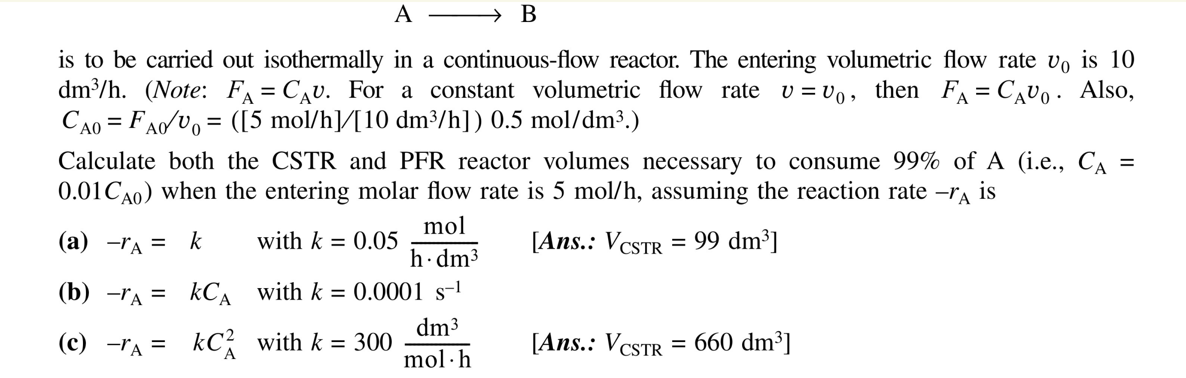
Ch.1

* Larger volume increase the amount of time the fluid spends in the reactor

↑ flow rate out ↑ volume in CSTR

Problems:-

Q5.



$$A \longrightarrow B$$

is to be carried out isothermally in a continuous-flow reactor. The entering volumetric flow rate v_0 is 10 dm³/h. (*Note*: $F_A = C_A v$. For a constant volumetric flow rate $v = v_0$, then $F_A = C_A v_0$. Also, $C_{A0} = F_{A0}/v_0 = ([5\ \text{mol/h}]/[10\ \text{dm}^3/\text{h}])\ 0.5\ \text{mol/dm}^3$.)

Calculate both the CSTR and PFR reactor volumes necessary to consume 99% of A (i.e., $C_A = 0.01 C_{A0}$) when the entering molar flow rate is 5 mol/h, assuming the reaction rate $-r_A$ is

(a) $-r_A = k$ with $k = 0.05 \dfrac{\text{mol}}{\text{h} \cdot \text{dm}^3}$ [***Ans.:*** $V_{CSTR} = 99\ \text{dm}^3$]

(b) $-r_A = kC_A$ with $k = 0.0001\ \text{s}^{-1}$

(c) $-r_A = kC_A^2$ with $k = 300 \dfrac{\text{dm}^3}{\text{mol} \cdot \text{h}}$ [***Ans.:*** $V_{CSTR} = 660\ \text{dm}^3$]

$v_0 = 10\ dm^3/h$ $C_A = 0.01\ C_{A0}$

$C_{A0} = 0.5\ mol/dm^3$ $F_{A0} = 5\ mol/h$

a) CSTR $V = \dfrac{F_{A0} - F_A}{-r_A}$

$F_A = C_A v$

$[0.01(0.5)](10) = 0.05\ mol/h$

$V = \dfrac{5-0.05}{0.05} = 99\ dm^3$

PFR $V = \displaystyle\int_{F_{A0}}^{F_A} \frac{dF}{r_A}$

$V = -\dfrac{1}{k}\left[F_A - F_{A0}\right]$

$-\dfrac{1}{0.05}\left[0.05 - 5\right] = 99\ dm^3$

* constant Rate of Reaction = Same Volume

(zero order)

b) CSTR $V = \frac{F_{A0} - F_A}{-r_A}$

$$V = \frac{5 - 0.05}{k C_A}$$

$k = 0.0001\ s^{-1}$

$C_A = 0.01\ C_{A0}$

$0.01\ (0.5) = 0.005\ \frac{mol}{dm^3}$

$$V = \frac{5 - 0.05\ \cancel{mol}}{\cancel{h}} \left| \frac{\cancel{s}}{0.0001} \right| \frac{dm^3}{0.005\ \cancel{mol}} \left| \frac{1\ \cancel{h}}{3600\cancel{s}} \right.$$

$V = 2750\ dm^3$

*CSTR always have higher value than PFR

c) CSTR:

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

$$V = \frac{5 - 0.05}{300\ (0.0005)^2} = 660\ dm^3$$

$F_{A0} = C_A v$

$C_A = \frac{F_{A0}}{v}$

PFR $V = \int_{F_{A0}}^{F_A} \frac{dF}{-kC_A}$

$$V = -\frac{1}{k} \int_{F_{A0}}^{F_A} \frac{dF_A}{\frac{F_A}{v}}$$

$$V = -\frac{v}{k} \left[\ln F_A - \ln F_{A0} \right]$$

$$V = -\frac{v}{k} \ln \frac{F_A}{F_{A0}}$$

$$V = \frac{-10\ dm^3}{h} \left| \frac{s}{0.0001} \right| \frac{1\ h}{3600s} \cdot \ln \left[\frac{0.05}{5} \right]$$

$V = 128\ dm^3$

PFR

$$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{-k\ C_A^2}$$

$$V = -\frac{1}{k} \int_{F_{A0}}^{F_A} \frac{dF_A}{\frac{F_A^2}{v_0^2}}$$

$$-\frac{v^2}{k} \left[-\frac{1}{F_A} + \frac{1}{F_{A0}} \right]$$

$$-\frac{10^2}{300} \left[-\frac{1}{0.05} + \frac{1}{5} \right]$$

$V = 6.6\ dm^3$

(d) Repeat **(a)**, **(b)**, and/or **(c)** to calculate the time necessary to consume 99.9% of species A in a 1000 dm^3 constant-volume batch reactor with $C_{A0} = 0.5\ mol/dm^3$.

Batch ∴ $-r_A = K$

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

$N_{A_0} = C_{A_0} V$

$N_{A_0} = 0.5(1000) = 500\ mol$

$N_A = 0.01\ N_{A0}$

$N_A = 0.01(500) = 5\ mol$

$$t = \int_{N_{A0}}^{N_{A0}} \frac{dN_A}{r_A V} \rightarrow t = \int_{N_{A0}}^{N_A} \frac{dN_A}{-kV}$$

$$t = \frac{-1}{kV} \int_{N_{A0}}^{N_A} dN_A$$

$$t = \frac{-1}{0.05\ \cancel{mol}} \left| \frac{dm^3 \cdot h}{1000\ \cancel{dm}^3} \right. \left[N_A - N_{A0} \right] \cancel{mol}$$

$$(5 - 500)$$

$$t = 9.9\ h$$

B) $-r_A = KC_A$ $K = 0.0001\ s^{-1}$

$$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A V} \qquad t = \int_{N_{A0}}^{N_A} \frac{dN_A}{-C_A k V}$$

$N_A = C_A V$

$$t = \frac{-1}{k} \int_{N_{A0}}^{N_A} \frac{dN_A}{N_A}$$

$$t = \frac{-1}{0.0001} \Big| s \left[\ln \frac{5}{500} \right]$$

$$t = 46051.7\ s = 12.8\ h$$

Q8: $2A \rightarrow B$ $\quad k = 0.03\ dm^3/mol \cdot s$ $\quad C_{A0} = 2$ molar $\quad v_0 = 3\ dm^3/s$

$C_A = 0.1$ molar

CSTR $\quad V = \dfrac{F_{A0} - F_A}{-r_A}$

$-r_A = k C_A^2$

$$V = \frac{F_{A0} - F_A}{k C_A^2}$$

$F_{A0} = C_{A0} v_0$

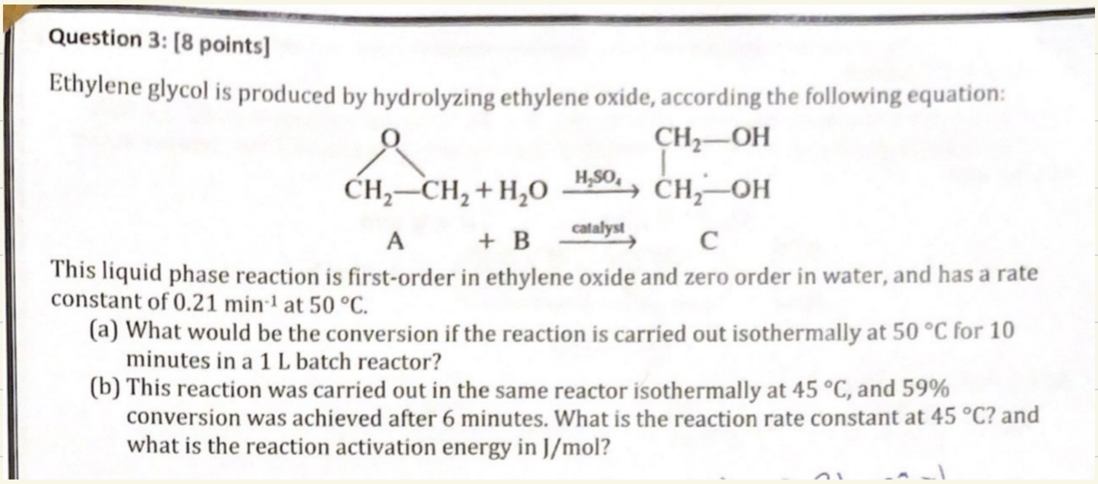
$2(3) = 6$ mol/s

$F_A = C_A v_0$

$0.1(3) = 0.3$ mol/s

$$V = \frac{6 - 0.3}{0.03(0.1)^2} = 19000\ dm^3$$

Ch.4



Question 3: [8 points]

Ethylene glycol is produced by hydrolyzing ethylene oxide, according the following equation:

$$\underset{A}{\overset{O}{CH_2\text{—}CH_2}} + \underset{B}{H_2O} \xrightarrow[\text{catalyst}]{H_2SO_4} \underset{C}{\begin{matrix} CH_2\text{—}OH \\ | \\ CH_2\text{—}OH \end{matrix}}$$

This liquid phase reaction is first-order in ethylene oxide and zero order in water, and has a rate constant of 0.21 min^{-1} at 50 °C.

(a) What would be the conversion if the reaction is carried out isothermally at 50 °C for 10 minutes in a 1 L batch reactor?

(b) This reaction was carried out in the same reactor isothermally at 45 °C, and 59% conversion was achieved after 6 minutes. What is the reaction rate constant at 45 °C? and what is the reaction activation energy in J/mol?

A) 1. Mole Balance Batch $N_{A0}\frac{dX}{dt} = -r_A V$ $C_A = \frac{N_T}{V}$

$$C_{A0}\frac{dX}{dt} = -r_A$$

$$\frac{-\cancel{r_A}\,dt}{\cancel{-r_A}} = \frac{C_{A0}\,dX}{-r_A}$$

$$t = \int_0^X \frac{C_{A0}}{-r_A}\,dX$$

2. Rate Law

$$-r_A = k C_A$$

3. Stoichiometry $C_A = C_{A0}(1-X)$

4. combine $-r_A = k C_{A0}(1-X)$

$$t = \int_0^X \frac{C_{A0}}{k C_{A0}(1-X)}\,dX$$

$$t = \frac{1}{k}\int_0^X \frac{1}{(1-X)}\,dX$$

$$10 = \frac{1}{0.21} -\ln(1-X)$$ $X = 0.877$

B)

$$t = \frac{1}{k} \int_0^x \frac{dx}{(1-X)}$$

$$6 = \frac{1}{k} - \ln(1 - 0.59) \qquad k = 0.149 \text{ min}^{-1}$$

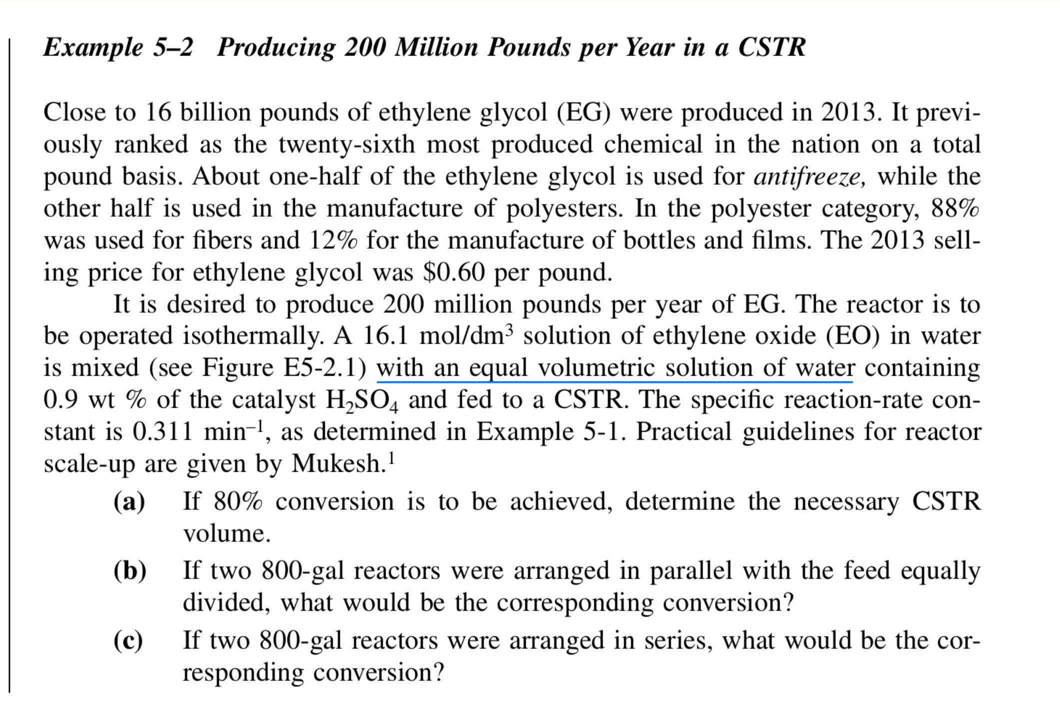
$$K(T_2) = K(T_1)\, e^{\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$0.149 = 0.21 \quad e^{\frac{E}{8.314}\left(\frac{1}{323} - \frac{1}{318}\right)}$$

$$E = 58609 \text{ J/mol}$$

$$58.6 \text{ kJ/mol}$$

Ch.5



Example 5–2 Producing 200 Million Pounds per Year in a CSTR

Close to 16 billion pounds of ethylene glycol (EG) were produced in 2013. It previously ranked as the twenty-sixth most produced chemical in the nation on a total pound basis. About one-half of the ethylene glycol is used for *antifreeze,* while the other half is used in the manufacture of polyesters. In the polyester category, 88% was used for fibers and 12% for the manufacture of bottles and films. The 2013 selling price for ethylene glycol was $0.60 per pound.

It is desired to produce 200 million pounds per year of EG. The reactor is to be operated isothermally. A 16.1 mol/dm^3 solution of ethylene oxide (EO) in water is mixed (see Figure E5-2.1) with an equal volumetric solution of water containing 0.9 wt % of the catalyst H_2SO_4 and fed to a CSTR. The specific reaction-rate constant is 0.311 min^{-1}, as determined in Example 5-1. Practical guidelines for reactor scale-up are given by Mukesh.[1]

- **(a)** If 80% conversion is to be achieved, determine the necessary CSTR volume.
- **(b)** If two 800-gal reactors were arranged in parallel with the feed equally divided, what would be the corresponding conversion?
- **(c)** If two 800-gal reactors were arranged in series, what would be the corresponding conversion?

Product

EG → 2×10^8 pounds/year

$C_{A0} = 16.1 \text{ mol/dm}^3$

C_B → dilute water

CSTR

$K = 0.311 \text{ min}^{-1}$

A) $X = 0.8$

1. mole Balance CSTR

$$V = \frac{F_{A0} X}{-r_A}$$

2 Rate Law $-r_A = k C_A$

* water is dilute

3. Stoichiometry $C_A = C_{A0}(1-X)$

4. combine

$$V = \frac{F_{A0} X}{k C_{A0}(1-X)} = \frac{v_0 C_{A0} X}{k C_{A0}(1-X)} = \frac{v_0 X}{k(1-X)}$$

→ to find v_0 [liq $v = v_0$]

$$F_c = \frac{2\times10^8 \text{ lbm}}{\text{year}} \left| \frac{1\text{year}}{12\text{months}} \right| \frac{1\text{month}}{30\text{ days}} \left| \frac{1\text{ day}}{24\text{h}} \right| \frac{1\text{ h}}{3600\text{s}} \left| \frac{454\text{g}}{1\text{ lbm}} \right| \frac{1\text{mol}}{62.07\text{g}}$$

$F_c = 47.03$ mol/s

$\Rightarrow F_c = F_{A0} X$

$47\,03 = F_{A0}\,(0.8)$ $\qquad F_{A0} = 58.8\ mol/s$

Entering for A

$\Rightarrow C_{A0} = \frac{F_{A0}}{v_0}$ $\qquad 16.1\ \frac{mol}{dm^3} = \frac{588\ mol/s}{v_0}$ $\qquad \boxed{v_{A0} = 3.62}\ dm^3/s$

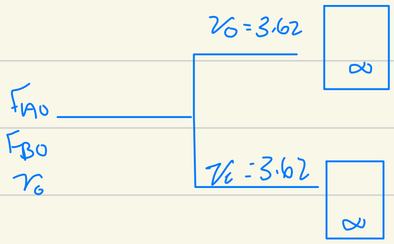
→ for water [Equal volumetric]

$v_{B0} = 3.62\ dm^3/s$

→ total $v_0 = 3.62 + 3.62 = 7.24\ dm^3/s$

$V_{CSTR} = \frac{7.24\,(0.8)}{0.0052\,(1-0.8)} = 5569.23\ dm^3$ $\qquad K = \frac{0.311}{min}\Big|\frac{1 min}{60 s} = 0.0052\ s^{-1}$

B)



V= 800 gallon

1. Mole Balance

$$V = \frac{F_{A0}\,X}{-r_A}$$

2. Rate Law $\qquad -r_A = K C_A$

3. Stoichiometry $\qquad C_A = C_{A0}(1-X)$

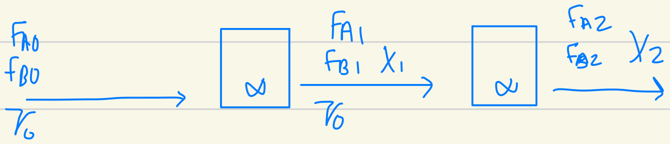
4. combine

$$V = \frac{C_{A0}\,v_0\,X}{K\,C_{A0}\,(1-X)} = \frac{v_0\,X}{K(1-X)}$$

$$\frac{800 gallon}{}\Big|\frac{3.785\ dm^3}{1 gallon} = \frac{3.62\ X}{0.0052\,(1-X)}$$

$$X = 0.81$$

c)



$V = 800$ gallon

1. mole Balance [first reactor]

$$V = \frac{F_{A0} X}{-r_A}$$

2. Rate law $-r_A = k C_A$

3. Stoichiometry $C_A = C_{A0}(1-X)$

4 combine $V = \dfrac{v_0 X}{k(1-X)}$

$$\tau = \frac{V}{v_0} = \frac{800 \times 3.785}{7.24} = 418.23 = \frac{X}{k(1-X)}$$

$$X = \frac{\tau k}{1+\tau k} = \frac{418.23(0.0052)}{1+418.23(0.0052)}$$

$$X = 0.684$$

→ Second Reactor

1. mole Balance $V = \dfrac{F_{A0}(X_2 - X_1)}{-r_A}$

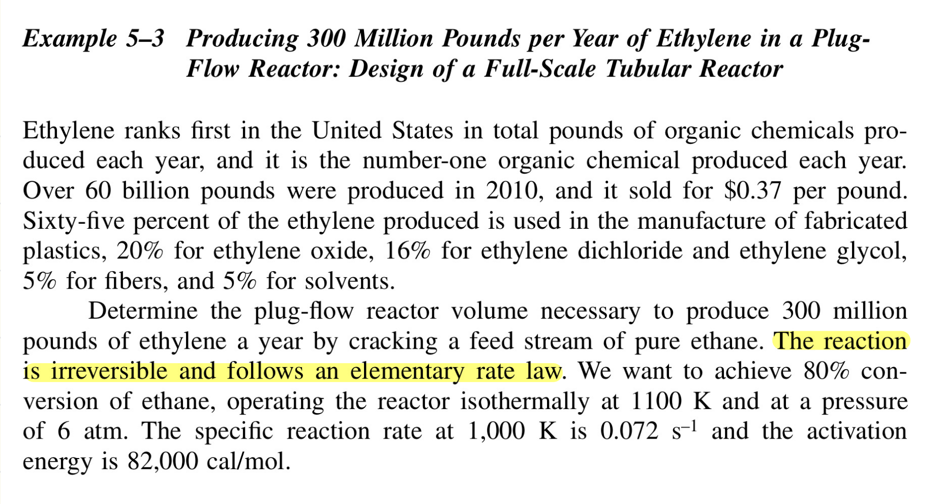
2. Rate law $-r_A = k C_{A2}$

3. Stoichiometry $C_{A2} = C_{A0}(1-X_2)$

4. combine $V = \dfrac{v_0 (X_2 - X_1)}{k(1-X_2)}$

$$800 \times 3.785 = \frac{7.24(X_2 - 0.684)}{0.0052(1-X_2)}$$

$$X_2 = 0.9$$



Example 5–3 Producing 300 Million Pounds per Year of Ethylene in a Plug-Flow Reactor: Design of a Full-Scale Tubular Reactor

Ethylene ranks first in the United States in total pounds of organic chemicals produced each year, and it is the number-one organic chemical produced each year. Over 60 billion pounds were produced in 2010, and it sold for \$0.37 per pound. Sixty-five percent of the ethylene produced is used in the manufacture of fabricated plastics, 20% for ethylene oxide, 16% for ethylene dichloride and ethylene glycol, 5% for fibers, and 5% for solvents.

Determine the plug-flow reactor volume necessary to produce 300 million pounds of ethylene a year by cracking a feed stream of pure ethane. The reaction is irreversible and follows an elementary rate law. We want to achieve 80% conversion of ethane, operating the reactor isothermally at 1100 K and at a pressure of 6 atm. The specific reaction rate at 1,000 K is 0.072 s^{-1} and the activation energy is 82,000 cal/mol.

Product

3×10^8 pounds/year

$X = 0.8$

isothermal $T = 1100\,K$

$P = 6\,atm$

$k = 0.072\,s^{-1}$ $E_A = 82000\,cal/mol$

$\delta > 0$ $v_0\uparrow$ $T\downarrow$ $X\downarrow$

$\varepsilon > 0$

$$A \longrightarrow B + C$$

1. mole Balance (PFR)

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \xrightarrow[\text{drop}]{\text{no pressure}} V = F_{A0}\int_0^X \frac{dX}{-r_A}$$

2. Elementary Rate Law $-r_A = k\,C_A$

3 Stoichiometry $C_A = \dfrac{C_{A0}(1-X)}{(1+\varepsilon X)}$

4. Combine $-r_A = k\,\dfrac{C_{A0}(1-X)}{(1+\varepsilon X)}$

$$V = \int_0^X \frac{F_{A0}}{kC_{A0}\frac{(1-X)}{(1+\varepsilon X)}}\,dX \qquad V = \frac{F_{A0}}{kC_{A0}}\int_0^X \frac{(1+\varepsilon X)}{(1-X)}\,dX$$

$$V = \frac{F_{A0}}{k\,C_{A0}}\left[(1+\varepsilon)\ln\frac{1}{1-X} - \varepsilon X\right]$$

→ Find F_{A0} from F_B

$$F_B = \frac{3\times10^8\ lbm}{year}\left|\frac{1\,year}{12\,months}\right|\frac{1\,month}{30\,days}\left|\frac{1\,day}{24\,h}\right|\frac{1\,h}{3600\,s}\left|\frac{454\,g}{1\,lbm}\right|\frac{mol}{28.05\,g} = 154.4\ mol/s$$

$$F_B = F_{A0} X$$

$$154.4 = F_{A0} (0.8) \qquad F_{A0} = 193 \text{ mol/s}$$

→ Find C_{A0}

$$C_{A0} = y_{A0} C_{T0} = y_{A0} \frac{P}{RT} = 1 \left[\frac{6 \text{atm}}{0.08206 \text{ atm dm}^3} \middle| \frac{\text{K mol}}{1100 \text{ K}} \right]$$

$$C_{A0} = 0.066 \text{ mol} / \text{dm}^3$$

→ k at 1100

$$k(T_2) = k(T_1) \exp\left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] \qquad k(1000) = 0.072$$

$$k(1100) = 0.072 \exp\left[\frac{82000 \text{ cal/mol}}{1.987 \text{ cal/mol·K}} \left(\frac{1}{1000} - \frac{1}{1100} \right) \right]$$

$$k(1100) = 3.07 \text{ s}^{-1}$$

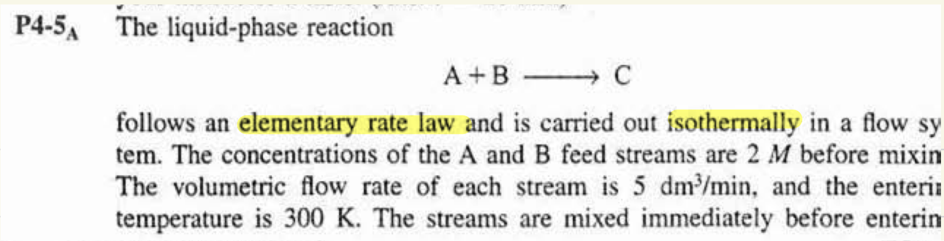
→ ε

$$\varepsilon = y_{A0} \delta \qquad \delta = 1 + 1 - 1 = 1$$

$$\varepsilon = (1)(1) = 1$$

$$V = \frac{193}{3.07 \times 0.066} \left[(1+1) \ln \frac{1}{1-0.8} - (1)(0.8) \right]$$

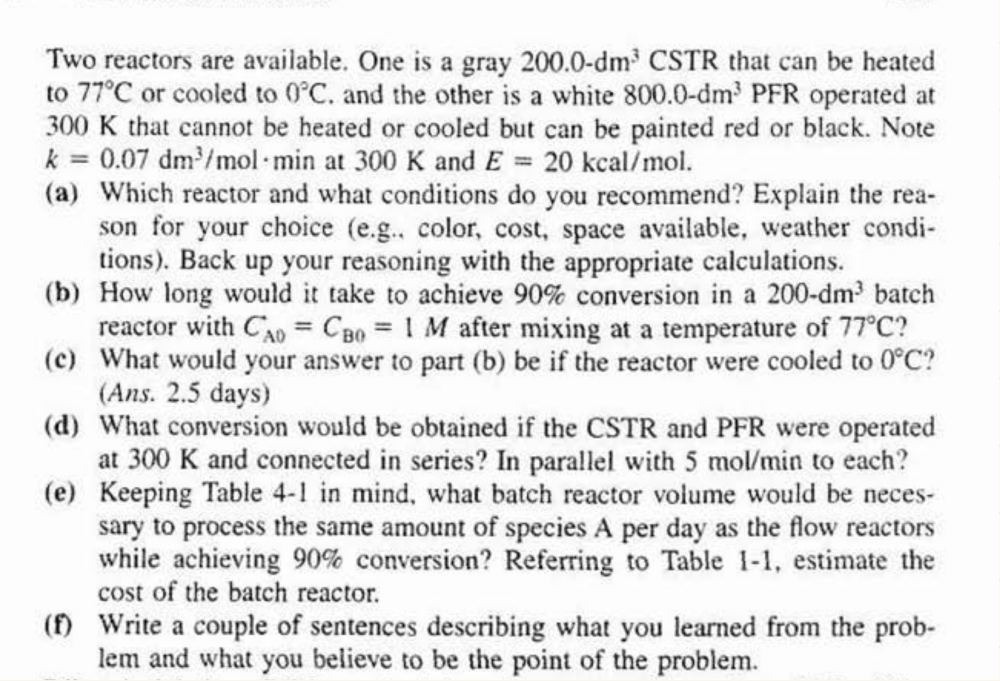
$$V = 2304 \text{ dm}^3$$



P4-5$_A$ The liquid-phase reaction

$$A + B \longrightarrow C$$

follows an elementary rate law and is carried out isothermally in a flow sy tem. The concentrations of the A and B feed streams are 2 *M* before mixin The volumetric flow rate of each stream is 5 dm³/min, and the enteri temperature is 300 K. The streams are mixed immediately before enterin



Two reactors are available. One is a gray 200.0-dm³ CSTR that can be heated to 77°C or cooled to 0°C, and the other is a white 800.0-dm³ PFR operated at 300 K that cannot be heated or cooled but can be painted red or black. Note $k = 0.07$ dm³/mol·min at 300 K and $E = 20$ kcal/mol.

(a) Which reactor and what conditions do you recommend? Explain the reason for your choice (e.g., color, cost, space available, weather conditions). Back up your reasoning with the appropriate calculations.

(b) How long would it take to achieve 90% conversion in a 200-dm³ batch reactor with $C_{A0} = C_{B0} = 1$ *M* after mixing at a temperature of 77°C?

(c) What would your answer to part (b) be if the reactor were cooled to 0°C? (*Ans.* 2.5 days)

(d) What conversion would be obtained if the CSTR and PFR were operated at 300 K and connected in series? In parallel with 5 mol/min to each?

(e) Keeping Table 4-1 in mind, what batch reactor volume would be necessary to process the same amount of species A per day as the flow reactors while achieving 90% conversion? Referring to Table 1-1, estimate the cost of the batch reactor.

(f) Write a couple of sentences describing what you learned from the problem and what you believe to be the point of the problem.

$C_{A0} = C_{B0} = 2M$

$v_0 = 5\ dm^3/min$

Reactor ① CSTR $V = 200\ dm^3$

Reactor ② PFR $V = 800\ dm^3$

$K = 0.07\ dm^3/mol \cdot min$

at 300K & $E = 20kcal/mol$

Reactor ① CSTR:

$F_{A0} = C_{A0} v_0$

$2 \times 5 = 10$

1. Mole Balance $\quad V = \frac{F_{A0} X}{-r_A}$

2. Rate Law $\quad -r_A = k C_A C_B$

3. Stoichiometry $\quad C_A = C_{A0}(1-X)$

$C_B = C_{A0}(1-X)$

4. Arrhenious Law for k at $77 + 273 = 350$

$$k = A \exp\left(\frac{E}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$K = 0.07 \exp\left(\frac{20000}{1.987}\right)\left(\frac{1}{300} - \frac{1}{350}\right)$$

$$k_2 = 8.45\ dm^3/mol \cdot min$$

5. Combine

$$-r_A = k_2 C_{A0}^2 (1-X)^2$$

$$V = \frac{F_{A0} X}{-r_A} = \frac{F_{A0}\ X}{k_2 C_{A0}^2 (1-X)^2} \qquad 200 = \frac{10X}{8.45 (1)^2 (1-X)^2}$$

$$X = 0.92$$

Reactor ② PFR :

1. Mole Balance $$V = \int_0^X \frac{F_{A0}}{-r_A}\, dX$$

2. Rate Law $$-r_A = k C_A C_B$$

3 Stoichiometry $$C_A = C_{A0}(1-X)$$

$$C_B = C_{A0}(1-X)$$

4. combine $$-r_A = k\, C_{A0}^2 (1-X)^2$$

$$V = \frac{F_{A0}}{k C_{A0}^2} \int_0^X \frac{dX}{(1-X)^2}$$

$$800 = \frac{10}{0.07\,(2)^2} \int_0^X \frac{dX}{(1-X)^2}$$

$$X = 0.85$$

B) $X = 0.9$ Batch Reactor $V = 200\ dm^3$ $C_{A0} = C_{B0} = 1\ M$

1 Mole Balance $$N_{A0} \frac{dX}{dt} = -r_A V$$

$$t = N_{A0} \int_0^X \frac{dX}{-r_A V}$$

$N_A = C_A V$

$1(200) = 200 mol$

2. Rate law $$-r_A = k C_A C_B$$

$$= k\, C_{A0}^2 (1-X)^2$$

$$t = \frac{N_{A0}}{V k_2 C_{A0}^2} \int_0^X \frac{dX}{(1-X)^2}$$

$$t = \frac{200}{200\,(8.45)\,(1)^2} \int_0^{0.9} \frac{dX}{(1-X)^2} = \frac{1}{8.45}\left[\frac{0.9}{1-0.9}\right] = 1.06\ min$$

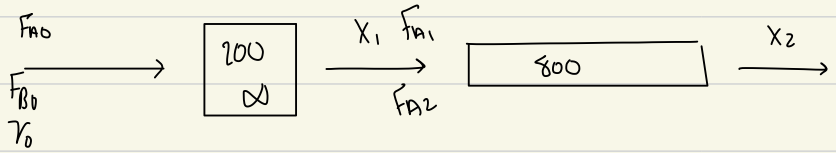
c) $T = 0^{\circ}C = 273\,K$

Arrhenius Law $$k = 0.07\ \exp\left(\frac{20{,}000}{1.987}\right)\left(\frac{1}{300} - \frac{1}{273}\right) = 2.54\times10^{-3}$$

$$t = \frac{200}{200\,(1)^2 \times 2.54\times10^{-3}} \int_0^{0.9} \frac{dX}{(1-X)^2}$$

$t = 3543.3$ min

D) Series



1. CSTR

$$V = \frac{F_{A0}X}{-r_A} = \frac{F_{A0}\,X}{k\,C_{A0}^2\,(1-X)^2}$$

$$200 = \frac{10\,X}{0.07\,(1)^2\,(1-X)^2} \qquad X_1 = 0.44$$

2. PFR

$$V = F_{A0}\int_{0.44}^{X} \frac{dX}{-r_A}$$

$$800 = \frac{10}{0.07\times(1)^2}\int_{0.44}^{X} \frac{dX}{(1-X)^2}$$

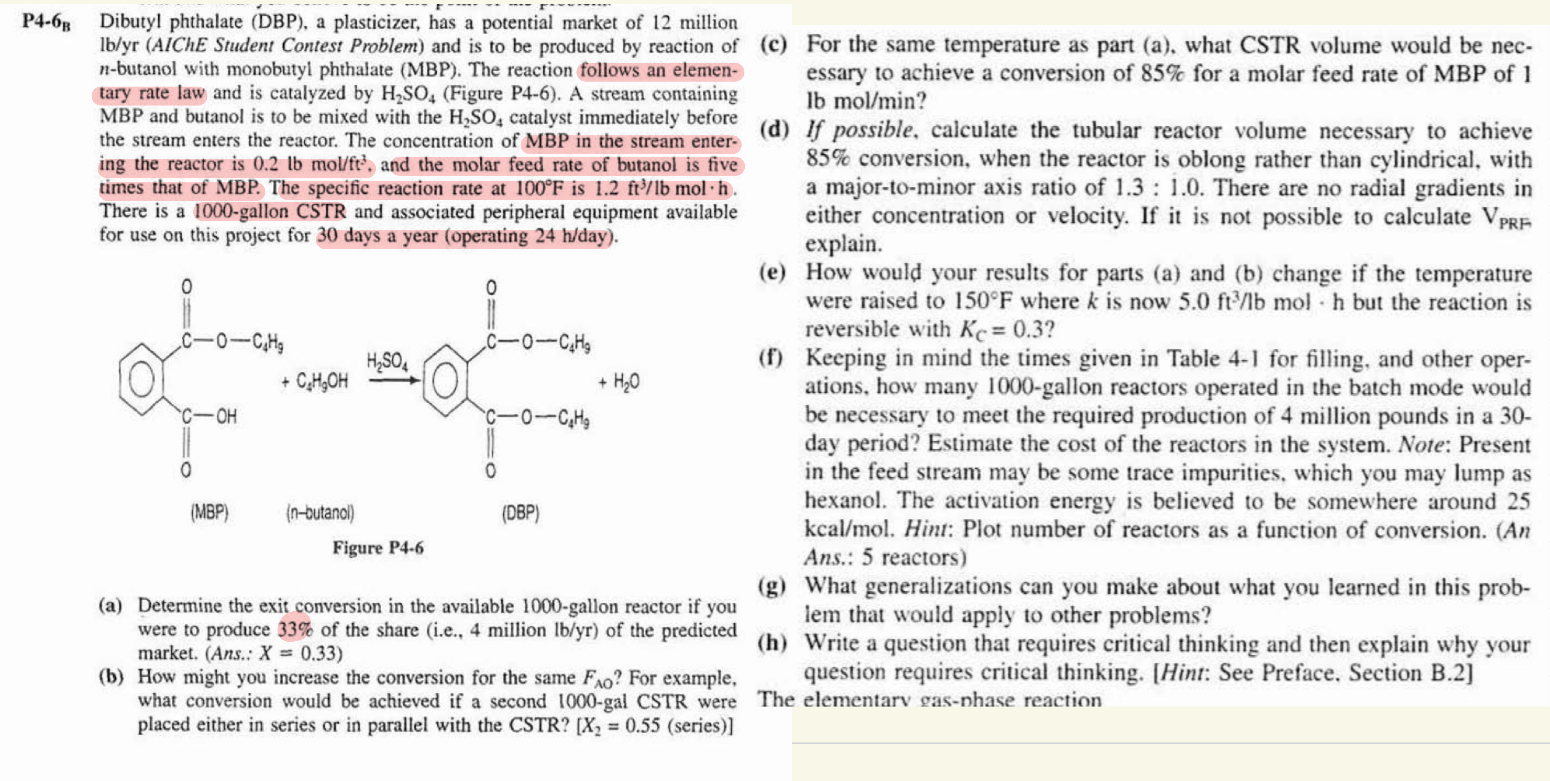
$X = 0.86$

Parallel

1. CSTR $$V = \frac{F_{A0}X}{-r_A} \qquad 200 = \frac{5\,X}{0.07\,(1)^2\,(1-X)^2} \qquad X = 0.55$$

2. PFR $$V = F_{A0}\int_0^X \frac{dX}{-r_A} \qquad 800 = \frac{5}{0.07(1)^2}\int_0^X \frac{dX}{(1-X)^2} \qquad X = 0.92$$

$$X_{overall} = \frac{0.56 + 0.92}{2} = 0.74$$



P4-6$_B$ Dibutyl phthalate (DBP), a plasticizer, has a potential market of 12 million lb/yr (*AIChE Student Contest Problem*) and is to be produced by reaction of *n*-butanol with monobutyl phthalate (MBP). The reaction follows an elementary rate law and is catalyzed by H_2SO_4 (Figure P4-6). A stream containing MBP and butanol is to be mixed with the H_2SO_4 catalyst immediately before the stream enters the reactor. The concentration of MBP in the stream entering the reactor is 0.2 lb mol/ft^3, and the molar feed rate of butanol is five times that of MBP. The specific reaction rate at 100°F is 1.2 ft^3/lb mol · h. There is a 1000-gallon CSTR and associated peripheral equipment available for use on this project for 30 days a year (operating 24 h/day).

Figure P4-6

(a) Determine the exit conversion in the available 1000-gallon reactor if you were to produce 33% of the share (i.e., 4 million lb/yr) of the predicted market. (*Ans.*: $X = 0.33$)

(b) How might you increase the conversion for the same F_{AO}? For example, what conversion would be achieved if a second 1000-gal CSTR were placed either in series or in parallel with the CSTR? [$X_2 = 0.55$ (series)]

(c) For the same temperature as part (a), what CSTR volume would be necessary to achieve a conversion of 85% for a molar feed rate of MBP of 1 lb mol/min?

(d) *If possible*, calculate the tubular reactor volume necessary to achieve 85% conversion, when the reactor is oblong rather than cylindrical, with a major-to-minor axis ratio of 1.3 : 1.0. There are no radial gradients in either concentration or velocity. If it is not possible to calculate V_{PFR}, explain.

(e) How would your results for parts (a) and (b) change if the temperature were raised to 150°F where k is now 5.0 ft^3/lb mol · h but the reaction is reversible with $K_C = 0.3$?

(f) Keeping in mind the times given in Table 4-1 for filling, and other operations, how many 1000-gallon reactors operated in the batch mode would be necessary to meet the required production of 4 million pounds in a 30-day period? Estimate the cost of the reactors in the system. *Note*: Present in the feed stream may be some trace impurities, which you may lump as hexanol. The activation energy is believed to be somewhere around 25 kcal/mol. *Hint*: Plot number of reactors as a function of conversion. (*An Ans.*: 5 reactors)

(g) What generalizations can you make about what you learned in this problem that would apply to other problems?

(h) Write a question that requires critical thinking and then explain why your question requires critical thinking. [*Hint*: See Preface, Section B.2]

The elementary gas-phase reaction

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

A) potenial market = 12 million lb/yr x 0.33 = 4 million lb/yr [Product]

1. mole Balance [CSTR]

$$V = \frac{F_{AO}\,X}{-r_A}$$

2. Rate law $-r_A = k\,C_A C_B$

$F_{AO} = 5F_{BO}$

3. Stoichiometry

$C_A = C_{AO}(1-X)$

$C_B = C_{AO}(5-X)$

$C_{A_0} = 0.2$ lb mole/ft^3

$F_{AO} = C_{AO}\,v_0$

$20 = 0.2\,v_0$

$v_0 = 100$ ft^3/s

4. combine

$$V = \frac{F_{AO}\,X}{k\,C_{AO}^2\,(1-X)(5-X)}$$

→ to find F_{Ao}

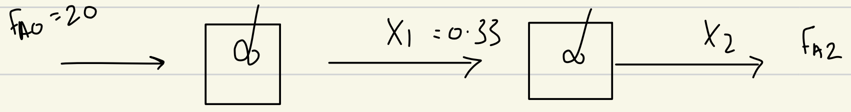
$$\dot{m}_c = \frac{4\times10^6\ \text{lb}}{\text{yr}}\left|\frac{1\ \text{yr}}{30\ \text{days}}\right|\frac{1\ \text{day}}{24\ \text{h}}\left|\frac{1\ \text{lb mol}}{278\ \text{lb}}\right. = 20\ \text{moles/h}$$

$F_{AO\,(\text{wet in})} = 20$ moles/h

$$V: \; 1000 \text{ gallon} \left| \frac{1 \text{ ft}^3}{7.48 \text{ gall}} \right. = 133.7 \text{ ft}^3$$

$$133.7 = \frac{20}{1.2(0.2)^2(1-X)(5-X)} \qquad X = 0.33$$

B)

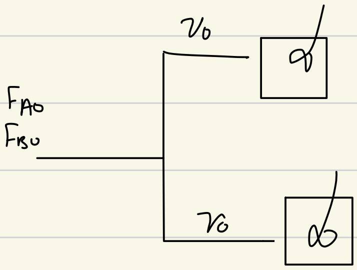


mole Balance on Reactor 2

$$V = F_{A0} \frac{(X_2 - X_1)}{-r_A}$$

$$133.7 = 20 \frac{(X_2 - 0.33)}{1.2(0.2)^2(1-X_2)(5-X_2)} \qquad X = 0.72$$

* For highest conv CSTR → PFR with high temp



$$V = \frac{C_{A0} v_0 \; X}{K \, C_{A0}^2 (1-X)(5-X)}$$

$$133.7 = \frac{50 \; X}{1.2(0.2)(1-X)(5-X)} \qquad X = 0.73$$

C) $X = 0.85$

$F_{A0} = 1$ lbmole/min

$$V = \frac{F_{A0} X}{-r_A}$$

$$F_{A0} = \frac{1 \text{ lbmole}}{\text{min}} \left| \frac{60 \text{ min}}{1 \text{ h}} \right. = 60 \text{ lbmole/h}$$

$$V = \frac{60 \quad 0.85}{1.2(0.2)^2(1-0.85)(5-0.85)}$$

$$V = 1706.83 \text{ dm}^3$$

D)

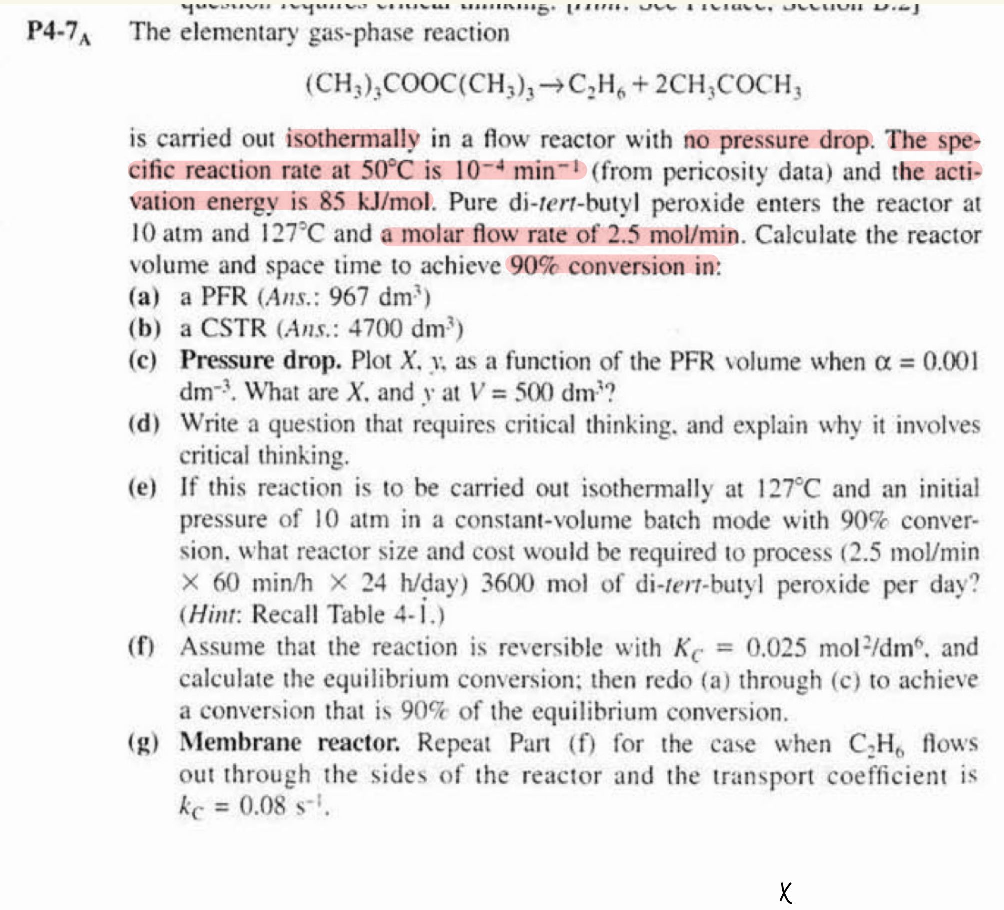
1. mole Balance PFR

$$V = F_{A0} \int_0^X \frac{dX}{-r_A}$$

$$V = F_{A0} \int_0^X \frac{dX}{k_1 C_{A0}^2 (1-X)(5-X)}$$

$$V = \frac{60}{1.2(0.2)^2} \int_0^{0.85} \frac{dX}{(1-X)(5-X)}$$

$V = 535 \quad dm^3$



question requires critical thinking. [*Hint*: See Preface, Section B.2]

P4-7$_A$ The elementary gas-phase reaction

$$(CH_3)_3COOC(CH_3)_3 \rightarrow C_2H_6 + 2CH_3COCH_3$$

is carried out isothermally in a flow reactor with no pressure drop. The specific reaction rate at 50°C is 10^{-4} min^{-1} (from pericosity data) and the activation energy is 85 kJ/mol. Pure di-*tert*-butyl peroxide enters the reactor at 10 atm and 127°C and a molar flow rate of 2.5 mol/min. Calculate the reactor volume and space time to achieve 90% conversion in:

(a) a PFR (*Ans.*: 967 dm^3)

(b) a CSTR (*Ans.*: 4700 dm^3)

(c) **Pressure drop.** Plot X, y, as a function of the PFR volume when $\alpha = 0.001$ dm^{-3}. What are X, and y at $V = 500$ dm^3?

(d) Write a question that requires critical thinking, and explain why it involves critical thinking.

(e) If this reaction is to be carried out isothermally at 127°C and an initial pressure of 10 atm in a constant-volume batch mode with 90% conversion, what reactor size and cost would be required to process (2.5 mol/min × 60 min/h × 24 h/day) 3600 mol of di-*tert*-butyl peroxide per day? (*Hint*: Recall Table 4-1.)

(f) Assume that the reaction is reversible with $K_C = 0.025$ mol^2/dm^6, and calculate the equilibrium conversion; then redo (a) through (c) to achieve a conversion that is 90% of the equilibrium conversion.

(g) **Membrane reactor.** Repeat Part (f) for the case when C_2H_6 flows out through the sides of the reactor and the transport coefficient is $k_C = 0.08$ s^{-1}.

$A \rightarrow B + 2C$

A) PFR

1. mole Balance $\quad V = F_{A0} \int_0^X \frac{dX}{-r_A}$

2. Rate Law $\quad -r_A = k C_A$

3. Stoichiometry $\quad C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}$

$\varepsilon = y_{A0}\,\delta = (1)(2) = 2$

$\delta = 2+1-1 = 2$

4. Arrhenius Law

$$k = 10^{-4} \times \exp\left(\frac{85000}{8.314}\right)\left(\frac{1}{323} - \frac{1}{400}\right)$$

$$k = 0.044 \text{ min}^{-1}$$

5. Combine $\quad V = F_{A0} \int_0^X \frac{dX}{k\,\frac{C_{A0}(1-X)}{(1+\varepsilon X)}}$

$$V = \frac{F_{A0}}{k\,C_{A0}} \int_0^X \frac{(1+\varepsilon X)}{(1-X)}\,dX$$

$$V = \frac{2.5}{0.044\,(0.3)} \int_0^{0.9} \frac{(1+\varepsilon X)}{(1-X)}\,dX$$

$C_{A0} = \frac{P_{A0}}{RT}$

$C_{A0} = \frac{10 \text{ atm}}{0.08206 \text{ atm}\cdot\text{dm}^3} \Big| \frac{k\,\text{mol}}{400} = 0.3 \text{ mol/dm}^3$

$$V = \frac{2.5}{0.044(0.3)}\left[(1+\varepsilon)\ln\frac{1}{1-X} - \varepsilon X\right]_0^{0.9}$$

$$V = 967\ 37\ dm^3$$

B) CSTR

1. mole Balance $$V = \frac{F_{A0}X}{-r_A}$$

2. $$-r_A = kC_A$$

3. $$C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}$$

4. $$V = \frac{F_{A0}X}{C_{A0}k}\,\frac{(1+\varepsilon X)}{(1-X)}$$

$$V = \frac{2.5(0.9)}{0.3(0.044)}\,\frac{(1+2(0.9))}{(1-0.9)} = 4772\ dm^3$$

---

f) $A \rightleftharpoons B + 2C$

1. $$-r_A = k\left[C_A - \frac{C_B C_C^2}{K_C}\right] = 0 \quad [\text{Equilibrium}] \qquad K_C = 0.025$$

2. $$C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}$$

$$C_B = \frac{C_{A0}X}{(1+\varepsilon X)}$$

$$C_C = \frac{C_{A0}2X}{(1+\varepsilon X)}$$

$$\theta_B = \frac{F_{B0}}{F_{A0}} = 0$$

$$\theta_C = \frac{F_{C0}}{F_{A0}} = 0$$

3. $$0 = k\left[\frac{C_{A0}(1-X)}{(1+\varepsilon X)} - \frac{C_{A0}X}{(1+\varepsilon X)}\,\frac{4C_{A0}^2X^2}{(1+\varepsilon X)^2}\,\frac{1}{K_C}\right]$$

$$0 = kC_{A0}\left[\frac{(1-X)}{(1+\varepsilon X)} - \frac{4C_{A0}^2X^3}{(1+\varepsilon X)^3K_C}\right]$$

$$K_C = \frac{C_B C_C^2}{C_A} = \frac{C_{A0} X}{(1+\varepsilon X)} \quad \frac{C_{A0}^2 4X}{(1+\varepsilon X)^2} \cdot \frac{(1+\varepsilon X)}{C_{A0}(1-X)}$$

$$0.025 = \frac{0.3X}{(1+2X)} \cdot \frac{(0.3)^2 4 \cdot X}{(1+2X)^2} \cdot \frac{(1+2X)}{0.3(1-X)}$$

$$X_{eq} = 0.52$$

$$X = 0.9(0.52) = 0.47$$

$$V_{CSTR} = \frac{F_{A0} X}{-r_A} = \frac{2.5(0.47)}{0.044(0.3)\left[\frac{1-0.47}{1+2(0.47)} - \frac{4(0.3)^2(0.47)^3}{(1+2(0.47))^3 \, 0.025}\right]}$$

$$V_{CSTR} = 1300 \text{ dm}^3$$

$$V_{PFR} = F_{A0} \int_0^{0.47} \frac{dX}{-r_A}$$ ⇝ on software for Integration.

$$\frac{F_{A0}}{k C_{A0}} \int_0^{0.47} \frac{(1+\varepsilon X)}{(1-X)} - \frac{(1+\varepsilon X)^3 k_c}{4 C_{A0}^2 X^3} \, dX$$

$$\frac{F_{A0} \cdot k_c}{k C_{A0}^3 \, 4} \int_0^{0.47} \frac{(1+\varepsilon X)}{(1-X)} - \frac{(1+\varepsilon X)}{X^3} \, dX$$

G) membrane Reactor

*swept

1. $\frac{dF_A}{dV} = r_A$ $\quad \frac{dF_B}{dV} = r_B - R_B$ $\quad \frac{dF_C}{dV} = r_C$

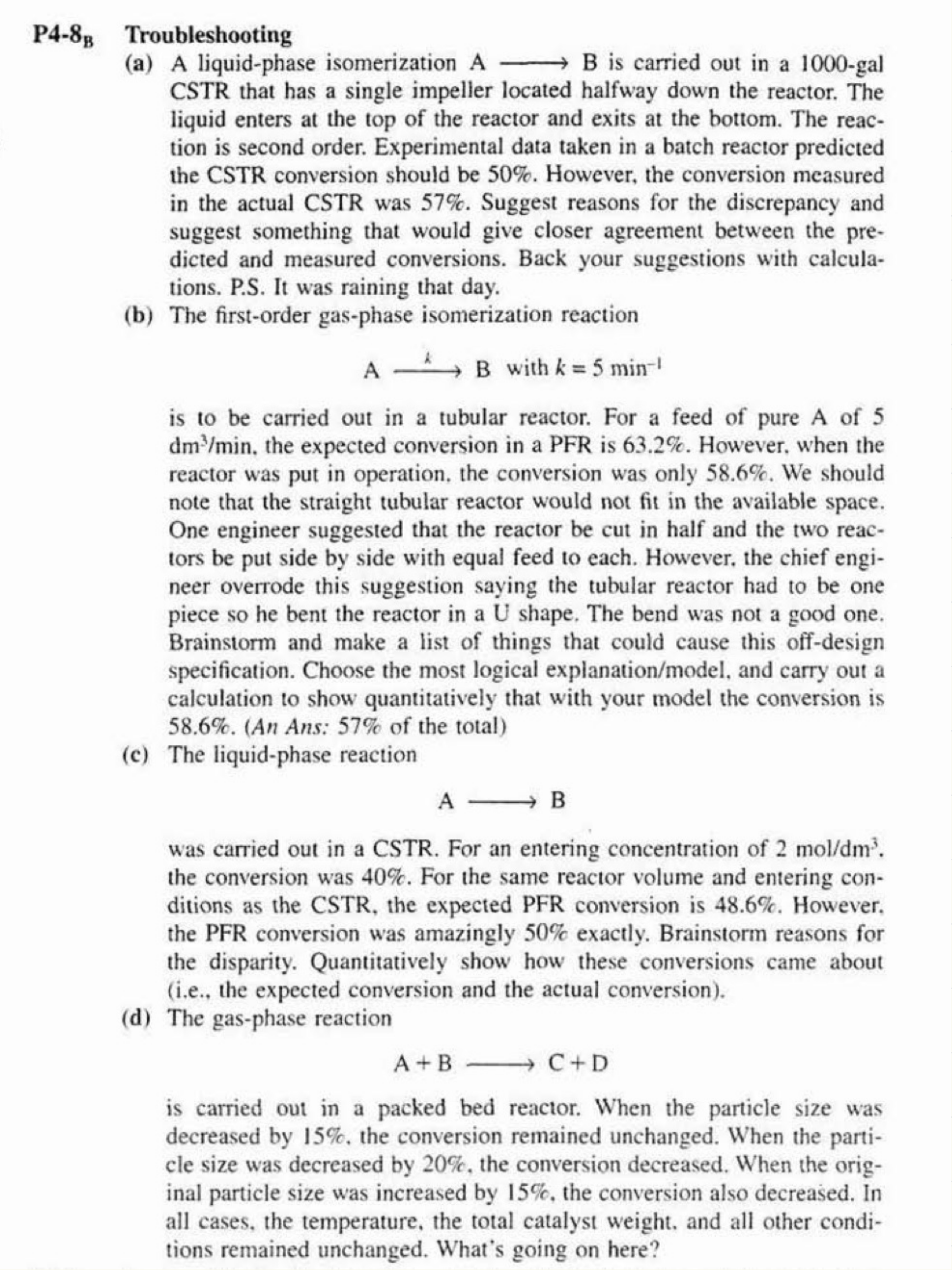
2. $-r_A = r_B = \frac{r_C}{2}$ $\quad R_B = k_c C_B$

3 $-r_A = k\left[C_A - \frac{C_B C_C^2}{K_c}\right]$

4. $C_A = C_{T0} \frac{F_A}{F_T}$ $C_B = C_{T0} \frac{F_B}{F_T}$ $C_c = C_{T0} \frac{F_C}{F_T}$

$F_T = F_A + F_B$

5. combine → polymath.



P4-8$_B$ **Troubleshooting**

(a) A liquid-phase isomerization $A \longrightarrow B$ is carried out in a 1000-gal CSTR that has a single impeller located halfway down the reactor. The liquid enters at the top of the reactor and exits at the bottom. The reaction is second order. Experimental data taken in a batch reactor predicted the CSTR conversion should be 50%. However, the conversion measured in the actual CSTR was 57%. Suggest reasons for the discrepancy and suggest something that would give closer agreement between the predicted and measured conversions. Back your suggestions with calculations. P.S. It was raining that day.

(b) The first-order gas-phase isomerization reaction

$$A \xrightarrow{k} B \quad \text{with } k = 5 \text{ min}^{-1}$$

is to be carried out in a tubular reactor. For a feed of pure A of 5 dm^3/min, the expected conversion in a PFR is 63.2%. However, when the reactor was put in operation, the conversion was only 58.6%. We should note that the straight tubular reactor would not fit in the available space. One engineer suggested that the reactor be cut in half and the two reactors be put side by side with equal feed to each. However, the chief engineer overrode this suggestion saying the tubular reactor had to be one piece so he bent the reactor in a U shape. The bend was not a good one. Brainstorm and make a list of things that could cause this off-design specification. Choose the most logical explanation/model, and carry out a calculation to show quantitatively that with your model the conversion is 58.6%. (*An Ans:* 57% of the total)

(c) The liquid-phase reaction

$$A \longrightarrow B$$

was carried out in a CSTR. For an entering concentration of 2 mol/dm^3, the conversion was 40%. For the same reactor volume and entering conditions as the CSTR, the expected PFR conversion is 48.6%. However, the PFR conversion was amazingly 50% exactly. Brainstorm reasons for the disparity. Quantitatively show how these conversions came about (i.e., the expected conversion and the actual conversion).

(d) The gas-phase reaction

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

is carried out in a packed bed reactor. When the particle size was decreased by 15%, the conversion remained unchanged. When the particle size was decreased by 20%, the conversion decreased. When the original particle size was increased by 15%, the conversion also decreased. In all cases, the temperature, the total catalyst weight, and all other conditions remained unchanged. What's going on here?

c) 1. $V_{CSTR} = \frac{F_{A0}\, X}{-r_A}$

2. $-r_A = k C_A$

3. $C_A = C_{A0}(1-X)$

4. $V = \frac{F_{A0}\, X}{k C_{A0}(1-X)}$ $\qquad V = \frac{C_{A0} v_0 (X)}{k C_{A0}(1-X)}$

$\tau = \frac{X}{k(1-X)}$

$\tau k = \frac{X}{1-X} \Rightarrow \frac{0.4}{1-0.4} = 0.67$

1. $V_{PFR} = F_{A0}\int_0^X \frac{dX}{-r_A}$

2. $-r_A = kC_A$

3. $C_A = C_{A0}(1-X)$

4 $V = \frac{C_{A0}v_0}{C_{A0}k}\int_0^X \frac{dX}{(1-X)}$

$$\tau k = \ln(1-X)\Big|_0^X$$

$0.67 = -\ln(1-X)$ $X = 0.486$

→ if it was in second order

$V_{CSTR} = \frac{C_{A0}v_0 X}{k C_{A0}^2(1-X)^2}$ $\tau k = \frac{X}{(1-X)^2}$

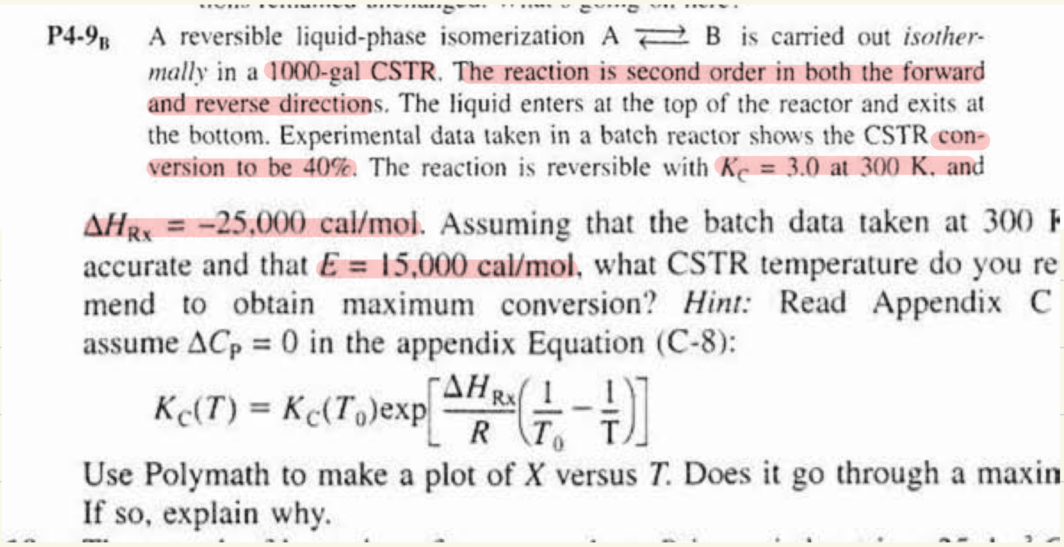
$C_{A0}\tau k = \frac{0.4}{(1-0.4)^2}$ $\tau k = 1.11$

$V_{PFR} = \frac{C_{A0}v_0}{C_{A0}^2 k}\int_0^X \frac{dX}{(1-X)^2}$ $C_{A0}\tau k = \frac{X}{1-X}$

$1.111 = \frac{X}{1-X}$ $X = 0.526$

→ PFR is in second order.

D)



P4-9$_B$ A reversible liquid-phase isomerization A $\rightleftarrows$ B is carried out *isothermally* in a 1000-gal CSTR. The reaction is second order in both the forward and reverse directions. The liquid enters at the top of the reactor and exits at the bottom. Experimental data taken in a batch reactor shows the CSTR conversion to be 40%. The reaction is reversible with $K_C = 3.0$ at 300 K, and

$\Delta H_{Rx} = -25{,}000$ cal/mol. Assuming that the batch data taken at 300 K accurate and that $E = 15{,}000$ cal/mol, what CSTR temperature do you re mend to obtain maximum conversion? *Hint:* Read Appendix C assume $\Delta C_P = 0$ in the appendix Equation (C-8):

$$K_C(T) = K_C(T_0)\exp\left[\frac{\Delta H_{Rx}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

Use Polymath to make a plot of X versus T. Does it go through a maxin If so, explain why.

1. mole Balance CSTR $\quad V = \frac{F_{A0}\,X}{-r_A}$

2. $-r_A = k\left[C_A^2 - \frac{C_B^2}{K_C}\right]$

3. $C_A = C_{A0}(1-X)$

$C_B = C_{A0}X$

4. $-r_A = k\left[C_{A0}^2(1-X)^2 - \frac{C_{A0}^2X^2}{K_C}\right]$

$Z =$

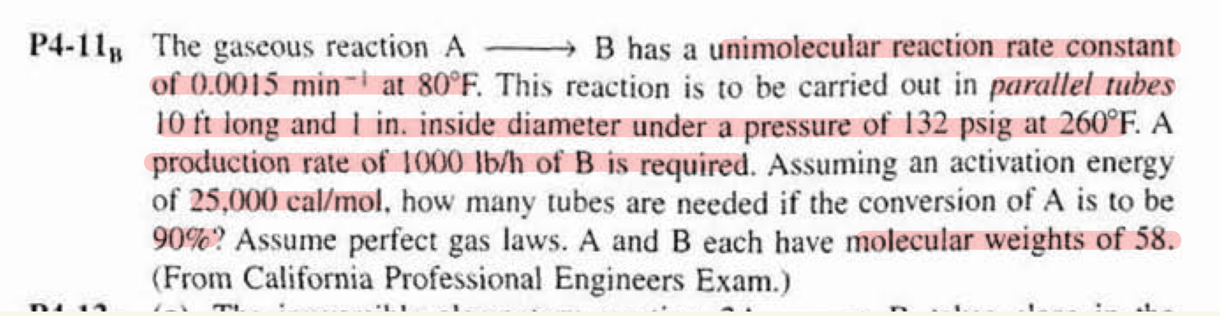
$$V = \frac{F_{A0}\,X}{k\,C_{A0}^2\left[(1-X)^2 - \frac{X^2}{K_C}\right]}$$

$$V = \frac{1000\text{ gallon} \;\big|\; 3.785\text{ dm}^3}{\;\big|\; 1\text{ gallon}} = 3785\text{ dm}^3$$

$$3785 = Z\,\frac{0.4}{\left[(1-0.4)^2 - \frac{0.4^2}{3}\right]} \qquad Z = 2902\text{ dm}^3$$

$$K_0 = k\,\exp\left(\frac{E}{R}\right)\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

$$z = \frac{k_0}{k} \qquad \frac{Z}{z} = \frac{F_{A0}}{\cancel{k}\,C_{A0}^2}\cdot\frac{\cancel{k}}{k_0} \Rightarrow \text{after change}$$



P4-11$_B$ The gaseous reaction A $\longrightarrow$ B has a unimolecular reaction rate constant of 0.0015 min^{-1} at 80°F. This reaction is to be carried out in *parallel tubes* 10 ft long and 1 in. inside diameter under a pressure of 132 psig at 260°F. A production rate of 1000 lb/h of B is required. Assuming an activation energy of 25,000 cal/mol, how many tubes are needed if the conversion of A is to be 90%? Assume perfect gas laws. A and B each have molecular weights of 58. (From California Professional Engineers Exam.)

$k = 0.0015\ min^{-1}$ 80°F

10ft long 1 inch ID

$P = 132\ psig$ 260°F

$F_B = 1000\ lb/h$

$E = 25000\ lb/mole$

$X = 0.9$

1. $V_{PFR} = F_{A0} \int_0^X \frac{dX}{-r_A}$

2. $-r_A = k C_A$

$$C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)} = C_{A0}(1-X) \qquad \varepsilon = 0$$

$$-r_A = k C_{A0}(1-X)$$

3. Arrhenious Law $k = 0.0015 \exp\left(\frac{25000}{1.104}\right)\left(\frac{1}{540} - \frac{1}{720}\right)$

$$k \approx \frac{53.6}{min} \cdot \frac{60\,min}{1\,h} = 3219\ h^{-1}$$

4. combine $-r_A = k C_{A0}(1-X)$

$$V = \frac{F_{A0}}{k C_{A0}} \int_0^{0.9} \frac{dX}{(1-X)}$$

→ find F_{A0}

$$F_B = \frac{1000\ lb}{h} \cdot \frac{lbmole}{58\ lb} = 17.24\ lbmole/h$$

$$F_B = F_{A0} X$$

$$17.2 = F_{A0}(0.9) \qquad F_{A0} = 19.1\ lbmole/h$$

→ find C_{A0}

$$C_{A0} = \frac{P_0}{RT_0} = \frac{146.7\ psia}{10.73\ ft^3\ psia} \cdot \frac{lbmole.R}{720\ R} = 0.0189$$

132 psig + 14.69 = 146.69 psia

5. Evaluate $V = \frac{19.1}{3219 \, (0.0189)} - \ln(1-0.9)$

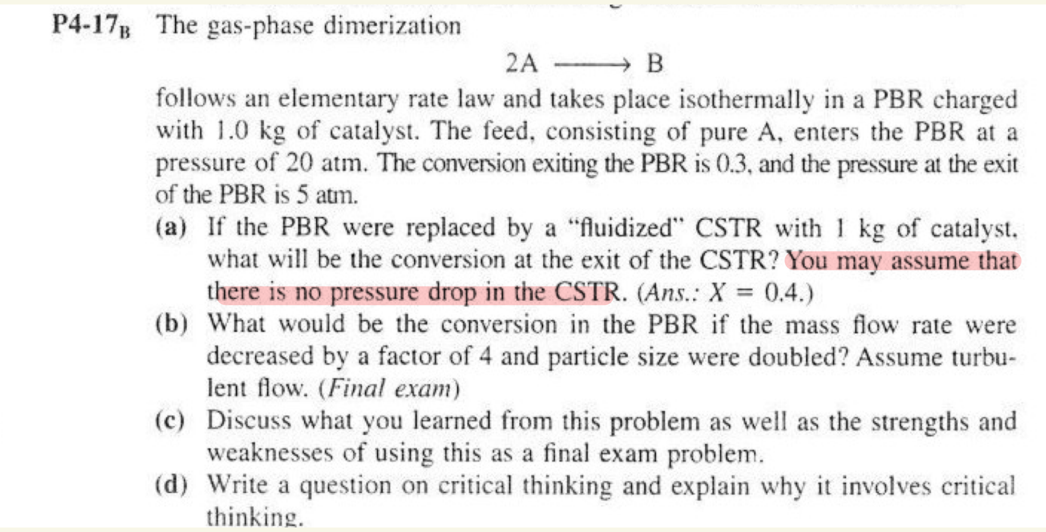
$V = 0.72 \text{ ft}^3$

$V = \frac{4}{\pi} D^2 L \, n_t$

$0.72 = \pi/4 \, (1/12)^2 \, 10 \, n_t$ $\qquad n_t = 13.2 \simeq 14$ tubes

P4-12$_B$ **(a)** The irreversible elementary reaction $2A \longrightarrow B$ takes place in the gas phase in an *isothermal tubular (plug-flow) reactor.* Reactant A and a diluent C are fed in equimolar ratio, and conversion of A is 80%. If the molar feed rate of A is cut in half, what is the conversion of A assuming that the feed rate of C is left unchanged? Assume ideal behavior and that the reactor temperature remains unchanged. What was the point of this problem? (From California Professional Engineers Exam.)

(b) Write a question that requires critical thinking, and explain why it involves critical thinking.



P4-17$_B$ The gas-phase dimerization

$$2A \longrightarrow B$$

follows an elementary rate law and takes place isothermally in a PBR charged with 1.0 kg of catalyst. The feed, consisting of pure A, enters the PBR at a pressure of 20 atm. The conversion exiting the PBR is 0.3, and the pressure at the exit of the PBR is 5 atm.

(a) If the PBR were replaced by a "fluidized" CSTR with 1 kg of catalyst, what will be the conversion at the exit of the CSTR? You may assume that there is no pressure drop in the CSTR. (*Ans.: X* = 0.4.)

(b) What would be the conversion in the PBR if the mass flow rate were decreased by a factor of 4 and particle size were doubled? Assume turbulent flow. (*Final exam*)

(c) Discuss what you learned from this problem as well as the strengths and weaknesses of using this as a final exam problem.

(d) Write a question on critical thinking and explain why it involves critical thinking.

$A \rightarrow \frac{1}{2}B$

A)

1 $W = \frac{F_{A0} X}{-r_A}$

2. $-r_A = k C_A^2$

3. $C_A = C_{A0} \frac{(1-X)}{(1+\varepsilon X)}$ * no DP in CSTR

$\varepsilon = y_{A0} \delta = -\frac{1}{2}$

$\delta = \frac{1}{2} - 1 = -\frac{1}{2}$

$y_{A0} = 1$

4. $W = \frac{F_{A0} X (1+\varepsilon X)^2}{k C_{A0}^2 (1-X)^2} = \frac{\cancel{C_{A0}} v_0 X (1+\varepsilon X)^2}{k C_{A0}^{\cancel{2}} (1-X)^2}$

⇒ to find $\frac{v_0}{k C_{A0}}$

PFR: 1. $\frac{dX}{dW} = \frac{-r_A'}{F_{A0}}$

2. $-r_A' = k C_A^2$

3. $C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)} \frac{P}{P_0}$

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

4. $\frac{dy}{dW} = -\frac{\alpha}{2y}(1+\varepsilon X)$

$2y\,dy = -\alpha(1+\varepsilon X)\,dW$

5. $\frac{dX}{dW} = \frac{k C_{A0}^{\cancel{2}} (1-X)^2 \left[-\alpha(1+\varepsilon X\,dW - 2y\,dy\right]^2}{\cancel{C_{A0}} v_0 (1+\varepsilon X)^2}$

ws solve by polymath $\frac{k\,C_{A0}}{v_0} = 0.7$ $\alpha = 1.043\ kg^{-1}$

$$W = \frac{v_0}{k C_{A0}} \frac{X(1+\varepsilon X)^2}{(1-X)^2}$$

$$1 = \frac{1}{0.7} \frac{X(1 + -\frac{1}{2} X)^2}{(1-X)^2}$$ $X = 0.4$

B) G↓4 Dp↑2 Turbulent

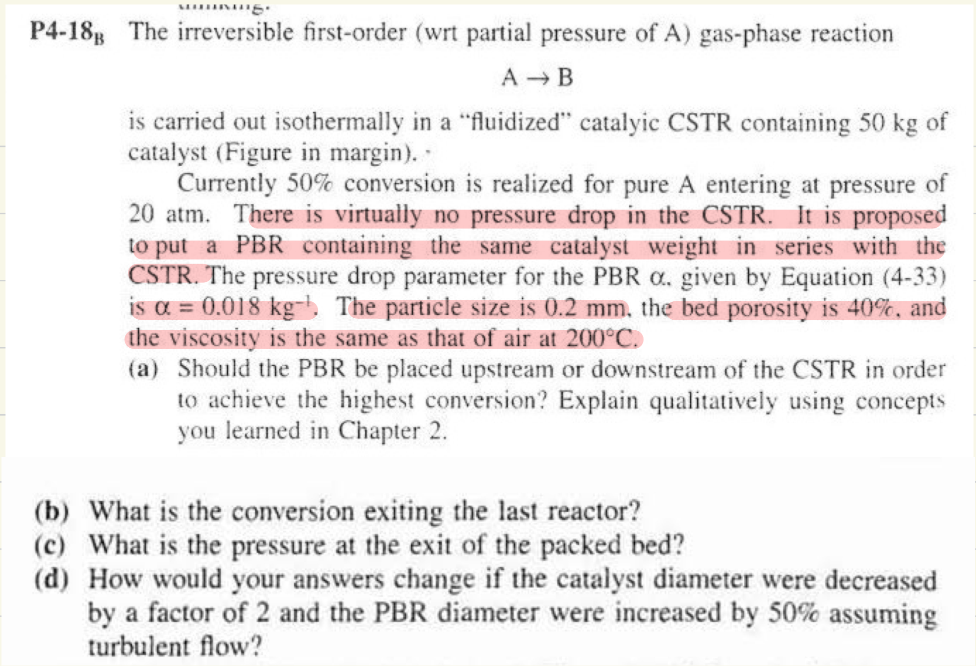
$G_2 = \frac{1}{4} G_1$

$Dp_2 = 2 Dp_1$

$$\alpha = \frac{G^2 \ T}{Dp \ A_c \ P_0^2}$$

$$\alpha_2 = \alpha_1 \left(\frac{G_2}{G_1}\right)^2 \left(\frac{Dp_1}{Dp_2}\right)$$

$$\alpha_2 = \alpha_1 \left(\frac{G_1}{4G_1}\right)^2 \left(\frac{Dp_1}{2Dp_1}\right) = \quad \frac{\alpha_2}{\alpha_1} = \frac{1}{32}$$



P4-18$_B$ The irreversible first-order (wrt partial pressure of A) gas-phase reaction

$$A \rightarrow B$$

is carried out isothermally in a "fluidized" catalytic CSTR containing 50 kg of catalyst (Figure in margin).

Currently 50% conversion is realized for pure A entering at pressure of 20 atm. There is virtually no pressure drop in the CSTR. It is proposed to put a PBR containing the same catalyst weight in series with the CSTR. The pressure drop parameter for the PBR α, given by Equation (4-33) is $\alpha = 0.018\ kg^{-1}$. The particle size is 0.2 mm, the bed porosity is 40%, and the viscosity is the same as that of air at 200°C.

(a) Should the PBR be placed upstream or downstream of the CSTR in order to achieve the highest conversion? Explain qualitatively using concepts you learned in Chapter 2.

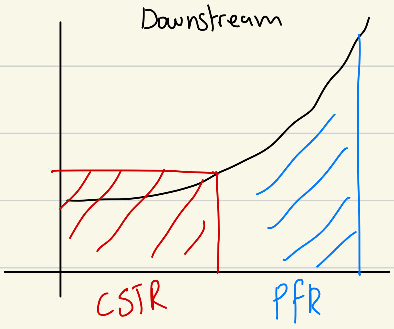
(b) What is the conversion exiting the last reactor?
(c) What is the pressure at the exit of the packed bed?
(d) How would your answers change if the catalyst diameter were decreased by a factor of 2 and the PBR diameter were increased by 50% assuming turbulent flow?

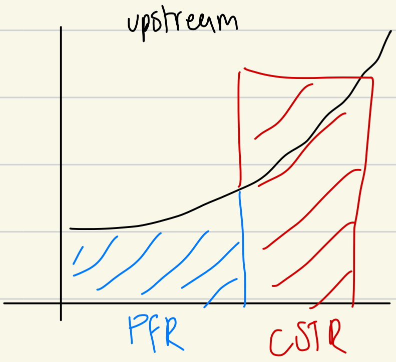
$w = 50kg$

$X = 0.5$

$P_0 = 20\ atm$

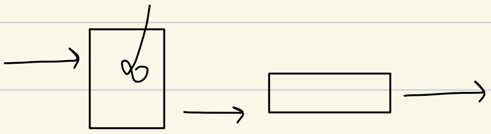
A)





→ PFR downstream (less wasted Volume)

B)



Reactor ①

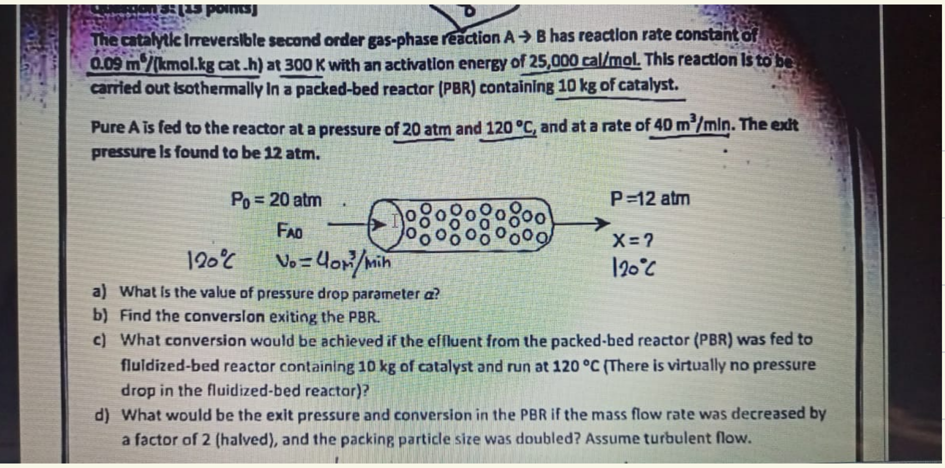
1. $$W = \frac{F_{A0} X}{-r_A'}$$

2- $$-r_A = kC_A$$

3. $$C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)} \frac{P}{P_0} \qquad \varepsilon = 0 \quad , no\ \Delta P$$

$$C_A = C_{A0}(1-X)$$

4 $$W = \frac{F_{A0}\ X}{k\ C_{A0}(1-X)}$$



Question 3: [15 points]

The catalytic irreversible second order gas-phase reaction A → B has reaction rate constant of 0.09 $m^6/(kmol.kg\ cat.h)$ at 300 K with an activation energy of 25,000 cal/mol. This reaction is to be carried out isothermally in a packed-bed reactor (PBR) containing 10 kg of catalyst.

Pure A is fed to the reactor at a pressure of 20 atm and 120 °C, and at a rate of 40 m^3/min. The exit pressure is found to be 12 atm.

a) What is the value of pressure drop parameter α?

b) Find the conversion exiting the PBR.

c) What conversion would be achieved if the effluent from the packed-bed reactor (PBR) was fed to fluidized-bed reactor containing 10 kg of catalyst and run at 120 °C (There is virtually no pressure drop in the fluidized-bed reactor)?

d) What would be the exit pressure and conversion in the PBR if the mass flow rate was decreased by a factor of 2 (halved), and the packing particle size was doubled? Assume turbulent flow.

A) $\boxed{\varepsilon = 0}$ $y = (1 - \alpha W)^{1/2}$

$$\frac{P}{P_0} = (1 - \alpha W)^{1/2} \qquad \frac{12}{20} = (1 - \alpha(10))^{1/2}$$

$$\alpha = 0.064 \ kg^{-1}$$

B) $$dW = F_{A0} \int_0^X \frac{dX}{-r_A}$$

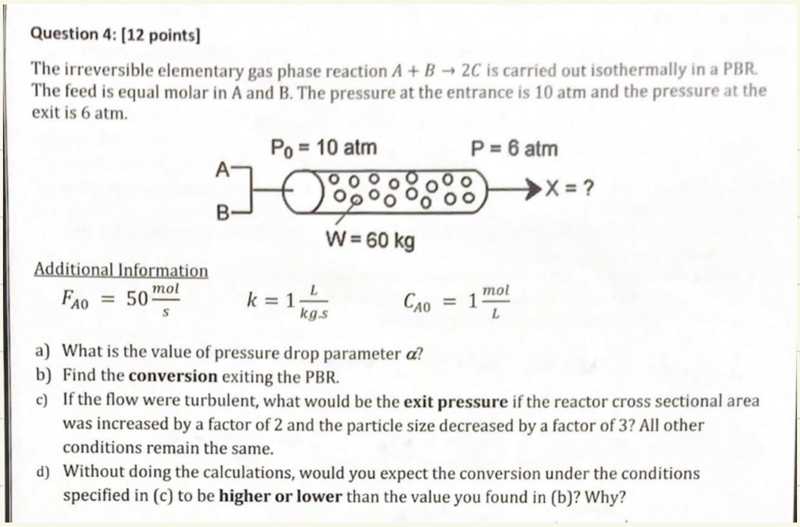
$$-r_A = KC_A^2$$

$$C_A = C_{A0}(1-X)\frac{P}{P_0} \qquad \frac{P}{P_0} = (1-\alpha W)^{1/2}$$

$$-r_A = k C_{A0}^2 (1-X)^2 (1-\alpha W)$$

$$dW = \frac{F_{A0}\ dX}{C_{A0}^2 (1-X)^2 (1-\alpha W)}$$

$$\int_0^{10} (1-\alpha W)\, dW = \frac{F_{A0}}{kC_{A0}^2} \int_0^X \frac{1}{(1-X^2)}$$



Question 4: [12 points]

The irreversible elementary gas phase reaction $A + B \rightarrow 2C$ is carried out isothermally in a PBR. The feed is equal molar in A and B. The pressure at the entrance is 10 atm and the pressure at the exit is 6 atm.

Additional Information

$F_{A0} = 50 \frac{mol}{s}$ $\quad k = 1 \frac{L}{kg.s}$ $\quad C_{A0} = 1 \frac{mol}{L}$

a) What is the value of pressure drop parameter α?
b) Find the **conversion** exiting the PBR.
c) If the flow were turbulent, what would be the **exit pressure** if the reactor cross sectional area was increased by a factor of 2 and the particle size decreased by a factor of 3? All other conditions remain the same.
d) Without doing the calculations, would you expect the conversion under the conditions specified in (c) to be **higher or lower** than the value you found in (b)? Why?

A) $\varepsilon = 0$ $\quad$ $\frac{P}{P_0} = (1 - \alpha W)^{1/2}$

$\frac{6}{10} = (1 - \alpha(60))^{1/2}$ $\quad$ $\alpha = 0.0107 \ kg^{-1}$

B) 1. $F_{A0} \frac{dX}{dW} = -r_A'$

2. $-r_A' = k C_A C_B$

3. $C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)} y$ $\quad$ $\varepsilon = 0$

$C_B = \frac{C_{A0}(1-X)}{(1+\varepsilon X)} y$

4 $F_{A0} \frac{dX}{dW} = C_{A0}^2 (1-X)^2 y^2$

5. $\frac{dy}{dW} = \frac{-\alpha}{2y}$ $\quad$ $y = (1 - \alpha W)^{1/2}$

$$\rightarrow \quad \frac{dX}{dW} = \frac{k C_{A0}^2 (1-X)^2 (1-\alpha W)}{F_{A0}}$$

$$F_{A0}\, dX = k C_{A0}^2 (1-X)^2 (1-\alpha W)\, dW$$

$$\int_0^X \frac{dX}{(1-X)^2} = \int_0^W \frac{k C_{A0}^2}{F_{A0}} (1-\alpha W)\, dW$$

$$\frac{X}{1-X} = \frac{K\, C_{A0}^{2}}{F_{A0}} \left(W - \frac{\alpha W^{2}}{2} \right)$$

$$\frac{X}{1-X} = \frac{(1)(1)^{2}}{50} \left[60 - 0.0107 \frac{(60)^{2}}{2} \right]$$

$$X = 0.449$$

c) Turbulent $A_c \uparrow 2$ $D_p \downarrow 3$

$A_{c2} = 2A_{c1}$ $D_{p2} = \frac{1}{3} D_{p1}$

$$\alpha_2 = \alpha_1 \left(\frac{A_{c1}}{A_{c2}} \right)^{3} \left(\frac{D_{p1}}{D_{p2}} \right)$$

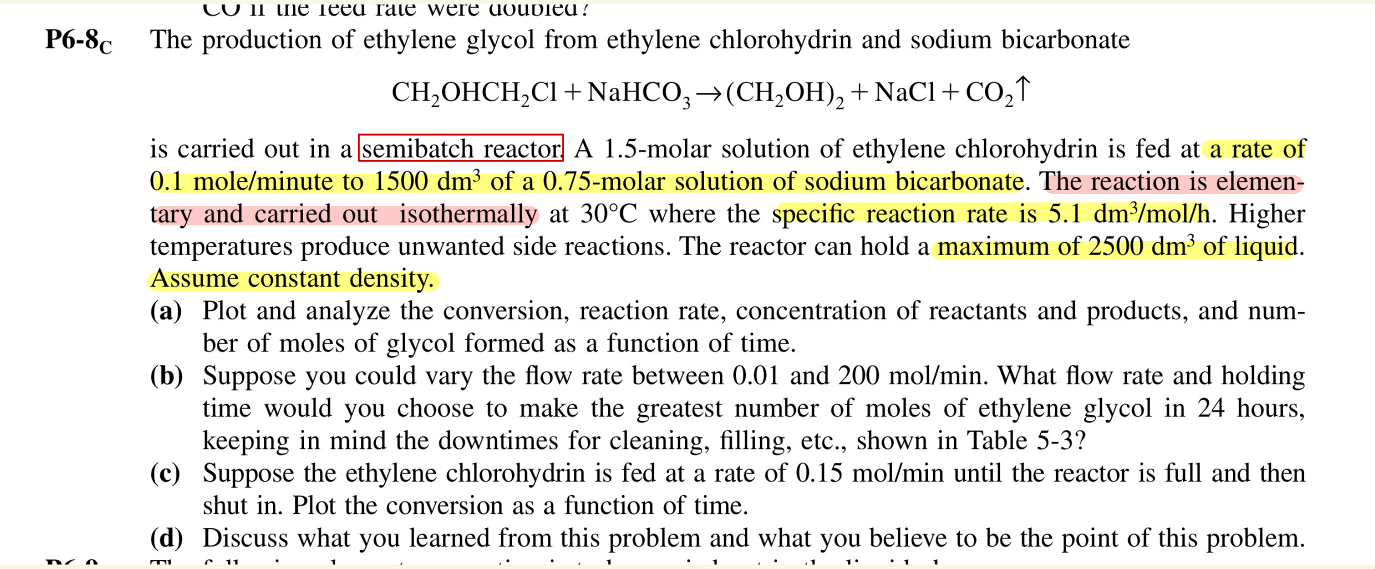
$$\alpha_2 = \alpha_1 \left(\frac{A_{c1}}{2A_{c1}} \right)^{3} \left(\frac{3D_{p1}}{D_{p1}} \right) = \frac{3}{8}\alpha_1 = \frac{3}{8}(0.0107) = 0.004\ \text{kg}^{-1}$$

$$\frac{P}{P_0} = (1 - \alpha W)^{\frac{1}{2}} \qquad \frac{P}{10} = (1 - 0.004(60))^{\frac{1}{2}} \qquad P = 8.72\ \text{atm}$$

c) higher conversion due to lower pressure drop

$\downarrow \Delta P$ $\downarrow \upsilon_0$ $\uparrow \tau$ $\uparrow X$

CH.6



CO if the feed rate were doubled?

P6-8$_C$ The production of ethylene glycol from ethylene chlorohydrin and sodium bicarbonate

$$CH_2OHCH_2Cl + NaHCO_3 \rightarrow (CH_2OH)_2 + NaCl + CO_2\uparrow$$

is carried out in a semibatch reactor. A 1.5-molar solution of ethylene chlorohydrin is fed at a rate of 0.1 mole/minute to 1500 dm^3 of a 0.75-molar solution of sodium bicarbonate. The reaction is elementary and carried out isothermally at 30°C where the specific reaction rate is 5.1 dm^3/mol/h. Higher temperatures produce unwanted side reactions. The reactor can hold a maximum of 2500 dm^3 of liquid. Assume constant density.

(a) Plot and analyze the conversion, reaction rate, concentration of reactants and products, and number of moles of glycol formed as a function of time.

(b) Suppose you could vary the flow rate between 0.01 and 200 mol/min. What flow rate and holding time would you choose to make the greatest number of moles of ethylene glycol in 24 hours, keeping in mind the downtimes for cleaning, filling, etc., shown in Table 5-3?

(c) Suppose the ethylene chlorohydrin is fed at a rate of 0.15 mol/min until the reactor is full and then shut in. Plot the conversion as a function of time.

(d) Discuss what you learned from this problem and what you believe to be the point of this problem.

$$A + B \longrightarrow C + D + CO_2\uparrow$$

1 Mole Balance

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

$$\frac{dN_B}{dt} = F_{B0} + r_A V$$

$$F_{CO_2} = r_{CO_2} V$$

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

$$\frac{dN_D}{dt} = r_D V$$

2. Relative Rates $-r_A = -r_B = r_C = r_D = r_{CO_2}$

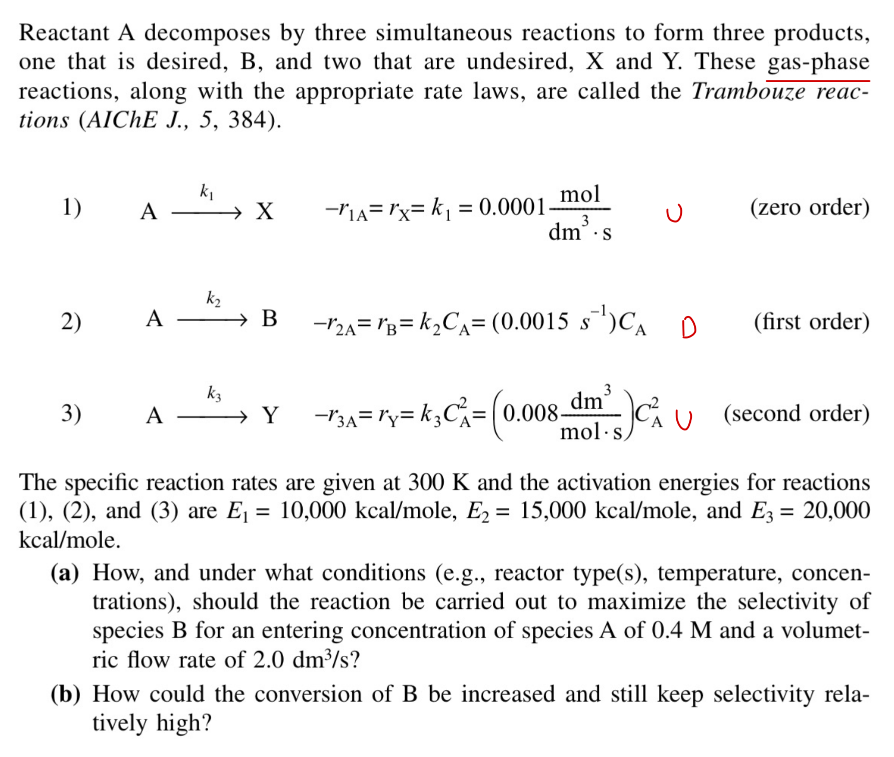
3. Rate of Reaction $-r_A = k C_A C_B$

4. Parameters: $X = \frac{N_{A0} - N_A}{N_{A0}}$

$$N_{A0} = V_0 C_{A0}$$

$$V = V_0 + v_0 t$$

CH.8



Reactant A decomposes by three simultaneous reactions to form three products, one that is desired, B, and two that are undesired, X and Y. These gas-phase reactions, along with the appropriate rate laws, are called the *Trambouze reactions* (*AIChE J.*, *5*, 384).

1) $A \xrightarrow{k_1} X \qquad -r_{1A} = r_X = k_1 = 0.0001 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$ U (zero order)

2) $A \xrightarrow{k_2} B \qquad -r_{2A} = r_B = k_2 C_A = (0.0015\ s^{-1}) C_A$ D (first order)

3) $A \xrightarrow{k_3} Y \qquad -r_{3A} = r_Y = k_3 C_A^2 = \left(0.008 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}}\right) C_A^2$ U (second order)

The specific reaction rates are given at 300 K and the activation energies for reactions (1), (2), and (3) are E_1 = 10,000 kcal/mole, E_2 = 15,000 kcal/mole, and E_3 = 20,000 kcal/mole.

- **(a)** How, and under what conditions (e.g., reactor type(s), temperature, concentrations), should the reaction be carried out to maximize the selectivity of species B for an entering concentration of species A of 0.4 M and a volumetric flow rate of 2.0 dm³/s?
- **(b)** How could the conversion of B be increased and still keep selectivity relatively high?

$$S_{D/U} = \frac{r_D}{r_{U1} + r_{U2}} = \frac{r_B}{r_X + r_Y} = \frac{k_2 C_A}{k_1 + k_3 C_A^2} \Rightarrow \text{CSTR}$$

→ to find max C_A

$$\frac{dS_{D/U}}{dC_A} = 0 = \frac{k_2(k_1 + k_3 C_A^2) - k_2 C_A(2k_3 C_A)}{(k_1 + k_3 C_A^2)^2}$$

$$0 = k_1 k_2 + k_2 k_3 C_A^2 - 2k_2 k_3 C_A^2$$

$$0 = k_1 k_2 - k_2 k_3 C_A^2$$

$$k_1 k_2 = k_2 k_3 C_A^2 \qquad C_A^2 = \frac{k_1 \cancel{k_2}}{\cancel{k_2} k_3}$$

$$C_A = \sqrt{\frac{k_1}{k_3}}$$

$$C_A = \sqrt{\frac{0.0001}{0.008}} = 0.112$$

→ Use max conc to maximize selectivity

$$S_{D/U} = \frac{0.0015(0.112)}{0.0001 + 0.008(0.112)^2} = 0.84$$

$C_{A0} = 0.4$

$C_A = 0.112$

→ Volume

$$V: \frac{C_{A0}v_0 - C_A v_0}{-r_A}$$

$$\frac{V}{v_0} = \frac{0.4 - 0.112}{-r_A = k_1 + k_2 C_A + k_3 C_A^2}$$

$$\tau = \frac{0.4 - 0.112}{0.0001 + 0.0015(0.112) + 0.008(0.112)^2} = 782$$

$$V = \tau v_0$$

$$V = 782 \quad (2) \quad = 1564 \text{ dm}^3$$

→ Temperature

$$S_{D/U} : \frac{k_2 \sqrt{\frac{k_1}{k_3}}}{k_1 + \cancel{k_3}\left(\frac{k_1}{\cancel{k_3}}\right)} \rightarrow \frac{k_2 \sqrt{\frac{k_1}{k_3}}}{k_1 + k_1} \rightarrow \frac{k_2}{2\sqrt{k_1 k_3}}$$

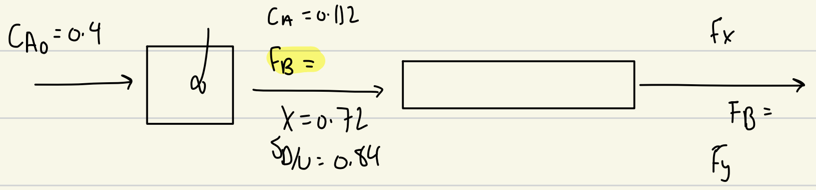
$$\frac{A_2}{2\sqrt{A_1 A_3}} \exp\left[\frac{\frac{E_1 + E_3}{2} - E_2}{R}\right]$$

$$\frac{E_1 + E_3}{2} - E_2 = \frac{10{,}000 + 20{,}000}{2} - 15\,000 = 0$$ → No temp effects.

→ Conversion

$$X = \frac{C_{A0} - C_A}{C_{A0}} = \frac{0.4 - 0.112}{0.4} = 0.72$$

B) to increase selectivity & conversion ⇒ add PFR after CSTR (conversion gradually increases)



→ to find F_B ⇒ mole Balance on CSTR

$$0 - C_B + r_B V = 0$$

$$C_B v_0 = r_B V$$

$$\frac{C_B}{\tau} = r_B$$

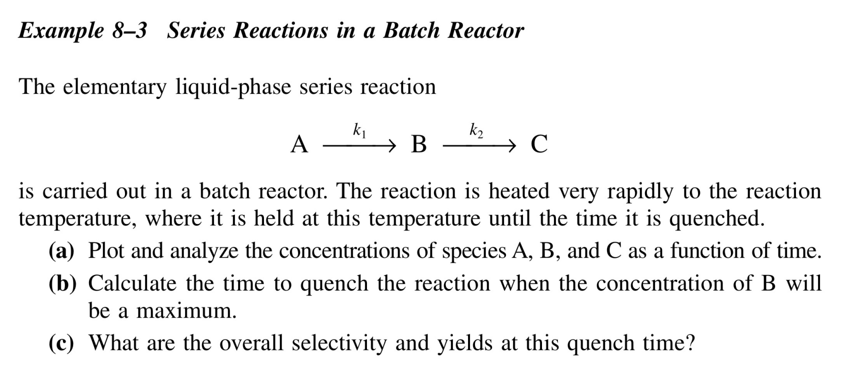
$$\frac{C_B}{782} = 0.0015(0.112)$$

$$C_B = 0.1313$$

$$C_B = \frac{F_B}{v_0}$$

$$0.1313 = \frac{F_B}{2}$$

$F_B = 0.26$ into PFR



Example 8–3   Series Reactions in a Batch Reactor

The elementary liquid-phase series reaction

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

is carried out in a batch reactor. The reaction is heated very rapidly to the reaction temperature, where it is held at this temperature until the time it is quenched.

(a) Plot and analyze the concentrations of species A, B, and C as a function of time.

(b) Calculate the time to quench the reaction when the concentration of B will be a maximum.

(c) What are the overall selectivity and yields at this quench time?

$A \rightarrow B \quad k_1$

$B \rightarrow C \quad k_2$

A)

$V = V_0$ (liq - batch)

1) Mole Balances

$$\frac{dN_A}{\partial t} = r_A V \qquad \frac{dC_A}{\partial t} = r_A$$

$$\frac{dN_B}{\partial t} = r_B V \qquad \frac{dC_B}{\partial t} = r_B$$

$$\frac{dN_C}{\partial t} = r_C V \qquad \frac{\partial C_C}{\partial t} = r_C$$

2) Rates

Rate law

$$r_{A_1} = -k_1 C_A$$

$$r_{B2} = -k_2 C_B$$

Relative Rates

$$\frac{r_{A1}}{-1} = \frac{r_{B1}}{1} \qquad r_{B1} = -r_A$$

$$\frac{r_{B2}}{-1} = \frac{r_{C2}}{1} \qquad r_{C2} = -r_{B2}$$

Net Rates

$$r_A = -k_1 C_{A_1}$$

$$r_B = r_{B1} + r_{B2} = k_1 C_A - k_2 C_{B2}$$

3) Combine Ⓐ

$$\frac{dC_A}{\partial t} = r_A$$

$$\frac{dC_A}{\partial t} = -k_1 C_{A1} \qquad \int_{C_{A0}}^{C_A} dC_A = \int_0^t -k\, C_{A1}\, dt$$

$$\ln \frac{C_A}{C_{A0}} = -k\, C_{A1}\, t$$

$$C_A = C_{A0} \exp(-k_1 t)$$

Ⓑ $$\frac{dC_B}{dt} = k_1 C_{A1} - k_2 C_{B2}$$

$$\frac{dC_B}{dt} + k_2 C_{B2} = k_1 C_{A0} e^{-k_1 t}$$

→ Integrating Factor

$$IF = \exp \int k_2 \, dt = e^{k_2 t}$$

$$\frac{d(C_B e^{k_2 t})}{dt} = k_1 C_{A0} e^{(k_2 - k_1)t}$$

at $t = 0$ $C_B = 0$ $$C_B = \frac{k_1 C_{A0}}{k_2 - k_1} \left[e^{-k_1 t} - e^{-k_2 t} \right]$$

Ⓒ $$\frac{dC_C}{dt} = k_2 C_B$$

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

at $t = 0$ $C_C = 0$ $$C_C = \frac{C_{A0}}{k_2 - k_1} \left[k_2 (1 - e^{-k_1 t}) - k_1 (1 - e^{-k_2 t}) \right]$$

3) Optimum yield

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

$$\frac{dC_B}{dt} = 0 = \frac{k_1 C_{A0}}{k_2 - k_1} \left[-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} \right]$$

$$-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} = 0$$

$$k_2 e^{-k_2 t} = k_1 e^{-k_1 t}$$

$$-k_2 t + \ln k_2 = -k_1 t + \ln k_1$$

$$\ln \frac{k_2}{k_1} + (-k_2 t) = -k_1 t$$

$$\frac{\ln \frac{k_2}{k_1}}{k_2 - k_1} = t_{max}$$

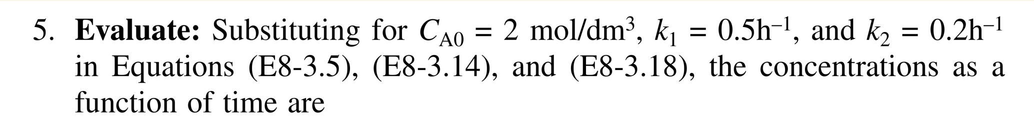
→ substitute in CA

$$C_A = C_{A0} \exp -k_1 \left(\frac{\ln \frac{k_2}{k_1}}{k_2 - k_1} \right)$$

→ Substitute in CB

$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1} \left[e^{-k_1 \left(\frac{\ln k_2/k_1}{k_2 - k_1} \right)} - e^{-k_2 \left(\frac{\ln k_2/k_1}{k_2 - k_1} \right)} \right]$$

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



5. **Evaluate:** Substituting for C_{A0} = 2 mol/dm^3, k_1 = 0.5h^{-1}, and k_2 = 0.2h^{-1} in Equations (E8-3.5), (E8-3.14), and (E8-3.18), the concentrations as a function of time are

$$t_{max} = \frac{1}{k_2 - k_1} \ln \frac{k_2}{k_1} = \frac{1}{0.2 - 0.5} \ln \frac{0.2}{0.5} = 3.05 \text{ h}$$

at tmax $C_A = C_{A0} e^{-k_1 t}$

$$C_A = 2 e^{-0.5(3.05)} = 0.44 \text{ mol/dm}^3$$

$$C_B = \frac{0.5(2)}{0.2 - 0.5} \left[\left(\frac{0.5}{0.2} \right)^{\frac{0.5}{0.2 - 0.5}} - \left(\frac{0.5}{0.2} \right)^{\frac{0.2}{0.2 - 0.5}} \right]$$

$$C_B = 1.07 \text{ mol/dm}^3$$

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

$2 - 0.44 - 1.08 = 0.49 \text{ mol/dm}^3$

c) Selectivity overall

$$\tilde{S}_{BC} = \frac{C_B}{C_C} = \frac{1.07}{0.49} = 2.2$$

Yield overall

$$\tilde{Y}_B = \frac{C_B}{C_{A0} - C_A} = \frac{1.07}{2 - 0.44} = 0.69$$

Example 8–4 Series Reaction in a CSTR

The reactions discussed in Example 8-3 are now to be carried out in a CSTR.

$$A \xrightarrow{k_1} B$$

$$B \xrightarrow{k_2} C$$

(a) Determine the exit concentrations from the CSTR.

(b) Find the value of the space time τ that will maximize the concentration of B.

1) Mole Balance

A

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

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

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

B

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

$$-C_B + r_B \tau = 0$$

C

$$-C_C + r_C \tau = 0$$

2) Rates

Rate Law

$$-r_{A1} = k_1 C_A$$

$$-r_{B2} = k_2 C_B$$

Relative Rates

$$\frac{r_{A1}}{-1} = \frac{r_{B1}}{1} \qquad r_{B1} = -r_A$$

$$\frac{r_{B2}}{-1} = \frac{r_{C2}}{1} \qquad r_{C2} = -r_{B2}$$

Net Rates

$$r_A = -r_{A1} = k_1 C_A$$

$$r_B = r_{B1} + r_{B2} = k_1 C_A - k_2 C_B$$

3) combine

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

B → $$-C_B + (k_1 C_A - k_2 C_B)\tau = 0$$

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

$$1 + k_1\tau + k_2\tau + k_1k_2\tau^2$$

C → $$-C_C + k_2 C_B \tau = 0$$

$$C_C = \frac{k_2 k_1 C_{A0} \tau^2}{(1+k_2\tau)(1+k_1\tau)}$$

b) optimum concentration of B

$$\frac{\partial C_B}{\partial \tau} = 0 = \frac{k_1 C_{A0}(1 + k_1\tau + k_2\tau + k_1k_2\tau^2) - k_1 C_{A0}\tau(k_1 + k_2 + 2k_1k_2\tau)}{(1 + k_1\tau + k_2\tau + 2k_1k_2\tau)^2}$$

$$k_1C_{A0} + k_1^2\cancel{C_{A0}}\tau + k_1k_2\cancel{C_{A0}}\tau + k_1^2k_2C_{A0}\tau^2 - k_1^2\cancel{C_{A0}}\tau - k_1k_2\cancel{C_{A0}}\tau - 2k_1^2k_2C_{A0}\tau^2 = 0$$

$$k_1C_{A0} - k_1^2k_2C_{A0}\tau^2 = 0$$

$$k_1C_{A0} = k_1^2k_2C_{A0}\tau^2$$

$$\tau^2 = \frac{\cancel{k_1}\,\cancel{C_{A0}}}{\cancel{k_1^2}\,k_2\,\cancel{C_{A0}}}$$

$$\tau_{max} = \sqrt{\frac{1}{k_1k_2}}$$

$$C_B = \frac{k_1 C_{A0}\sqrt{\frac{1}{k_1k_2}}}{\left(1+k_2\sqrt{\frac{1}{k_1k_2}}\right)\left(1+k_1\sqrt{\frac{1}{k_1k_2}}\right)}$$

Evaluation

$$\tau_{max} : \sqrt{\frac{1}{0.2 \times 0.5}} = \sqrt{10}\ h$$

$$C_A = \frac{C_{A0}}{1+k_1\tau} = \frac{2}{1+0.5\sqrt{10}} = 0.78\ mol/dm3$$

$$C_B = \frac{0.5(2)\sqrt{10}}{(1+0.2\sqrt{10})(1+0.5\sqrt{10})} = 0.75\ mol/dm^3$$

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

$$2 - 0.78 - 0.75 = 0.47\ mol/dm^3$$

Conversion

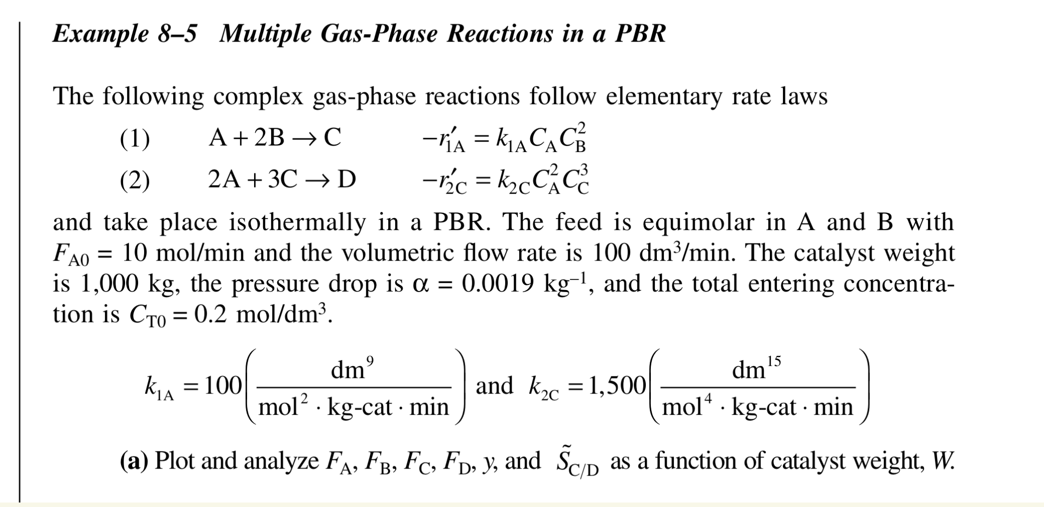
$$X = \frac{C_{A0} - C_A}{C_{A0}} = \frac{2-0.78}{2} = 0.61$$

Overall selectivity

$$\tilde{S}_{B/C} = \frac{C_B}{C_C} = \frac{0.75}{0.47} = 1.6$$

Overall yield

$$\tilde{Y}_B = \frac{C_B}{C_{A0} - C_A} = \frac{0.75}{2-0.78} = 0.614$$



Example 8–5 Multiple Gas-Phase Reactions in a PBR

The following complex gas-phase reactions follow elementary rate laws

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

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

and take place isothermally in a PBR. The feed is equimolar in A and B with F_{A0} = 10 mol/min and the volumetric flow rate is 100 dm³/min. The catalyst weight is 1,000 kg, the pressure drop is $\alpha = 0.0019\ \text{kg}^{-1}$, and the total entering concentration is $C_{T0} = 0.2\ \text{mol/dm}^3$.

$$k_{1A} = 100\left(\frac{\text{dm}^9}{\text{mol}^2 \cdot \text{kg-cat} \cdot \text{min}}\right) \text{ and } k_{2C} = 1{,}500\left(\frac{\text{dm}^{15}}{\text{mol}^4 \cdot \text{kg-cat} \cdot \text{min}}\right)$$

(a) Plot and analyze F_A, F_B, F_C, F_D, y, and $\tilde{S}_{C/D}$ as a function of catalyst weight, W.

$F_{A0} = 10\text{mol}/\text{min}$

$v_0 = 100\ \text{dm}^3/\text{min}$

$W = 1000\ \text{kg}$

$\alpha = 0.0019\ \text{kg}^{-1}$

$C_{T0} = 0.2$

1) Mole Balance

$$\frac{dF_A}{dW} = r'_A \qquad \frac{dF_C}{dW} = r'_C$$

$$\frac{dF_B}{dW} = r'_B \qquad \frac{dF_D}{dW} = r'_D$$

$W = 1000\ \text{kg}$

$F_{A0} = 10\ \text{mol}/\text{min}$

$F_{B0} = 10\ \text{mol}/\text{min}$

2) Rates

rate laws

$$-r'_{1A} = k_{1A} C_A C_B^2$$

$$-r'_{2C} = k_{2C} C_A^2 C_B^3$$

$k_{1A} = 100$

$k_{2C} = 1500$

Relative Rates

$$\frac{r'_{1A}}{-1} = \frac{r'_{1B}}{-2} = \frac{r'_{1C}}{1} \qquad r'_{1B} = 2r'_{1A} \qquad r'_{1C} = -r'_{1A}$$

$$\frac{r'_{2A}}{-2} = \frac{r'_{2C}}{-3} = \frac{r'_{2D}}{1} \qquad r'_{2A} = \tfrac{2}{3} r'_C \qquad r'_{2D} = -\tfrac{1}{3} r'_{2C}$$

Net Rates

$$r'_A = r'_{1A} + r'_{2A}$$

$$r_A = -k_1 C_A C_B^2 - \tfrac{2}{3} k_2 C_A^2 C_C^3$$

$$r'_B = r'_{1B}$$

$$r_B = -2 k_1 C_A C_B^2$$

$$r'_C = r'_{1C} + r'_{2C}$$

$$r'_C = k_1 C_A C_B^2 - k_2 C_A^2 C_C^3$$

$$r'_D = \tfrac{1}{3} k_2 C_A^2 C_C^3$$

3) Stoichiometry (Gas)

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

$C_{T0} = 0.2$

$F_{T0} = 20 \text{ mol/min}$

$$C_B = C_{T0}\left(\frac{P}{P_0}\right)\left(\frac{F_B}{F_T}\right)$$

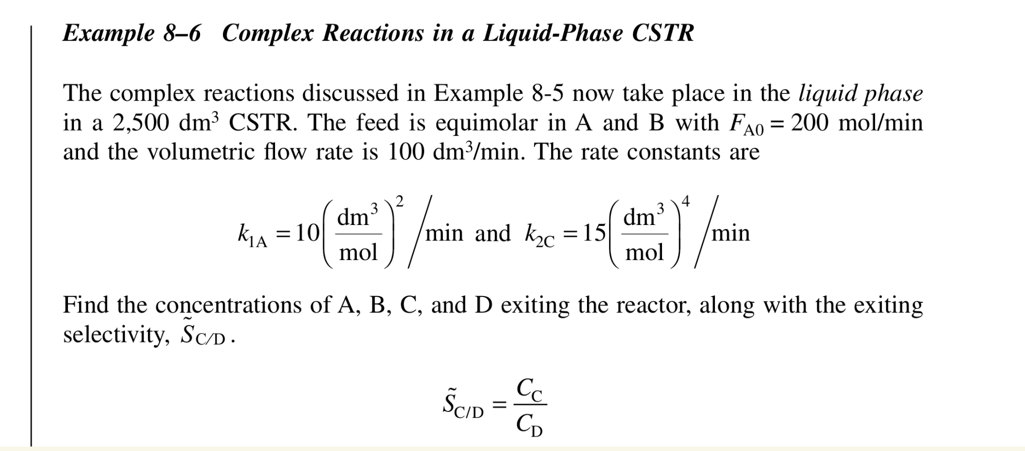
$$C_C = C_{T0}\left(\frac{P}{P_0}\right)\left(\frac{F_C}{F_T}\right)$$

$$C_D = C_{T0}\left(\frac{P}{P_0}\right)\left(\frac{F_D}{F_T}\right)$$

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

$y = \frac{P}{P_0}$ $\qquad \frac{dy}{dW} = -\frac{\alpha}{2y}\left(\frac{F_T}{F_{T0}}\right)$ $\qquad \alpha = 0.0019$

$$\tilde{S}_{C/D} = \frac{F_C}{F_D} \quad \text{if } W > 0.0001$$



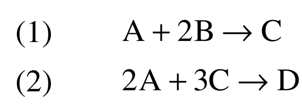
Example 8–6 Complex Reactions in a Liquid-Phase CSTR

The complex reactions discussed in Example 8-5 now take place in the *liquid phase* in a 2,500 dm^3 CSTR. The feed is equimolar in A and B with $F_{A0} = 200$ mol/min and the volumetric flow rate is 100 dm^3/min. The rate constants are

$$k_{1A} = 10\left(\frac{\text{dm}^3}{\text{mol}}\right)^2 \Big/ \text{min} \quad \text{and} \quad k_{2C} = 15\left(\frac{\text{dm}^3}{\text{mol}}\right)^4 \Big/ \text{min}$$

Find the concentrations of A, B, C, and D exiting the reactor, along with the exiting selectivity, $\tilde{S}_{C/D}$.

$$\tilde{S}_{C/D} = \frac{C_C}{C_D}$$



(1) $A + 2B \rightarrow C$

(2) $2A + 3C \rightarrow D$

1) Mole Balance $C_{A0}v_0 - C_Av_0 + r_AV = f(C_A)$

$C_{B0}v_0 - C_Bv_0 + r_BV = f(C_B)$

$-C_Cv_0 + r_CV = f(C_C)$

$-C_Dv_0 + r_DV = f(C_D)$

Rates → same as last ex.

Selectivity $S_{C/D} = \dfrac{F_C}{F_D+0.001}$

↳ to prevent $S_{C/D}$ from going to infinity when $F_D=0$

→ Define parameters

Ch 11

Example 11–2 Heat of Reaction

Calculate the heat of reaction for the synthesis of ammonia from hydrogen and nitrogen at 150°C in kcal/mol of N_2 reacted *and also* in kJ/mol of H_2 reacted.

Solution

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

→ ΔH° at 25°C are: $H^\circ_{NH_3} = -11{,}020$ cal/mol NH_3

$H^\circ_{N_2} = 0$

$H^\circ_{H_2} = 0$

$$\Delta H^\circ_{RX} = \frac{2}{1}(-11{,}020) - \frac{3}{1}(0) - (0)$$

$$\Delta H^\circ_{RX}\ (298) = -22{,}040 \text{ cal/mol } N_2 \text{ reacted}$$

↳ Indicates that the reaction is exothermic

→ Cp at 150°C

$C_{P_{H_2}} = 6.992$ cal/mol $H_2 \cdot K$

$C_{P_{N_2}} = 6.984$ cal/mol $N_2 \cdot K$

$C_{P_{NH_3}} = 8.92$ cal/mol $NH_3 \cdot K$

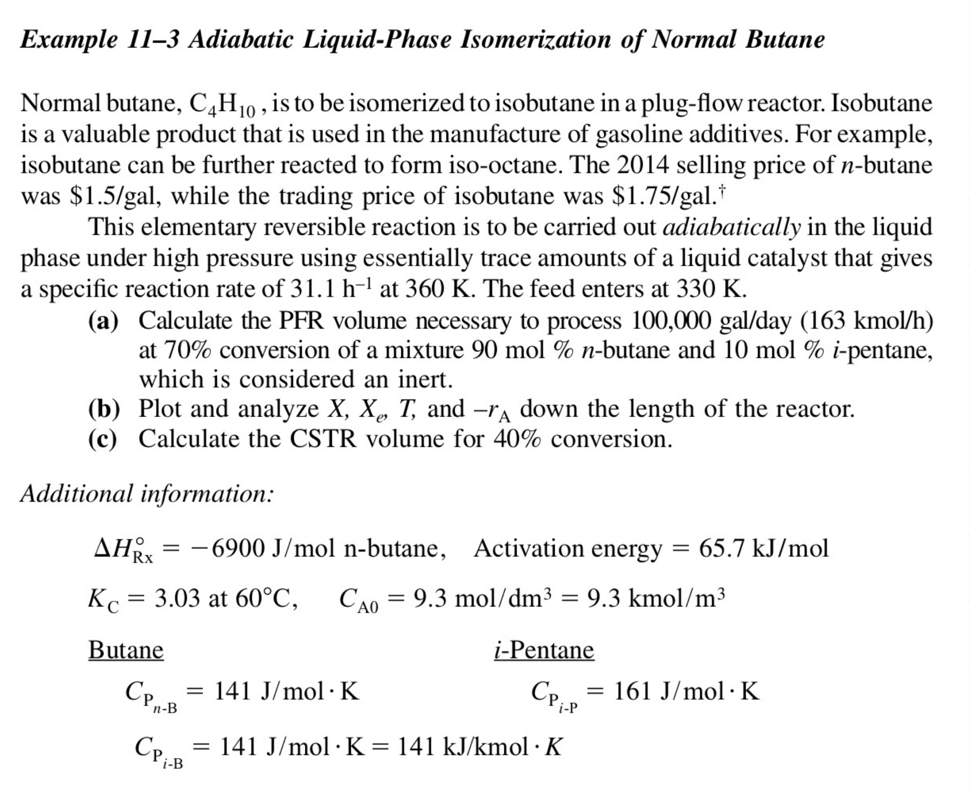
$$\Delta C_p = 2(8.92) - 3(6.992) - (6.984)$$

$$\Delta C_p = -10.12 \text{ cal/mol } N_2 \text{ reacted}$$

$$\Delta H_{Rxn}(T) = \Delta H^\circ_{Rxn}(T_R) + \Delta C_p (T - T_R)$$

$$\Delta H_{Rxn}(423) = -22{,}040 + -10.12\,(423 - 298)$$

$$\Delta H_{Rxn} = -23{,}305 \text{ cal/mol } N_2$$



Example 11–3 Adiabatic Liquid-Phase Isomerization of Normal Butane

Normal butane, C_4H_{10}, is to be isomerized to isobutane in a plug-flow reactor. Isobutane is a valuable product that is used in the manufacture of gasoline additives. For example, isobutane can be further reacted to form iso-octane. The 2014 selling price of *n*-butane was \$1.5/gal, while the trading price of isobutane was \$1.75/gal.†

This elementary reversible reaction is to be carried out *adiabatically* in the liquid phase under high pressure using essentially trace amounts of a liquid catalyst that gives a specific reaction rate of 31.1 h^{-1} at 360 K. The feed enters at 330 K.

- **(a)** Calculate the PFR volume necessary to process 100,000 gal/day (163 kmol/h) at 70% conversion of a mixture 90 mol % *n*-butane and 10 mol % *i*-pentane, which is considered an inert.
- **(b)** Plot and analyze X, X_e, T, and $-r_A$ down the length of the reactor.
- **(c)** Calculate the CSTR volume for 40% conversion.

Additional information:

$$\Delta H^\circ_{Rx} = -6900 \text{ J/mol n-butane}, \quad \text{Activation energy} = 65.7 \text{ kJ/mol}$$

$$K_C = 3.03 \text{ at } 60°C, \qquad C_{A0} = 9.3 \text{ mol/dm}^3 = 9.3 \text{ kmol/m}^3$$

Butane	*i*-Pentane
$C_{P_{n\text{-B}}} = 141 \text{ J/mol}\cdot\text{K}$	$C_{P_{i\text{-P}}} = 161 \text{ J/mol}\cdot\text{K}$
$C_{P_{i\text{-B}}} = 141 \text{ J/mol}\cdot\text{K} = 141 \text{ kJ/kmol}\cdot K$	

PFR, Adiabatic

$k = 31.1\ h^{-1}$ at $T = 360\ K$

$T_{in} = 330\ K$

A) $X = 0.7$ $F_{i0} = 163\ kmol/h$ $A \rightleftharpoons B$

90% A

10% I

1) Mole Balance $$\frac{dV}{dX} = \frac{F_{A0}}{-r_A}$$

2) Rate Law $$-r_A = k\left[C_A - \frac{C_B}{K_C}\right]$$

3) Stoichiometry $$C_A = C_{A0}(1-X)$$ $$C_B = C_{A0}X$$

4) Energy Balance (Adiabatic) → Check $\Delta C_P = 141 - 141 = 0$

$$T = T_0 + \frac{-\Delta H_{rxn} X}{\sum \Theta_i C_{Pi}}$$

5) Evaluate $$V = \frac{F_{A0} X}{k\left[C_{A0}(1-X) - \frac{C_{A0}X}{K_C}\right]}$$

$F_{A0} = 0.9 (F_{T0})$

$0.9(163) = 146.7$

$F_{I0} = 0.1(163) = 16.3$

$\theta_I = \frac{F_{I0}}{F_{A0}} = \frac{16.3}{146.7} = \frac{1}{9}$

$$T = 330 + \frac{-(-6900)\ X}{1(141) + \left(\frac{0.1}{0.9}\right)(161)}$$

$$T = 330 + 43.4X$$

at $X = 0.7$ $\quad T = 330 + 43.4(0.7)$

$T = 360.38\ K$

$\rightarrow k = 31.1 \exp\left[\frac{65700}{8.314}\left(\frac{1}{360} - \frac{1}{360.38}\right)\right] = 31.82$

$\rightarrow K_C = 3.03 \exp\left[\frac{-6900}{8.314}\left(\frac{1}{333} - \frac{1}{360.38}\right)\right] = 2.5$

$\rightarrow -r_A = k\left[C_{A0}(1-X) - \frac{C_{A0}X}{K_C}\right]$

$r_A = k C_{A0}\left[(1-X) - \frac{X}{K_C}\right]$

$-r_A = k C_{A0}\left[1 - \left(1 + \frac{1}{K_C}\right)X_e\right]$

$X_e = \frac{K_C}{1+K_C}$

$X_e = \frac{2.5}{1+2.5} = 0.714$

$-r_A = 31.82(9.3)\left[1 - \left(1 + \frac{1}{2.5}\right)0.7\right]$

$-r_A \cong 6.2$

$\rightsquigarrow \frac{F_{A0}}{-r_A} = \frac{146.7}{6.2} = 23.29$

↳ to find Volume carry out a table for $\frac{-F_{A0}}{r_A}$ & numerical Integration

13) mole Balance CSTR $V = \frac{F_{A0} X}{-r_A}$

$$-r_A = k_1 \left[C_A - \frac{C_B}{k_C} \right]$$

$$k = k_1 \exp\left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right]$$

$$k_C = k_{C1} \exp\left[\frac{\Delta H_{rxn}}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right]$$

$$C_A = C_{A0}(1-X)$$

$$C_B = C_{A0} X$$

$$T = 330 + 43.4 X$$

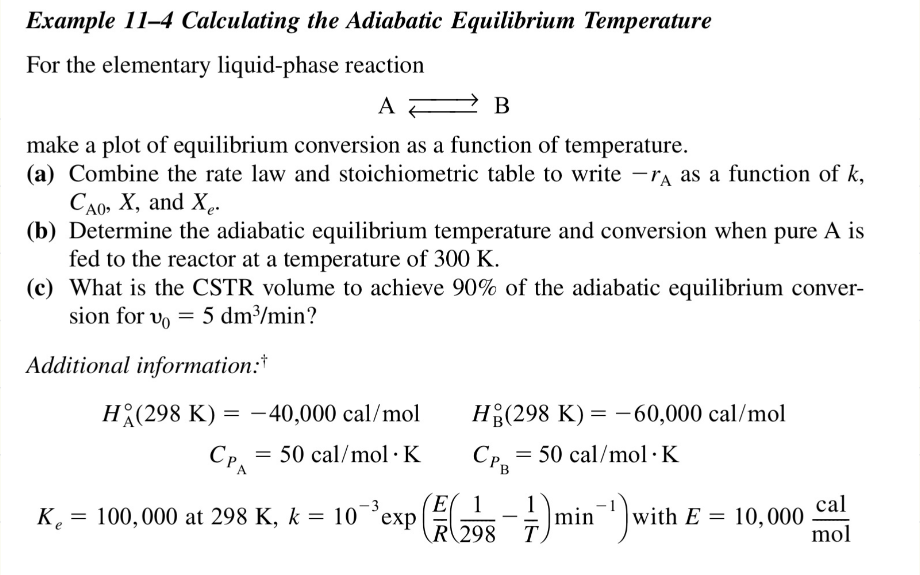
$$\rightarrow T = 330 + 43.4 (0.4) = 347.36$$

$$\rightarrow k = 31.1 \exp\left[\frac{65700}{8.314} \left(\frac{1}{360} - \frac{1}{347.36} \right) \right] = 14.02$$

$$\rightarrow k_C = 3.03 \exp\left[\frac{-6900}{8.314} \left(\frac{1}{333} - \frac{1}{347.36} \right) \right] = 2.73$$

$$-r_A = 14.02 (9.3) \left[(1-0.4) - \frac{0.4}{2.73} \right] \therefore 59.12$$

$$V = \frac{F_{A0} X}{-r_A} = \frac{146.7 (0.4)}{59.12} = 1 m^3$$



Example 11–4 Calculating the Adiabatic Equilibrium Temperature

For the elementary liquid-phase reaction

$$A \rightleftarrows B$$

make a plot of equilibrium conversion as a function of temperature.

(a) Combine the rate law and stoichiometric table to write $-r_A$ as a function of k, C_{A0}, X, and X_e.

(b) Determine the adiabatic equilibrium temperature and conversion when pure A is fed to the reactor at a temperature of 300 K.

(c) What is the CSTR volume to achieve 90% of the adiabatic equilibrium conversion for $\upsilon_0 = 5\ \text{dm}^3/\text{min}$?

Additional information:†

$$H_A^\circ(298\text{ K}) = -40{,}000\ \text{cal/mol} \qquad H_B^\circ(298\text{ K}) = -60{,}000\ \text{cal/mol}$$

$$C_{P_A} = 50\ \text{cal/mol}\cdot\text{K} \qquad C_{P_B} = 50\ \text{cal/mol}\cdot\text{K}$$

$$K_e = 100{,}000 \text{ at } 298\text{ K},\ k = 10^{-3}\exp\left(\frac{E}{R}\left(\frac{1}{298} - \frac{1}{T}\right)\text{min}^{-1}\right)\text{with } E = 10{,}000\ \frac{\text{cal}}{\text{mol}}$$

1) Rate law $\quad -r_A = k\left[C_A - \frac{C_B}{K_C}\right]$

equilibrium $\quad -r = 0 \qquad K_C = \frac{C_B}{C_A}$

2) Stoichiometry

$$C_A = C_{A0}(1-X)$$

$$C_B = C_{A0}X$$

4) combine

$$k_C = \frac{C_{A0}X}{C_{A0}(1-X)} \qquad K_C = \frac{X_e}{1-X_e}$$

$$-r_A = kC_{A0}\left((1-X) - \frac{X}{\frac{X_e}{1-X_e}}\right)$$

$$-r_A = kC_{A0}\left(1 - \frac{X}{X_e}\right)$$

$$X_e = \frac{K_C}{1+K_C}$$

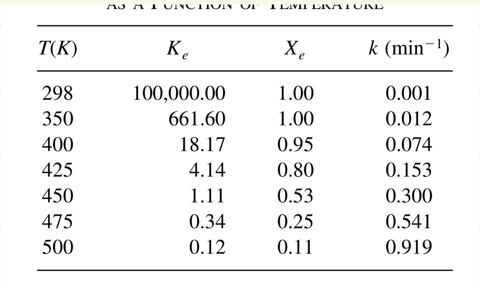
→ Calculate Equilibrium constant k_C

1. $\Delta C_p = 50 - 50 = 0$

2. $\Delta H_{rxn} = -60{,}000 - -40{,}000 = -20{,}000$

3. $K_C = 100{,}000 \exp\left[\frac{-20{,}000}{1.989}\left(\frac{1}{298} - \frac{1}{T}\right)\right]$

$$\frac{X_e}{1-X_e} = 100{,}000 \exp\left[\frac{-20{,}000}{1.989}\left(\frac{1}{298}-\frac{1}{T}\right)\right]$$



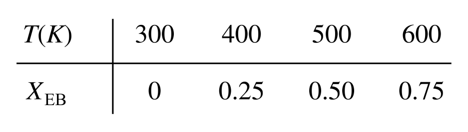
$T(K)$	K_e	X_e	k (min^{-1})
298	100,000.00	1.00	0.001
350	661.60	1.00	0.012
400	18.17	0.95	0.074
425	4.14	0.80	0.153
450	1.11	0.53	0.300
475	0.34	0.25	0.541
500	0.12	0.11	0.919

→ Calculate X_e at every T

5) Energy Balance

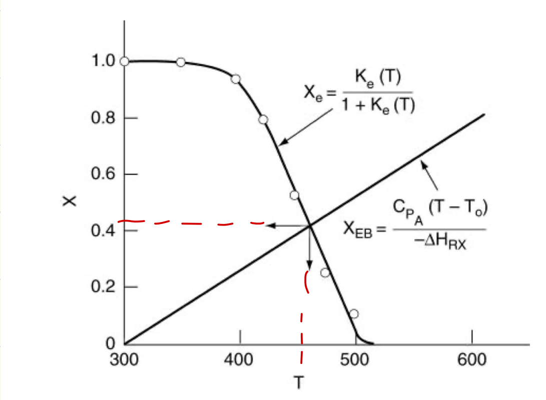
$$T = T_o + \frac{-\Delta H_{rxn} X_{EB}}{\sum \Theta_i C_{Pi}}$$

$$T = 298 + \frac{-(-20{,}000)\, X_{EB}}{1(50)}$$



$T(K)$	300	400	500	600
X_{EB}	0	0.25	0.50	0.75

→ plot



The Intersection of $X_{\text{Energy Balance}}$ & $X_{\text{equilibrium}}$

$X_e = 0.42$ → Adiabatic equilibrium Conversion.

$T = 465$ → Adiabatic equilibrium temp

B) $$V_{CSTR} = \frac{F_{A0} X}{-r_A} = \frac{C_{A0} v_0 X}{k C_{A0}\left[1 - \frac{X}{X_e}\right]}$$

$$X = 0.9(0.42) = 0.378$$

$$T = T_0 + \frac{-\Delta H_{rxn} X}{\Sigma \theta_i C_{pi}}$$

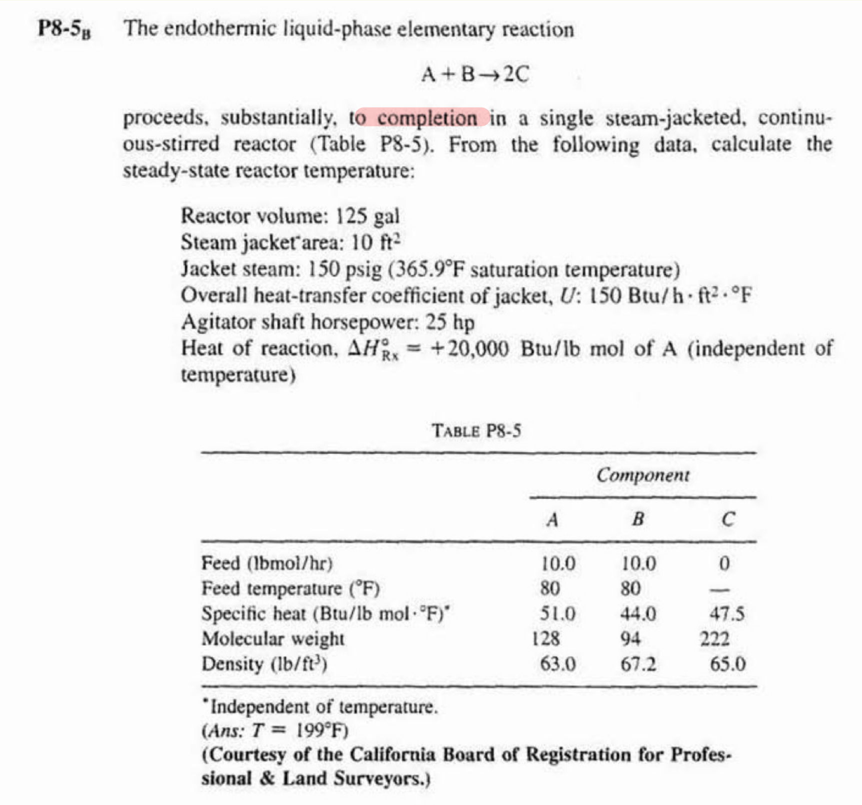
$$T = 298 + \frac{-(-20{,}000)(0.38)}{50} \quad = 452\ K$$

$$k = 10^{-3} \exp\left[\frac{10{,}000}{1.989}\left(\frac{1}{298} - \frac{1}{452}\right)\right] = 0.322$$

$$K_C = 100{,}000 \exp\left[\frac{-20{,}000}{1{,}989}\left(\frac{1}{298} - \frac{1}{452}\right)\right] = 1.016$$

$$X_e = \frac{K_C}{1+K_C} = \frac{1.016}{1+1.016} = 0.5$$

$$V = \frac{5(0.38)}{0.322\left(1 - \frac{0.38}{0.5}\right)} = 24.5$$



P8-5$_B$ The endothermic liquid-phase elementary reaction

$$A + B \rightarrow 2C$$

proceeds, substantially, to completion in a single steam-jacketed, continuous-stirred reactor (Table P8-5). From the following data, calculate the steady-state reactor temperature:

Reactor volume: 125 gal
Steam jacket area: 10 ft^2
Jacket steam: 150 psig (365.9°F saturation temperature)
Overall heat-transfer coefficient of jacket, U: 150 Btu/h · ft^2 · °F
Agitator shaft horsepower: 25 hp
Heat of reaction, ΔH°_{Rx} = +20,000 Btu/lb mol of A (independent of temperature)

TABLE P8-5

	Component		
	A	*B*	*C*
Feed (lbmol/hr)	10.0	10.0	0
Feed temperature (°F)	80	80	—
Specific heat (Btu/lb mol · °F)*	51.0	44.0	47.5
Molecular weight	128	94	222
Density (lb/ft^3)	63.0	67.2	65.0

*Independent of temperature.
(*Ans:* T = 199°F)
(Courtesy of the California Board of Registration for Professional & Land Surveyors.)

$X = 1$

$V = 125 \text{gal}$

$A = 10 \text{ft}^2$

$P = 150 \text{ Psig}$

$U = 150 \text{ Btu/h} \cdot \text{ft}^2 \text{ °F}$

$\dot{W}_s = 25 \text{ hp}$

$\Delta H^\circ_{rxn} = 20{,}000$

$\dot{W}_s = 63525 \text{ Btu/h}$

$\Theta_A = 1$

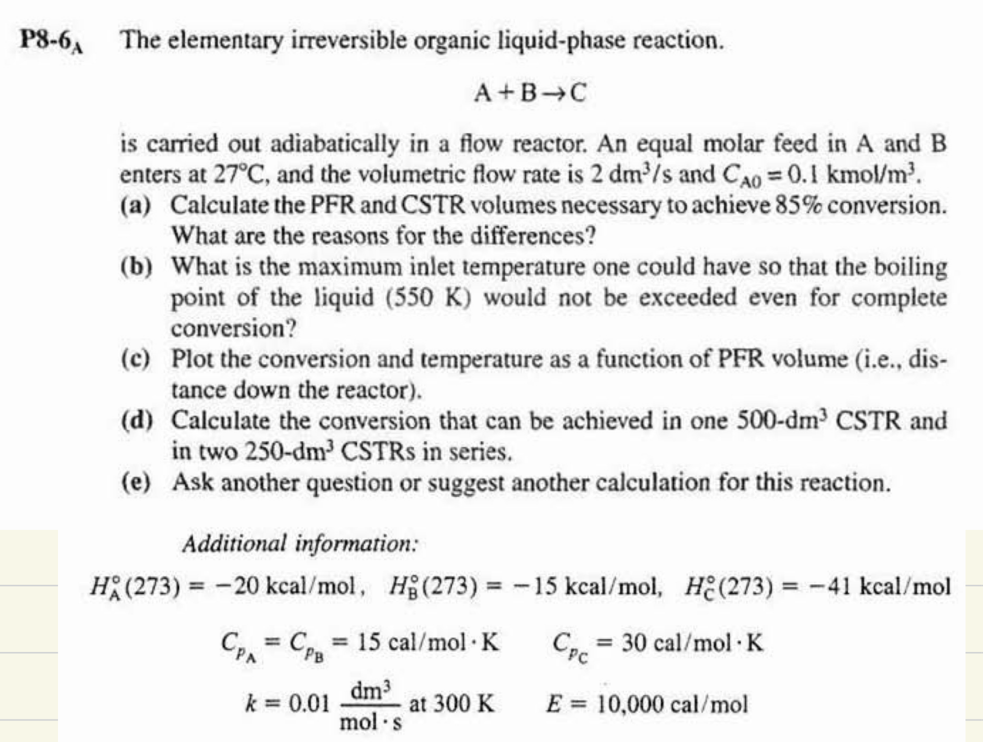
$\Theta_B = 1$

Energy Balance [CSTR with heat Exchange]

$$X_{EB} = \frac{\left(\frac{UA}{F_{A0}}(T - T_a)\right) + \sum \Theta_i C_{pi} (T - T_0) - \left(\frac{\dot{W}_s}{F_{A0}}\right)}{-\Delta H_{rxn}}$$

$$1 = \frac{\left[\frac{150(10)}{10}(T - 365.9)\right] + \left[((1(5)) + 1(44)))(T - 80)\right] - \left[\frac{63525}{10}\right]}{-20{,}000}$$

$T = 199 °F$



P8-6$_A$ The elementary irreversible organic liquid-phase reaction.

$$A + B \rightarrow C$$

is carried out adiabatically in a flow reactor. An equal molar feed in A and B enters at 27°C, and the volumetric flow rate is 2 dm^3/s and $C_{A0} = 0.1$ kmol/m^3.

- **(a)** Calculate the PFR and CSTR volumes necessary to achieve 85% conversion. What are the reasons for the differences?
- **(b)** What is the maximum inlet temperature one could have so that the boiling point of the liquid (550 K) would not be exceeded even for complete conversion?
- **(c)** Plot the conversion and temperature as a function of PFR volume (i.e., distance down the reactor).
- **(d)** Calculate the conversion that can be achieved in one 500-dm^3 CSTR and in two 250-dm^3 CSTRs in series.
- **(e)** Ask another question or suggest another calculation for this reaction.

Additional information:

$$H_A^\circ(273) = -20 \text{ kcal/mol}, \quad H_B^\circ(273) = -15 \text{ kcal/mol}, \quad H_C^\circ(273) = -41 \text{ kcal/mol}$$

$$C_{P_A} = C_{P_B} = 15 \text{ cal/mol}\cdot\text{K} \qquad C_{P_C} = 30 \text{ cal/mol}\cdot\text{K}$$

$$k = 0.01 \frac{\text{dm}^3}{\text{mol}\cdot\text{s}} \text{ at } 300 \text{ K} \qquad E = 10{,}000 \text{ cal/mol}$$

$X = 0.85$

$C_{A0} = 0.1$ Kmol /m3

$v_0 = 2$ dm^3/s

1) PFR volume

1. $\dfrac{dX}{dV} = \dfrac{-r_A}{F_{A0}}$ $\qquad V = \displaystyle\int_0^X \frac{F_{A0}}{-r_A}\, dX$

2. $-r_A = k C_A C_B$ $\qquad k = k_1 \exp\left(\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$

$k = 0.01 \exp\left(\frac{10000}{2}\left(\frac{1}{300} - \frac{1}{T}\right)\right)$

3. $C_A = C_{A0}(1-X)$
$C_B = C_{A0}(1-X)$] → Equimolar

4. $dV = \dfrac{F_{A0}}{k_1 \exp\left(\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right) C_{A0}^2 (1-X)^2}$

5 check $\Delta C_p = 30 - 15 - 15 = 0$ ⇒ simplified

$T = T_0 + \dfrac{-\Delta H_{rxn}(X)}{\Sigma \theta_i C_{p_i}}$ $\qquad \Sigma \theta_i C_{p_1} = C_{PA} + C_{PB}$

$15 + 15 = 30$cal/mol·K

→ $-\Delta H_{rxn} = -41 - (-15) - (-20) = -6$kcal/mol·K

$T = 300 + \dfrac{-(-6)\cancel{kcal}}{\cancel{mol}} \Big| \dfrac{K}{30\ \cancel{cal}} \Big| \dfrac{\cancel{mol}\cdot K}{} \Big| \dfrac{1000\ \cancel{cal}}{1\ k\cancel{cal}} \Big| X$

$T = 300 + 200X$

$$V = \frac{F_{A0}}{k_1 C_{A0}^2} \int_0^{0.85} \frac{dx}{(1-x)^2 \exp\left(\frac{10{,}000}{1.989}\left(\frac{1}{300} - \frac{1}{300+200x}\right)\right)}$$

$$V = \frac{\cancel{C_{A0}}\, v_0}{k_1\, C_{A0}^{\cancel{2}}} \left(0.154 \right)$$

$$\frac{2}{0.01\,(0.1)} (0.154) : 308.3 \text{ dm}^3$$

CSTR volume:

$$V = \frac{F_{A0}\, X}{-r_A}$$

$$V = \frac{0.1\,(2)\,(0.85)}{0.01 \exp\left(\frac{10000}{2}\left(\frac{1}{300} - \frac{1}{300+200(0.85)}\right)\right) (0.1)^2 (1-0.85)^2}$$

$$V = 182 \text{ dm}^3$$

B) $T_{out} = 550$

Do not exceed $X = 1$

$$T = T_0 + 200X$$

$$550 = T_0 + 200(1) \qquad T_0 = 350K$$

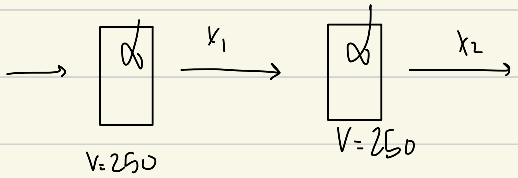
D) one 500 dm^3 CSTR

$$V = \frac{F_{A0}\, X}{k_1 \exp\left(\frac{E}{R}\left(\frac{1}{300} - \frac{1}{300+200X}\right)\right) C_{A0}^2 (1-X)^2}$$

$$500 = \frac{0.1\,(2)\,X}{0.01 \exp\left(\frac{10000}{2}\left(\frac{1}{300} - \frac{1}{300+200X}\right)\right) (0.1)^2 (1-X)^2}$$

$$X = 0.922$$

→ 2 250dm³ CSTR



→ for X_1

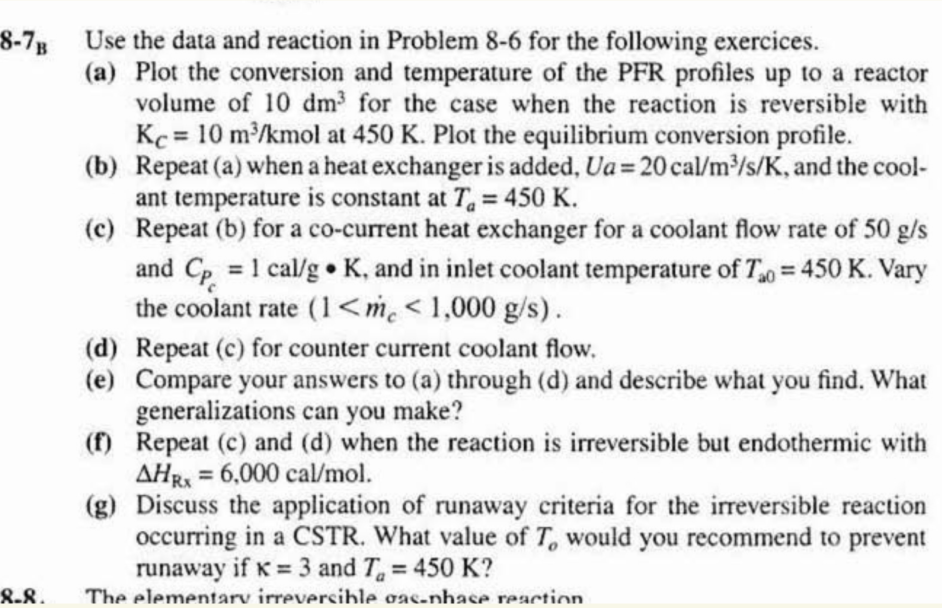
$$250 = \frac{2(X)}{0\ 01 \exp\left(\frac{10000}{2}\left(\frac{1}{300} - \frac{1}{300+200X}\right)\right)(0.1)(1-X)^2}$$

$$X = 0.88$$

→ for X_2

$$250 = \frac{2(X_2 - X_1)}{0.01 \exp\left(\frac{10000}{2}\left(\frac{1}{300} - \frac{1}{300+200X}\right)\right)(0.1)(1-X_2)^2}$$

$$X_2 = 0.97$$



8-7$_B$ Use the data and reaction in Problem 8-6 for the following exercices.

(a) Plot the conversion and temperature of the PFR profiles up to a reactor volume of 10 dm^3 for the case when the reaction is reversible with $K_C = 10$ m^3/kmol at 450 K. Plot the equilibrium conversion profile.

(b) Repeat (a) when a heat exchanger is added, $Ua = 20$ cal/m^3/s/K, and the coolant temperature is constant at $T_a = 450$ K.

(c) Repeat (b) for a co-current heat exchanger for a coolant flow rate of 50 g/s and $C_{P_c} = 1$ cal/g • K, and in inlet coolant temperature of $T_{a0} = 450$ K. Vary the coolant rate $(1 < \dot{m}_c < 1{,}000 \text{ g/s})$.

(d) Repeat (c) for counter current coolant flow.

(e) Compare your answers to (a) through (d) and describe what you find. What generalizations can you make?

(f) Repeat (c) and (d) when the reaction is irreversible but endothermic with $\Delta H_{Rx} = 6{,}000$ cal/mol.

(g) Discuss the application of runaway criteria for the irreversible reaction occurring in a CSTR. What value of T_o would you recommend to prevent runaway if $\kappa = 3$ and $T_a = 450$ K?

8-8. The elementary irreversible gas-phase reaction

$A + B \rightleftharpoons C$

1. $$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

2. $$-r_A = k\left[C_A C_B - \frac{C_C}{K_C}\right]$$

$$k = k_1 \exp\left(\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$$

$k_1 = 0.01$ $T_1 = 300$

$$K_C = K_{C1} \exp\left(\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$$

$K_{C1} = 10$ $T_1 = 450$

3. $$C_A = C_{A0}(1-X)$$
$$C_B = C_{A0}(1-X)$$
$$C_C = C_{A0}X$$

$$X_e = \frac{K_C}{1+K_C}$$

4. $$T = T_0 + \frac{-\Delta H_{rxn} X}{\sum \Theta_i C_{Pi}}$$

$T = 300 + 200X$

B) $\frac{dT_a}{dV} = 0$ → constant T_a

$$\frac{dT}{dV} = \frac{r_A \Delta H_{rxn} - Ua(T - T_a)}{F_{A0}(\sum \Theta_i C_{Pi} + \Delta C_p X)}$$

$\Rightarrow \Delta C_p = 0$

$$\frac{dT}{dV} = \frac{r_A \Delta H_{rxn} - UA(T - T_a)}{F_{A0}(\Sigma \Theta_i C_{pi})}$$

$\Delta H_{rxn} = 6000$

$Ua = 20$ $A = 10$

$\Sigma \Theta_i C_{pi} = 30$

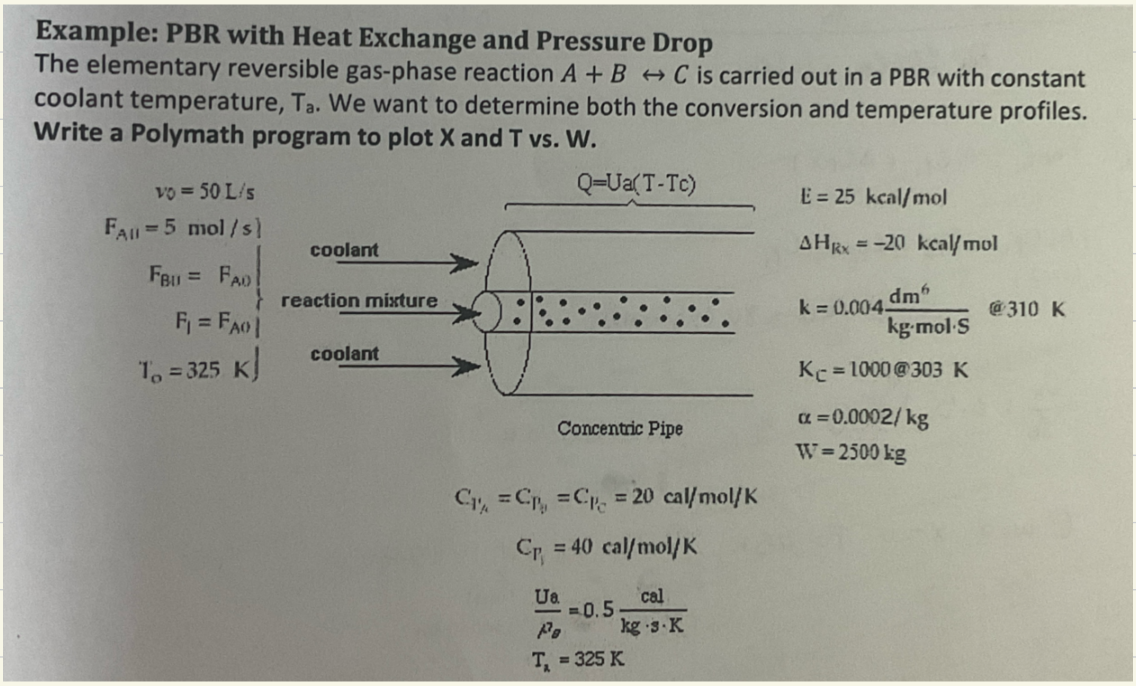
$T_a = 450$

() Co-current

$$\frac{dT_a}{dV} = \frac{UA(T - T_a)}{\dot{m}_c C_{pc}}$$

$\dot{m}_c = 50\ g$

$C_{pc} = 1$



Example: PBR with Heat Exchange and Pressure Drop

The elementary reversible gas-phase reaction $A + B \leftrightarrow C$ is carried out in a PBR with constant coolant temperature, T_a. We want to determine both the conversion and temperature profiles. **Write a Polymath program to plot X and T vs. W.**

$v_0 = 50\ L/s$

$F_{A0} = 5\ mol/s$

$F_{B0} = F_{A0}$

$F_I = F_{A0}$

$T_0 = 325\ K$

$E = 25\ kcal/mol$

$\Delta H_{Rx} = -20\ kcal/mol$

$k = 0.004 \frac{dm^6}{kg \cdot mol \cdot S}$ @310 K

$K_C = 1000$ @303 K

$\alpha = 0.0002/kg$

$W = 2500\ kg$

$C_{P_A} = C_{P_B} = C_{P_C} = 20\ cal/mol/K$

$C_{P_I} = 40\ cal/mol/K$

$\frac{Ua}{\rho_B} = 0.5 \frac{cal}{kg \cdot s \cdot K}$

$T_a = 325\ K$

1. Mole Balance $\frac{dX}{dV} = \frac{-r_A'}{F_{A0}}$

2. Rate Law $-r_A' = k\left[C_A C_B - \frac{C_C}{K_C}\right]$

$k = k_1 \exp\left(\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$ $k_1 = 0.004$ $T_1 = 310$

$E = 25000$

$K_C = K_{C_1} \exp\left(\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$ $K_{C_1} = 1000$ $T_1 = 303$

$\Delta H_{rxn} = -20\,000$

3. Stoichiometry $C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)} \frac{T_0}{T} \frac{P}{P_0}$

$C_{A0} = \frac{F_{A0}}{V_0} = \frac{5}{50} = 0.1\ mol/L$

$\varepsilon = \delta y_{A0}$ $\delta = 1 + 1 - 1 = -1$ $\varepsilon = -1/3$

$y_{A0} = \frac{F_{A0}}{F_{T0}} = \frac{5}{15} = \frac{1}{3}$

$C_B = \frac{C_{A0}(\Theta_B - X)}{1+\varepsilon X} \frac{T_0}{T} \frac{P}{P_0}$ $\Theta_B = \frac{F_{B0}}{F_{A0}} = 1$

$C_C = \frac{C_{A0}(X)}{1+\varepsilon X} \frac{T_0}{T} \frac{P}{P_0}$

4. Pressure

$$\frac{dy}{dW} = -\frac{\alpha}{2y}(1+\varepsilon X)\frac{T}{T_0}$$

$\alpha = 0.0002$

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

$F_{T0} = 15$ $\quad v_0 = 50$

$R = 0.08206$ L·atm/mol·K

$T_0 = 325K$

$$P_0 = \frac{F_{T0} R T_0}{v_0}$$

4. Heat

$$\frac{dT}{dW} = \frac{r_A' \Delta H_{rxn} - \frac{Ua}{\rho_B}(T - Ta)}{F_{A0}\left(\Sigma \theta_i Cp_i + \Delta Cp X\right)}$$

$\Delta Cp = 20 - 20 - 20 = -20$

$\Sigma \theta_i Cp_i = Cp_A + Cp_B + Cp_I$

$20 + 20 + 40 = 80$

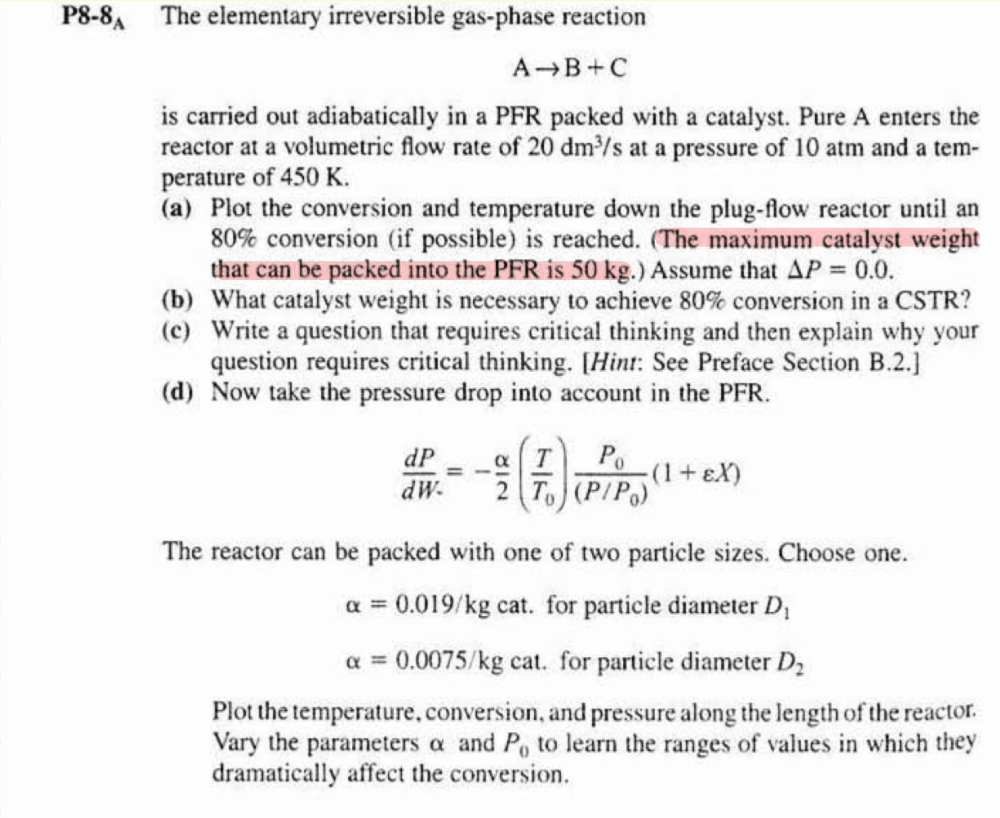
$\Delta H_{rxn} = -20{,}000$

$\frac{Ua}{\rho_B} = 0.5$ $\qquad T_a = 325K$

at $W = 0$ $\quad X = 0$ $\quad T = 325$ $\quad y = 1$

$W(F) = 2500$

↳ final condition



P8-8$_A$ The elementary irreversible gas-phase reaction

$$A \rightarrow B + C$$

is carried out adiabatically in a PFR packed with a catalyst. Pure A enters the reactor at a volumetric flow rate of 20 dm^3/s at a pressure of 10 atm and a temperature of 450 K.

- **(a)** Plot the conversion and temperature down the plug-flow reactor until an 80% conversion (if possible) is reached. (The maximum catalyst weight that can be packed into the PFR is 50 kg.) Assume that $\Delta P = 0.0$.
- **(b)** What catalyst weight is necessary to achieve 80% conversion in a CSTR?
- **(c)** Write a question that requires critical thinking and then explain why your question requires critical thinking. [*Hint*: See Preface Section B.2.]
- **(d)** Now take the pressure drop into account in the PFR.

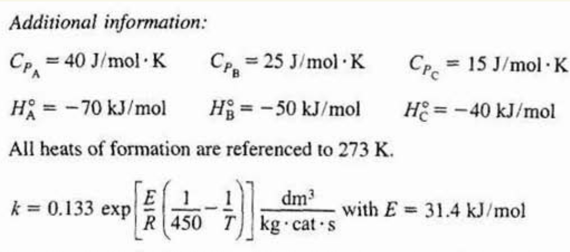
$$\frac{dP}{dW} = -\frac{\alpha}{2}\left(\frac{T}{T_0}\right)\frac{P_0}{(P/P_0)}(1+\varepsilon X)$$

The reactor can be packed with one of two particle sizes. Choose one.

$\alpha = 0.019$/kg cat. for particle diameter D_1

$\alpha = 0.0075$/kg cat. for particle diameter D_2

Plot the temperature, conversion, and pressure along the length of the reactor. Vary the parameters α and P_0 to learn the ranges of values in which they dramatically affect the conversion.



Additional information:

$C_{P_A} = 40$ J/mol·K $C_{P_B} = 25$ J/mol·K $C_{P_C} = 15$ J/mol·K

$H_A^\circ = -70$ kJ/mol $H_B^\circ = -50$ kJ/mol $H_C^\circ = -40$ kJ/mol

All heats of formation are referenced to 273 K.

$$k = 0.133 \exp\left[\frac{E}{R}\left(\frac{1}{450}-\frac{1}{T}\right)\right] \frac{dm^3}{kg \cdot cat \cdot s} \text{ with } E = 31.4 \text{ kJ/mol}$$

$v_0 = 20 dm^3/s$

$P_0 = 10$ atm $T_0 = 450K$

A) 1. Mole Balance $\frac{dX}{dW} = \frac{-r_A'}{F_{A0}}$ $v_0 = 20 dm^3/s$

2. Rate Law $-r_A' = k C_A$ $k = k_1 \exp\left(\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$

$k_1 = 0.133$ $E = 31400$ $T_1 = 450$

3. Stoichiometry $C_A = C_{A0} \frac{(1-X)}{(1+\varepsilon X)} \frac{T_0}{T}$

$\varepsilon = y_{A0}(\delta) = 1(1-1+1) = 1$ $T_0 = 450K$

4. Energy Balance $T = T_0 + \frac{-\Delta H_{rxn}(X)}{\Sigma \Theta_i C_{pi}}$ $\Sigma \Theta_i C_{pi} = 40$

Adiabatic $Ua = 0$ $\Delta H_{rxn} = -40 + -50 - -70$

$\Delta C_p = 0$ $= -20{,}000$

$$T = 450 + \frac{-(-20{,}000)(X)}{40}$$

$$T = 450 + 500X$$

→ Find W at $X = 0.8$

$$W = \frac{F_{A0}}{k_1 C_{A0} T_0} \int_0^{0.8} \frac{(1+\varepsilon X)(450+500X) \, dX}{(1-X) \exp\left(\frac{E}{R}\left(\frac{1}{450} - \frac{1}{450+500X}\right)\right)}$$

$$W = \frac{C_{A0} v_0}{k_1 C_{A0} T_0} \int_0^{0.8} \frac{(1+\varepsilon x)(450+500x)}{(1-X)\exp\left(\frac{E}{R}\left(\frac{1}{450} - \frac{1}{450+500x}\right)\right)} \, dx$$

$$W = \frac{20}{0.133(450)} \int_0^{0.8} \frac{(1+X)(450+500X)}{(1-X)\exp\left(\frac{31400}{8.314}\left(\frac{1}{450} - \frac{1}{450+500x}\right)\right)}$$

$$W = 0.3341 \, (129.087)$$

$W = 43.13$ Kg < 50 (catalyst max in PFR)

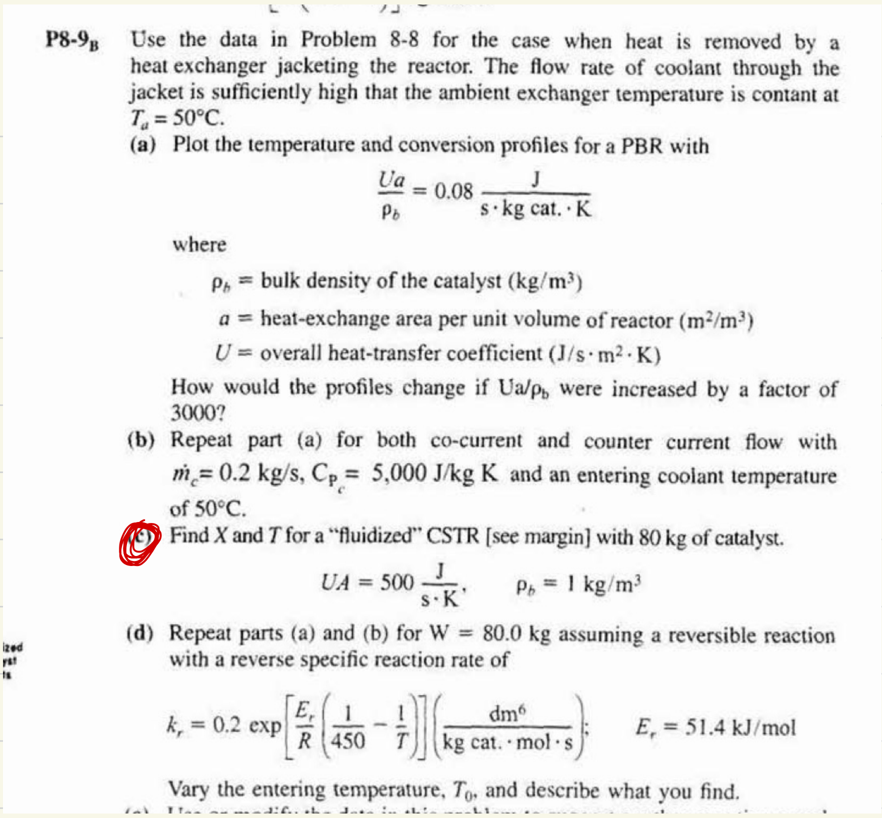
B) W_{CSTR}

$$W = \frac{F_{A0} X}{-r_A'}$$

$$W = \frac{C_{A0} v_0 X \quad (1+\varepsilon x)(450+500X)}{C_{A0}(1-X) \quad T_0 \quad k_1 \exp\left(\frac{E}{R}\left(\frac{1}{450} - \frac{1}{450+500X}\right)\right)}$$

$$W = \frac{20(0.8)\,(1+0.8)\,(450+500(0.8))}{(1-0.8)\,(450)\,(0.133)\,\exp\left(\frac{31400}{8.314}\left(\frac{1}{450} - \frac{1}{450+500x}\right)\right)}$$

$W = 39.39$ Kg



P8-9$_B$ Use the data in Problem 8-8 for the case when heat is removed by a heat exchanger jacketing the reactor. The flow rate of coolant through the jacket is sufficiently high that the ambient exchanger temperature is contant at $T_a = 50°C$.

(a) Plot the temperature and conversion profiles for a PBR with

$$\frac{Ua}{\rho_b} = 0.08 \frac{J}{s \cdot kg\ cat. \cdot K}$$

where

ρ_b = bulk density of the catalyst (kg/m³)

a = heat-exchange area per unit volume of reactor (m²/m³)

U = overall heat-transfer coefficient (J/s · m² · K)

How would the profiles change if Ua/ρ_b were increased by a factor of 3000?

(b) Repeat part (a) for both co-current and counter current flow with $\dot{m}_c = 0.2$ kg/s, $C_{P_c} = 5{,}000$ J/kg K and an entering coolant temperature of 50°C.

(c) Find X and T for a "fluidized" CSTR [see margin] with 80 kg of catalyst.

$$UA = 500 \frac{J}{s \cdot K}, \qquad \rho_b = 1\ kg/m^3$$

(d) Repeat parts (a) and (b) for W = 80.0 kg assuming a reversible reaction with a reverse specific reaction rate of

$$k_r = 0.2 \exp\left[\frac{E_r}{R}\left(\frac{1}{450} - \frac{1}{T}\right)\right]\left(\frac{dm^6}{kg\ cat. \cdot mol \cdot s}\right); \qquad E_r = 51.4\ kJ/mol$$

Vary the entering temperature, T_0, and describe what you find.

$T_a = 50°C$

↑ same equations as 8-8

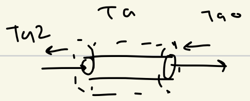
A)

$$\frac{dT}{dW} = \frac{r_A'(\Delta H_{rxn}) - \frac{Ua}{\rho_B}(T - T_a)}{F_{A0}(\Sigma \theta_i C_{P_i} + \Delta C_p X)}$$

B) co-current

$$\frac{dT_a}{dW} = \frac{\frac{Ua}{\rho_B}(T - T_a)}{\dot{m}_c C_{P_c}}$$

$\dot{m}_c = 0.2$ $\quad C_{P_c} = 5000$ $\quad T_a = 50$



counter-current

$$\frac{dT_a}{dW} = \frac{\frac{Ua}{\rho_B}(T_a - T)}{\dot{m}_c C_{P_c}}$$

$T_{a0} = T_a$ at Exit $W = 50$

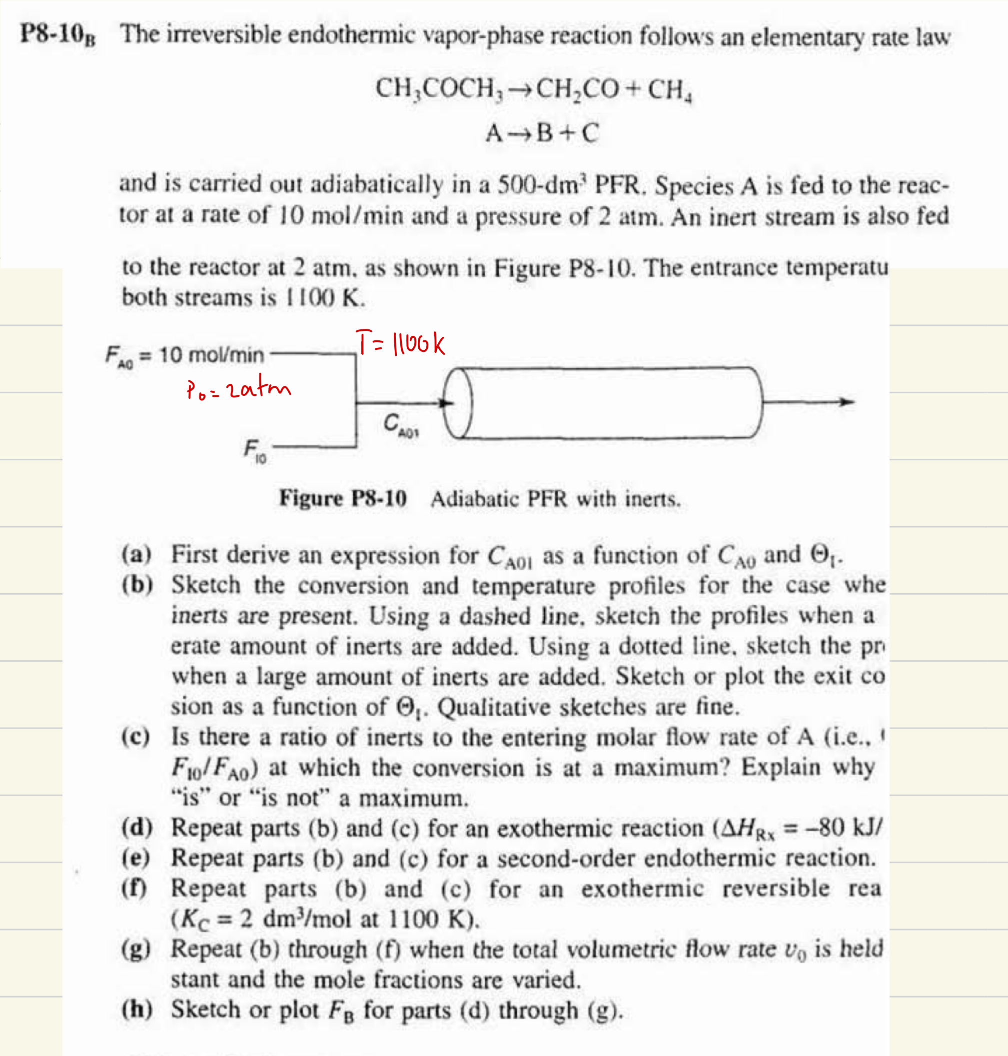
$T_a = 323$

$T_{a0} = 438.8$

C) W_{CSTR}

$$X_{MB} = \frac{\tau k}{1 + \tau k} \qquad \tau = \frac{\frac{W}{\rho_B} C_{A0}}{F_{A0}}$$

$$X_{EB} = \frac{\left[\left(\frac{Ua}{F_{A0}}\right)(T - T_a)\right] + \Sigma \theta_i C_{P_i}(T - T_a)}{-\Delta H_{rxn}} \qquad X_{MB} = X_{EB}$$



P8-10$_B$ The irreversible endothermic vapor-phase reaction follows an elementary rate law

$$CH_3COCH_3 \rightarrow CH_2CO + CH_4$$

$$A \rightarrow B + C$$

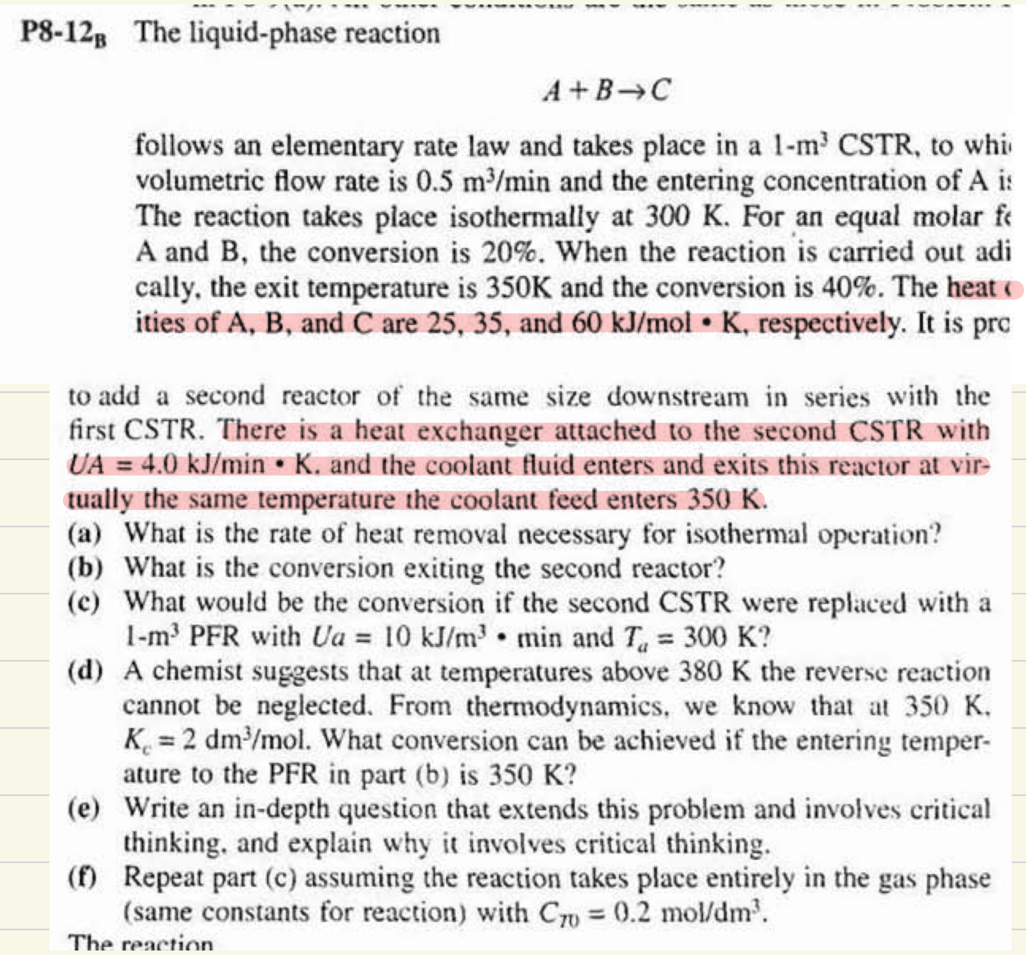
and is carried out adiabatically in a 500-dm^3 PFR. Species A is fed to the reactor at a rate of 10 mol/min and a pressure of 2 atm. An inert stream is also fed to the reactor at 2 atm, as shown in Figure P8-10. The entrance temperatu both streams is 1100 K.

Figure P8-10 Adiabatic PFR with inerts.

- (a) First derive an expression for C_{A01} as a function of C_{A0} and Θ_I.
- (b) Sketch the conversion and temperature profiles for the case whe inerts are present. Using a dashed line, sketch the profiles when a erate amount of inerts are added. Using a dotted line, sketch the pr when a large amount of inerts are added. Sketch or plot the exit co sion as a function of Θ_I. Qualitative sketches are fine.
- (c) Is there a ratio of inerts to the entering molar flow rate of A (i.e., F_{I0}/F_{A0}) at which the conversion is at a maximum? Explain why "is" or "is not" a maximum.
- (d) Repeat parts (b) and (c) for an exothermic reaction (ΔH_{Rx} = −80 kJ/
- (e) Repeat parts (b) and (c) for a second-order endothermic reaction.
- (f) Repeat parts (b) and (c) for an exothermic reversible rea (K_C = 2 dm^3/mol at 1100 K).
- (g) Repeat (b) through (f) when the total volumetric flow rate v_0 is held stant and the mole fractions are varied.
- (h) Sketch or plot F_B for parts (d) through (g).

c) when θ is low ⇒ keeps temp down ⇒ Favors endothermic reactions

D) maximum is at even lower θ because the reaction is now exothermic [no advantage to adding inerts & lowering the temp]



P8-12$_B$ The liquid-phase reaction

$$A + B \rightarrow C$$

follows an elementary rate law and takes place in a 1-m³ CSTR, to whi volumetric flow rate is 0.5 m³/min and the entering concentration of A i The reaction takes place isothermally at 300 K. For an equal molar fe A and B, the conversion is 20%. When the reaction is carried out adi cally, the exit temperature is 350K and the conversion is 40%. The heat c ities of A, B, and C are 25, 35, and 60 kJ/mol • K, respectively. It is pro to add a second reactor of the same size downstream in series with the first CSTR. There is a heat exchanger attached to the second CSTR with UA = 4.0 kJ/min • K. and the coolant fluid enters and exits this reactor at virtually the same temperature the coolant feed enters 350 K.

(a) What is the rate of heat removal necessary for isothermal operation?

(b) What is the conversion exiting the second reactor?

(c) What would be the conversion if the second CSTR were replaced with a 1-m³ PFR with Ua = 10 kJ/m³ • min and T_a = 300 K?

(d) A chemist suggests that at temperatures above 380 K the reverse reaction cannot be neglected. From thermodynamics, we know that at 350 K, K_c = 2 dm³/mol. What conversion can be achieved if the entering temperature to the PFR in part (b) is 350 K?

(e) Write an in-depth question that extends this problem and involves critical thinking, and explain why it involves critical thinking.

(f) Repeat part (c) assuming the reaction takes place entirely in the gas phase (same constants for reaction) with C_{T0} = 0.2 mol/dm³.

The reaction

$V_{CSTR} = 1 m^3$ $T = 300$

$v_0 = 0.5 m^3/min$ $C_A = 1000 mol/m^3$

isothermal, equimolar

$X = 0.2$

$T_0 = 300$

Adiabatically → $T = 350$

$X = 0.4$

A) Energy Balance

isothermal $T = T_0$

$$\frac{\dot{Q}}{F_{A0}} - \cancelto{0}{\frac{\dot{W}_s}{F_{A0}}} - X\left[\Delta H_R^\circ + \Delta C_p(\cancelto{0}{T - T_R})\right] = \cancelto{0}{\Sigma\Theta_i C_{p_i}(T - T_{i0})}$$

$\Delta C_p = 60 - 35 - 25 = 0$

$$\frac{\dot{Q}}{F_{A0}} - X[\Delta H_{rxn}] = 0$$

→ Find ΔH_{rxn} from Adiabatic

$\dot{Q} = 0$ $\dot{W}_s = 0$ $\Delta C_p = 0$

$$\cancelto{0}{\frac{\dot{Q}}{F_{A0}}} - \cancelto{0}{\frac{\dot{W}}{F_{A0}}} - X[\Delta H_{rxn}] = \Sigma\Theta_i C_{p_i}(T - T_0)$$

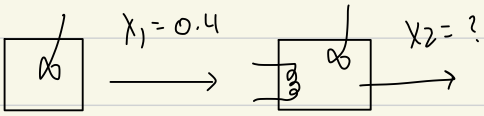
$$-(0.4)(\Delta H_{rxn}) = 1(25) + 1(35)\ (350 - 300)$$

$$\Delta H_{rxn} = -7500 \text{ kJ/mol}$$

$$\rightarrow \frac{\dot{Q}}{C_{A0}v_0} - X[\Delta H_{rxn}] = 0$$

$$\frac{\dot{Q}}{1000 \times 0.5} - (0.2)(-7500) = 0 \qquad \dot{Q} = -750{,}000 \text{ kJ/min}$$

B)



$V = 1 m^3$

$V = 1 m^3$

$UA = 4 kJ/min \cdot K$

$T_{a0} = 350 K$

Energy Balance

$$\frac{UA}{F_{A0}} - (X_2 - X_1)\Delta H_{rxn} = \Sigma \Theta_i C_{p_i}(T - T_0)$$

1. Mole Balance $\quad V = \frac{F_{A0}(X_2 - X_1)}{-r_A}$

2. Rate law $\quad -r_A = k C_A C_B \qquad k = k_1 \exp\left(\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$

3. Stoichiometry

$$\left.\begin{aligned} C_A &= C_{A0}(1-X) \\ C_B &= C_{A0}(1-X) \end{aligned}\right] \rightarrow \text{equimolar}$$

4. Combine $\quad -r_A = k\, C_{A0}^2 (1-X)^2$

$$V = \frac{F_{A0}(X_2 - X_1)}{k C_{A0}^2 (1-X_2)^2}$$

→ to find k from first Reactor (Isothermal & Adiabatic)

1. Mole Balance $\quad V = \frac{F_{A0} X_1}{k C_{A0}^2 (1-X_1)^2}$

$$k = \frac{F_{A0} X_1}{V C_{A0}^2 (1-X_1)^2}$$

1. Isothermal Reactor $X = 0.2$ $T = 300$

$$k = \frac{\cancel{C_{A0}} v_0 X_1}{V C_{A0}^{\cancel{2}} (1-X_1)^2} = \frac{0.5(0.2)}{1(1000)(1-0.2)^2} = 1.56 \times 10^{-4}$$

2. Adiabatic Reactor $X = 0.4$ $T = 350$

$$k = \frac{0.5(0.4)}{1(1000)(1-0.4)^2} = 5.55 \times 10^{-4}$$

→ Arrhenius Law $k(350) = k(300)\exp\left(\frac{E}{R}\left(\frac{1}{300} - \frac{1}{350}\right)\right)$

$$5.55\times10^{-4} = 1.56\times10^{-4}\exp\left[\frac{E}{R}\left(\frac{1}{300} - \frac{1}{350}\right)\right]$$

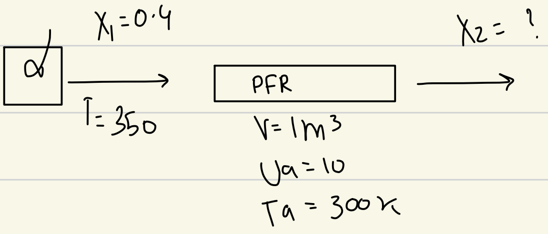
$$\frac{E}{R} = 2665.13$$

$$1 = \frac{\cancel{C_{A0}}\, v_0 (X_2 - X_1)}{5.55\times10^{-4}\exp\left(2265.13\left(\frac{1}{350} - \frac{1}{T}\right)\right) C_{A0}^{\cancel{2}} (1-X_2)^2}$$

$$1 = \frac{0.5(1000)(X_2 - 0.4)}{5.55\times10^{-4}\exp\left[2265.13\left(\frac{1}{350} - \frac{1}{T}\right)\right](1000)(1-X_2)^2}$$

↳ polymath solution $X = 0.423$

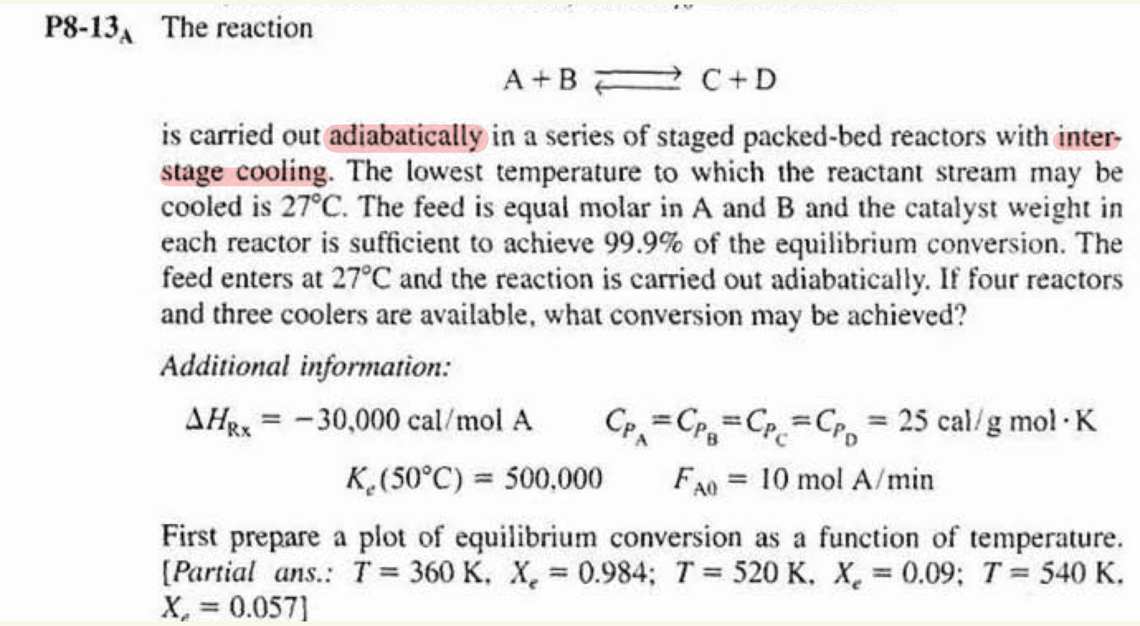
c) Second Reactor PFR



1 Mole Balance $\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$ $\quad \partial V = F_{A0}\int_{X_1}^{X_2} \frac{dX}{-r_A}$

⋮ Same as last ex.

Energy Balance $\frac{dT}{dV} = \frac{r_A \Delta H_{rxn} - Ua(T - Ta)}{F_{A0}(\Sigma \Theta_i C_{pi})}$



P8-13$_A$ The reaction

$$A + B \rightleftharpoons C + D$$

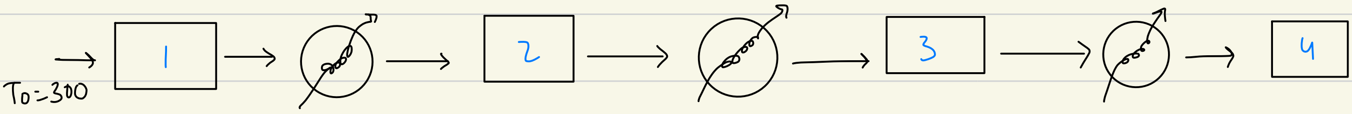
is carried out adiabatically in a series of staged packed-bed reactors with interstage cooling. The lowest temperature to which the reactant stream may be cooled is 27°C. The feed is equal molar in A and B and the catalyst weight in each reactor is sufficient to achieve 99.9% of the equilibrium conversion. The feed enters at 27°C and the reaction is carried out adiabatically. If four reactors and three coolers are available, what conversion may be achieved?

Additional information:

$\Delta H_{Rx} = -30{,}000$ cal/mol A $\qquad C_{P_A} = C_{P_B} = C_{P_C} = C_{P_D} = 25$ cal/g mol · K

$K_e(50°C) = 500{,}000 \qquad F_{A0} = 10$ mol A/min

First prepare a plot of equilibrium conversion as a function of temperature. [*Partial ans.:* $T = 360$ K, $X_e = 0.984$; $T = 520$ K, $X_e = 0.09$; $T = 540$ K, $X_e = 0.057$]

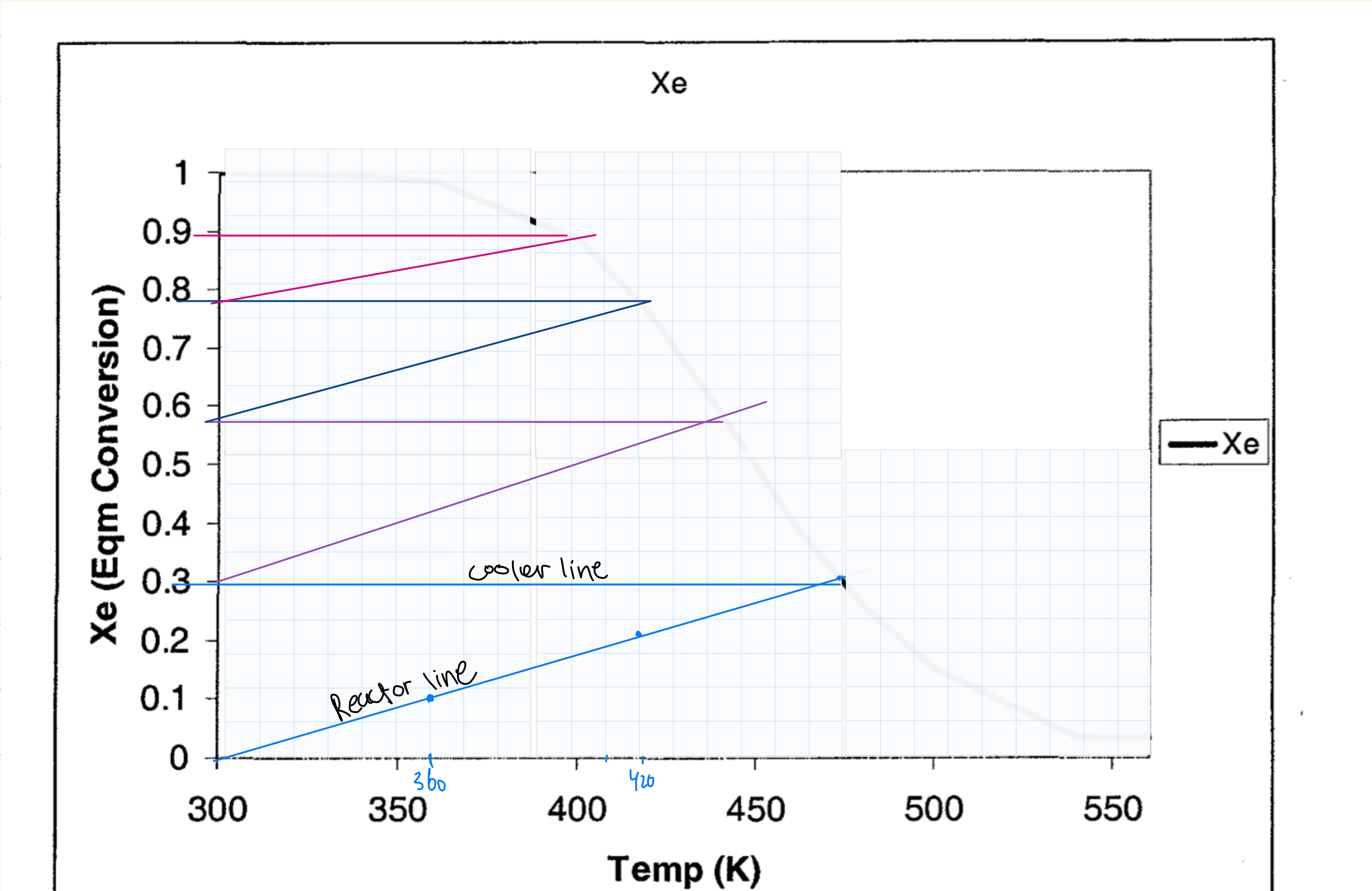


1. Energy Balance (Adiabatic)

$$T = T_0 + \frac{-\Delta H_{rxn}\ X}{\sum \theta_i C_{pi}}$$

$$T = 300 + \frac{-(-30{,}000)\ X}{25+25}$$

$$T = 300 + 600X$$



Reactor ①

$T = 300 + 600X$

$T = 300 + 600(0.1)$ $T = 360$

$T = 300 + 600(0.2)$ $T = 420$ $X = 0.3$

$T = 300 + 600(0.3)$ $T = 480$

Reactor ② $T = 300 + 600(0.3)$ $(T_2 - 300) = 600(X - 0)$

⋮ all 4 Reactors

$X_1 = 0.29$ $T_1 = 475$

$X_2 = 0\ 53$ $T_2 = 445$

$X_3 = 0.74$ $T_3 = 420$

$X_4 = 0\ 9$ $T_4 = 400$

→ to find W of the reactor (At X_1, T_1)

1. $W = \dfrac{F_{A0}\,X}{-r_A}$

2. $-r_A = K\left[C_A C_B - \dfrac{C_C C_D}{K_C}\right]$

$K = K_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$

$K_C = K_{C1} \exp\left[\frac{\Delta H_{Rx}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$

3. Stoichiometry

$C_A = C_{A0}(1 - X)$

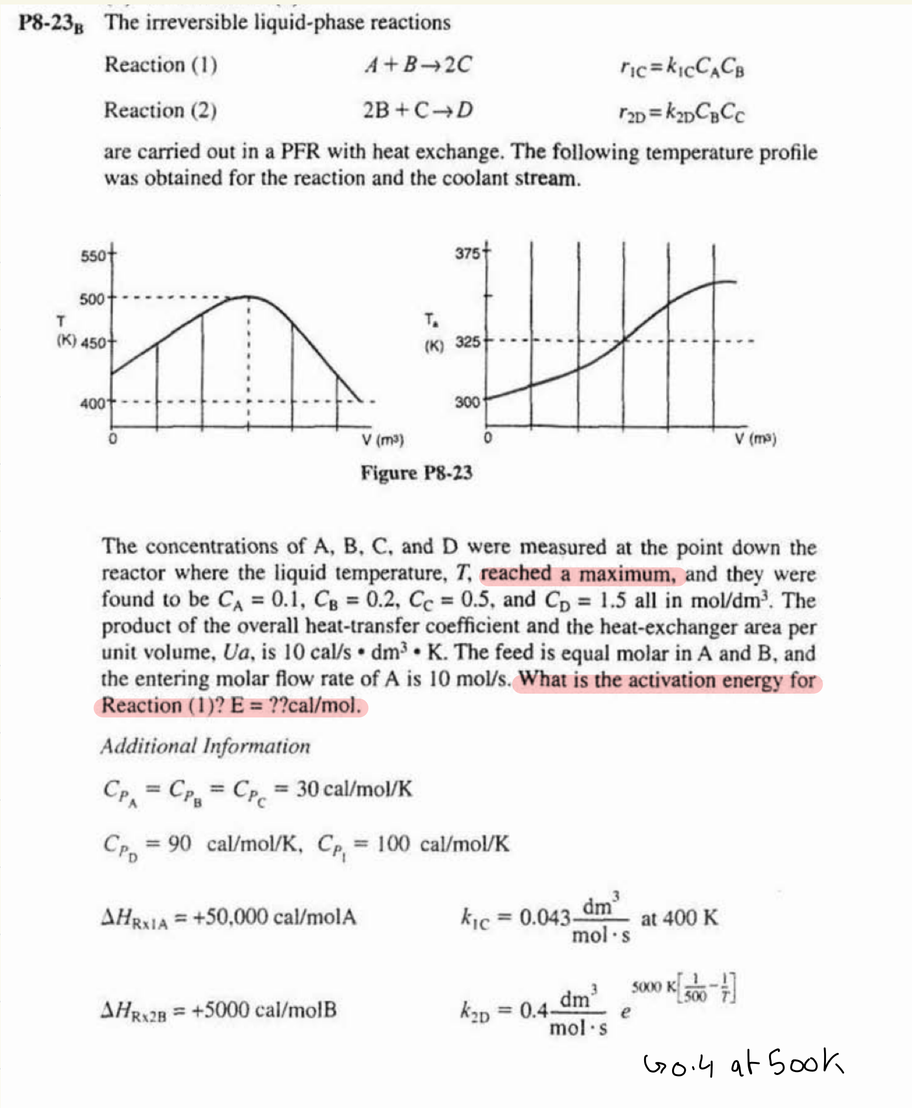
$C_B = C_{A0}(1 - X_1)$

$C_C = C_{A0} X_1$

$C_D = C_{A0} X_1$

⋮

all reactors



P8-23$_B$ The irreversible liquid-phase reactions

Reaction (1)	$A+B\rightarrow 2C$	$r_{1C}=k_{1C}C_AC_B$
Reaction (2)	$2B+C\rightarrow D$	$r_{2D}=k_{2D}C_BC_C$

are carried out in a PFR with heat exchange. The following temperature profile was obtained for the reaction and the coolant stream.

Figure P8-23

The concentrations of A, B, C, and D were measured at the point down the reactor where the liquid temperature, T, reached a maximum, and they were found to be $C_A = 0.1$, $C_B = 0.2$, $C_C = 0.5$, and $C_D = 1.5$ all in mol/dm³. The product of the overall heat-transfer coefficient and the heat-exchanger area per unit volume, Ua, is 10 cal/s • dm³ • K. The feed is equal molar in A and B, and the entering molar flow rate of A is 10 mol/s. What is the activation energy for Reaction (1)? E = ??cal/mol.

Additional Information

$C_{P_A} = C_{P_B} = C_{P_C} = 30$ cal/mol/K

$C_{P_D} = 90$ cal/mol/K, $C_{P_I} = 100$ cal/mol/K

$\Delta H_{Rx1A} = +50{,}000$ cal/molA $\qquad k_{1C} = 0.043\dfrac{dm^3}{mol\cdot s}$ at 400 K

$\Delta H_{Rx2B} = +5000$ cal/molB $\qquad k_{2D} = 0.4\dfrac{dm^3}{mol\cdot s}\,e^{5000\,K\left[\frac{1}{500}-\frac{1}{T}\right]}$

↳0.4 at 500K

Reaction 1 $\Delta Cp = 2(30) - 30 - 30 = 0$

Reaction 2 $\Delta Cp = 90 - 30 - 2(30) = 0$

Energy Balance $\dfrac{dT}{dV} = \dfrac{\Sigma r_{ij}\,\Delta H_{rxn} - Ua(T-Ta)}{\Sigma F_i C_{pi}}$

→ At maximum $\dfrac{dT}{dV} = 0 = \dfrac{r_{1C}(\Delta H_{rxn\,1C}) + r_{2D}(\Delta H_{rxn\,2D}) - Ua(T-Ta)}{\Sigma F_i C_{pi}}$

$0 = r_{1C}(\Delta H_{rxn\,1C}) + r_{2D}(\Delta H_{rxn\,2D}) - Ua(T-Ta)$

→ solve for r_{1C} $\quad 0 = r_{1C}(50000) + 0.4(0.2)(0.5)(5000) - 10(500-325)$

$r_{1C} = 0.039$

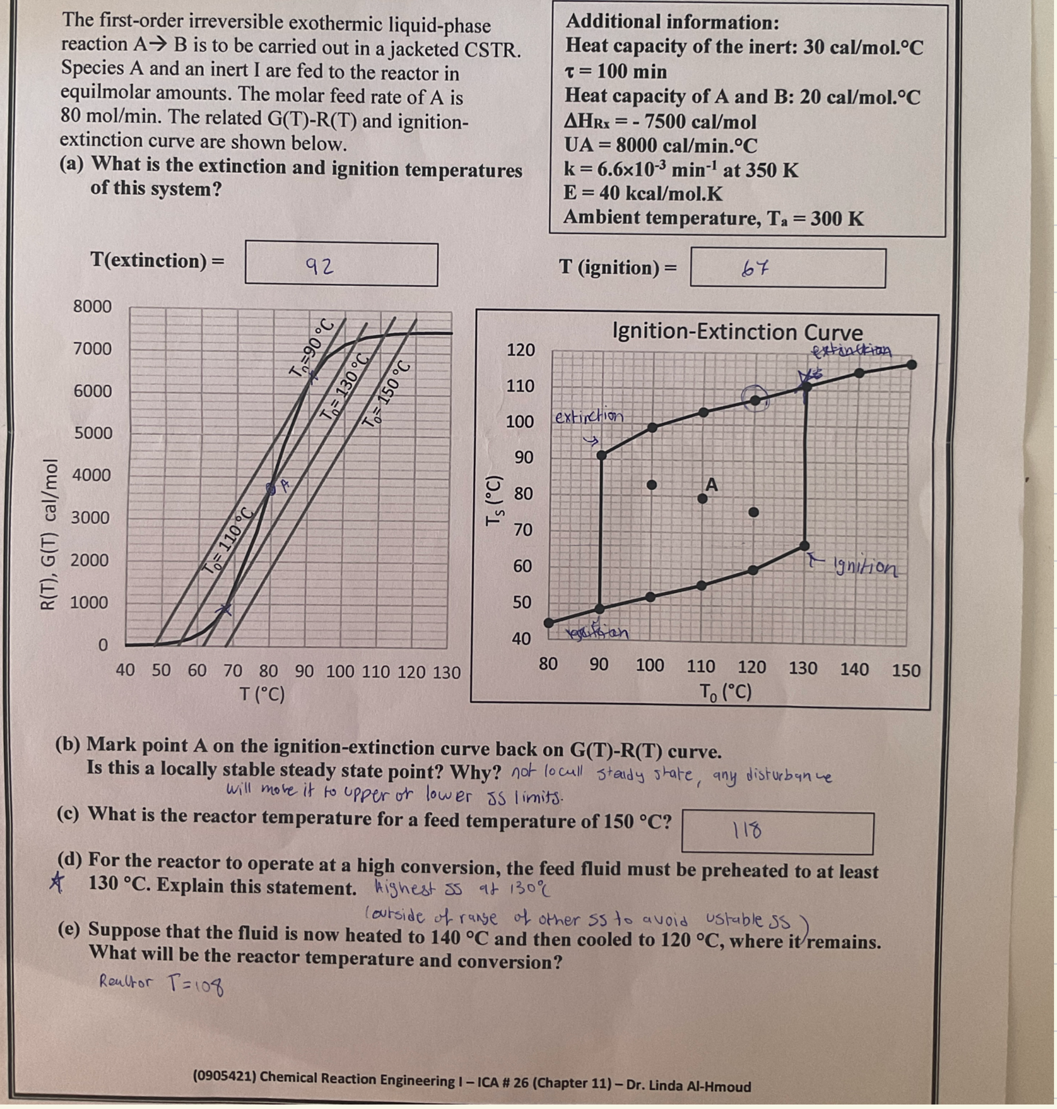
$r_K = k\,C_A C_B$

$0.039 = k\,(0.1)(0.2)$ $\quad\quad k = 1.95$ at 500K

$k(500) = k(400)\exp\left(\frac{E}{R}\left(\frac{1}{400} - \frac{1}{500}\right)\right)$

$\frac{E}{R} = 7628$ $\quad\quad R = 1.989$

$E = 15{,}172$



The first-order irreversible exothermic liquid-phase reaction A→ B is to be carried out in a jacketed CSTR. Species A and an inert I are fed to the reactor in equilmolar amounts. The molar feed rate of A is 80 mol/min. The related G(T)-R(T) and ignition-extinction curve are shown below.

(a) What is the extinction and ignition temperatures of this system?

Additional information:
Heat capacity of the inert: 30 cal/mol.°C
τ = 100 min
Heat capacity of A and B: 20 cal/mol.°C
ΔH_{Rx} = - 7500 cal/mol
UA = 8000 cal/min.°C
k = 6.6×10^{-3} min^{-1} at 350 K
E = 40 kcal/mol.K
Ambient temperature, T_a = 300 K

T(extinction) = 92

T (ignition) = 67

(b) Mark point A on the ignition-extinction curve back on G(T)-R(T) curve. Is this a locally stable steady state point? Why? not locull staidy state, any disturbance will move it to upper or lower SS limits.

(c) What is the reactor temperature for a feed temperature of 150 °C? 118

(d) For the reactor to operate at a high conversion, the feed fluid must be preheated to at least ☆ **130 °C. Explain this statement.** highest SS at 130°C (outside of range of other SS to avoid ustable SS)

(e) Suppose that the fluid is now heated to 140 °C and then cooled to 120 °C, where it remains. What will be the reactor temperature and conversion?

Reactor T=108

(0905421) Chemical Reaction Engineering I – ICA # 26 (Chapter 11) – Dr. Linda Al-Hmoud

E) T= 107°C ⇒ from plot

→ Conv:

1. $V = \frac{F_{A0}\,X}{-r_A}$

2. $-r_A = k C_A$

$k = k_1 \exp\left(\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$

3. $C_A = C_{A0}(1-X)$

$k = 6.6\times10^{-3} \exp\left[\frac{40000}{1.987}\left(\frac{1}{350} - \frac{1}{380}\right)\right]$

4. $V = \frac{F_{A0}\,X}{k\,C_{A0}(1-X)}$

$k = 0.6188$

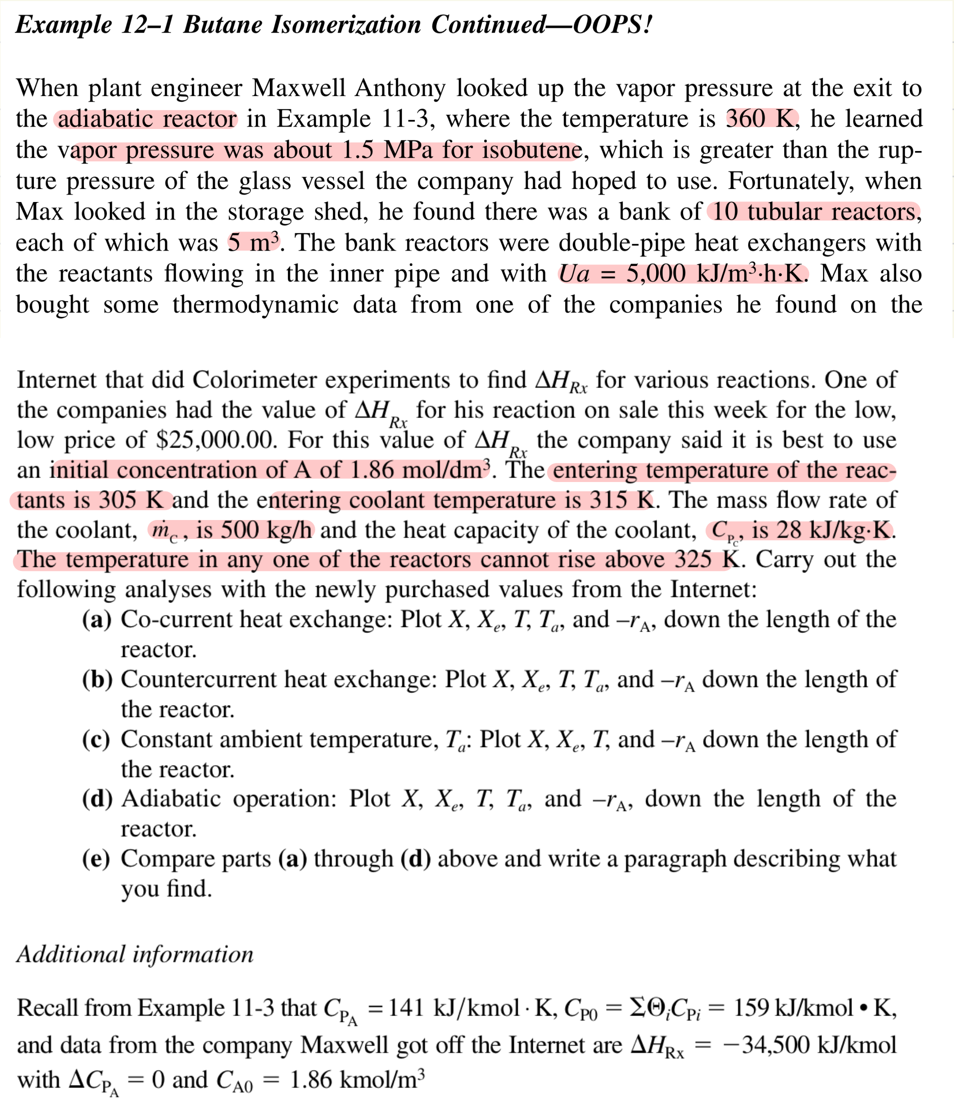
$V = \frac{\cancel{C_{A0}}\,v_0\,X}{k\,\cancel{C_{A0}}(1-X)}$

$\frac{V}{v_0} = \tau = \frac{X}{k(1-X)}$

$100 = \frac{X}{0.6188(1-X)}$

$X = 0.98$

Ch.12



Example 12–1 Butane Isomerization Continued—OOPS!

When plant engineer Maxwell Anthony looked up the vapor pressure at the exit to the adiabatic reactor in Example 11-3, where the temperature is 360 K, he learned the vapor pressure was about 1.5 MPa for isobutene, which is greater than the rupture pressure of the glass vessel the company had hoped to use. Fortunately, when Max looked in the storage shed, he found there was a bank of 10 tubular reactors, each of which was 5 m^3. The bank reactors were double-pipe heat exchangers with the reactants flowing in the inner pipe and with Ua = 5,000 kJ/m^3·h·K. Max also bought some thermodynamic data from one of the companies he found on the Internet that did Colorimeter experiments to find ΔH_{Rx} for various reactions. One of the companies had the value of ΔH_{Rx} for his reaction on sale this week for the low, low price of \$25,000.00. For this value of ΔH_{Rx} the company said it is best to use an initial concentration of A of 1.86 mol/dm^3. The entering temperature of the reactants is 305 K and the entering coolant temperature is 315 K. The mass flow rate of the coolant, $\dot{m}_c$, is 500 kg/h and the heat capacity of the coolant, C_{P_c}, is 28 kJ/kg·K. The temperature in any one of the reactors cannot rise above 325 K. Carry out the following analyses with the newly purchased values from the Internet:

- **(a)** Co-current heat exchange: Plot X, X_e, T, T_a, and $-r_A$, down the length of the reactor.
- **(b)** Countercurrent heat exchange: Plot X, X_e, T, T_a, and $-r_A$ down the length of the reactor.
- **(c)** Constant ambient temperature, T_a: Plot X, X_e, T, and $-r_A$ down the length of the reactor.
- **(d)** Adiabatic operation: Plot X, X_e, T, T_a, and $-r_A$, down the length of the reactor.
- **(e)** Compare parts **(a)** through **(d)** above and write a paragraph describing what you find.

Additional information

Recall from Example 11-3 that $C_{P_A} = 141$ kJ/kmol·K, $C_{P0} = \Sigma\Theta_i C_{Pi} = 159$ kJ/kmol • K, and data from the company Maxwell got off the Internet are $\Delta H_{Rx} = -34{,}500$ kJ/kmol with $\Delta C_{P_A} = 0$ and $C_{A0} = 1.86$ kmol/m^3

$A \rightleftharpoons B$

A) Co-current:

→ from last example $F_{A0} = 0.9(163) = \frac{146.7}{10 \text{ tubes}} = 14.67$ kmol/h

1. Mole Balance $\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$

2. Rate Law $-r_A = k\left[C_A - \frac{C_B}{K_C}\right]$

$k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$

$K_C = K_{C1} \exp\left[\frac{\Delta H_{Rx}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$

3. Stoichiometry $C_A = C_{A0}(1-X)$

$C_B = C_{A0}X$

4. Combine $-r_A = kC_{A0}\left[1 - \left(1 + \frac{1}{K_C}\right)X\right]$

$X_e = \frac{K_C}{1+K_C}$

$$\frac{dT}{dV} = \frac{r_A \Delta H_{rxn} - Ua(T-Ta)}{\sum F_i C_{pi}}$$

5. Energy Balance [co-current]

$$\frac{dTa}{dV} = \frac{Ua(T-Ta)}{\dot{m}_c C_{pc}}$$

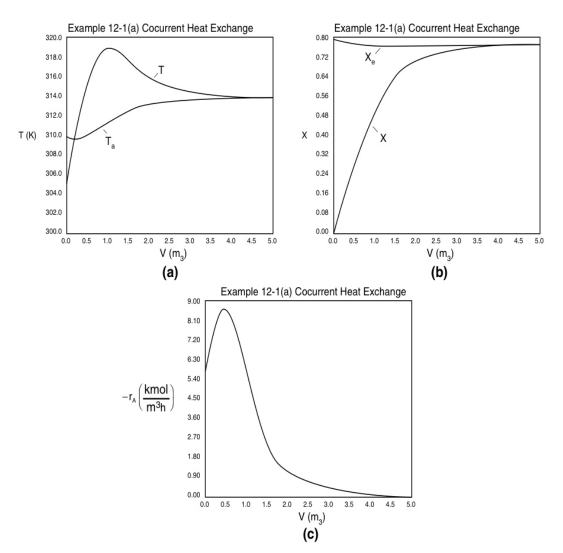


Figure E12-1.1 Profiles down the reactor for co-current heat exchange **(a)** temperature, **(b)** conversion, **(c)** reaction rate.

Analysis: Reactor temp goes through a maximum

Reactant concentrations are high ⇒ high reaction rate

Temp & conv ↑ as ↑V , Xe↓ as T↑

Reaction Rate becomes very small approaching equilibrium

when T & Ta are essentially equal , there is no longer a temp driving force to cool the reactor

B) counter-current

: same as before

:

5. Energy Balance [counter-current]

$$\frac{dTa}{dV} = \frac{Ua(Ta-T)}{\dot{m}_c C_{pc}}$$

Guess for Ta at V=0 so T = Ta

↳ at V = 5 (end) (final value Ta)

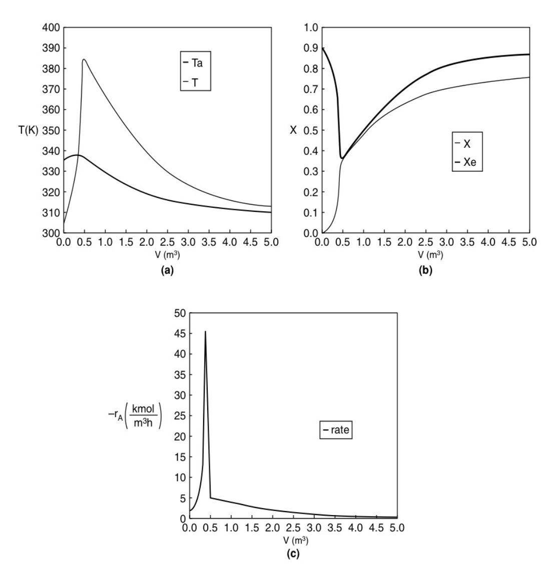


Figure E12-1.2 Profiles down the reactor for counter current heat exchange **(a)** temperature, **(b)** conversion, **(c)** reaction rate.

Near the enterance, Ta is higher than T

Reaction generates heat causing T to become higher than Ta

Xe reaches minimum near the enterance [X cannot increase above Xe]

→ Reactants are cooled & reactor T↓ allowing X & Xe to increase

Higher exit X & Xe in counter-current than in co-current

C) Constant Ta

5. Energy Balance

$$\frac{dT}{dV} = \frac{r_A \Delta H_{rxn} - Ua(T - Ta)}{F_{A0} C_{PA}}$$

$$\frac{dTa}{dV} = 0$$

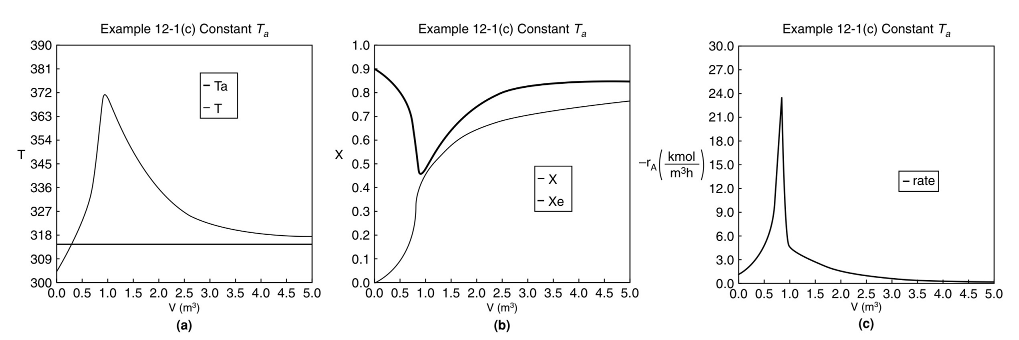


Figure E12-1.3 Profiles down the reactor for constant heat-exchange fluid temperature T_a; **(a)** temperature, **(b)** conversion, **(c)** reaction rate.

when coolant flowrate is sufficiently large ⇒ Ta is constant

if the reactor volume is sufficiently large ⇒ T will approach Ta

lowest exit temp ⇒ highest Xe

D) Adiabatic operation

$Ua = 0$ $\Delta Cp = 0$

$$\frac{dT}{dV} = \frac{r_A \Delta H_{rxn} - Ua(T - Ta)}{F_{A0} C_{PA}}$$

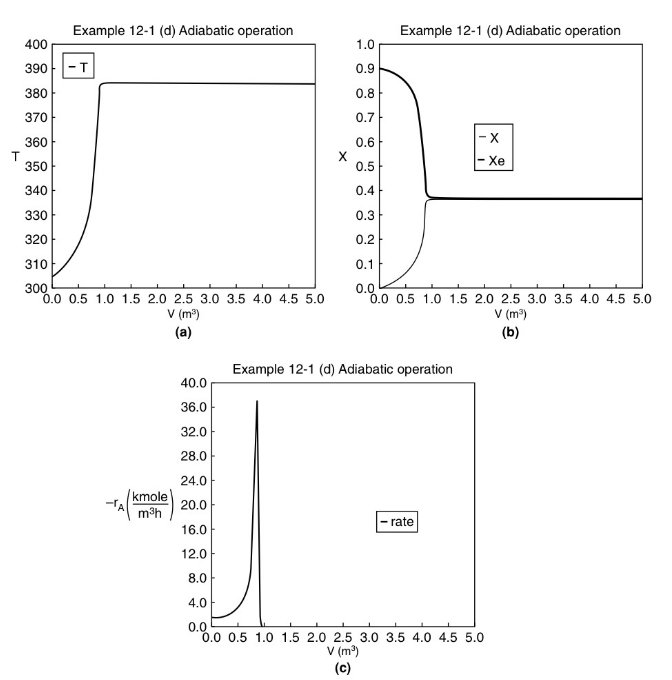


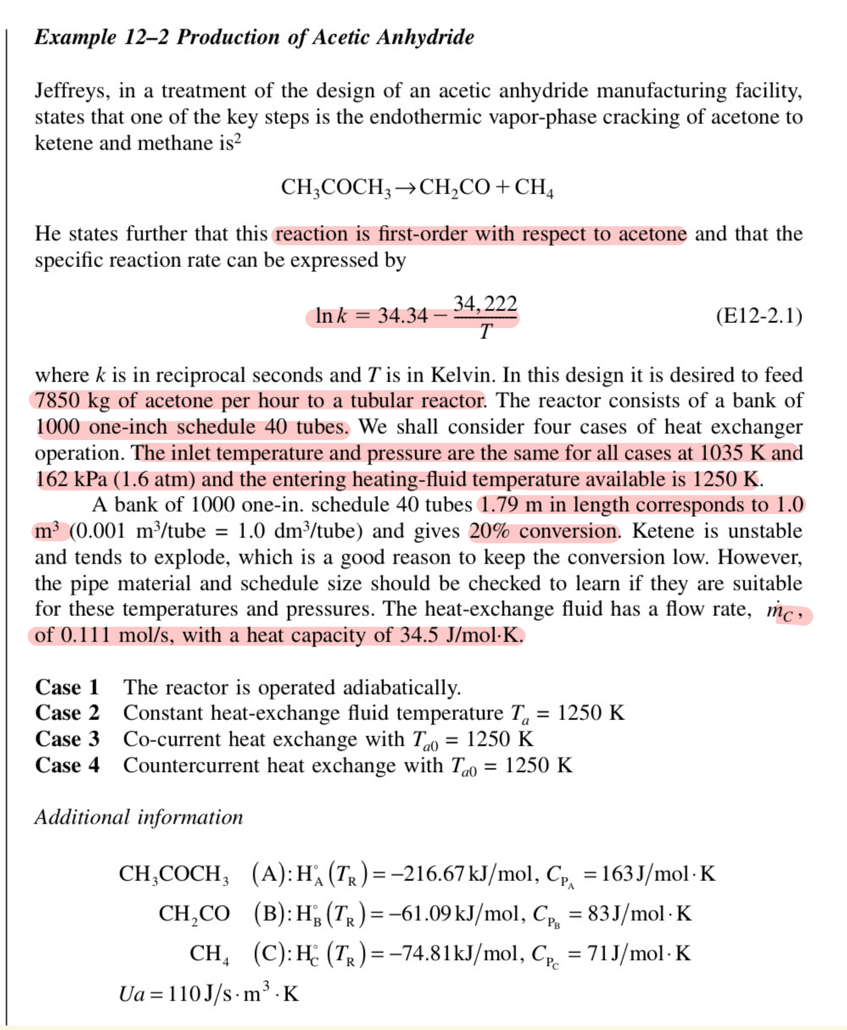
Figure E12-1.4 Profiles down the reactor for adiabatic reactor; **(a)** temperature, **(b)** conversion, **(c)** reaction rate.

Due to no cooling, Temp will keep increasing [Exo] until equilibrium is reached at $X = X_e = 0.365$ & $T = 384$

Xe decreases because T increases until $(X = Xe)$

There is no change in T at this point → reaction rate is zero

lowest X



Example 12–2 Production of Acetic Anhydride

Jeffreys, in a treatment of the design of an acetic anhydride manufacturing facility, states that one of the key steps is the endothermic vapor-phase cracking of acetone to ketene and methane is[2]

$$CH_3COCH_3 \rightarrow CH_2CO + CH_4$$

He states further that this reaction is first-order with respect to acetone and that the specific reaction rate can be expressed by

$$\ln k = 34.34 - \frac{34,222}{T} \tag{E12-2.1}$$

where k is in reciprocal seconds and T is in Kelvin. In this design it is desired to feed 7850 kg of acetone per hour to a tubular reactor. The reactor consists of a bank of 1000 one-inch schedule 40 tubes. We shall consider four cases of heat exchanger operation. The inlet temperature and pressure are the same for all cases at 1035 K and 162 kPa (1.6 atm) and the entering heating-fluid temperature available is 1250 K.

A bank of 1000 one-in. schedule 40 tubes 1.79 m in length corresponds to 1.0 m^3 (0.001 m^3/tube = 1.0 dm^3/tube) and gives 20% conversion. Ketene is unstable and tends to explode, which is a good reason to keep the conversion low. However, the pipe material and schedule size should be checked to learn if they are suitable for these temperatures and pressures. The heat-exchange fluid has a flow rate, $\dot{m}_C$, of 0.111 mol/s, with a heat capacity of 34.5 J/mol·K.

Case 1 The reactor is operated adiabatically.
Case 2 Constant heat-exchange fluid temperature T_a = 1250 K
Case 3 Co-current heat exchange with T_{a0} = 1250 K
Case 4 Countercurrent heat exchange with T_{a0} = 1250 K

Additional information

CH_3COCH_3 (A): $H_A^\circ(T_R) = -216.67$ kJ/mol, $C_{P_A} = 163$ J/mol·K
CH_2CO (B): $H_B^\circ(T_R) = -61.09$ kJ/mol, $C_{P_B} = 83$ J/mol·K
CH_4 (C): $H_C^\circ(T_R) = -74.81$ kJ/mol, $C_{P_C} = 71$ J/mol·K
$Ua = 110$ J/s·m^3·K

$A \rightarrow B + C$

1. Mole Balance $\qquad \frac{dX}{dV} = \frac{-r_A}{F_{A0}}$

2. Rate law $\qquad -r_A = KC_A$

$$-r_A = \exp\left(34.34 - \frac{34222}{T}\right) C_A$$

3. Stoichiometry

Gas phase, no ΔP

$$C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)} \frac{T_0}{T}$$

$\varepsilon = y_{A0}\delta$
$\delta = 1+1-1 = 1$
$\varepsilon = 1(1) = 1$

4. Combine

$$-r_A = 8.2\times10^{14} \exp\left(\frac{-34,222}{T}\right) \frac{C_{A0}(1-X)}{(1+X)} \frac{T}{T_0}$$

5. Energy Balance

i) Co-current

$$\frac{dT_a}{dV} = \frac{Ua(T-T_a)}{\dot{m}_c C_{P_c}}$$

$$\frac{dT}{dV} = \frac{r_A(DH_{rxn}) - Ua(T-T_a)}{F_{A0} \sum \Theta_i C_{P_i} + X \Delta C_p}$$

6. Evaluation of parameters (mole Balance)

→ $F_{A0} = \frac{7850\ \text{kg}}{\text{h}} \times \frac{\text{kmol}}{58\ \text{kg}} = 135.35\ \text{kmol/h} = 0.0376\ \text{mol/s}$

$\frac{135.35}{1000\ \text{tube}} = 0.135\ \text{kmol/h}$

→ $C_{A0} = \frac{P}{RT} = \frac{1.6\ \text{atm}}{1035\ \text{K}} \left| \frac{\text{K} \cdot \text{kmol}}{0.08206\ \text{m}^3 \cdot \text{atm}} \right. = 0.0188\ \text{kmol/m}^3 = 18.8\ \text{mol/m}^3$

→ $v_0 = \frac{F_{A0}}{C_{A0}} = \frac{0.0376}{18.8} = 2\times10^{-3}\ \text{m}^3/\text{s} = 2\ \text{dm}^3/\text{s}$

(Energy Balance)

$DH_{rxn} = -74.81 + -61.09 - (-216.67) = 80.77\ \text{kJ/mol}$

$\Delta C_p = 71 - 83 + 163 = -9\ \text{J/mol} \cdot \text{K}$

(Heat Exchange)

$a = \frac{4}{D} = \frac{4}{0.0266} = 150\ \text{m}^{-1}$

$U = 110\ \text{J/sm}^2 \cdot \text{K} \times 150\ \text{m}^{-1} = 16500\ \text{J/sm}^3 \cdot \text{K}$

case 1 : Adiabatic

$U_a = 0$ $\Delta C_p = 0$

$$\frac{dT}{dV} = \frac{r_A \, \Delta H_{rxn}}{F_{A0} \left(\Sigma \theta_i C_{pi} \right)}$$

$$\frac{dT_a}{dV} = \frac{U_a \left(T - T_a \right)}{\dot{m}_c \, C_{pc}}$$

case 2 : Constant Ta

$$\frac{dT_a}{dV} = 0$$

$$\frac{dT}{dV} = \frac{r_A \, \Delta H_{rxn} - U_a \left(T - T_a \right)}{F_{A0} \left(\Sigma \theta_i C_{pi} + \Delta C_p X \right)}$$

case 3 : co-current

$$\frac{dT}{dV} = \frac{r_A \, \Delta H_{rxn} - U_a \left(T - T_a \right)}{F_{A0} \left(\Sigma \theta_i C_{pi} + \Delta C_p X \right)}$$

$$\frac{dT_a}{dV} = \frac{U_a \left(T - T_a \right)}{C_{pc} \, \dot{m}_c}$$

case 4 : counter - current

$$\frac{dT}{dV} = \frac{r_A \, \Delta H_{rxn} - U_a \left(T - T_a \right)}{F_{A0} \left(\Sigma \theta_i C_{pi} + \Delta C_p X \right)}$$

$$\frac{dT_a}{dV} = \frac{U_a \left(T_a - T \right)}{C_{pc} \, \dot{m}_c}$$

Guess for T_a $(V = 0)$

Ex 12-3

12-4