Chemical Reaction Engineering I

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CHAPTER 6 – MULTIPLE REACTIONS

The breakfast of champions is not cereal, it's your opposition.

Nick Seitz

Learning Outcomes

- After completing chapter 6, you will be able to
  - 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 semibatch reactor, a CSTR, a PFR, and a PBR, in systems with multiple reactions.

Multiple Reactions

- Selectivity and Yield
- Parallel Reactions

$$A \xrightarrow{k_D} D$$

$$A \xrightarrow{k_U} U$$

- Series Reactions

$$A \longrightarrow B \longrightarrow C$$

- Complex Reactions

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

$$A + C \longrightarrow E$$

4 Types of Multiple Reactions

- Series: $A \rightarrow B \rightarrow C$
- Parallel: $A \rightarrow D$
  $A \rightarrow U$
- Independent: $A \rightarrow B$
  $C \rightarrow D$
- Complex: $A + B \rightarrow C + D$
  $A + C \rightarrow E$

With multiple reactors, either molar flow or number of moles must be used (**NO CONVERSION!**)

Selectivity and Yield

There are two types of selectivity and yield: Instantaneous and Overall.

	Instantaneous	Overall
Selectivity	$S_{DU} = \frac{r_D}{r_U}$	$\tilde{S}_{DU} = \frac{F_D}{F_U}$
Yield	$Y_D = \frac{r_D}{-r_A}$	$\tilde{Y}_D = \frac{F_D}{F_{A0} - F_A}$

Selectivity and Yield

Example: $\mathrm{A} + \mathrm{B} \xrightarrow{\mathrm{k_1}} \mathrm{D}$ Desired Product:

$$r_D = k_1 C_A^2 C_B$$

$\mathrm{A} + \mathrm{B} \xrightarrow{\mathrm{k_2}} \mathrm{U}$ Undesired Product:

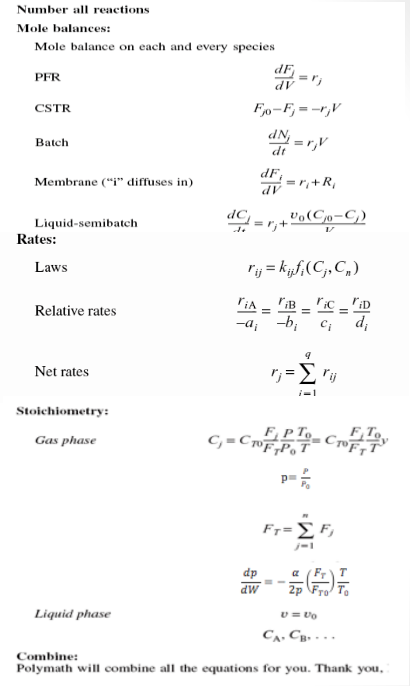
$$r_U = k_2 C_A C_B$$

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

To maximize the selectivity of D with respect to U run at high concentration of A and use PFR.

Multiple Reactions Algorithm

Following the Algorithm



Number all reactions

Mole balances:

Mole balance on each and every species

PFR	$\frac{dF_j}{dV} = r_j$
CSTR	$F_{j0} - F_j = -r_j V$
Batch	$\frac{dN_j}{dt} = r_j V$
Membrane ("i" diffuses in)	$\frac{dF_i}{dV} = r_i + R_i$
Liquid-semibatch	$\frac{dC_j}{dt} = r_j + \frac{v_0(C_{j0} - C_j)}{V}$

Rates:

Laws	$r_{ij} = k_{ij} f_i(C_j, C_n)$
Relative rates	$\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i}$
Net rates	$r_j = \sum_{i=1}^{q} r_{ij}$

Stoichiometry:

Gas phase	$C_j = C_{T0} \frac{F_j}{F_T} \frac{P}{P_0} \frac{T_0}{T} = C_{T0} \frac{F_j}{F_T} \frac{T_0}{T} y$
	$p = \frac{P}{P_0}$
	$F_T = \sum_{j=1}^{n} F_j$
	$\frac{dp}{dW} = -\frac{\alpha}{2p}\left(\frac{F_T}{F_{T0}}\right)\frac{T}{T_0}$
Liquid phase	$v = v_0$
	$C_A, C_B, \ldots$

Combine:

Polymath will combine all the equations for you. Thank you,

Multiple Reactions

A) Mole Balance of each and every species

Flow	Batch
$\frac{dF_A}{dV} = r_A$	$\frac{dN_A}{dt} = r_A V$
$\frac{dF_B}{dV} = r_B$	$\frac{dN_B}{dt} = r_B V$

Multiple Reactions

B) Rates

A. **Rate Law** for each reaction:

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

$$-r_{2A} = k_{2A} C_C C_A$$

B. Net **Rates**:

$$r_A = \sum_{i=1} r_{iA} = r_{1A} + r_{2A}$$

C. Relative **Rates**:

$$\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i}$$

Multiple Reactions

C) Stoichiometry

Gas:

$$C_A = C_{T0} \frac{F_A}{F_T} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

Liquid:

$$C_A = F_A / \upsilon_0$$

Batch Series Reactions

Example

$$A \rightarrow B \rightarrow C$$

$$(1)\ A \rightarrow B \quad k_1$$

$$(2)\ B \rightarrow C \quad k_2$$

Batch Series Reactions

1) Mole Balances

$$\frac{dN_A}{dt} = r_A V$$

$$\frac{dN_B}{dt} = r_B V$$

$$\frac{dN_C}{dt} = r_C V$$

$V = V_0$ (constant batch)

$$\frac{dC_A}{dt} = r_A \qquad \frac{dC_B}{dt} = r_B \qquad \frac{dC_C}{dt} = r_C$$

$$\boxed{\begin{array}{l} \mathbf{A \rightarrow B \rightarrow C} \\ \mathbf{(1)\ A \rightarrow B \quad k_1} \\ \mathbf{(2)\ B \rightarrow C \quad k_2} \end{array}}$$

Batch Series Reactions

2) Rate Laws

A → B → C

(1) A → B k_1

(2) B → C k_2

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

Laws

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

Net rates

$$\frac{r_{1A}}{-1} = \frac{r_{1B}}{1}$$
$$\frac{r_{2B}}{-1} = \frac{r_{2C}}{1}$$

Relative rates

Batch Series Reactions

3) Combine

Species A:

$$-\frac{dC_A}{dt} = -r_A = k_1C_A$$
$$C_A = C_{A0}\exp\left(-k_1t\right)$$

Species B:

$$\frac{dC_B}{dt} = r_B$$
$$r_B = r_{B\,NET} = r_{1B} + r_{2B} = k_1C_A - k_2C_B$$
$$\frac{dC_B}{dt} + k_2C_B = k_1C_{A0}\exp(-k_1t)$$

Batch Series Reactions

Using the integrating factor, $I.F. = \exp\left(\int k_2 dt\right) = \exp(k_2 t)$

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

at t = 0, C_B=0

$$\boxed{C_B = \frac{k_1 C_{A0}}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right]}$$

$$C_C = C_{A0} - C_A - C_B$$

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

CSTR Series Reactions

$A \rightarrow B \rightarrow C$

What is the optimal τ ?

1) Mole Balances

A: $F_{A0} - F_A + r_A V = 0$

$$C_{A0} v_0 - C_A v_0 + r_A V = 0$$

$$\boxed{C_{A0} - C_A + r_A \tau = 0}$$

B: $0 - v_0 C_B + r_B V = 0$

$$\boxed{-C_B + r_B \tau = 0}$$

CSTR Series Reactions

$$A \rightarrow B \rightarrow C$$

2) Rate Laws

Laws:

$$r_{1A} = -k_1 C_A$$

$$r_{2B} = -k_2 C_B$$

Relative:

$$\frac{r_{1A}}{-1} = \frac{r_{1B}}{1} \qquad \frac{r_{2B}}{-1} = \frac{r_{2C}}{1}$$

Net:

$$r_A = r_{1A} + 0 = -k_1 C_A$$

$$r_B = -r_{1A} + r_{2B} = k_1 C_A - k_2 C_B$$

CSTR Series Reactions

$$A \rightarrow B \rightarrow C$$

3) Combine

$$C_{A0} - C_A - k_1 C_A t = 0$$

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

$$-C_B + \left(k_1 C_A - k_2 C_B\right)t = 0$$

$$C_B = \frac{k_1 C_A t}{1 + k_2 t}$$

$$C_B = \frac{k_1 C_{A0} t}{\left(1 + k_2 t\right)\left(1 + k_1 t\right)}$$

CSTR Series Reactions

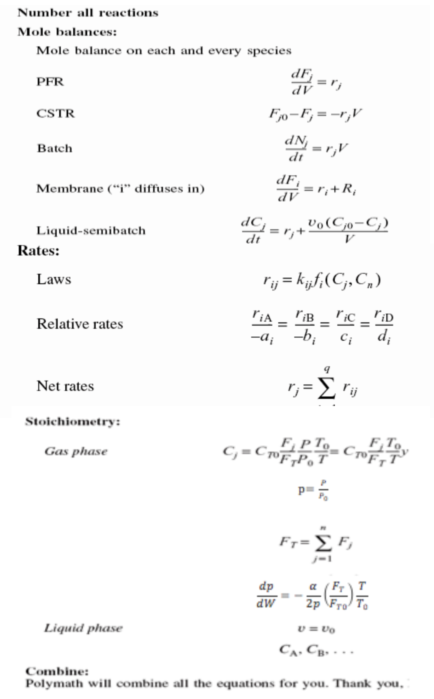
$$A \rightarrow B \rightarrow C$$

Find τ that gives maximum concentration of B

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

$$\frac{dC_B}{d\tau} = 0 \qquad \boxed{\tau_{\max} = \frac{1}{\sqrt{k_1 k_2}}}$$

Following the Algorithm



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Mole balance on each and every species

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Batch $\frac{dN_j}{dt} = r_j V$

Membrane ("i" diffuses in) $\frac{dF_i}{dV} = r_i + R_i$

Liquid-semibatch $\frac{dC_j}{dt} = r_j + \frac{\upsilon_0 (C_{j0} - C_j)}{V}$

Rates:

Laws $r_{ij} = k_{ij} f_i(C_j, C_n)$

Relative rates $\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i}$

Net rates $r_j = \sum^{q} r_{ij}$

Stoichiometry:

Gas phase $C_j = C_{T0} \frac{F_j}{F_T} \frac{P}{P_0} \frac{T_0}{T} = C_{T0} \frac{F_j}{F_T} \frac{T_0}{T} y$

$$p = \frac{P}{P_0}$$

$$F_T = \sum_{j=1}^{n} F_j$$

$$\frac{dp}{dW} = -\frac{\alpha}{2p} \left(\frac{F_T}{F_{T0}}\right) \frac{T}{T_0}$$

Liquid phase $\upsilon = \upsilon_0$

$$C_A, C_B, \ldots$$

Combine:
Polymath will combine all the equations for you. Thank you,

What Type of Reaction is Taking Place?

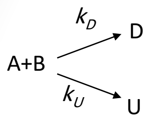
Three species were found in a CSTR. The following concentration data were obtained as a function of temperature. The initial concentration of the single reactant, A, was the same at all temperatures. Both B and C are products. C_{A0} = 2mol/dm^3

Run	T (°C)	C_A (mol/dm^3)	C_B (mol/dm^3)	C_C (mol/dm^3)
1	30	1.7	0.01	0.29
2	50	1.4	0.03	0.57
3	70	1.0	0.1	0.90
4	100	0.5	0.75	0.75
5	120	0.1	1.80	0.1
6	130	0.01	1.98	0.01

Explain the above data, what type of reaction is taking place, independent, complex, series or parallel ?

Parallel Reactions

Purpose: maximizing the desired product in parallel reactions



(desired) $r_D = k_D C_A^{\alpha 1} C_B^{\beta 1} \rightarrow r_D = A_D e^{\frac{-E_D}{RT}} C_A^{\alpha 1} C_B^{\beta 1}$

(undesired) $r_U = k_U C_A^{\alpha 2} C_B^{\beta 2} \rightarrow r_U = A_U e^{\frac{-E_U}{RT}} C_A^{\alpha 2} C_B^{\beta 2}$

$$k(T) = Ae^{\frac{-E}{RT}}$$

Rate of disappearance of A: $-r_A = r_D + r_U$

$$-r_A = A_D e^{\frac{-E_D}{RT}} C_A^{\alpha 1} C_B^{\beta 1} + A_U e^{\frac{-E_U}{RT}} C_A^{\alpha 2} C_B^{\beta 2}$$

Define the *instantaneous rate selectivity*, $S_{D/U}$

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

$$S_{D/U} = \frac{A_D e^{\frac{-E_D}{RT}} C_A^{\alpha_1} C_B^{\beta_1}}{A_U e^{\frac{-E_U}{RT}} C_A^{\alpha_2} C_B^{\beta_2}}$$

$$S_{D/U} = \frac{k_D}{k_U}\left(C_A^{\alpha 1-\alpha 2}\right) C_B^{\beta 1-\beta 2} \rightarrow \boxed{S_{D/U} = \frac{A_D}{A_U} e^{\frac{-(E_D-E_U)}{RT}} \left(C_A^{\alpha 1-\alpha 2}\right) C_B^{\beta 1-\beta 2}}$$

Goal: Maximize $S_{D/U}$ to maximize production of the desired product

Maximizing $S_{D/U}$ for Parallel Reactions: Temperature Control

$$\boxed{S_{D/U}=\frac{A_D}{A_U}e^{\frac{-(E_D-E_U)}{RT}}\left(C_A^{\alpha_1-\alpha_2}\right)C_B^{\beta_1-\beta_2}}$$

What reactor conditions and configuration maximizes the selectivity?

Start with temperature (affects k):

a) If $E_D > E_U$

$$\frac{E_D-E_U}{RT}>0\rightarrow e^{\frac{-(E_D-E_U)}{RT}}<1$$

Specific rate of desired reaction k_D increases more rapidly with increasing T

Use higher temperature to favor desired product formation

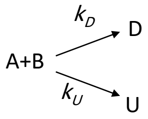
b) If $E_D < E_U$

$$\frac{E_D-E_U}{RT}<0\rightarrow e^{\frac{-(E_D-E_U)}{RT}}>1$$

Specific rate of desired reaction k_D increases less rapidly with increasing T

Use lower T to favor desired product formation (not so low that the reaction rate is tiny)

Maximizing $S_{D/U}$ for Parallel Reactions: Concentration



$$\boxed{S_{D/U}=\frac{A_D}{A_U}e^{\frac{-(E_D-E_U)}{RT}}\left(C_A^{\alpha_1-\alpha_2}\right)C_B^{\beta_1-\beta_2}}$$

What reactor conditions and configuration maximizes the selectivity?

Now evaluate concentration:

a) $\alpha_1>\alpha_2\rightarrow\alpha_1-\alpha_2>0$

$C_A^{\alpha_1-\alpha_2}$

$\longrightarrow$ Use large C_A

b) $\alpha_1<\alpha_2\rightarrow\alpha_1-\alpha_2<0$

$C_A^{\alpha_1-\alpha_2}$

$\longrightarrow$ Use small C_A

c) $\beta_1>\beta_2\rightarrow\beta_1-\beta_2>0$

$C_B^{\beta_1-\beta_2}$

$\longrightarrow$ Use large C_B

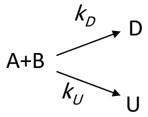
d) $\beta_1<\beta_2\rightarrow\beta_1-\beta_2<0$

$C_B^{\beta_1-\beta_2}$

$\longrightarrow$ Use small C_B

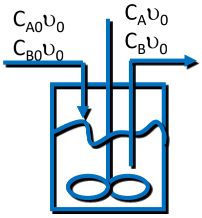
How do these concentration requirements affect reactor selection?

Concentration Requirements & Reactor Selection

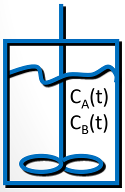


How do concentration requirements play into reactor selection?

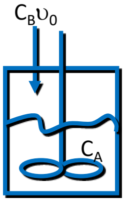
PFR (or PBR): concentration is high at the inlet & progressively drops to the outlet concentration



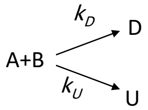
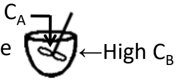
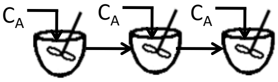
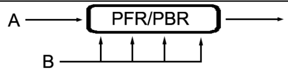
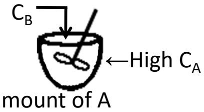
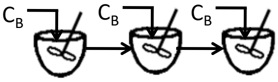
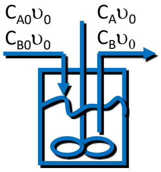
CSTR: concentration is always at its lowest value (that at outlet)



Batch: concentration is high at t=0 & progressively drops with increasing time



Semi-batch: concentration of one reactant (A as shown) is high at t=0 & progressively drops with increasing time, whereas concentration of B can be kept low at all times

	$\alpha_1 > \alpha_2$ High C_A favors desired product formation	$\alpha_1 < \alpha_2$ High C_A favors <u>undesired</u> product formation (keep C_A low)
$\beta_1 > \beta_2$ High C_B favors desired product formation	**Batch reactor**  When C_A & C_B are low (end time or position), all rxns will be slow  High P for gas-phase rxn, do not add inert gas (dilutes reactants)	**PFR/PBR**  Side streams feed low C_A **Semi-batch reactor** slowly feed A to large amt of B  **CSTRs in series** 
$\beta_1 < \beta_2$ High C_B favors <u>undesired</u> product formation (keep C_B low)	 **PFR/PBR** w/ side streams feeding low C_B **Semi-batch reactor**, slowly feed B to large amount of A  **CSTRs in series**  B consumed before leaving $CSTR_n$	 **CSTR**  **PFR/PBR** w/ high recycle • Dilute feed with inert that can be easily separated from product • Low P if gas phase

What reactor/reactors scheme and conditions would you use to maximize the selectivity parameters for the following parallel reaction?

$A+C \xrightarrow{k_D} D$ desired

$A+C \xrightarrow{k_{U1}} U_1$ undesired

$$r_D = 800e^{\frac{-\boxed{2000}}{T}} C_A^{0.5} C_C \quad \xleftarrow{\quad} E/R \xrightarrow{\quad} \quad r_{U_1} = 10e^{\frac{-\boxed{300}}{T}} C_A C_C$$

Need to maximize $S_{D/U1}$

$$k(T) = Ae^{\frac{-E}{RT}}$$

$$S_{D/U_1} = \frac{r_D}{r_{U_1}} = \frac{A_D}{A_{U_1}} e^{\frac{-(E_D-E_{U_1})}{T}} \left(C_A^{\alpha_D-\alpha_{U_1}}\right) C_C^{\beta_D-\beta_{U_1}}$$

Plug in numbers: $S_{D/U_1} = \frac{800}{10} e^{\frac{-(2000-300)}{T}} \left(C_A^{0.5-1}\right) C_C^{1-1} \rightarrow \boxed{S_{D/U_1} = 80e^{\frac{-1700}{T}} C_A^{-0.5}}$

Question 1: To maximize the production of the desired product, the temperature should be

a) As high as possible (without decomposing the reactant or product)
b) Neither very high or very low
c) As low as possible (but not so low the rate = 0)
d) Doesn't matter, T doesn't affect the selectivity
e) Not enough info to answer the question

$E_D > E_U$, so use higher T

What reactor/reactors scheme and conditions would you use to maximize the selectivity parameters for the following parallel reaction?

$A+C \xrightarrow{k_D} D$ desired

$A+C \xrightarrow{k_{U1}} U_1$ undesired

$$r_D = 800e^{\frac{-2000}{T}} \boxed{C_A^{0.5}} C_C \qquad r_{U_1} = 10e^{\frac{-300}{T}} \boxed{C_A} C_C$$

Need to maximize $S_{D/U1}$

$$k(T) = Ae^{\frac{-E}{RT}}$$

$$S_{D/U_1} = \frac{r_D}{r_{U_1}} = \frac{A_D}{A_{U_1}} e^{\frac{-(E_D-E_{U_1})}{T}} \left(C_A^{\alpha_D-\alpha_{U_1}}\right) C_C^{\beta_D-\beta_{U_1}}$$

Plug in numbers: $S_{D/U_1} = \frac{800}{10} e^{\frac{-(2000-300)}{T}} \left(C_A^{0.5-1}\right) C_C^{1-1} \rightarrow \boxed{S_{D/U_1} = 80e^{\frac{-1700}{T}} C_A^{-0.5}}$

Question 2: To maximize the production of the desired product, C_A should be

a) As high as possible
b) Neither very high or very low
c) As low as possible
d) Doesn't matter, C_A doesn't affect the selectivity
e) Not enough info to answer the question

$\alpha_D < \alpha_{U1}$, so high C_A favors undesired product formation (keep C_A low)

What reactor/reactors scheme and conditions would you use to maximize the selectivity parameters for the following parallel reaction?

$A+C \xrightarrow{k_D} D$ desired

$A+C \xrightarrow{k_{U1}} U_1$ undesired

$$r_D = 800e^{\frac{-2000}{T}} C_A^{0.5} C_C \qquad r_{U_1} = 10e^{\frac{-300}{T}} C_A C_C$$

Need to maximize $S_{D/U1}$

$$S_{D/U_1} = \frac{r_D}{r_{U_1}} = \frac{A_D}{A_{U_1}} e^{\frac{-(E_D - E_{U_1})}{T}} \left(C_A^{\alpha_D - \alpha_{U_1}}\right) C_C^{\beta_D - \beta_{U_1}}$$

Plug in numbers:

$$S_{D/U_1} = \frac{800}{10} e^{\frac{-(2000-300)}{T}} \left(C_A^{0.5-1}\right) C_C^{1-1} \rightarrow \boxed{S_{D/U_1} = 80e^{\frac{-1700}{T}} C_A^{-0.5}}$$

- Since $E_D > E_{U1}$, k_D increases faster than k_{U1} as the temperature increases
- Operate at a high temperature to maximize C_D with respect to C_{U1}
- $\alpha_D < \alpha_{U1}$, keep C_A low to maximize C_D with respect to C_{U1}
- r_D and r_{U1} are 1st order in C_C, so changing C_C does not influence selectivity
- HOWEVER, high C_C will increase the reaction rate and offset the slow reaction rate that is caused by low C_A (that's a good thing)

What reactor should we use?

What reactor/reactors scheme and conditions would you use to maximize the selectivity parameters for the following parallel reaction?

$A+C \xrightarrow{k_D} D$ desired

$A+C \xrightarrow{k_{U1}} U_1$ undesired

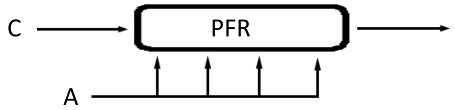
$$r_D = 800e^{\frac{-2000}{T}} C_A^{0.5} C_C \qquad r_{U_1} = 10e^{\frac{-300}{T}} C_A C_C$$

Need to maximize $S_{D/U1}$

$$S_{D/U_1} = 80e^{\frac{-1700}{T}} C_A^{-0.5}$$

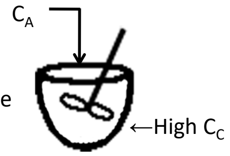
- $E_D > E_{U1}$, **operate at a high temperature** to maximize C_D with respect to C_{U1}
- $\alpha_D < \alpha_{U1}$, **keep C_A low** to maximize C_D with respect to C_{U1}
- r_D and r_{U1} are 1st order in C_C, so changing C_C does not influence selectivity
- HOWEVER, **high C_C** will increase the reaction rate and offset the slow reaction rate that is caused by low C_A (that's a good thing)

What reactor should we use?



PFR/PBR w/ side streams feeding low C_A

Semi-batch reactor
slowly feed A to large amount of C



How does the selection of reactor/reactors scheme and conditions change if D can react with C and form another undesired product?

$A+C \xrightarrow{k_D} D$ desired $\quad A+C \xrightarrow{k_{U1}} U_1$ undesired $\quad D+C \xrightarrow{k_{U2}} U_2$ undesired

$$r_D = 800e^{\frac{-2000}{T}} C_A^{0.5} C_C \qquad r_{U_1} = 10e^{\frac{-300}{T}} C_A C_C \qquad r_{U_2} = 10^6 e^{\frac{-8000}{T}} C_C C_D$$

Need to maximize $S_{D/U1}$ and $S_{D/U2}$

$$\boxed{S_{D/U_1} = 80e^{\frac{-1700}{T}} C_A^{-0.5}}$$

- $E_D > E_{U1}$, operate at a high T
- $\alpha_D < \alpha_{U1}$, keep C_A low
- High C_C increases rxn rate & offsets slow rxn from low C_A

$$S_{D/U_2} = \frac{r_D}{r_{U_2}} = \frac{800e^{\frac{-2000}{T}} C_A^{0.5} C_C}{10^6 e^{\frac{-8000}{T}} C_C C_D} \rightarrow \boxed{S_{D/U_2} = 8\times10^{-4} e^{\frac{6000}{T}} C_A^{0.5} C_D^{-1}}$$

- Since $E_D < E_{U21}$, k_D increases slower than k_{U2} as T increases ⇨ operate at low T to maximize C_D Conflicts with maximizing $S_{D/U1}$!
- $\alpha_D > \alpha_{U2}$, keep C_A high to maximize C_D Conflicts with maximizing $S_{D/U1}$!
- r_D, r_{U1} & r_{U2} are all 1st order in C_C, so changing C_C does not influence selectivity, but high C_C will offset the rate decrease due to low C_A
- Low C_D reduces the production of U_2 Conflicts with producing the product D!!!

$A+C \xrightarrow{k_D} D$ desired $\quad A+C \xrightarrow{k_{U1}} U_1$ undesired $\quad D+C \xrightarrow{k_{U2}} U_2$ undesired

$$\boxed{S_{D/U_1} = 80e^{\frac{-1700}{T}} C_A^{-0.5}}$$

Maximize $S_{D/U1}$ & $S_{D/U2}$

$$\boxed{S_{D/U_2} = 8\times10^{-4} e^{\frac{6000}{T}} C_A^{0.5} C_D^{-1}}$$

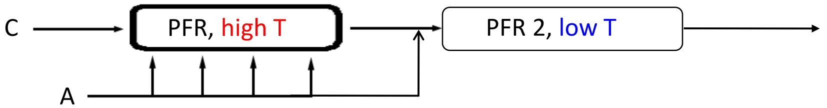
- $E_D > E_{U1}$, operate at a high T
- $\alpha_D < \alpha_{U1}$, keep C_A low
- Want to maximize C_D

- $E_D < E_{U2}$, operate at low T
- $\alpha_D > \alpha_{U2}$, keep C_A high
- Low C_D reduces production of U_2

- High C_C increases rxn rate & offsets slow rate caused by low C_A

Consider relative magnitude of $S_{D/U1}$ and $D_{D/U2}$ as a function of position in PFR

PFR w/ side streams feeding low C_A



High T, C_C is initially high, C_A is low

→ high $S_{D/U1}$

Initially C_D=0 → r_{U2}=0. Both gradually increase down reactor

Initially high $S_{D/U2}$ (because C_D is low), but $S_{D/U2}$ gradually decreases down reactor

- At some distance down the reactor, significant amounts of D have formed
- $S_{D/U2}$ becomes significant with respect to $S_{D/U1}$
- At this point, want low T, high C_A & low C_C

If a CSTR were used with C_A = 1 mol/L and C_D= 1 mol/L, at what temperature should the reactor be operated?

$A+C \xrightarrow{k_D} D$ desired $\quad$ $A+C \xrightarrow{k_{U1}} U_1$ undesired $\quad$ $D+C \xrightarrow{k_{U2}} U_2$ undesired

$$r_D = 800e^{\frac{-2000}{T}} C_A^{0.5} C_C \qquad r_{U_1} = 10e^{\frac{-300}{T}} C_A C_C \qquad r_{U_2} = 10^6 e^{\frac{-8000}{T}} C_C C_D$$

Need to maximize $S_{D/(U1+U2)}$

$$S_{D/(U_1+U_2)} = \frac{r_D}{r_{U_1}+r_{U_2}} = \frac{800e^{\frac{-2000}{T}} C_A^{0.5} \cancel{C_C}}{10e^{-\left(\frac{300}{T}\right)} C_A \cancel{C_C} + 10^6 e^{\frac{-8000}{T}} \cancel{C_C} C_D}$$

C_A=1

C_D=1

$$S_{\frac{D}{U_1+U_2}} = \frac{\frac{800}{10} e^{\frac{-2000}{T}} (1)^{0.5}}{\frac{10}{10} e^{-\left(\frac{300}{T}\right)} (1) + \frac{10^6}{10} e^{\frac{-8000}{T}} (1)} \rightarrow S_{\frac{D}{U_1+U_2}} = \frac{80e^{\frac{-2000}{T}}}{e^{-\left(\frac{300}{T}\right)} + 10^5 e^{\frac{-8000}{T}}}$$

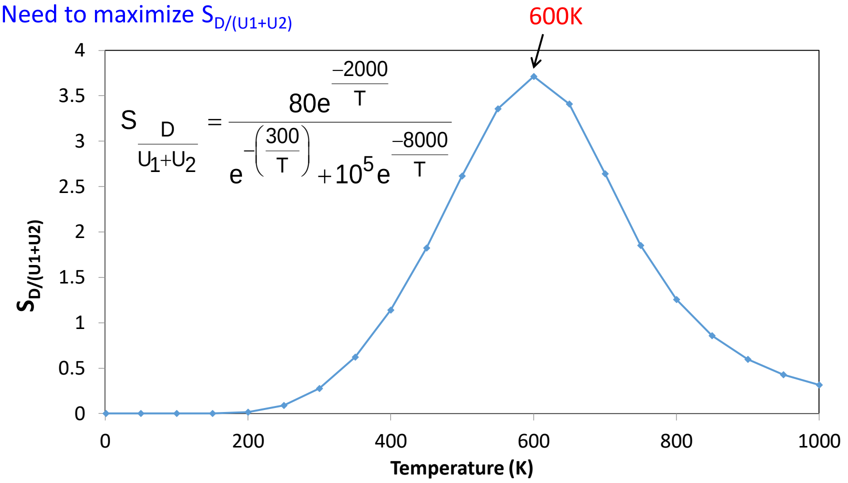
Plot $S_{D/(U1+U2)}$ vs temperature to find the temperature that maximizes $S_{D/(U1+U2)}$

If a CSTR were used with C_A = 1 mol/L and C_D= 1 mol/L, at what temperature should the reactor be operated?

$A+C \xrightarrow{k_D} D$ desired $\quad$ $A+C \xrightarrow{k_{U1}} U_1$ undesired $\quad$ $D+C \xrightarrow{k_{U2}} U_2$ undesired

$$r_D = 800e^{\frac{-2000}{T}} C_A^{0.5} C_C \qquad r_{U_1} = 10e^{\frac{-300}{T}} C_A C_C \qquad r_{U_2} = 10^6 e^{\frac{-8000}{T}} C_C C_D$$

Need to maximize $S_{D/(U1+U2)}$



$$S_{\frac{D}{U_1+U_2}} = \frac{80e^{\frac{-2000}{T}}}{e^{-\left(\frac{300}{T}\right)} + 10^5 e^{\frac{-8000}{T}}}$$

Calculate the yield of forming B in a **CSTR** and PFR when the conversion of A is 90% and C_{A0} = 4 mol/L. The following reactions occur in the reactor:

$$A \xrightarrow{k_B} B \quad r_B = k_B = 2\frac{mol}{L\cdot min} \qquad A \xrightarrow{k_C} C \quad r_C = k_C C_A \quad k_C = 1\ min^{-1}$$

What is the expression for the yield of B for a CSTR?

$$\tilde{Y}_B = \frac{F_B}{F_{A0}-F_A} \quad \text{(overall yield)} \quad \tilde{Y}_B = \frac{C_B\upsilon_0}{C_{A0}\upsilon_0 - C_A\upsilon_0} \rightarrow \tilde{Y}_B = \frac{C_B}{C_{A0}-C_A}$$

We know C_{A0} and C_A when X_A=0.9. How do we get C_B?

In - Out + Gen. = Accum.

$$\underset{0}{\cancel{F_{B0}}} - F_B + r_B V = \underset{0}{\cancel{\frac{dN_B}{dt}}} \rightarrow -F_B + r_B V = 0 \rightarrow r_B = \frac{C_B\upsilon_0}{V}$$

$$\rightarrow r_B = \frac{C_B}{\tau} \quad \rightarrow r_B = 2\frac{mol}{L\cdot min} = \frac{C_B}{\tau} \rightarrow 2\frac{mol}{L\cdot min}\tau = C_B$$

Use the mole balance on A to find τ (at 90% conversion)

In - Out + Gen. = Accum.

$$F_{A0} - F_A + r_A V = \underset{0}{\cancel{\frac{dN_A}{dt}}} \quad \rightarrow C_{A0}\upsilon_0 - C_A\upsilon_0 = -r_A V$$

$$C_{A0}-C_A = -r_A\frac{V}{\upsilon_0} \rightarrow C_{A0}-C_A = -r_A\tau \rightarrow \frac{C_{A0}-C_A}{-r_A} = \tau$$

Calculate the yield of forming B in a **CSTR** and PFR when the conversion of A is 90% and C_{A0} = 4 mol/L. The following reactions occur in the reactor:

$$A \xrightarrow{k_B} B \quad r_B = k_B = 2\frac{mol}{L\cdot min} \qquad A \xrightarrow{k_C} C \quad r_C = k_C C_A \quad k_C = 1\ min^{-1}$$

$$\tilde{Y}_B = \frac{C_B}{C_{A0}-C_A} \qquad 2\frac{mol}{L\cdot min}\tau = C_B \qquad \frac{C_{A0}-C_A}{-r_A} = \tau$$

What is $-r_A$? $\quad -r_A = r_B + r_C$

$$\rightarrow -r_A = k_B + k_C C_A \rightarrow -r_A = 2\frac{mol}{L\cdot min} + \frac{1}{min}C_A$$

Plug $-r_A$ back into expression for τ

$$\tau = \frac{C_{A0}-C_A}{-r_A} \rightarrow \tau = \frac{C_{A0}-C_A}{2\frac{mol}{L\cdot min} + \frac{1}{min}C_A}$$

C_{A0} = 4 mol/L, and at X_A=0.9, C_A= 0.4 mol/L

$$\tau = \frac{4\frac{mol}{L} - 0.4\frac{mol}{L}}{2\frac{mol}{L\cdot min} + \frac{1}{min}\left(0.4\frac{mol}{L}\right)} \rightarrow \tau = 1.5\ min$$

Residence time for $X_A = 0.9$

$$\tilde{Y}_B = \frac{r_B\tau}{C_{A0}-C_A} \quad \rightarrow \tilde{Y}_B = \frac{2\frac{mol}{L\cdot min}(1.5\,min)}{4\frac{mol}{L} - 0.4\frac{mol}{L}} \rightarrow \boxed{\tilde{Y}_B = 0.83}$$

Calculate the yield of forming B in a CSTR and **PFR** when the conversion of A is 90% and C_{A0} = 4 mol/L. The following reactions occur in the reactor:

$$A \xrightarrow{k_B} B \quad \boxed{r_B = k_B = 2\frac{mol}{L\cdot min}} \qquad A \xrightarrow{k_C} C \quad r_C = k_C C_A \quad k_C = 1\ min^{-1}$$

$$\rightarrow -r_A = k_B + k_C C_A \rightarrow -r_A = 2\frac{mol}{L\cdot min} + \frac{1}{min}C_A$$

What is the expression for the yield of B for a PFR?

$$\tilde{Y}_B = \frac{F_B}{F_{A0}-F_A} \quad \text{(overall yield)} \quad \tilde{Y}_B = \frac{C_B\upsilon_0}{C_{A0}\upsilon_0 - C_A\upsilon_0} \rightarrow \tilde{Y}_B = \frac{C_B}{C_{A0}-C_A}$$

Use the mole balance on B to find C_B

$$\frac{dF_B}{dV}=r_B \quad \rightarrow \frac{dC_B\upsilon_0}{dV}=r_B \quad \rightarrow \frac{dC_B}{d\tau}=r_B \quad \rightarrow \frac{dC_B}{d\tau}=2\frac{mol}{L\cdot min}$$

$$\rightarrow \int_{C_{B0}}^{C_B} dC_B = 2\frac{mol}{L\cdot min}\int_0^\tau d\tau \rightarrow C_B - \underset{0}{\cancel{C_{B0}}} = 2\frac{mol}{L\cdot min}(\tau-0) \rightarrow C_B = 2\frac{mol}{L\cdot min}\tau$$

Use the mole balance on A to find τ (at 90% conversion)

$$\frac{dF_A}{dV}=r_A \quad \rightarrow \frac{dC_A\upsilon_0}{dV}=r_A \quad \rightarrow \frac{dC_A}{d\tau}=r_A \quad \rightarrow \frac{dC_A}{d\tau} = -\left(2\frac{mol}{L\cdot min}+\frac{1}{min}C_A\right)$$

$$\rightarrow \frac{dC_A}{d\tau} = -\left(2\frac{mol}{L}+C_A\right)\frac{1}{min} \quad \rightarrow \int_{C_{A0}}^{C_A}\frac{dC_A}{-(2\,mol/L + C_A)} = \frac{1}{min}\int_0^\tau d\tau$$

Calculate the yield of forming B in a CSTR and **PFR** when the conversion of A is 90% and C_{A0} = 4 mol/L. The following reactions occur in the reactor:

$$A \xrightarrow{k_B} B \quad r_B = k_B = 2\frac{mol}{L\cdot min} \qquad A \xrightarrow{k_C} C \quad r_C = k_C C_A \quad k_C = 1\ min^{-1}$$

$$\rightarrow -r_A = k_B + k_C C_A \rightarrow -r_A = 2\frac{mol}{L\cdot min} + \frac{1}{min}C_A$$

$$\tilde{Y}_B = \frac{C_B}{C_{A0}-C_A} \qquad C_B = 2\frac{mol}{L\cdot min}\tau$$

Use mole balance on A to find τ (at X_A = 0.9)

$$\rightarrow \int_{C_{A0}}^{C_A}\frac{dC_A}{-\left(2\frac{mol}{L}+C_A\right)} = \frac{1}{min}\int_0^\tau d\tau \qquad \rightarrow \ln\frac{-\left(2\frac{mol}{L}+C_{A0}\right)}{-\left(2\frac{mol}{L}+C_A\right)} = \frac{1}{min}(\tau-0)$$

C_{A0} = 4 mol/L

C_A = 0.4 mol/L

$$\rightarrow \ln\frac{\left(2\frac{mol}{L}+4\frac{mol}{L}\right)}{\left(2\frac{mol}{L}+0.4\frac{mol}{L}\right)} = \frac{1}{min}\tau \quad \rightarrow 0.92\ min = \tau$$

$$\tilde{Y}_B = \frac{C_B}{C_{A0}-C_A} = \frac{r_B\tau}{C_{A0}-C_A} \rightarrow \tilde{Y}_B = \frac{2\frac{mol}{L\cdot min}0.92\,min}{4\frac{mol}{L}-0.4\frac{mol}{L}} \rightarrow \tilde{Y}_B = 0.51$$

Yield was better in the CSTR, but the residence time was longer

Complex Reactions – Algorithm

1. **Number Every Reaction**
2. **Mole Balance on every species**
3. **Rate Laws**

(a) Net **Rates** of Reaction for every species

$$r_A = \sum_{i=1}^{N} r_{iA}$$

(b) **Rate** Laws for every reaction

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

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

(c) Relative **Rates** of Reaction for every reaction

For a given reaction i: $\boldsymbol{a_i} A + \boldsymbol{b_i} B \rightarrow \boldsymbol{c_i} C + \boldsymbol{di} D$

$$\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i}$$

Reactor Mole Balance Summary

Reactor Type	Gas Phase	Liquid Phase
Batch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A$
Semibatch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A - \frac{\upsilon_0 C_A}{V}$
	$\frac{dN_B}{dt} = r_B V + F_{B0}$	$\frac{dC_B}{dt} = r_B + \frac{\upsilon_0 [C_{B0} - C_B]}{V}$

Reactor Mole Balance Summary

Reactor Type	Gas Phase	Liquid Phase
CSTR	$V = \dfrac{F_{A0} - F_A}{-r_A}$	$V = \upsilon_0 \dfrac{(C_{A0} - C_A)}{-r_A}$
PFR	$\dfrac{dF_A}{dV} = r_A$	$\upsilon_0 \dfrac{dC_A}{dV} = r_A$
PBR	$\dfrac{dF_A}{dW} = r'_A$	$\upsilon_0 \dfrac{dC_A}{dW} = r'_A$

Note: The reaction **rates** in the above **mole balances** are net rates.

Batch	Flow
$C_B = \dfrac{N_B}{V}$	$C_B = \dfrac{F_B}{\upsilon}$
$V = V_0 \dfrac{N_T}{N_{T0}} \dfrac{P_0}{P} \dfrac{T}{T_0}$	$\upsilon = \upsilon_0 \dfrac{F_T}{F_{T0}} \dfrac{P_0}{P} \dfrac{T}{T_0}$
$C_B = \dfrac{N_B}{N_T} \dfrac{N_{T0}}{V_0} \dfrac{P}{P_0} \dfrac{T_0}{T}$	$C_B = \dfrac{F_B}{F_T} \dfrac{F_{T0}}{\upsilon_0} \dfrac{P}{P_0} \dfrac{T_0}{T}$
$C_B = C_{T0} \dfrac{N_B}{N_T} \dfrac{P}{P_0} \dfrac{T_0}{T}$	$C_B = C_{T0} \dfrac{F_B}{F_T} \dfrac{P}{P_0} \dfrac{T_0}{T}$

Complex Reactions – Algorithm

4. Stoichiometry

Concentration of Gas:

$$C_A = C_{T0}\left(\frac{F_A}{F_T}\right)y\left(\frac{T_0}{T}\right) \qquad F_T = F_A + F_B + F_C + F_D$$

Note: We could use the gas phase mole balances for **liquids** and then just express the concentration as:

Flow: $C_A = \frac{F_A}{\upsilon_0}$

Batch: $C_A = \frac{N_A}{V_0}$

Complex Reactions

Example A: Liquid Phase PFR

$$(1) \quad \mathrm{A} + 2\mathrm{B} \rightarrow \mathrm{C} \qquad r_{1A} = -k_{1A}C_A C_B^2$$

$$(2) \quad \mathrm{A} + 3\mathrm{C} \rightarrow \mathrm{D} \qquad r_{2C} = -k_{2C}C_A^2 C_C^3$$

NOTE: The specific reaction rate k_{1A} is defined with respect to species A, and the specific reaction rate k_{2C} is defined with respect to species C.

1) Mole Balance on each and every species

$$(1) \quad \frac{dF_A}{dV} = r_A \qquad (2) \quad \frac{dF_B}{dV} = r_B$$

$$(3) \quad \frac{dF_C}{dV} = r_C \qquad (4) \quad \frac{dF_D}{dV} = r_D$$

Complex Reactions

Example A: Liquid Phase PFR

2) Rate Laws:

$$\boxed{\begin{array}{ll}(1) & \mathrm{A}+2\mathrm{B}\rightarrow\mathrm{C}\\ (2) & \mathrm{A}+3\mathrm{C}\rightarrow\mathrm{D}\end{array}}$$

(a) Net Rates

$$(5)\ r_A = r_{1A} + r_{2A} \qquad (7)\ r_B = r_{1B} + r_{2B}$$

$$(6)\ r_C = r_{1C} + r_{2C} \qquad (8)\ r_D = 0 + r_{2D}$$

(b) Rate Laws

$$(9)\ r_{1A} = -k_{1A} C_A C_B^2$$

$$(10)\ r_{2C} = -k_{2C} C_A^2 C_C^3$$

(c) Relative Rates

Reaction 1

$A + 2B \rightarrow C$

$$\frac{r_{1A}}{-1} = \frac{r_{1B}}{-2} = \frac{r_{1C}}{1}$$

$$(11)\ r_{1B} = 2 r_{1A}$$

$$(12)\ r_{1C} = -r_{1A}$$

Complex Reactions

Example A: Liquid Phase PFR

(c) Relative Rates

Reaction 2

$A + 3C \rightarrow D$

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

$$(13)\ r_{2A} = \frac{2}{3} r_{2C}$$

$$(14)\ r_{2D} = -\frac{r_{2C}}{3}$$

(d) Combine Net Rates

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

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

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

$$r_D = \frac{k_{2C}}{3} C_A^2 C_C^3$$

Complex Reactions

Example A: Liquid Phase PFR

3) Stoichiometry

Liquid

(15) $C_A = F_A / \upsilon_0$

(16) $C_B = F_B / \upsilon_0$

(17) $C_C = F_C / \upsilon_0$

(18) $C_D = F_D / \upsilon_0$

(19) $\tilde{S}_{C/D} = if\ (V > 0.00001)\ \text{then} \left(\frac{F_C}{F_D}\right) \text{else}\ 0$

Complex Reactions

Example A: Liquid Phase PFR

Others

$F_T = \text{Liquid} - \text{Not Needed}$

(19) $\alpha = \text{Liquid} - \text{Not Needed}$

(20) $C_{T0} = \text{Liquid} - \text{Not Needed}$

4) Parameters

(21) $k_{1A} = 10$

(22) $k_{2C} = 20$

(23) $\alpha = \text{Liquid}$

(24) $C_{T0} = \text{Liquid}$

(25) $V_f = 2500$

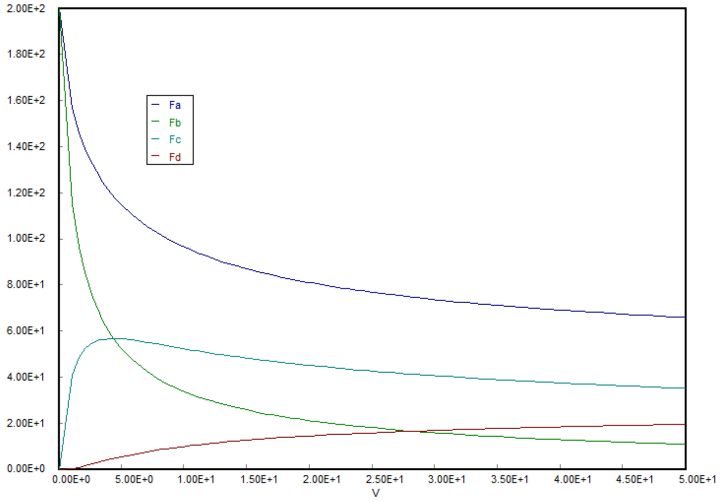
(26) $F_{A0} = 200$

(28) $F_{B0} = 200$

(26) $\upsilon_0 = 100$

Complex Reactions

Example A: Liquid Phase PFR



Complex Reactions

Example A: Liquid Phase

$$A + 2B \rightarrow C$$

$$A + 3C \rightarrow D$$

Net Rates

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

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

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

$$r_D = \frac{k_{2C}}{3} C_A^2 C_C^3$$

What is the best configuration to be used to maximize $S_{C/D}$?

Complex Reactions
Example E: Liquid Phase Semibatch

Same reactions, rate laws, and rate constants as Example A:

$$(1)\quad A + 2B \rightarrow C \qquad -r_{1A} = k_{1A} C_A C_B^2$$

NOTE: The specific reaction rate k_{1A} is defined with respect to species A.

$$(2)\quad 3C + 2A \rightarrow D \qquad -r_{2C} = k_{2C} C_C^3 C_A^2$$

NOTE: The specific reaction rate k_{2C} is defined with respect to species C.

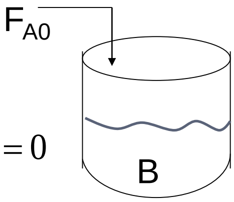
Complex Reactions
Example E: Liquid Phase Semibatch

The complex liquid phase reactions take place in a semibatch reactor where A is fed to B with F_{A0}= 3 mol/min. The volumetric flow rate is 10 dm^3/min and the initial reactor volume is 1,000 dm^3.

The maximum volume is 2,000 dm^3 and C_{A0}=0.3 mol/dm^3 and C_{B0}=0.2 mol/dm^3. Plot C_A, C_B, C_C, C_D and $S_{S/D}$ as a function of time.

Complex Reactions
Example E: Liquid Phase Semibatch

(1) A + 2B →C (2) 2A + 3C → D



1) Mole Balances:

$$\frac{dN_A}{dt} = r_A V + F_{A0} \qquad N_{A0} = 0$$

$$\frac{dN_B}{dt} = r_B V \qquad N_{B0} = C_{B0}V_0 = 2.000$$

$$\frac{dN_C}{dt} = r_C V \qquad N_{C0} = 0$$

$$\frac{dN_D}{dt} = r_D V \qquad N_{D0} = 0$$

Complex Reactions
Example E: Liquid Phase Semibatch

2) Rate Laws: (5)-(14)

Net Rate, Rate Laws and relative rate – are the same as Liquid and Gas Phase PFR and Liquid Phase CSTR

$$V = V_0 + v_0 t \quad (15)$$

$$C_A = \frac{N_A}{V} \quad (16) \qquad C_B = \frac{N_B}{V} \quad (17)$$

$$C_C = \frac{N_C}{V} \quad (18) \qquad C_D = \frac{N_D}{V} \quad (19)$$

3) Selectivity and Parameters:

$$S_{C/D} = \text{if } (t > 0.0001) \text{ then } \left(\frac{N_C}{N_D}\right) \text{ else } (0) \quad (20)$$

$$\upsilon_0 = 10\,\text{dm}^3/\text{min} \quad V_0 = 100\,\text{dm}^3 \quad F_{A0} = 3\,\text{mol/min}$$

Complex Reactions
Example E: Liquid Phase Semibatch