Problem 1 (40 points):

Consider the gas-phase decomposition reaction:

$$A \rightarrow B + \mathbf{c}C$$

where the rate law is given by $r=kC_A$, and **c** is the stoichiometric coefficient of product C.

You are told to design a constant volume batch-stirred tank reactor (BSTR) for this reaction in a new chemical plant that your company is building. The reactor has volume V, and the reaction will be run isothermally at a temperature T. Initially, an equimolar mixture of A and inert species I are present with a total pressure $P_{Total,o}$. Assume ideal gas behavior.

a) Calculate the initial concentration of A in the reactor in terms of the variables given in the problem statement. **(2 pts.)**

Assuming ideal gas law for species A and inert I, the following relation results,

$$C_{A0} = \frac{N_A}{V} = \frac{P_A}{RT} = \frac{P_{Total,o}}{2RT}$$

2 pts. for correct answer (No Partial Credit)

b) Calculate the pressure in the reactor as a function of conversion, X_A using only variables given in the problem statement and define any new variables that you may need. (8 pts total)

Using the ideal gas law again Fogler's equation 3-38 gives for a batch reactor system.

$$V = V_0\left(\frac{P_0}{P}\right)(1+\epsilon X_A)\left(\frac{T}{T_0}\right)$$

Since this is a constant volume and temperature system, the above equation reduces to:

$$P = P_0\,(1+\epsilon X_A)$$

ε is defined as:

$$\epsilon = y_{A0}\delta$$

$$\epsilon = \frac{1}{2}(c+1-1) = \frac{c}{2}$$

$$P = P_{Total,o}\left(1+\frac{c}{2}X_A\right)$$

More rigorously, using a stoichiometric table, assuming constant volume,

Species	Initial	Change	Final
A	C_{A0}	$-X_AC_{A0}$	$C_{A0}(1-X_A)$
B	0	X_AC_{A0}	X_AC_{A0}
C	0	cX_AC_{A0}	cX_AC_{A0}
I	C_{A0}	0	C_{A0}
Total	$2C_{A0}$	cX_AC_{A0}	$C_{A0}(2+cX_A)$

Using the ideal gas law the pressure can be expressed as:

$$P = C_T RT = C_{A0}\left(2 + cX_A\right)RT = 2C_{A0}RT\left(1 + \frac{c}{2}X_A\right) = P_{total,o}\left(1 + \frac{c}{2}X_A\right)$$

This is the same result as above!

c) Consider the case of the same reaction with the same rate law in a CSTR, with an equimolar feed of species A and inert species I with a molar flowrate of F_0. The reactor is isobaric at a pressure P_{total} and isothermal at a temperature T. What is the volume of the CSTR needed to reach conversion X_A*? Your answer <u>should not include</u> v_0, C_{A0}, or F_{A0} in the final expression. **(12 pts.)**

The design equation for a CSTR is:

$$V_{CSTR} = \frac{F_{A0}X_A^*}{-r_A}$$

The key here is to get the concentration in the right expression. The stoichiometric table in Part B can be modified for the flow reactor system by making the concentrations change to molar flowrates.

Species	Initial	Change	Final
A	F_{A0}	$-X_AF_{A0}$	$F_{A0}(1-X_A)$
B	0	X_AF_{A0}	X_AF_{A0}
C	0	cX_AF_{A0}	cX_AF_{A0}
I	F_{A0}	0	$0.5F_0$
Total	$2F_{A0}$	cX_AF_{A0}	$F_{A0}(2+cX_A)$

Expressing the concentration of species A:

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X_A)}{v_0\frac{F_T}{F_{T0}}} = \frac{F_{A0}(1-X_A)}{v_0\frac{F_{A0}(2+cX_A)}{2F_{A0}}}$$

Using the ideal gas law, v_0 is written as:

$$v_0 = \frac{F_{T0}RT}{P_{total}} = \frac{2F_{A0}RT}{P_{total}}$$

Substitute v_0 into the previous expression for C_A:

$$C_A = \frac{P_{total}}{RT}\frac{1-X_A}{2+cX_A}$$

Finally, substitute into the design equation:

$$V_{CSTR} = \frac{F_0RTX_A^*}{2kP_{total}}\left(\frac{2+cX_A^*}{1-X_A^*}\right)$$

d) Experimentally it is observed that , $V_{PFR} < V_{CSTR}$ to achieve the same conversion X_A*. Why is this true? Answers longer than 2 sentences will receive a 0. **(8 pts.)**

For positive order kinetics, the concentration driving force for the reaction is higher in the PFR since there is no back mixing while in the CSTR there is perfect mixing. The volume of the reactor is inversely proportional to the reaction rate, which is directly proportional to the concentration driving force.

e) Suppose now that you discover that species C condenses at a vapor pressure of P_c^{vap} at the reactor temperature. Assuming conditions otherwise similar to the CSTR situation in Part C, at what conversion, $X_{A,cond}$ will C begin to condense? Write $X_{A,cond}$ as a function of <u>only</u> P_{total}, P_c^{vap}, and the stoichiometric coefficient **c**. **(10 pts.)**

C will begin to condense when the partial pressure of C produced by the reaction equals the vapor pressure of C at the reactor temperature.

$$P_C = P_C^{vap}$$

$$P_C^{vap} = C_C RT = \left(\frac{P_{total}}{RT}\right)\left(\frac{cX_{A,cond}}{2 + cX_{A,cond}}\right) RT$$

$$X_{A,cond} = \frac{2P_C^{vap}}{\left(P_{total} - P_C^{vap}\right) c}$$

Problem 2 (35 points):

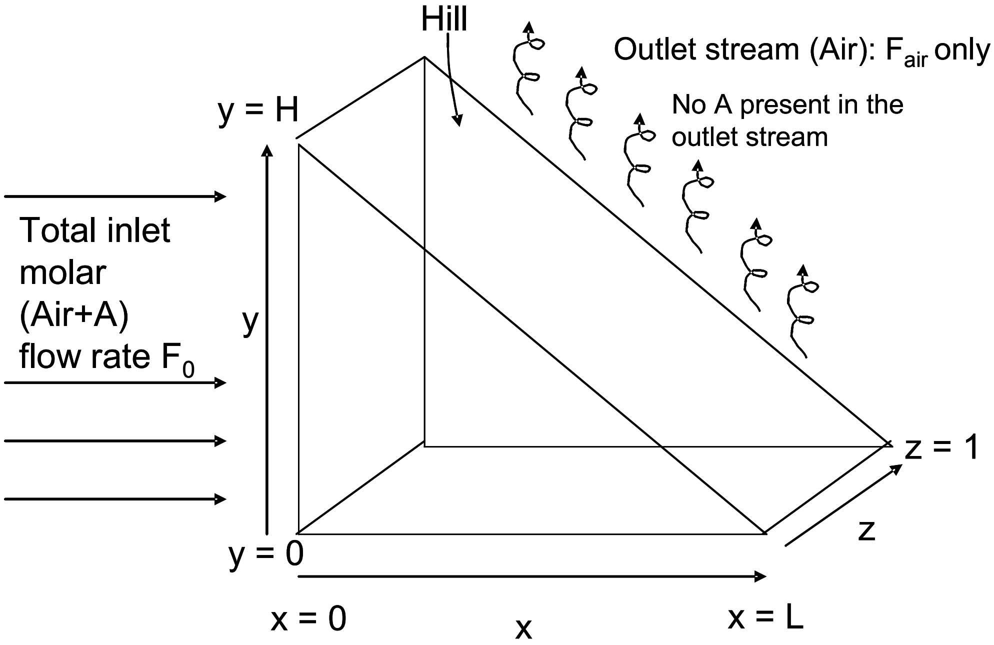
A new enzyme is implemented to clean up the soil on a hill (dimension z = 1, x=L, and y=H, see Figure below) that is contaminated with hazardous chemical waste (A). The enzyme (tyrosinase) converts the hazardous chemical waste (A) to a non-toxic substance according to the reaction:

$$A \xrightarrow{k} \text{non-toxic substance}$$

The reaction rate of A by the enzyme follows first-order (in A) irreversible kinetics with rate constant ***k***.

A fresh air mixture containing A enters the soil at a total molar flowrate of F_0. This mixture is saturated with A at a partial pressure of A of 0.01 atm, and exits the soil essentially *depleted* of A due to A's very favorable absorption by the soil. The diffusion of A is rapid within the soil, such that there is no concentration gradient of A within the soil whatsoever. Assume that because A is present in such small amounts relative to the soil volume, the volume of the hill always remains ***fixed*** in time regardless of the A concentration. The temperature of the hill is constant and uniform, and the total pressure is 1 atm.

Derive the concentration of A with respect to time in terms of the variables above.



$$-r_A = kC_A$$

Initial conditions:

$$C_A(t = 0) = C_{A0}$$

for all x, y and z

Mass balance $\rho v_{in} - \rho v_{out} = \frac{d\rho V}{dt}$

$\frac{dV}{dt} \approx 0$ Note that V is constant.

Perform a species mol balance of A:

$$F_{A_{in}} - F_{A_{out}} + r_A V = \frac{dN_A}{dt}$$

Relate the molar flow rate of A in the inlet stream to vapor pressure of A:

$$F_{A_{in}} = F_0 \frac{P_A}{P_{total}}$$

We also know the volume of the hill:

$$V = \frac{1}{2} HL(1)$$

Substituting into the species A balance equation to yield:

$$F_0 \frac{P_A}{P_{total}} - 0 - kC_A V = \frac{d(VC_A)}{dt}$$

$$\frac{F_0}{V} \frac{P_A}{P_{total}} - kC_A = \frac{dC_A}{dt}$$

$$\frac{2F_0}{HL} \frac{P_A}{P_{total}} - kC_A = \frac{dC_A}{dt}$$

$$\frac{2F_0}{HL} 0.01 - kC_A = \frac{dC_A}{dt}$$

$$\int dt = \int \frac{dC_A}{(\frac{2F_0}{HL} \frac{P_A}{P_{total}} - kC_A)}$$

$$t = -\frac{\ln(\frac{2F_0}{HL} \frac{P_A}{P_{total}} - kC_A)}{k} + C_1$$

$$C_2 e^{-kt} = \frac{2F_0}{HL} \frac{P_A}{P_{total}} - kC_A$$

$$C_A = \frac{2F_0}{kHL} \frac{P_A}{P_{total}} - \frac{C_2}{k} e^{-kt}$$

Initial condition: t=0 $C_A = C_{A0}$

$$C_2 = \frac{2F_0}{HL}\frac{P_A}{P_{total}} - kC_{A0}$$

$$C_A = \frac{2F_0}{kHL}\frac{P_A}{P_{total}} - (\frac{2F_0}{kHL}\frac{P_A}{P_{total}} - C_{A0})e^{-kt}$$

$$C_A = \frac{2F_0}{kHL}\frac{P_A}{P_{total}}(1 - e^{-kt}) + C_{A0}e^{-kt}$$

$$C_A(t) = \frac{2F_0}{kHL}0.01(1 - e^{-kt}) + C_{A0}e^{-kt}$$

Problem 3 (25 points):
Olefin cis-trans isomerization occurs in the presence of molecular iodine according to the mechanism below. Answer the questions below, and show all steps toward final solution for credit. An answer without full justification receives zero credit.

step general reaction: cis $\longrightarrow$ trans

1 $I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,I\bullet$

2 $I\bullet + \text{cis} \xrightarrow{k_2} \text{IDC}$

3 $\text{IDC} \xrightarrow{k_3} I\bullet + \text{trans}$

where cis represents a cis olefin; trans represents a trans olefin and IDC represents a iodine-cis radical complex

I• and IDC are reactive intermediates

a) (9 points total) Using the pseudo-steady-state hypothesis (3 points), derive an expression for the rate of the general reaction (6 points).

for I·, PSSH: $-2k_1(I_2) + 2k_{-1}(I\cdot)^2 - k_2(I\cdot)(cis) + k_3(IDC) = 0$

+3/3

for IDC, PSSH: $k_2(I\cdot)(cis) - k_3(IDC) = 0$

so $I\cdot = \sqrt{\frac{k_1 I_2}{k_{-1}}} = \sqrt{K_1(I_2)}$

and $IDC = \frac{k_2}{k_3}(I\cdot)(cis) = \frac{k_2}{k_3}\sqrt{K_1(I_2)}(cis)$

6/6 so $\boxed{r_{overall} = r_3 = k_3(IDC) = k_2\sqrt{K_1(I_2)}(cis)}$

note: PSSH requires $r_1 = r_{-1}$,

Now – for parts b – d below – assume that step 2 is also reversible so that the mechanism is as below:

step general reaction: cis $\longrightarrow$ trans

1 $I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,I\bullet$

2 $I\bullet + \text{cis} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{IDC}$

3 $\text{IDC} \xrightarrow{k_3} I\bullet + \text{trans}$

where cis represents a cis olefin; trans represents a trans olefin and IDC represents a iodine-cis radical complex

I • and IDC are reactive intermediates

b) (8 points) Assuming steps 1 and 2 are quasi-equilibrated, determine the rate of the general reaction.

QE on step 1: $\frac{(I\cdot)^2}{(I_2)} = K_1 = \frac{k_1}{k_{-1}}$

+4/4

step 2: $\frac{(IDC)}{(I\cdot)(cis)} = K_2 = \frac{k_2}{k_{-2}}$

so $I\cdot = \sqrt{K_1 (I_2)}$

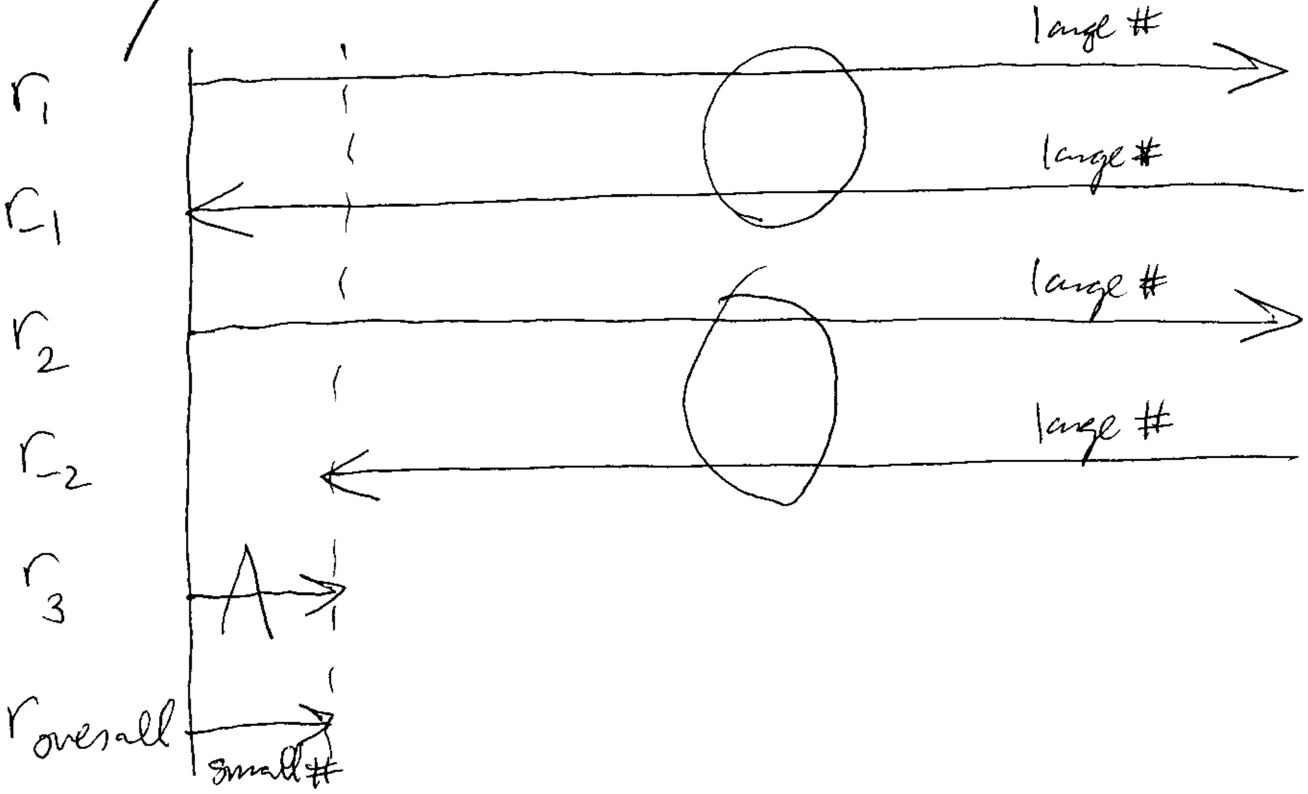
and $(IDC) = K_2 (I\cdot)(cis) = K_2 \sqrt{K_1}\sqrt{(I_2)}(cis)$

so $\boxed{r_{overall} = r_3 = k_3 (IDC) = k_3 K_2 \sqrt{K_1}\sqrt{(I_2)}\, cis}$

4/4

c) (8 points) Sketch a rate-arrow diagram for the case of quasi-equilibrated steps 1 and 2, showing clearly the rate of each relevant forward and reverse step and the rate of the general reaction on the diagram.

+8/8



note: PSSH in part (a) requires $r_1 = r_{-1}$; initiation negligible

need to clearly demonstrate

$|r_1|, |r_{-1}|, |r_2|, |r_{-2}| >> |r_{overall}|$