



**Bright Future Institute**  
FOR PRIVATE TRAINING

**AMERICAN UNIVERSITY OF MIDDLE  
EAST**

**CHEMICAL REACTION  
ENGINEERING**

**CHE 348**

**Spring (2023)**

**Chapter # 8**

**(Multiple Reactions)**

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## Chapter 8 Multiple Reactions

### ❖ For multiple reactions:

- 1- More than one reaction occurs within a chemical reactor
- 2- Minimization of undesired side reactions that occur with the desired reaction contributes to the economic success of a chemical plant
- 3- Use of selectivity factor to select the proper reactor that minimizes unwanted side reactions

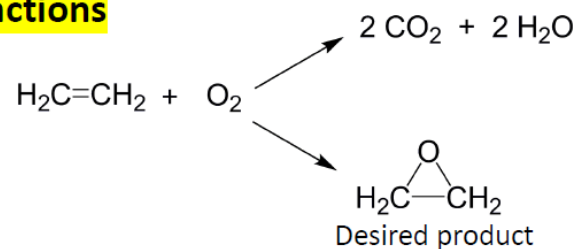
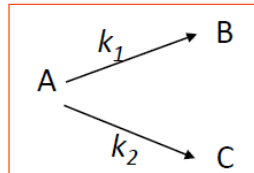
**Goal:** Determine the reactor conditions and configuration that maximizes product formation

### ❖ Types of multiple reactions:

- 1- Parallel Reaction 2- Series Reactions 3- Independent Reactions 4- Complex Reactions

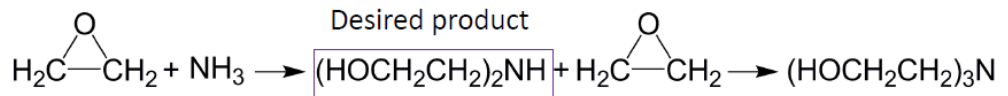
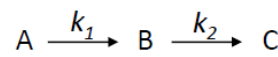
#### 1) Parallel or competing reactions

reactions in which the reactant is consumed by two different reaction pathways to form different products



reactions where the reaction forms an intermediate product which reacts further to form another product

#### 2) Series reactions

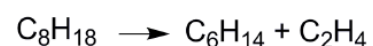
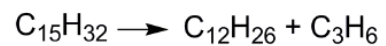


#### 3) Independent reactions

neither the product nor the reactants react with themselves or one another

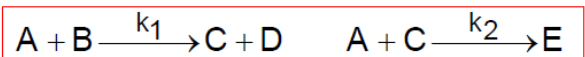


Crude oil cracking



combination of both series and parallel reactions

#### 4) Complex reactions

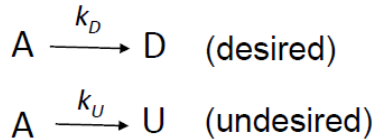


**Note:** With multiple reactors, either molar flow or number of moles must be used (No conversion)

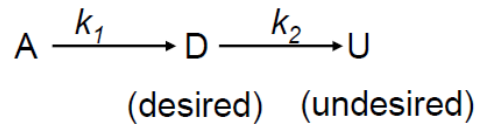


## Desired and Undesired Reactions

parallel reactions



series reactions



**Purpose:** Minimizing the formation of U (undesired product) and maximizing the formation of D (desired products) in parallel and series reactions.

### ❖ Selectivity & Yield:

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

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

### Instantaneous Selectivity

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

### Instantaneous Yield

$$Y_D = \frac{\text{rate of formation of D}}{\text{rate of consumption of A}} = \frac{r_D}{-r_A}$$

### Overall Selectivity

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

$$\tilde{S}_{D/U} = \frac{N_D}{N_U} = \frac{\text{Final moles of desired product}}{\text{Final moles of undesired product}}$$

### Overall Yield

flow

$$\tilde{Y}_D = \frac{F_D}{F_{A0} - F_A} \quad \leftarrow \text{Evaluated at outlet}$$

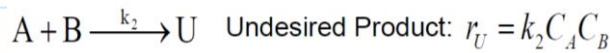
batch

$$\tilde{Y}_D = \frac{N_D}{N_{A0} - N_A} \quad \leftarrow \text{Evaluated at } t_{\text{final}}$$



**Example:**

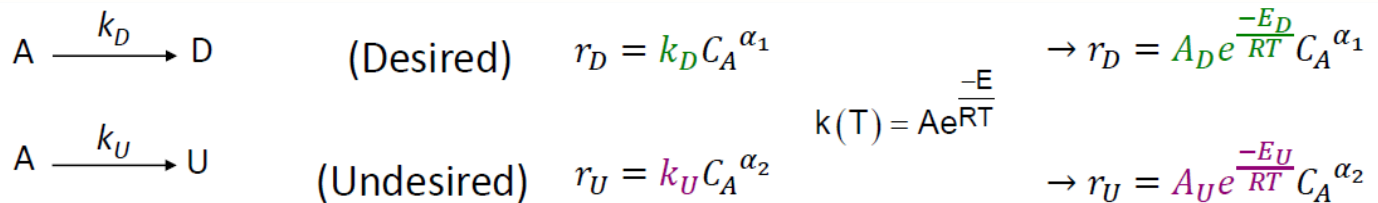
Find the instantaneous selectivity for the following multiple reactions?



**“Solution”**

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

## Parallel Reactions



Rate of disappearance of A:

$$-r_A = r_D + r_U$$

$$-r_A = k_D C_A^{\alpha_1} + k_U C_A^{\alpha_2}$$

$$-r_A = A_D e^{\frac{-E_D}{RT}} C_A^{\alpha_1} + A_U e^{\frac{-E_U}{RT}} C_A^{\alpha_2}$$

**Instantaneous Selectivity,  $S_{D/U}$  :**

$$S_{D/U} = \frac{\text{rate of formation of } D}{\text{rate of formation of } U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$$

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

❖ **How to maximize  $S_{D/U}$  for parallel reactions by concentration:**

$$S_{D/U} = \frac{\text{rate of formation of } D}{\text{rate of formation of } U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$$

**Case 1:  $\alpha_1 > \alpha_2$**

**Make  $C_A$  as large as possible:**





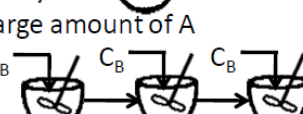
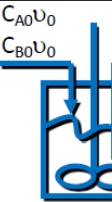
- If gas phase  $\rightarrow$  run it without inerts and high pressure
- If liquid phase  $\rightarrow$  the use of a diluents should be kept to a minimum
- Use a PFR or batch reactor
- Do not use a CSTR

**Case 2:  $\alpha_2 > \alpha_1$**

**Make  $C_A$  as low as possible:**

- Dilute the feed with inerts
- Use a CSTR

❖ **How do concentration play into reactor selection:**

$A+B \xrightarrow[k_U]{k_D} D$ $\alpha_1 > \alpha_2$	<p><b>High <math>C_A</math> favors desired product formation</b></p>	<p><math>\alpha_1 &lt; \alpha_2</math> <b>High <math>C_A</math> favors undesired product formation (keep <math>C_A</math> low)</b></p>
<p><math>\beta_1 &gt; \beta_2</math></p> <p><b>High <math>C_B</math> favors desired product formation</b></p>	<p><b>Batch reactor</b> </p> <p>When <math>C_A</math> &amp; <math>C_B</math> are low (end time or position), all rxns will be slow</p> <p><b>PFR/PBR</b></p> <p>High P for gas-phase rxn, do not add inert gas (dilutes reactants)</p>	<p><b>PFR/PBR</b></p> <p>Side streams feed low <math>C_A</math></p> <p><b>Semi-batch reactor</b>  <math>\leftarrow</math> High <math>C_B</math></p> <p>slowly feed A to large amt of B</p> <p><b>CSTRs in series</b> </p>
<p><math>\beta_1 &lt; \beta_2</math></p> <p><b>High <math>C_B</math> favors undesired product formation (keep <math>C_B</math> low)</b></p>	<p><b>PFR/PBR w/ side streams feeding low <math>C_B</math></b></p> <p><b>Semi-batch reactor</b>, slowly feed B to large amount of A  <math>\leftarrow</math> High <math>C_A</math></p> <p><b>CSTRs in series</b> </p> <p>B consumed before leaving CSTR<sub>n</sub></p>	<p><b>CSTR</b> </p> <p><b>PFR/PBR w/ high recycle</b></p> <ul style="list-style-type: none"> <li>• Dilute feed with inerts that are easily separated from product</li> <li>• Low P if gas phase</li> </ul>

**Very important to know that:**

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

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

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

**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

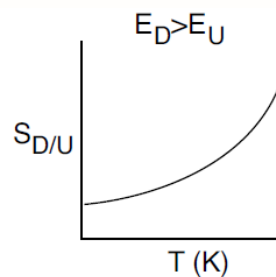


❖ **How to maximize  $S_{D/U}$  for parallel reactions by Temperature Control:**

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

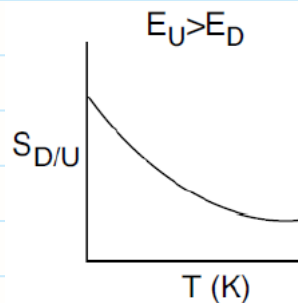
**Case 1:  $E_D > E_U$**

Specific reaction rate of the desired reaction increases **more** rapidly with increasing temperature → Operate at the **highest possible temperature**



**Case 2:  $E_U > E_D$**

Specific rate of desired reaction  $k_D$  increases **less** rapidly with increasing temperature → Operate at the **lowest possible temperature**

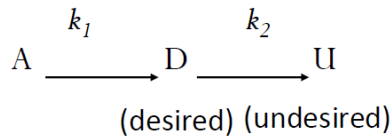


❖ **Reactor Selection criteria:**

- Safety
- Selectivity
- Yield
- Temperature control
- Cost



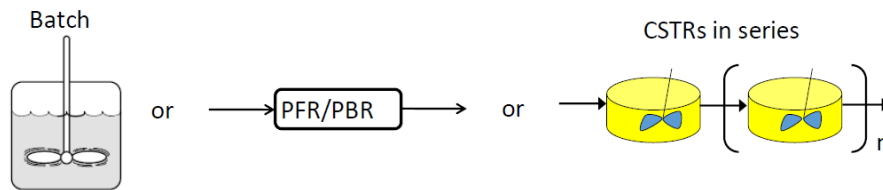
## Series (Consecutive) Reactions



**Time** is the key factor here!!!

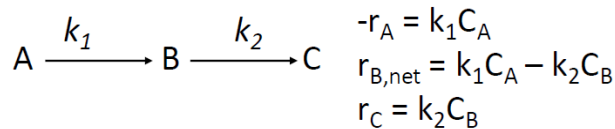
Space time ( $\tau$ ) for a flow reactor    Real time ( $t$ ) for a batch reactor

To maximize the production of D, use:



and carefully select the time (batch) or space time (flow)

❖ **How the concentration changes with time constant  $\tau$ :**



How does  $C_A$  depend on  $\tau$ ?

$$\frac{dF_A}{dV} = -k_1 C_A \rightarrow \nu_0 \frac{dC_A}{dV} = -k_1 C_A \rightarrow \boxed{C_A = C_{A0} e^{-k_1 \tau}} \quad \text{Substitute } \frac{V}{\nu_0} = \tau$$

How does  $C_B$  depend on  $\tau$ ?

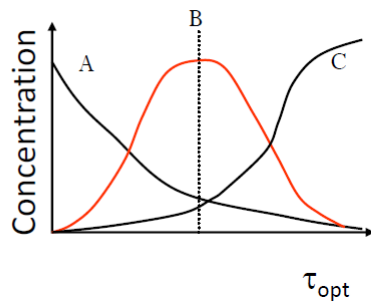
$$\frac{dF_B}{dV} = k_1 C_A - k_2 C_B \rightarrow \nu_0 \frac{dC_B}{dV} = k_1 (C_{A0} e^{-k_1 \tau}) - k_2 C_B$$

$$\rightarrow \frac{dC_B}{d\tau} = k_1 (C_{A0} e^{-k_1 \tau}) - k_2 C_B \rightarrow \frac{dC_B}{d\tau} + k_2 C_B = k_1 (C_{A0} e^{-k_1 \tau})$$

Use integrating factor  $\rightarrow \frac{d(C_B e^{k_2 \tau})}{d\tau} = k_1 C_{A0} e^{(k_2 - k_1)\tau} \rightarrow \boxed{C_B = k_1 C_{A0} \left( \frac{e^{-k_1 \tau} - e^{-k_2 \tau}}{k_2 - k_1} \right)}$

Find  $C_C$ ?

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



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

$$C_B = k_1C_{A0}\left(\frac{e^{-k_1\tau} - e^{-k_2\tau}}{k_2 - k_1}\right)$$

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

The reactor V (for a given  $\nu_0$ ) and  $\tau$  that maximizes  $C_B$  occurs when  $dC_B/d\tau=0$

$$\frac{dC_B}{d\tau} = \left(\frac{k_1C_{A0}}{k_2 - k_1}\right)(-k_1e^{-k_1\tau} + k_2e^{-k_2\tau}) = 0$$

$$\tau_{opt} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

$$\frac{V}{\nu_0} = \tau \quad \text{so} \quad V_{opt} = \nu_0 \tau_{opt}$$





## "Problem Solving"

### Example 1:

Liquid phase reaction takes place in a CSTR. The inlet and outlet concentrations of species A are 10 mol/L and 2 mol/L respectively. If the space time is 8 min, what is the rate of consumption of A ( $-r_A$ ) in mol/(L.min)?

### "Solution"

$$(C_{Ao} - C_A) = -r_A \tau$$
$$-r_A = \frac{(C_{Ao} - C_A)}{\tau}$$
$$-r_A = \frac{(10 - 2)}{8} = 1 \frac{\text{mol}}{\text{L.min}}$$

### Example 2:

What is the space time (in minutes) for a PFR having a volume of 100 L if the volumetric flow rate is constant and is equal to 20 L/min?

### "Solution"

$$\tau = \frac{V}{v_0}$$
$$\tau = \frac{100}{20} = 5 \text{ min}$$

### Example 3:

Multiple reactions take place in a continuous reactor producing species E, H, and G.

- The overall selectivity of E with respect to D is 5 mol E/ mol D.

What is the molar flow rate of D (in mol/s) at the outlet given that the outlet molar flow rate of E is 10 mol/s?

### "Solution"

$$\tilde{S}_{ED} = \frac{F_E}{F_D}$$
$$F_D = \frac{F_E}{\tilde{S}_{ED}} \longrightarrow F_D = \frac{10}{5} = 2 \text{ mol/s}$$



**Example 4:**

The following reactions occur in a batch reactor:

- First reaction:  $A+B \rightarrow C$
- Second reaction:  $2A+D \rightarrow E$
- The net rate of production of A is  $-5 \text{ mol/(L.s)}$
- If the rate of consumption of A in the first reaction is  $4 \text{ mol/(L.s)}$ , what will be the rate of consumption of A in the second reaction (in  $\text{mol/(L.s)}$ )?

**“Solution”**

$$\text{net production } r_A = r_{1A} + r_{2A}$$

$$-5 = (-4) + r_{2A}$$

$$\text{consumption rate of A in reaction 2 } -r_{2A} = 1 \frac{\text{mol}}{\text{L.s}}$$

**Example 5:**

Multiple reactions occur in a CSTR producing products X, W, Y, and Z. These species have outlet concentrations that are equal to 0.1, 0.5, 0.03, and 0.005 mol/L respectively.

- Assume isothermal steady state and constant volumetric flow rate.

What is the overall selectivity of X with respect to Z in (mol X/ mol Z)?

**“Solution”**

$$\tilde{S}_{XZ} = \frac{C_X}{C_Z} \quad \text{at const. } v_0$$

$$\tilde{S}_{XZ} = \frac{0.1}{0.005} = 20$$



**Example 6:**

The following liquid multiple reactions occur in a CSTR at isothermal steady state conditions.

- First reaction:  $A + 2B \rightarrow C + 4D$
- Second reaction:  $2A + D \rightarrow 3E$

The rate of consumption of D in the second reaction is 3 mol/(L.s). What is the net production rate of E in mol/(L.s)?

**“Solution”**

$$\frac{r_D}{-d} = \frac{r_E}{e}$$

$$\frac{-3}{-1} = \frac{r_E}{3}$$

$$r_E = \frac{-3 \times 3}{-1} = 9 \frac{\text{mol}}{\text{L.s}}$$

**Example 7:**

The following liquid multiple reactions occur in a CSTR at isothermal steady state conditions.

- Reaction (1):  $A + 2B \rightarrow C + 4D$
- Reaction (2):  $2A + 2D \rightarrow 3E$

The net rate of production of C is 1.5 mol/(L.s).

What is the net consumption rate of B in mol/(L.s)?

**“Solution”**

$$\frac{r_B}{-b} = \frac{r_C}{c}$$

$$\frac{r_B}{-2} = \frac{1.5}{1}$$

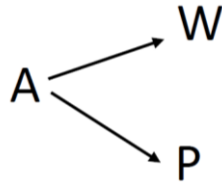
$$-r_B = \frac{-2 \times 1.5}{1} = 3 \frac{\text{mol}}{\text{L.s}}$$



**Example 8:**

Consider the reaction network below in a batch reactor: if the overall selectivity of W to P is 4.0, what is the overall yield of P?

**“Solution”**



$$\tilde{S}_{WP} = \frac{N_W}{N_P} = 4$$

$$\tilde{Y}_P = \frac{N_P}{N_{A0} - N_A} = \frac{N_P}{N_P + N_W}$$

$$\tilde{Y}_P = 0.2$$

**Example 9:**

Consider the series reaction below in a batch reactor: if the overall yield of D is 75%, at 50% conversion of A what is the overall selectivity to D with respect to U, i.e  $\tilde{S}_{DU}$ ?

**“Solution”**



$$\begin{aligned} N_A &= N_{A0} - N_{A0}X = N_{A0}(1 - 0.5) \\ N_A &= 0.5N_{A0} \end{aligned}$$

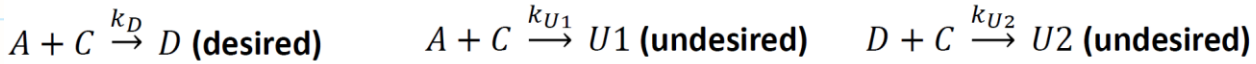
$$\tilde{Y}_D = \frac{N_D}{N_{A0} - N_A} = \frac{N_D}{0.5N_{A0}} = 0.75 \rightarrow N_D = (0.5)(0.75)N_{A0}$$

$$\tilde{S}_{DU} = \frac{N_D}{N_U} = \frac{N_D}{N_{A0} - N_A - N_D} = 3$$



### Example 10:

If a CSTR were used with  $C_A = 1 \frac{\text{mol}}{\text{L}}$  and  $C_D = 1 \frac{\text{mol}}{\text{L}}$ , at which temperature should the reactor be operated?



$$r_D = 800e^{\frac{-2000}{T}} C_A^{0.5} C_C \quad r_{U1} = 10e^{\frac{-300}{T}} C_A C_C \quad r_{U2} = 10^6 e^{\frac{-8000}{T}} C_C C_D$$

### "Solution"

Need to Maximize  $S_{\frac{D}{U1+U2}}$

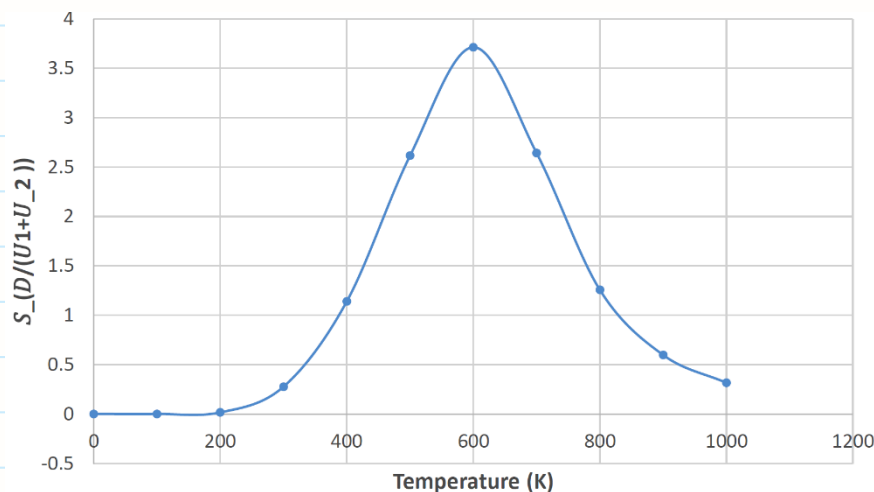
$$S_{\frac{D}{U1+U2}} = \frac{r_D}{r_{U1} + r_{U2}}$$

$$= \frac{800e^{\frac{-2000}{T}} C_A^{0.5} C_C}{10e^{\frac{-300}{T}} C_A C_C + 10^6 e^{\frac{-8000}{T}} C_C C_D}$$

At  $C_A = 1 \frac{\text{mol}}{\text{L}}$  and  $C_D = 1 \frac{\text{mol}}{\text{L}}$

$$S_{\frac{D}{U1+U2}} = \frac{800e^{\frac{-2000}{T}} 1^{0.5}}{10e^{\frac{-300}{T}} * 1 + 10^6 e^{\frac{-8000}{T}} * 1}$$

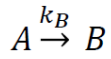
Plot  $S_{\frac{D}{U1+U2}}$  vs temperature to find the temperature that maximize  $S_{\frac{D}{U1+U2}}$



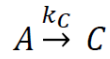


**Example 11:**

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



$$r_B = k_C = 2 \frac{\text{mol}}{\text{L} \cdot \text{min}}$$



$$r_C = k_C C_A, k_C = 1 \text{ min}^{-1}$$





**Given:**

$$C_{Ao} = 4 \frac{\text{mol}}{\text{L}} \rightarrow X_A = 0.4$$

$$\text{Rxn (1): } A \xrightarrow{k_B} B \approx r_B = k_B = 2 \frac{\text{mol}}{\text{L} \cdot \text{min}}$$

$$\text{Rxn (2): } A \xrightarrow{k_c} C \approx r_c = k_c C_A \rightarrow k_c = 1 \frac{1}{\text{min}}$$

**“Solution”**

To find the overall yield of B:

$$Y_B = \frac{F_B}{F_{Ao} - F_A} \approx Y_B = \frac{C_B}{C_{Ao} - C_A} \rightarrow (1)$$

**For CSTR:**

**Carry out mole balance on A:**

$$F_{Ao} - F_A + r_A V = \frac{dNa}{dt} \rightarrow v_o C_{Ao} - v_o C_A + r_A V = 0 \rightarrow -r_A V = v_o C_{Ao} - v_o C_A \div v_o$$

$$-r_A \tau = C_{Ao} - C_A \rightarrow (2)$$

$$C_A = C_{Ao}(1 - X_A) = 4(1 - 0.9) = 0.4 \frac{\text{mol}}{\text{L}}$$

$$-r_A = -r_{A1} - r_{A2} \rightarrow \text{using relative rate law}$$

$$-r_{A1} = -r_b = k_B \approx -r_{A1} = 2 \frac{\text{mol}}{\text{L} \cdot \text{min}} \rightarrow \text{sub in } -r_A$$

$$-r_{A2} = -r_c = k_c C_A \approx -r_{A2} = (1)(0.4) = 0.4 \frac{\text{mol}}{\text{L} \cdot \text{min}} \rightarrow \text{sub in } -r_A$$

$$-r_A = 2 + 0.4 = 2.4 \frac{\text{mol}}{\text{L} \cdot \text{min}} \rightarrow \text{sub in (2) to find } \tau$$

$$2.4\tau = 4 - 0.4 \rightarrow \tau = 1.5 \text{ min}$$



**Carry out mole balance on B:**

$$0 - F_B + r_B V = \cancel{\frac{dN_B}{dt}} \rightarrow -v_o C_B + r_B V = 0 \rightarrow r_B V = v_o C_B \div v_o$$

$$r_B \tau = C_B \approx C_B = (1.5)(2) = 3 \frac{\text{mol}}{L} \rightarrow \text{sub in (1) to find } Y_B$$

$$Y_B = \frac{C_B}{C_{A0} - C_A} = \frac{3}{4 - 0.4} = 0.83 \rightarrow \boxed{Y_B = 0.83}$$

**For PFR:**

**Carry out mole balance on A:**

$$\frac{dF_A}{dV} = r_A \rightarrow \frac{v_o dC_A}{dV} = r_A \rightarrow (1)$$

$$-r_A = -r_{A1} - r_{A2} = 2 + C_A \rightarrow r_A = -(2 + C_A) \rightarrow (2)$$

Sub (2) in (1):

$$\frac{v_o dC_A}{dV} = -(2 + C_A) \rightarrow \text{Separate } -v_o \frac{dC_A}{(2 + C_A)} = dV \rightarrow \text{Integrate}$$

$$-v_o \int_{C_{A0}}^{C_A} \frac{dC_A}{(2 + C_A)} = \int_0^V dV \rightarrow -v_o \int_4^{0.4} \frac{dC_A}{(2 + C_A)} = \int_0^V dV \rightarrow -v_o(-0.9162) = V \div v_o$$

$$\tau = 0.92 \text{ min}$$

**Carry out mole balance on B:**

$$\frac{dF_B}{dV} = r_B \rightarrow \frac{v_o dC_B}{dV} = 2 \rightarrow \text{Separate } \frac{v_o}{2} dC_B = dV \rightarrow \text{Integrate}$$

$$v_o \int_0^{C_B} dC_B = \int_0^V dV \rightarrow \frac{v_o}{2} C_B = V \div v_o$$

$$C_B = 2\tau = (2)(0.92) = 1.84 \frac{\text{mol}}{L} \rightarrow \text{sub in (1) to find } Y_B$$



$$Y_B = \frac{C_B}{C_{Ao} - C_A} = \frac{1.84}{4 - 0.4} = 0.83 \rightarrow Y_B = 0.51$$

**Analysis:**

The yield was better in the CSTR, but the residence time was longer.

	$\bar{Y}_B$	$\tau$
CSTR	0.83	1.5
PFR	0.51	0.92



**Table of Equations**

Reference Number of Equation	Equation	Notes
1	$\tilde{S}_{ij} = \frac{F_i}{F_j}$	Overall Selectivity in Flow reactors of species (i) with respect to species (j)
2	$\tilde{S}_{ij} = \frac{C_i}{C_j} \quad \text{at const. } v_0$	Overall Selectivity in Flow reactors of species (i) with respect to species (j) at constant volumetric flow rate
3	$\tau = \frac{V}{v_0}$	Space time in Flow reactors
4	$v_0 \frac{dC_W}{dV} = r_W$	General Mole Balance in PFR
5	$(C_{W0} - C_W) = -r_W \tau$	General Mole Balance in CSTR
6	$\text{net } r_W = -((-r_{1W}) + (-r_{2W}))$	Net Production Rate of species W
7	$\frac{dN_W}{dt} = r_W V$	General Mole Balance in Batch reactor
8	$a(t) = \frac{-r'_W(t)}{-r'_W(t=0)}$	Catalyst activity
9	$\frac{r_M}{-m} = \frac{r_P}{-p} = \frac{r_Q}{q} = \frac{r_Y}{y}$ $\text{for } mM + pP \rightarrow qQ + yY$	Lowercase letters represent stoichiometric coefficients while Uppercase letters represent species
10	$C_W = \frac{N_W}{V}$	Concentration in Batch reactor