B}{r_B}$$

$$V = \frac{v_0 C_B}{k_1 C_A - k_2 C_B}$$

$$C_B = \frac{\tau k_1 C_A}{1 + \tau k_2} = \frac{\tau k_1 C_{A0}}{(1 + \tau k_1)(1 + \tau k_2)}$$



Finding the Selectivity

Species Balance on C

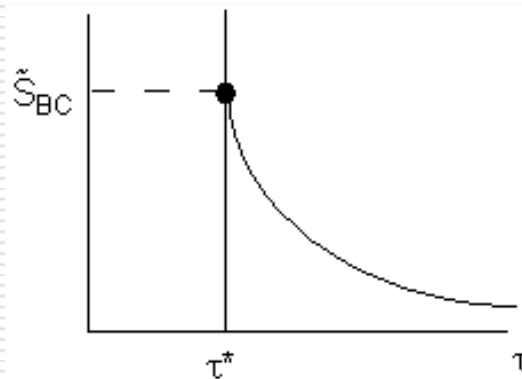
$$V = \frac{0 - C_C v_0}{-r_C} =$$

$$\tau = \frac{V}{V_0}$$

$$r_C = k_2 C_B$$

$$\tau = \frac{C_C}{k_2 C_B}$$

$$\tilde{S}_{BC} = \frac{C_B}{k_2 \tau C_B} = \frac{1}{k_2 \tau}$$



$$F_B = v_0 C_B = \frac{\tau^* k_1 F_{A0}}{(1 + k_1 \tau^*)(1 + k_2 \tau^*)}$$

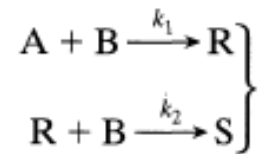
The space time, τ^* is the minimum value of V (i.e. τ^*) at which there is an acceptable molar flow rate of the desired product B from the CSTR.

Algorithm for Complex Reactions



**FOLLOW THE
ALGORITHM**

Complex Reactions



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

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

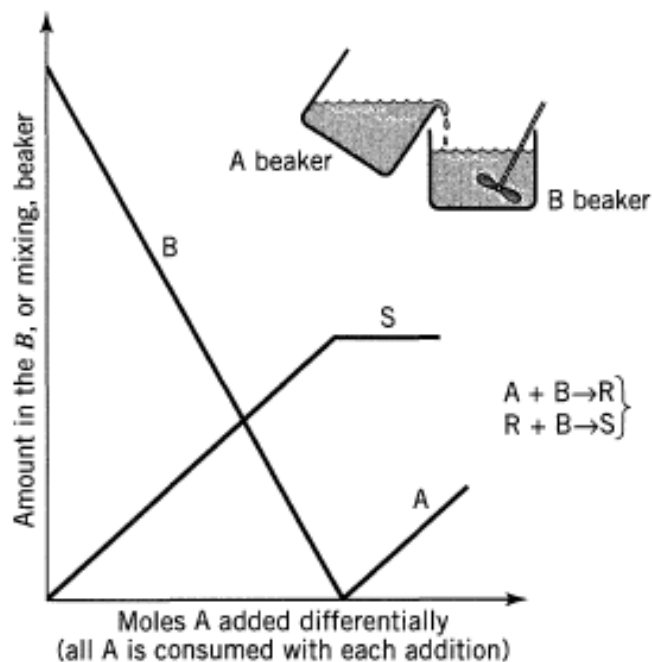
$$r_B = \frac{dC_B}{dt} = -k_1 C_A C_B - k_2 C_R C_B$$

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

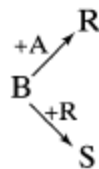
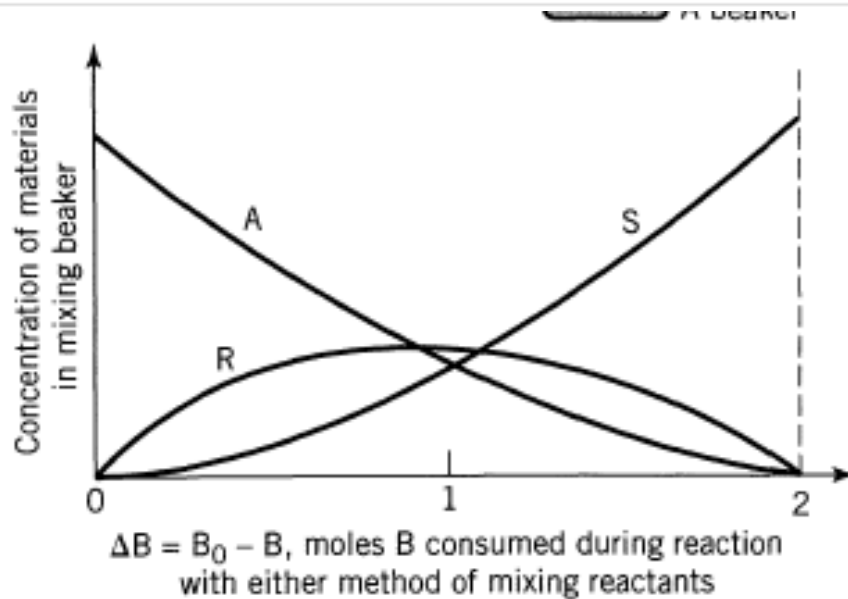
$$r_S = \frac{dC_S}{dt} = k_2 C_R C_B$$

Complex Reactions

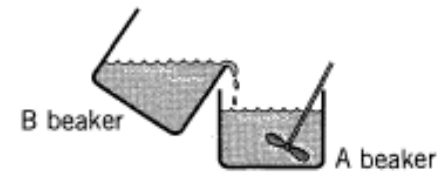
Add A Slowly to B.



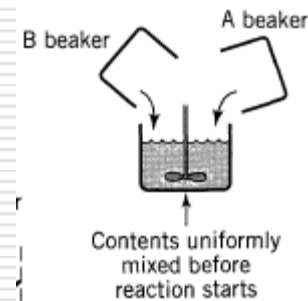
Complex Reactions



Add B Slowly to A.



Mix A and B Rapidly.



Complex Reactions

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.

Multiple Reactions

Reactions

- 1 Number each reaction

$(1) \quad A + 2B \longrightarrow C$
 $(2) \quad 3A + C \longrightarrow 2D$

Mole Balance

- 2 Write mole balance on each and every species

$\frac{dF_A}{dW} = r'_A, \quad \frac{dF_B}{dW} = r'_B, \quad \frac{dF_C}{dW} = r'_C, \quad \text{and} \quad \frac{dF_D}{dW} = r'_D$

Net Rate Laws

- 3 Write the net rate of reaction for each species
 $r'_A = r'_{1A} + r'_{2A}, \quad r'_B = r'_{1B} + r'_{2B}, \quad r'_C = r'_{1C} + r'_{2C}, \quad \text{and} \quad r'_D = r'_{1D} + r'_{2D}$
- 4 Write rate law for one species in every reaction
 $r'_{1A} = -k_{1A} C_A C_B^2 \quad \text{and} \quad r'_{2A} = -k_{2A} C_A C_C$
- 5 In each reaction relate the rates of reaction of each species to one another
 $r'_{1B} = 2r'_{1A}, \quad r'_{1C} = -r'_{1A}, \quad r'_{2B} = 0, \quad r'_{1D} = 0, \quad r'_{2C} = r'_{2A} / 3 \quad \text{and} \quad r'_{2D} = -\frac{2}{3} r'_{2A}$
- 6 Combine net rates, rate laws, and relative rates to write the net rates in terms of concentrations
 $r'_A = -k_{1A} C_A C_B^2 - k_{2A} C_A C_C, \quad r'_B = -2k_{1A} C_A C_B^2$
 $r'_C = k_{1A} C_A C_B^2 - k_{2A} C_A C_C / 3, \quad r'_D = \frac{2}{3} k_{2A} C_A C_C$

Stoichiometry

- 7 For isothermal ($T = T_0$) *gas-phase* reactions, write the concentrations in terms of molar flow rates
 $\text{e.g., } C_A = C_{T_0} \frac{F_A}{F_T} \quad \text{y, } C_B = C_{T_0} \frac{F_B}{F_T} \quad \text{y with } F_T = F_A + F_B + F_C + F_D$
 For *liquid-phase* reactions, just use concentrations as they are, e.g., C_A, C_B

Pressure Drop

- 8 Write the *gas-phase* pressure drop term in terms of molar flow rates
 $\frac{dy}{dW} = -\frac{\alpha}{2y} \frac{F_T}{F_{T_0}} \frac{T}{T_0}, \quad \text{with } y = \frac{P}{P_0}$

Combine

- 9 Use an ODE solver (e.g. Polymaht) to combine steps 1 through 8 to solve for the profiles of molar flow rates, concentration, and pressure, for example



Following the Algorithm

Mole balance

Reactor Type	Gas Phase	Liquid Phase
Batch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A$
Semi-batch (B added to A)	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A - \frac{u_0 C_A}{V}$
	$\frac{dN_B}{dt} = r_B V + F_{B0}$	$\frac{dC_B}{dt} = r_B + \frac{u_0 [C_{B0} - C_B]}{V}$
CSTR	$V = \frac{F_{A0} - F_A}{-r_A}$	$V = u_0 \frac{[C_{A0} - C_A]}{-r_A}$
PFR	$\frac{dF_A}{dV} = r_A$	$u_0 \frac{dC_A}{dV} = r_A$
PBR	$\frac{dF_A}{dW} = r'_A$	$u_0 \frac{dC_A}{dW} = r'_A$

Application of the algorithm

Example: Liquid Phase Reaction



$$-r_{1A} = k_{1A} C_A C_B^2$$



$$-r_{2C} = k_{2C} C_C^3 C_A^2$$

Case 1: PFR (Mole balance for A, B, C and D)

$$\frac{dF_A}{dV} = r_A$$

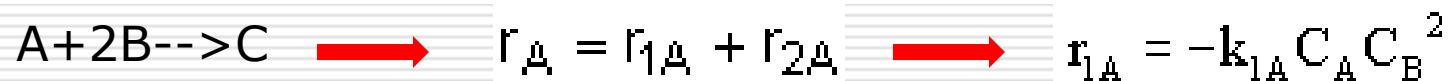
$$\frac{dF_B}{dV} = r_B$$

$$\frac{dF_C}{dV} = r_C$$

$$\frac{dF_D}{dV} = r_D$$

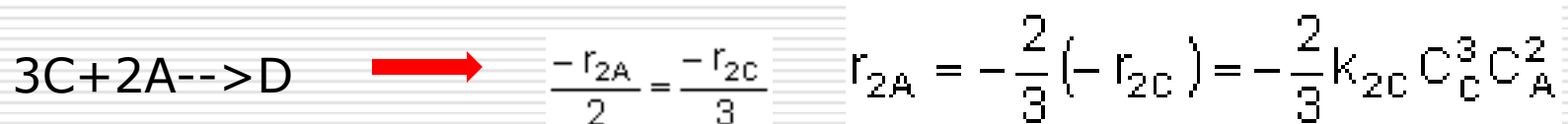
Application of the algorithm

Write the rate laws



$$r_{1B} = 2r_{1A}$$

$$r_{1C} = -r_{1A}$$



$$r_{2D} = -\frac{1}{3}r_{2C}$$

Application of the algorithm

SPECIES A \longrightarrow $r_A = -k_{1A} C_A C_B^2 - \frac{2}{3} k_{2C} C_C^3 C_A^2$

SPECIES B \longrightarrow $r_B = r_{1B} = -2k_{1A} C_A C_B^2$

SPECIES C \longrightarrow $r_C = k_{1A} C_A C_B^2 - k_{2C} C_C^3 C_A^2$

SPECIES D \longrightarrow $r_D = r_{2D} = -\frac{r_{2C}}{3} = \frac{1}{3} k_{2C} C_C^3 C_A^2$

Application of the algorithm

STOICHIOMETRY

liquid : $v = v_0$

$$F_A = C_A v_0$$

SPECIES A



$$\frac{dC_A}{dV} = \frac{r_A}{v_0}$$

$$\frac{dC_A}{dV} = \frac{-k_{1A} C_A C_B^2 - \frac{2}{3} k_{2C} C_C^3 C_A^2}{v_0}$$

SPECIES B



$$\frac{dC_B}{dV} = \frac{r_B}{v_0}$$

$$\frac{dC_B}{dV} = \frac{-2k_{1A} C_A C_B^2}{v_0}$$

SPECIES C



$$\frac{dC_C}{dV} = \frac{r_C}{v_0}$$

$$\frac{dC_C}{dV} = \frac{k_{1A} C_A C_B^2 - k_{2C} C_C^3 C_A^2}{v_0}$$

SPECIES D



$$\frac{dC_D}{dV} = \frac{r_D}{v_0}$$

$$\frac{dC_D}{dV} = \frac{1}{3} \frac{k_{2C} C_C^3 C_A^2}{v_0}$$

Application of the algorithm



**THINGS GETTING
OUT OF HAND**

TIME TO USE POLYMATH

$$k_{1A}=0.5$$

$$k_{2C}=2.0$$

$$v_0 = 5.0$$

$$\text{at } t=0: V=0, C_{AO}=4, \\ C_{BO}=4, C_{CO}=0, C_{DO}=0$$

$$V_f=5 \text{ dm}^3$$

Polymath Solution - 1

Differential equations as entered by the user

[1] $d(Ca)/d(V) = -(k1a*Ca*Cb^2 + 2/3*k2c*Cc^3*Ca^2)/vo$

[2] $d(Cb)/d(V) = -2*k1a*Ca*Cb^2/vo$

[3] $d(Cc)/d(V) = (k1a*Ca*Cb^2 - k2c*Cc^3*Ca^2)/vo$

[4] $d(Cd)/d(V) = k2c*Cc^3*Ca^2/3/vo$

Explicit equations as entered by the user

[1] $k1a = .5$

[2] $k2c = 2$

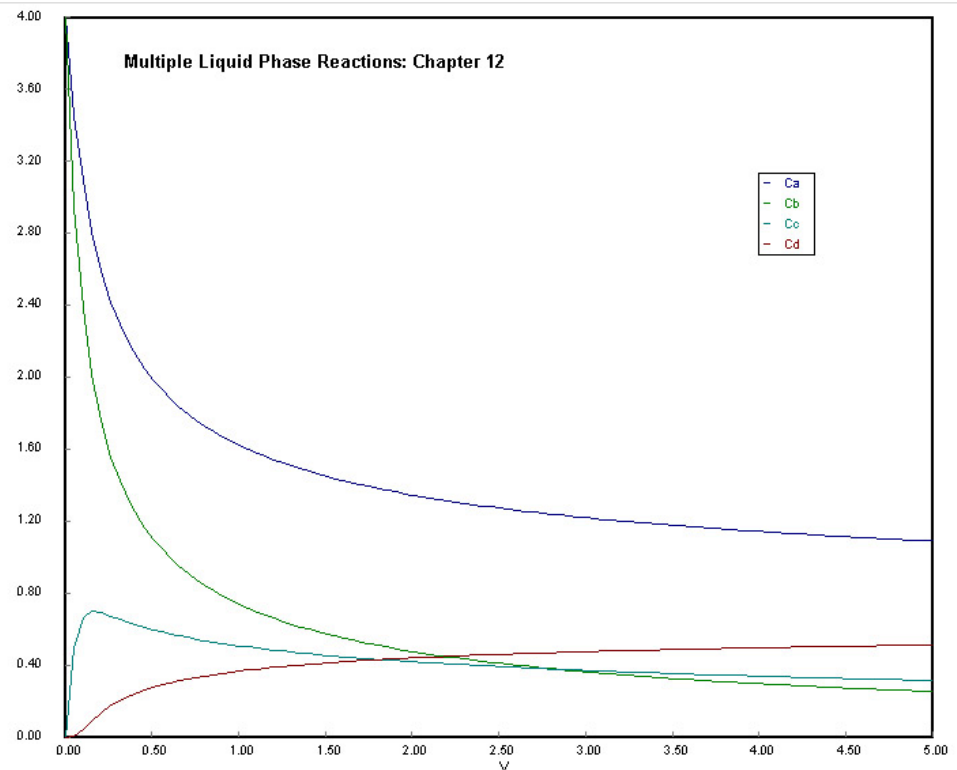
[3] $vo = 2$

Independent variable

variable name : V

initial value : 0

final value : 5



Mole balance

Reactor Type	Gas Phase	Liquid Phase
Batch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A$
Semi-batch (B added to A)	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A - \frac{u_0 C_A}{V}$
	$\frac{dN_B}{dt} = r_B V + F_{B0}$	$\frac{dC_B}{dt} = r_B + \frac{u_0 [C_{B0} - C_B]}{V}$
CSTR	$V = \frac{F_{A0} - F_A}{-r_A}$	$V = u_0 \frac{[C_{A0} - C_A]}{-r_A}$
PFR	$\frac{dF_A}{dV} = r_A$	$u_0 \frac{dC_A}{dV} = r_A$
PBR	$\frac{dF_A}{dW} = r'_A$	$u_0 \frac{dC_A}{dW} = r'_A$

Application of the algorithm

Case 2: CSTR : Liquid Phase

SPECIES A



$$V = \frac{F_{A0} - F_A}{-r_A} = \frac{v_0(C_{A0} - C_A)}{k_{1A}C_A C_B^2 + \frac{2}{3}k_{2C}C_C^3 C_A^2}$$

SPECIES B



$$V = \frac{F_{B0} - F_B}{-r_B} = \frac{v_0(C_{B0} - C_B)}{2k_{1A}C_A C_B^2}$$

SPECIES C



$$V = \frac{F_{C0} - F_C}{-r_C} = \frac{F_C}{r_C} = \frac{v_0 C_C}{k_{1A}C_A C_B^2 - k_{2C}C_C^3 C_A^2}$$

SPECIES D



$$V = \frac{F_{D0} - F_D}{-r_D} = \frac{F_D}{r_D} = \frac{v_0 C_D}{\frac{1}{3}k_{2C}C_C^3 C_A^2}$$

Application of the algorithm

$$\begin{aligned}f(C_A) &= -V \left[k_{1A} C_A C_B^2 + \frac{2}{3} k_{2C} C_C^3 C_A^2 \right] + v_o [C_{Ao} - C_A] \\f(C_B) &= -V \left[2k_{1A} C_A C_B^2 \right] + v_o [C_{Bo} - C_B] \\f(C_C) &= V \left[k_{1A} C_A C_B^2 - k_{2C} C_C^3 C_A^2 \right] - v_o C_C \\f(C_D) &= V \left[\frac{k_{2C} C_C^3 C_A^2}{3} \right] - v_o C_D\end{aligned}$$

We will specify V , C_{Ao} , C_{Bo} along with the specific reaction rates k_{ij} .

This formulation leaves us with four equations and four unknowns (C_A , C_B , C_C , and C_D).

Polymath Solution - 2

Nonlinear equations

$$[1] f(Ca) = v_o*(C_{ao}-Ca)-$$

$$V*(k_{1a}*Ca*C_b^2+2/3*k_{2c}*Ca^2*C_c^3) = 0$$

$$[2] f(C_b) = v_o*(C_{bo}-C_b)-V*(2*k_{1a}*Ca*C_b^2) = 0$$

$$[3] f(C_c) = -v_o*C_c+V*(k_{1a}*Ca*C_b^2-k_{2c}*Ca^2*C_c^3) = 0$$

$$[4] f(C_d) = -v_o*C_d+V*(k_{2c}*Ca^2*C_c^3)/3 = 0$$

Explicit equations

$$[1] C_{ao} = 4$$

$$[2] C_{bo} = 4$$

$$[3] k_{1a} = 0.5$$

$$[4] k_{2c} = 2$$

$$[5] V = 5$$

$$[6] v_o = 5$$

<u>Variable</u>	<u>Value</u>
Ca	1.9839539
Cb	1.1900914
Cc	0.4883166
Cd	0.3055459

Application of the algorithm

Case 2: Semi Batch: Liquid Phase

SPECIES A \longrightarrow
$$\frac{dC_A}{dt} = -k_{1A} C_A C_B^2 - \frac{2}{3} k_{2C} C_C^3 C_A^2 - \frac{u_0 C_A}{V}$$

SPECIES B \longrightarrow
$$\frac{dC_B}{dt} = \frac{u_0 [C_{B0} - C_B]}{V} - 2k_{1A} C_A C_B^2$$

SPECIES C \longrightarrow
$$\frac{dC_C}{dt} = k_{1A} C_A C_B^2 - k_{2C} C_C^3 C_A^2 - \frac{u_0 C_C}{V}$$

SPECIES D \longrightarrow
$$\frac{dC_D}{dt} = \frac{1}{3} k_{2C} C_C^3 C_A^2 - \frac{u_0 C_D}{V}$$

$$V = V_0 + v_0 t$$

Polymath Solution - 3

Differential equations as entered by the user

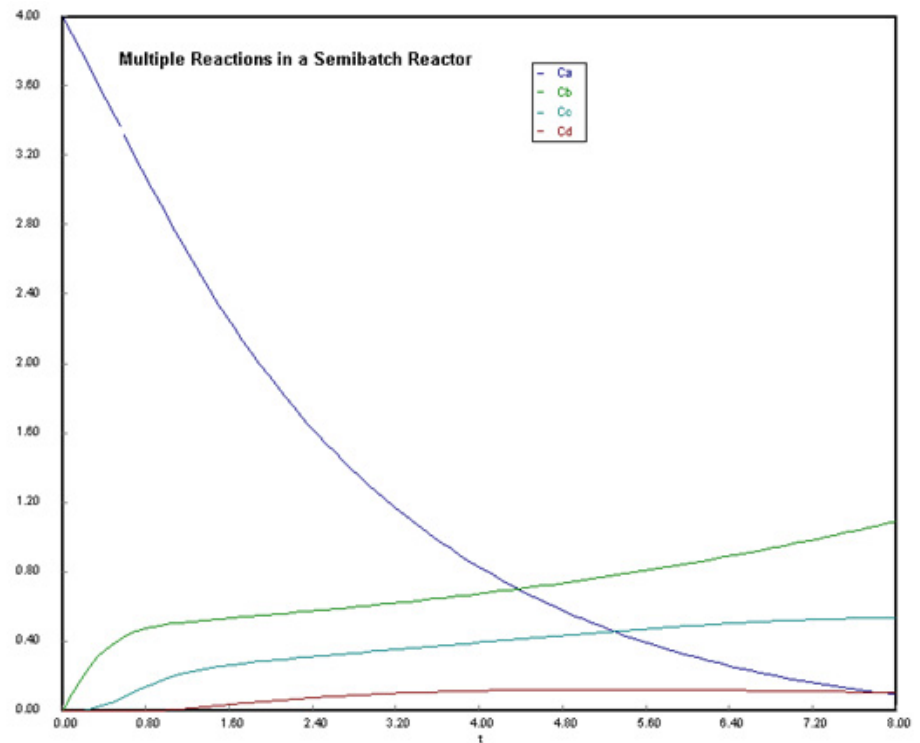
- [1] $d(Ca)/dt = -k_1 a^* Ca^* Cb^2 - 2/3 * k_2 c^* Cc^3 * Ca^2 - v_o^* Ca/V$
- [2] $d(Cb)/dt = v_o^*(Cbo - Cb)/V - 2 * k_1 a^* Ca^* Cb^2$
- [3] $d(Cc)/dt = k_1 a^* Ca^* Cb^2 - k_2 c^* Cc^3 * Ca^2 - v_o^* Cc/V$
- [4] $d(Cd)/dt = k_2 c^* Cc^3 * Ca^2 / 3 - v_o^* Cd/V$

Explicit equations as entered by the user

- [1] $V_o = 4$
- [2] $k_1 a = .5$
- [3] $k_2 c = 2$
- [4] $v_o = 1.2$
- [5] $Cbo = 4$
- [6] $V = V_o + v_o * t$

Independent variable

variable name : t
initial value : 0
final value : 8



Mole balance

Reactor Type	Gas Phase	Liquid Phase
Batch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A$
Semi-batch (B added to A)	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A - \frac{u_0 C_A}{V}$
	$\frac{dN_B}{dt} = r_B V + F_{B0}$	$\frac{dC_B}{dt} = r_B + \frac{u_0 [C_{B0} - C_B]}{V}$
CSTR	$V = \frac{F_{A0} - F_A}{-r_A}$	$V = u_0 \frac{[C_{A0} - C_A]}{-r_A}$
PFR	$\frac{dF_A}{dV} = r_A$	$u_0 \frac{dC_A}{dV} = r_A$
PBR	$\frac{dF_A}{dW} = r'_A$	$u_0 \frac{dC_A}{dW} = r'_A$

Multiple reactions: Gas Phase (PFR)



$$-r_{1A} = k_{1A} C_A C_B^2$$



$$-r_{2C} = k_{2C} C_C^3 C_A^2$$

$$C_i = C_{Tb} \left(\frac{F_i}{F_T} \right) \left(\frac{P}{P_o} \right) \left(\frac{T_o}{T} \right)$$

$$C_{Tb} = \frac{P_o}{RT_o}$$

$$F_T = F_A + F_B + F_C + F_D + F_I$$

Multiple reactions: Gas Phase (PFR)

$$\frac{dF_A}{dV} = r_A$$

$$\frac{dF_B}{dV} = r_B$$

$$\frac{dF_C}{dV} = r_C$$

$$\frac{dF_D}{dV} = r_D$$

SPECIES A \longrightarrow

$$r_A = r_{1A} + r_{2A}$$

SPECIES B \longrightarrow

$$r_B = r_{1B}$$

SPECIES C \longrightarrow

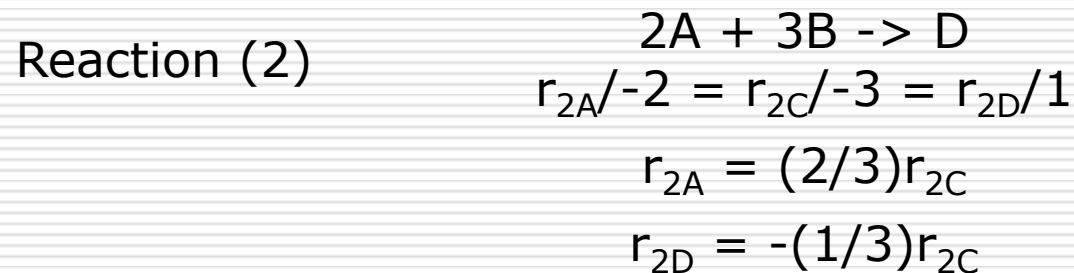
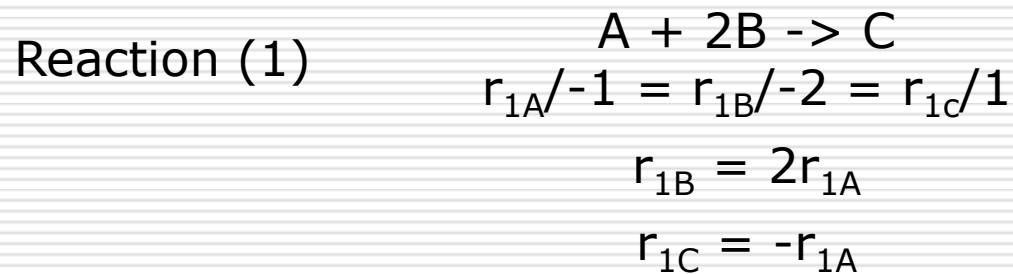
$$r_C = r_{1C} + r_{2C}$$

SPECIES D \longrightarrow

$$r_D = r_{2D}$$

Multiple reactions: Gas Phase (PFR)

RELATIVE RATES $r_{2C} = -k_{2C}C_A^2C_C^3$ $r_{1A} = -k_{1A}C_AC_B^2$



Multiple reactions: Gas Phase (PFR)

Species A $r_B = r_{1B} = -2k_{1A} C_A C_B^2$ (1)

Species B $r_A = -k_{1A} C_A C_B^2 - \frac{2}{3} k_{2C} C_C^3 C_A^2$ (2)

Species C $r_C = k_{1A} C_A C_B^2 - k_{2C} C_C^3 C_A^2$ (3)

Species D $r_D = r_{2D} = -\frac{r_{2C}}{3} = \frac{1}{3} k_{2C} C_C^3 C_A^2$ (4)

Multiple reactions: Gas Phase (PFR)

Stoichiometry

$$C_A = \frac{F_{T0}}{V_0} \frac{F_A}{F_T} \frac{P}{P_0} \frac{T_0}{T} = C_{T0} \frac{F_A}{F_T} \frac{P}{P_0} \frac{T_0}{T}$$

$$F_T = F_D + F_C + F_B + F_A$$

$$\Delta P = 0, P = P_0, T = T_0$$

$$C_i = C_{T0} \frac{F_i}{F_T}$$

Combine

Species A

$$\frac{dF_A}{dV} = -k_{1A} C_A C_B^2 - \frac{2}{3} k_{2C} C_A^2 C_B^3$$

$$\frac{dF_C}{dV} = k_{1A} C_{T0}^3 \left(\frac{F_A}{F_T} \right) \left(\frac{F_B}{F_T} \right)^2 - k_{2C} C_{T0}^5 \left(\frac{F_C}{F_T} \right)^3 \left(\frac{F_A}{F_T} \right)^2$$

Species B

Species C

Species D

$$\frac{dF_B}{dV} = -2k_{1A} C_{T0}^3 \left(\frac{F_A}{F_T} \right) \left(\frac{F_B}{F_T} \right)^2$$

$$\frac{dF_D}{dV} = \frac{1}{3} k_{2C} C_{T0}^5 \left(\frac{F_C}{F_T} \right)^3 \left(\frac{F_A}{F_T} \right)^2$$

Polymath Solution

$$k_{1A} = 0.05$$

$$k_{2C} = 1.3$$

$$C_{T0} = 0.8$$

Initial Conditions

$$V = 0, F_A = 10, F_B = 20, F_C = 0, F_D = 0, V_f = 200$$

Use the Polymath ordinary differential equation solver

Multiple reactions: Gas Phase (CSTR)

All equations apply as do initial conditions

$$A: \quad V = \frac{F_{A0} - F_A}{-r_A}$$

$$B: \quad V = \frac{F_{B0} - F_B}{-r_B}$$

$$C: \quad V = \frac{F_{C0} - F_C}{-r_C}$$

$$D: \quad V = \frac{F_{D0} - F_D}{-r_D}$$

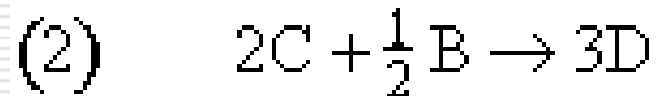
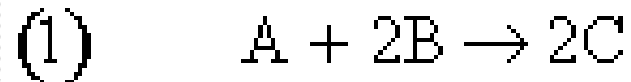
$$\text{Total: } F_T = F_A + F_B + F_C + F_D$$

$$X_A = \frac{F_{A0} - F_A}{F_{A0}}$$

Use the Polymath nonlinear equation solver

Practice Problem

- Write the net rates of formation for A, B, C and D (Reactions are elementary)

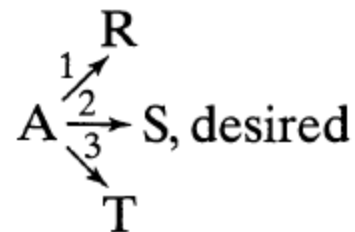


In a CSTR for gas phase, all the equations mentioned in last few slides apply.

Problems

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

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



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

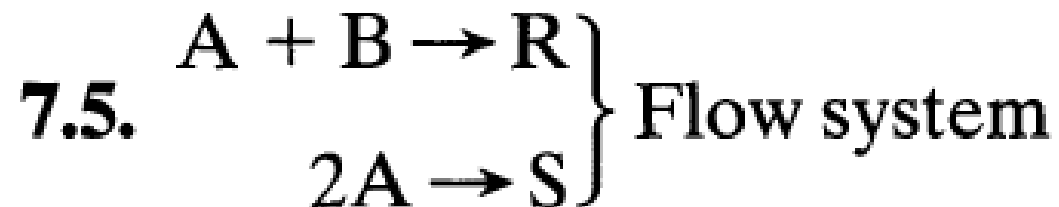
(a) $n_1 = 1, n_2 = 2, n_3 = 3$

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

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

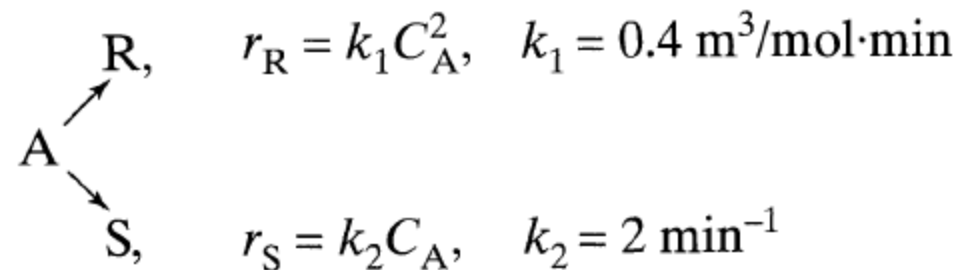
Problems

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.



Problems

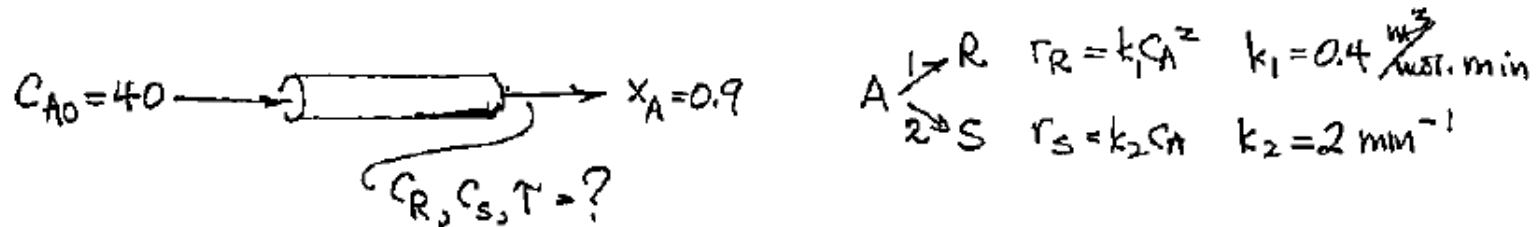
Liquid reactant A decomposes as follows:



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

Find C_{R} , and C_{S} and τ for $X_{\text{A}} = 0.9$ in a plug flow reactor.

Solution



First determine $Q(S/A)$..

$$Q(S/A) = \frac{r_S}{r_R + r_S} = \frac{2C_A}{0.4C_A^2 + 2C_A} = \frac{1}{1 + 0.2C_A}$$

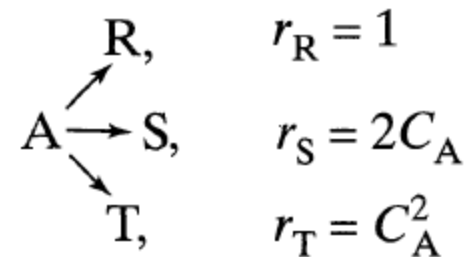
$$C_S = \int_4^{40} Q(S/A) dC_A = \int_4^{40} \frac{dC_A}{1 + 0.2C_A} = \frac{1}{0.2} \ln(1 + 0.2C_A) \Big|_4^{40} = 5 \ln \frac{9}{1.8} = 8$$

$$\therefore \left. \begin{array}{l} C_A = 4 \\ C_S = 8 \\ C_R = 28 \end{array} \right\}$$

$$T = \int \frac{dC_A}{-r_A} = \int \frac{dC_A}{2C_A + 0.4C_A^2} = \frac{1}{0.4} \int \frac{dC_A}{5C_A + C_A^2} = 2.5 \left[\frac{1}{5} \ln \frac{C_A}{C_A + 5} \right]_4^{40} = \frac{1}{2} \ln 2 = 0.347$$

Problems

Consider the parallel decomposition of A of different orders

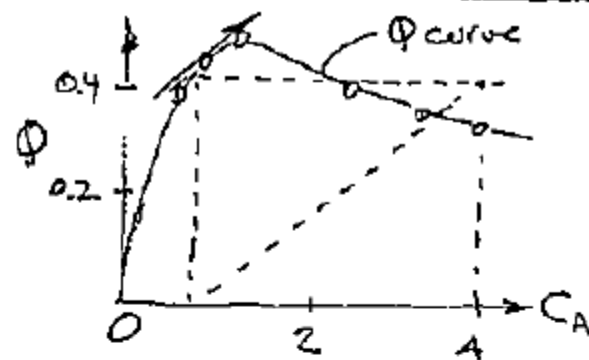
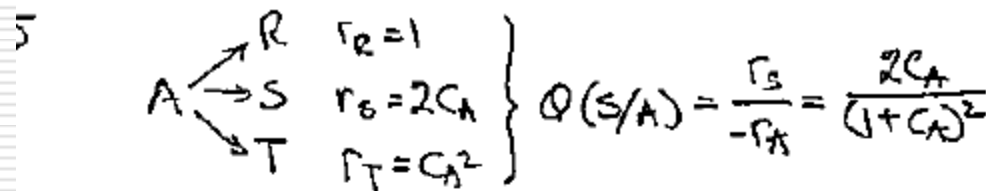


Determine the maximum concentration of desired product obtainable in

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

S is the desired product and $C_{\text{A}0} = 4$.

Solution



a) For plug flow go to $C_{Af} = 0$ for maximum area

$$C_S = \int_0^4 \frac{2C_A}{(1+C_A)^2} dC_A \approx (0.3984)4 = 1.59$$

graphical integration

b) For mixed flow let's solve analytically. Note we could also solve graphically.

$$C_S = Q(-\Delta C_A) = \frac{2C_A}{(1+C_A)^2} (4-C_A)$$

differentiating & setting to zero gives

$$\frac{dC_S}{dC_A} = \frac{[2(4-C_A) + 2C_A(-1)](1+C_A)^2 - 2C_A(4-C_A)2(1+C_A)}{(1+C_A)^4} = 0$$

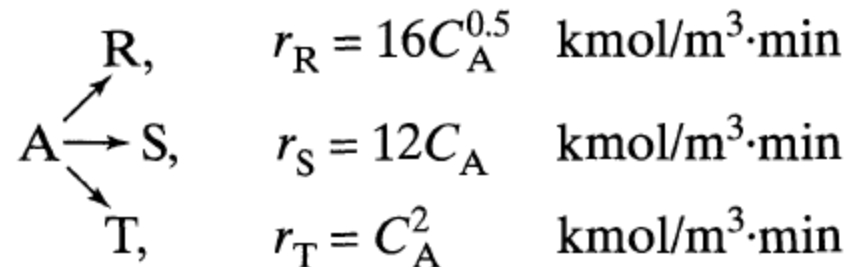
$$\therefore C_A(\text{at } C_{S\text{opt}}) = \frac{2}{3}$$

$$Q(\text{at } C_A = \frac{2}{3}) = \frac{2(\frac{2}{3})}{(1+\frac{2}{3})^2} = \frac{12}{25}$$

$$\therefore C_{S\text{max}} = \frac{12}{25} \left(4 - \frac{2}{3}\right) = 1.6$$

Problems

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



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

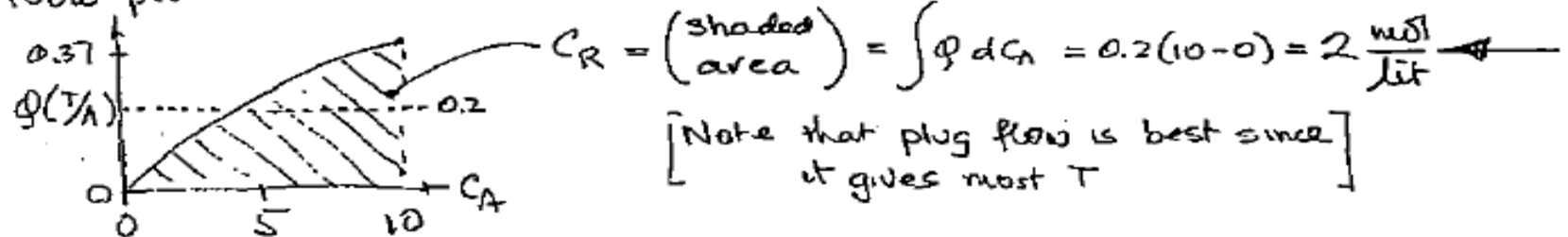
Product T is the desired material.

Solution

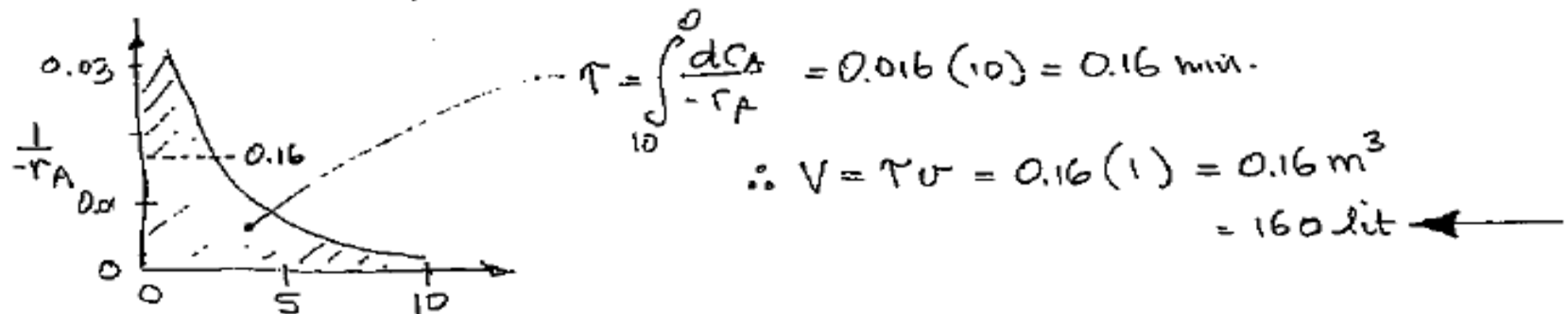
First find the ϕ vs C_A curve, then decide which reactor type to use

C_A	$\phi(T/A) = \frac{C_A^2}{16C_A^{1/2} + 12C_A + C_A^2}$	$-\frac{1}{r_A} = \frac{1}{16C_A^{1/2} + 12C_A + C_A^2}$
10	0.37	0.0037
9	0.34	0.0042
4	0.167	0.0104
1	0.03	0.03
0.1		0.16

Now plot



Next, to find τ plot $-1/r_A$ vs C_A



Objective Assessment of Chapter

- ❑ Define different types of selectivity and yield
- ❑ Choose the appropriate reactor and reaction system that would maximize the selectivity of the desired product given the rate laws for all the reactions occurring in the system
- ❑ Describe the algorithm used to design reactors with multiple reactions
- ❑ Apply the CRE algorithm to size reactors in order to maximize the selectivity and to determine the species concentrations in a batch reactor, a semi-batch reactor, a CSTR, a PFR, and a PBR, in systems with multiple reactions

The only way of finding the limits of the possible is by going beyond them into the impossible.

Arthur C. Clarke