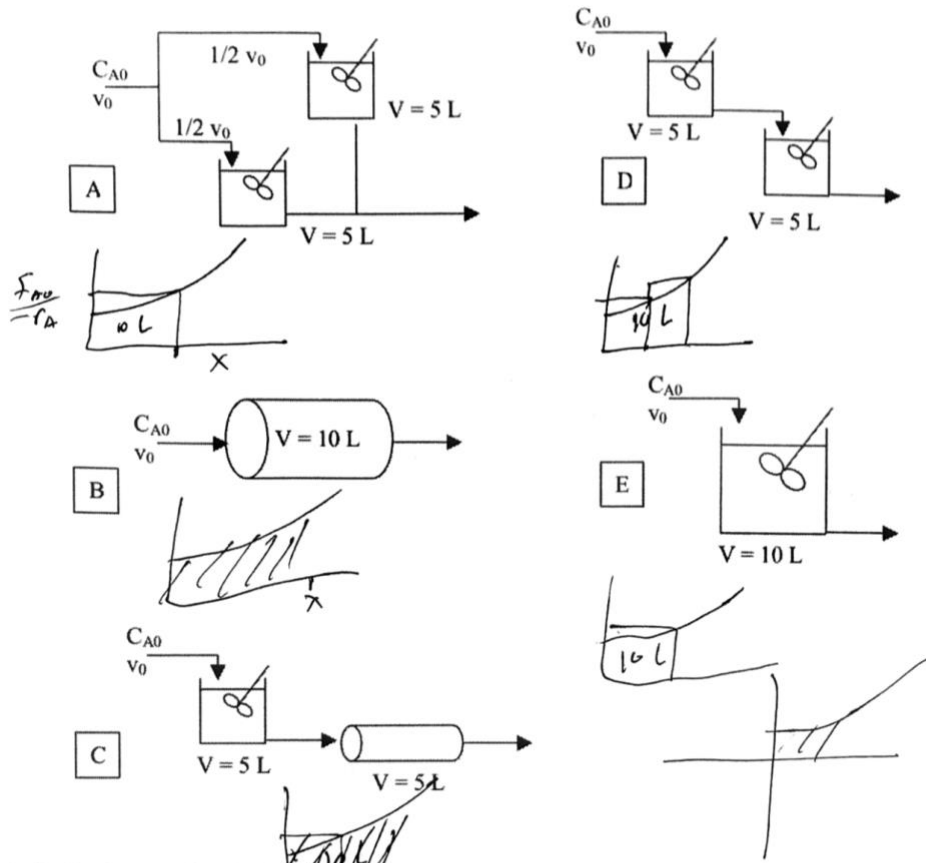


Problem 1 (25 points)

- a) (10 points) Rank the following reactor configurations in order of conversion from highest to lowest (ties are not impossible) when a 1st order, isothermal, isobaric, liquid-phase reaction is considered at steady-state.

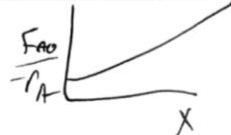


Write final answer in this box

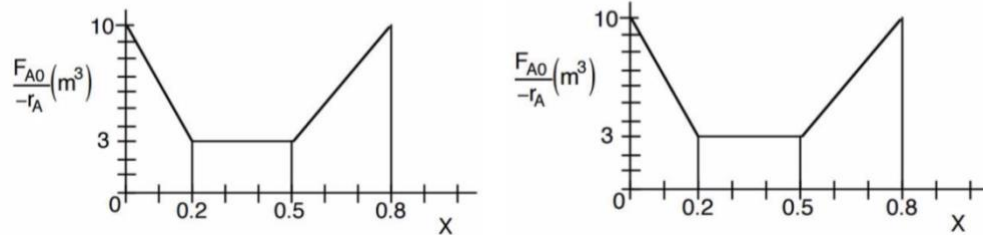
Ultimately: PFR > max of PFR/CSTR > CSTRs in series > CSTR = CSTR in parallel

B > C > D > A = E

for the kinetics following



- b) (15 points) Consider the following (identical) Levenspiel plots for the reaction $A \rightarrow B$. Assume the reactor feed is pure A and that operation is isothermal, isobaric, liquid-phase and at steady-state. Duplicate plots are provided to help you when solving the problem.



- 3 points i. At which conversion(s) (X) is the volume of a single CSTR **less** than a single PFR? Select all answers that apply:

- a) 0.2 b) 0.5
c) 0.7 d) 0.8

From the plot, we see the y-axis is $\frac{F_{A0}}{-r_A}$ and the x-axis is conversion (X).

For a PFR, the differential form of the PFR mole balance is $F_{A0} \frac{dX}{dV} = -r_A$, and the integral form is $V = F_{A0} \int_0^X \frac{dX}{-r_A}$

For a CSTR, we will use $V = \frac{F_{A0}X}{-r_A} = \frac{F_{A0}(X_2 - X_1)}{-r_A}$

Thus, the volume of a PFR is simply the area under the Levenspiel plot. CSTR volume is a rectangular area whose width is the conversion and height is the point on the Levenspiel plot where $x = X_{final}$. Recall that CSTR reaction rate depends on exit concentration (exit conversion).

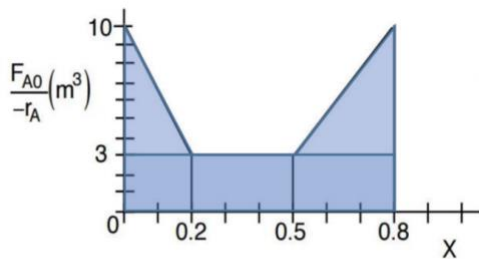


Figure 1: PFR Volumes

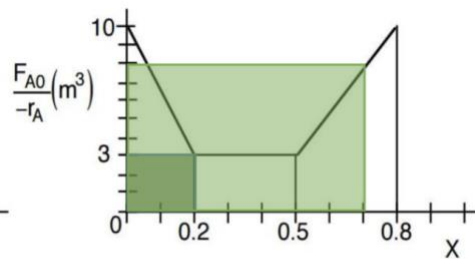


Figure 2: CSTR Volumes at $X = 0.2$ (dark green) and $X = 0.7$ (light green)

From $X = 0$ to $X = 0.2$, CSTR volume (dark green rectangle) is less than the volume for a PFR. From $X = 0.2$ to $X = 0.5$, the additional volume for both a CSTR and PFR is the same (middle rectangle), so the total volume of a CSTR from $X = 0$ to 0.5 is less than a PFR.

3 points ii. At which conversion(s) (X) is the volume of a single PFR **less** than a single CSTR?
Select all answers that apply:

- a) 0.2 b) 0.5
c) 0.7 **d) 0.8**

From X = 0 to X = 0.7, we see from Figure 2 (CSTR) that the rectangle area is greater than the area under the curve in Figure 1 (PFR). Therefore, the volume of a single PFR is less than a single CSTR for X = 0.7 and, by identical reasoning, for X= 0.8

4 points iii. Calculate the difference in volume of a CSTR and a PFR used for this reaction to bring conversion from X = 0 to 0.4. Which reactor is smaller?

From X range from 0 to 0.4,

$$\text{CSTR: } V = \left(\frac{F_{A0}}{-r_A}\right) X = \left(\frac{F_{A0}}{-r_A}\right) (X_{\text{final}}) = (3) * 0.4 = 1.2 \text{ m}^3 \quad (\text{determined graphically})$$

$$\text{PFR: } V = F_{A0} \int_0^{0.4} \frac{dX}{-r_A} \quad (\text{determine graphically})$$

To determine volume, find area under curve for the given range of X from 0 to 0.4,

$$V = (0.4 - 0.2)(3) + \frac{(3 + 10) * 0.2}{2} = 1.9 \text{ m}^3$$

Thus, CSTR volume is smaller

$$\text{PFR volume} - \text{CSTR volume} = 1.9 - 1.2 = 0.7 \text{ m}^3$$

5 points iv. Propose a reactor configuration that minimizes the number of reactors and their volumes while achieving 80% conversion. State the number, volume of each, type, and order of reactors you would choose.

Two possible arrangements are possible if we only want to use two reactors

1) CSTR (X range: 0 – 0.5, volume = 1.5 m³) ; PFR (X range: 0.5 – 0.8, volume = 1.95 m³)

2) CSTR (X range: 0 – 0.2, volume = 0.6 m³) ; PFR (X range: 0.2 – 0.8, volume = 2.85 m³)

Two more possible arrangements are possible if we want to use three reactors

1) CSTR (X range: 0 – 0.2, volume = 0.6 m³) ; PFR (X range: 0.2 – 0.5, volume = 0.9 m³);

PFR (X range: 0.5 – 0.8, volume = 1.95 m³)

2) CSTR (X range: 0 – 0.2, volume = 0.6 m³) ; CSTR (X range: 0.2 – 0.5, volume =

0.9 m³) ; PFR (X range: 0.5 – 0.8, volume = 1.95 m³)

We would normally choose one of the arrangements involving 2 reactors for economic reasons pertaining to fixed costs (it is very costly add additional reactors; more reactors means more instrumentation, piping, valves, etc).

Problem: Lobree et al. published a paper in 1998 describing how methane reduces supported Pd ions on ZSM-5 zeolites into Pd product. We provide a simplified mechanism in terms of letters below:

Elementary Steps	Rate constants	σ
$A + CH_4 \leftrightarrow B + H_2O$	k_1, k_{-1}	
$B \rightarrow 2C$	k_2	
$C \rightarrow D + CO$	k_3	
$2D \rightarrow 2E + Pd$	k_4	

The overall reaction stoichiometry is as follows: $A + CH_4 \rightarrow 2E + Pd + 2CO + H_2O$
 Assume all intermediates are reactive intermediates.

- a. Derive the rate law expression for the formation of Pd in terms of reactants and products. Also find the stoichiometric number for each step.

Elementary Steps	Stoichiometric number	Rates
$A + CH_4 \leftrightarrow B + H_2O$	1	$r_1 = k_1[A][CH_4]$ $r_{-1} = k_{-1}[B][H_2O]$
$B \rightarrow 2C$	1	$r_2 = k_2[B]$
$C \rightarrow D + CO$	2	$r_3 = k_3[C]$
$2D \rightarrow 2E + Pd$	1	$r_4 = k_4[D]^2$

Rate of Pd formation = $r_4 = k_4[D]^2$

PSSH on $[D]^2$

$$r_D \approx 0 = r_3 - 2r_4 = k_3[C] - 2k_4[D]^2$$

$$2k_4[D]^2 = k_3[C]$$

PSSH on $[C]$

$$r_C \approx 0 = 2r_2 - r_3 = 2k_2[B] - k_3[C]$$

$$k_3[C] = 2k_2[B]$$

PSSH on $[B]$

$$r_B \approx 0 = r_1 - r_{-1} - r_2 = k_1[A][CH_4] - k_{-1}[B][H_2O] - k_2[B]$$

$$[B] = \frac{k_1[A][CH_4]}{k_{-1}[H_2O] + k_2}$$

$$\text{Rate of Pd formation} = r_4 = k_4[D]^2 = 0.5k_3[C] = k_2[B] = \frac{k_1k_2[A][CH_4]}{k_{-1}[H_2O] + k_2}$$

+1 for each stoichiometric number (+4)

- +2 for doing a PSSH on intermediate C
- +2 for doing a PSSH on intermediate D (accept D²)
- +2 for PSSH on intermediate B
- +2 for correct rate of Pd formation

b. Using your result in part a, find the rate of formation of CO in terms of reactants and products.

Overall reaction is:



$$\text{Net rate } r = \frac{r_4}{1} = \frac{r_{CO}}{2} = \frac{k_1 k_2 [A][CH_4]}{k_{-1}[H_2O] + k_2}$$

$$r_{CO} = \frac{2k_1 k_2 [A][CH_4]}{k_{-1}[H_2O] + k_2}$$

- +2 for correctly using stoichiometry to say rate of CO is half that of net rate
- +2 for correct rate of formation of CO

c. Derive the Pd rate of formation expression if step 1 is QE.

If step 1 is QE, $r_1 = r_{-1}$, $k_1[A][CH_4] = k_{-1}[B][H_2O]$

$$[B] = \frac{k_1[A][CH_4]}{k_{-1}[H_2O]}$$

$$\text{rate of Pd formation} = \frac{k_1 k_2 [A][CH_4]}{k_{-1}[H_2O]}$$

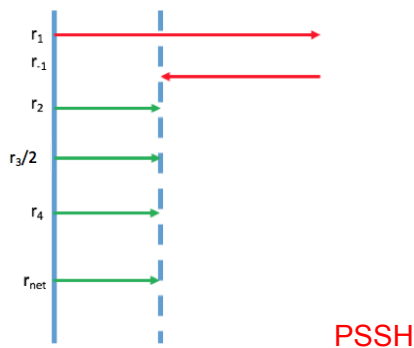
- +1 for saying $r_1 = r_{-1}$
- +2 for getting expression for concentration of B
- +2 for final rate of Pd formation

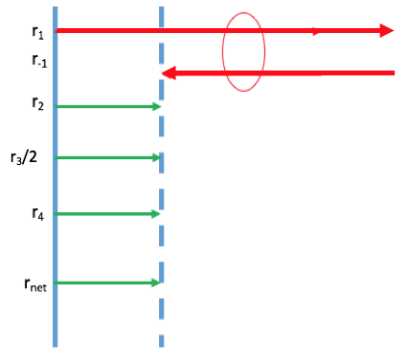
d. Under what conditions does your solution for part a collapse into your solution for part c? This is a rigorous justification for QEA. Draw a rate diagram for the PSSH and QEA cases and provide a specific inequality.

+2 for the inequality

+1 for each rate arrow diagram (+2)

This condition holds when $k_{-1}[H_2O] \gg k_2$

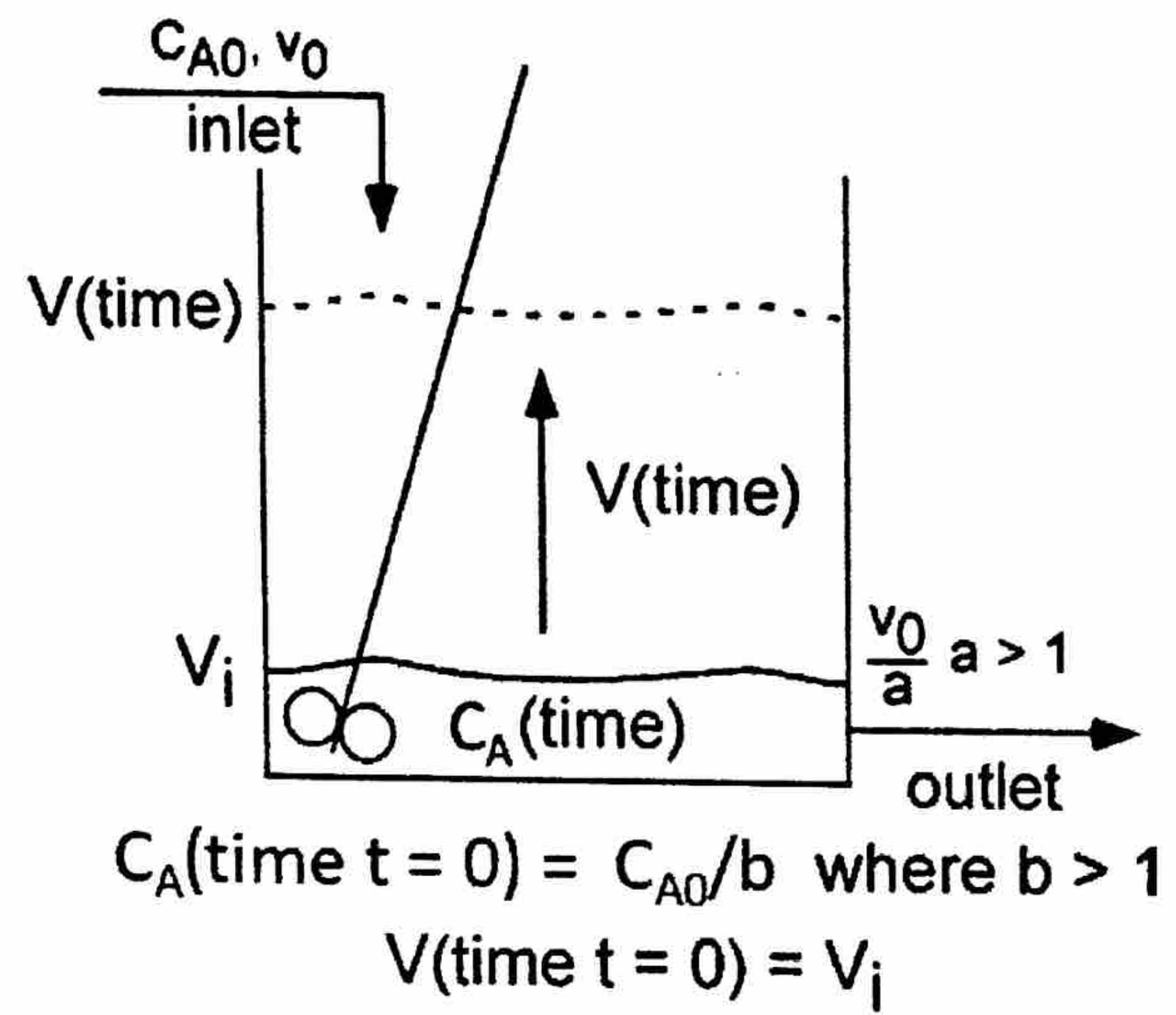




QEA

KEY

Problem 3 (25 points)



Consider the start-up of an ideal isothermal CSTR reactor. The vessel initially contains a solution of dye with a concentration, C_{A0}/b , where b is a constant that is greater than 1, and a volume V_i . Both inlet and outlet ports are turned on at time $t=0$. The inlet port flows with a volumetric flow rate, v_0 , and a concentration, C_{A0} . The outlet port flows with a volumetric flowrate v_0/a , where a is a constant that is greater than 1. Assume that the reactor vessel is large enough that it does not overflow in the timescale with which we are concerned.

a) (5 points) Write an expression for the reactor volume as a function of time, $V(t)$.

$$V = V_i + (v_0 - v) \cdot t$$

$$V = V_i + v_0 \left(1 - \frac{1}{a}\right) t$$

From mass balance

in - out = accumulation

$$\textcircled{1} \quad \rho_0 \cdot v_0 - \rho \cdot v = \frac{dm_{\text{Total}}}{dt}$$

$$\text{"} \quad \quad \quad = \frac{d(\rho \cdot V)}{dt}$$

$\textcircled{2}$ liquid phase, $\rho_0 = \rho$, $v = \frac{v_0}{a}$

$$\left(v_0 - \frac{v_0}{a}\right) = \frac{dV}{dt}$$

$$\textcircled{3} \quad \int_0^t dt = \int_{V_i}^V dV$$

$$V = V_i + v_0 \left(1 - \frac{1}{a}\right) t$$

Grading:

- +5 correct answer.
- OR:
- +1 for mass bal. $\textcircled{1}$
- +1 for assume ρ constant
- +1 trying to integrate mass balance

b) (10 points) Derive an expression for the change in concentration of A in the reactor over time, dC_A/dt , as a function of C_A , t and constants given in the problem statement.

$$\text{in} - \text{out} + \text{gen} = \text{accum.}$$

$$\textcircled{1} \quad \begin{matrix} \bar{F}_{A0} - F_A + 0 \\ \text{(no rxn)} \end{matrix} = \frac{dN_A}{dt} \quad \left[= \right] \frac{\text{mol}}{t} \quad \left. \vphantom{\frac{dN_A}{dt}} \right\}$$

$$\textcircled{2} \quad N_A = C_A \cdot V + 1$$

$$\textcircled{4} \quad (C_{A0} \cdot v_0 - C_A \cdot v) = \frac{d(C_A \cdot V)}{dt}$$

$$\textcircled{3} \quad \left. \begin{matrix} F_A = C_A \cdot v \\ F_{A0} = C_{A0} \cdot v_0 \end{matrix} \right\} + 1$$

$$\textcircled{5} \quad (\quad) = V \frac{dC_A}{dt} + C_A \frac{dV}{dt} + 1$$

$\textcircled{6}$ Substitute $v = \frac{v_0}{a}$, $\frac{dV}{dt} = v_0 - v$ into $\textcircled{5}$

$$C_{A0} v_0 - C_A \frac{v_0}{a} = V \cdot \frac{dC_A}{dt} + C_A (v_0 - \frac{v_0}{a})$$

$$\frac{1}{V} \left[C_{A0} v_0 - C_A \frac{v_0}{a} - C_A (v_0 - \frac{v_0}{a}) \right] = \frac{dC_A}{dt}$$

$$\frac{v_0}{V} \left[C_{A0} - \cancel{\frac{C_A}{a}} - C_A + \cancel{\frac{C_A}{a}} \right] = \frac{dC_A}{dt}$$

Partial credit:

+3 for balance $\textcircled{1}$

+1 for $N_A = C_A \cdot V$

+1 for $F_A = C_A \cdot v$

+1 for $\frac{d(C_A V)}{dt}$ $\textcircled{5}$

~~rule~~ product rule

$$\boxed{\frac{v_0 \cdot (C_{A0} - C_A)}{V_i + v_0(1 - 1/a) \cdot t} = \frac{dC_A}{dt}}$$

Full credit,
+10 pts

-2 if includes v , V or other non-constants, or algebra error.

grading

- +5 correct sign + explanation
- +4 correct sign + $C_{A0} > C_{A0/b}$ but no physical explanation
- +3 correct sign + partially correct explanation
- +1 correct sign, incorrect explanation.

c) (5 points) What is the sign of dC_A/dt ? Explain why in 1 sentence.

~~(+2 $dC_A/dt > 0$)~~
~~(+3 AND good physical explanation OR)~~
~~(+2 mathematical negativity without explanation.)~~

Sign is positive because inlet concentration C_{A0} is larger than initial tank concentration $C_{A0/b}$, so $(C_{A0} - C_A)$ is always positive. Tank conc. continuously increases approaching $C_A = C_{A0}$.

d) (5 points) Now assume that A can undergo an irreversible, monomolecular rearrangement to B with rate k_1 . Write an expression for dC_A/dt for this case.

Adjust approach in part b):

$$F_{A0} - F_A - k_1 C_A \cdot V = \frac{dN_A}{dt}$$

Partial credit:

+2 for balance with $k_1 C_A V$ term with negative sign.

Full credit: adjust answer from part b):

$$\boxed{\frac{V_0 (C_{A0} - C_A)}{V_i + V_0(1 - \alpha)t} - k_1 C_A = \frac{dC_A}{dt}} + 5 \text{ pts}$$

no credit for $(-k_1 C_A)$

a) $N_{T0} = 2N_{A0}$ Force balance : $(z_0 = P_0 \cdot A_c)$

I & L: $P_0 V_0 = N_{T0} R T_0 \Rightarrow V_0 =$

$$P_0 = \frac{C \cdot z_0}{A_c}$$

$$\frac{C \cdot z_0}{A_c} (z_0 \cdot A_c) = 2N_{A0} R T_0$$

$$V_0 = z_0 \cdot A_c$$

$$\Rightarrow z_0 = \sqrt{\frac{2N_{A0} R T_0}{C}}$$

	N_{j0}	ΔN_j	N_j
b) A	N_{A0}	$-N_{A0} X_A$	$N_{A0}(1-X_A)$
B	0	$3N_{A0} X_A$	$3N_{A0} X_A$
I	N_{A0}	0	N_{A0}

$$r = k_1 C_A - k_{-1} C_B^3 \quad C_A = \frac{N_A}{V} \quad C_B = \frac{N_B}{V}$$

Just need V now, but its changing due to

X_A : $V = V_0 (1 + \epsilon X_A) \frac{P_0}{P}$ from notes and books

\downarrow \downarrow \downarrow
 $z_0 \cdot A_c$ $\epsilon = \gamma_{A0} \delta$ $\frac{P_0}{P}$
 $= \frac{1}{2} \cdot 2 = 1$ *isothermal*

$$\Rightarrow V = z_0 \cdot A_c (1 + X_A) \frac{\frac{C \cdot z_0}{A_c}}{\frac{\epsilon \cdot z}{A_c}} = \frac{(z_0)^2 A_c (1 + X_A)}{z}$$



$$b) z = \sqrt{\frac{N_T R T}{C}} \quad T = T_0, \quad N_T = 2N_{A0} + 2N_{A0}X_A$$

$$= \sqrt{\frac{2N_{A0}(1+X_A)RT_0}{C}}$$

Thus,

$$V = \frac{\frac{2N_{A0}RT_0}{C} A_c (1+X_A)}{\sqrt{\frac{2N_{A0}(1+X_A)RT_0}{C}}} = A_c \sqrt{\frac{2N_{A0}RT_0(1+X_A)}{C}}$$

Plug into (C_A, C_B) then into rate law.

c) Set $r_{net} = 0$ @ equilibrium and
the X_A becomes $X_{A,eq}$