NAME ______________________________

Problem 1. (15 points)

a. Rank the conversion you expect to achieve for the elementary reaction 2A → B in each of the following isothermal and isobaric, liquid phase reactors that all have the same total volume (4 L). "1" denotes the HIGHEST conversion. If there are two reactors with the same conversion, give them the same number. The total volumetric flow rate (v_o) and concentrations of the inlet stream are the same in all cases.

5 points max

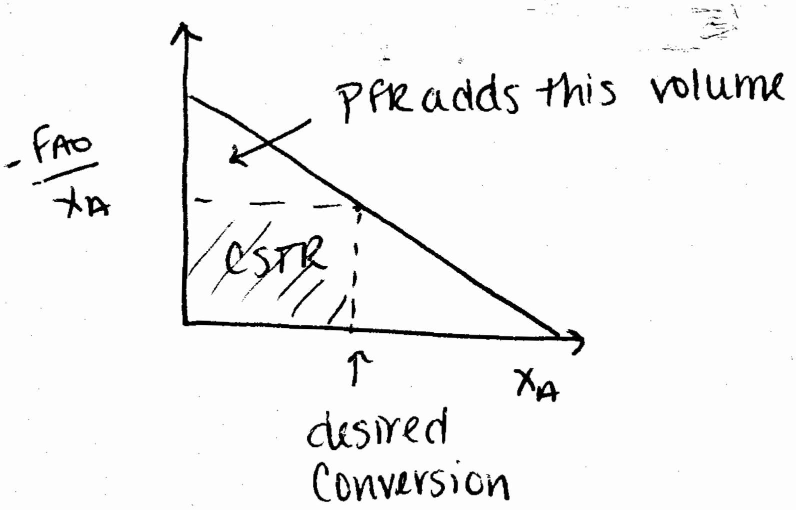
__1__ A single PFR with volume 4 L
__4__ A single CSTR with volume 4 L
__2__ A 2 L PFR followed by a 2 L CSTR
__3__ A 2 L CSTR followed by a 2 L PFR
__1__ Two 2 L PFRs in parallel, each with an inlet volumetric flow rate $v_o/2$
__4__ Two 2 L CSTRs in parallel, each with an inlet volumetric flow rate $v_o/2$

b. Which reactor of total volume V will yield a larger conversion for the isothermal and isobaric, liquid-phase negative order reaction, A→B? Your two choices are either CSTR or PFR. Explain both graphically AND in ONE sentence why. Answers without correct explanation receive zero credit.

5 points max

Levenspiel Plot

$V = \frac{F_{A0} X_A}{-r_A}$ CSTR

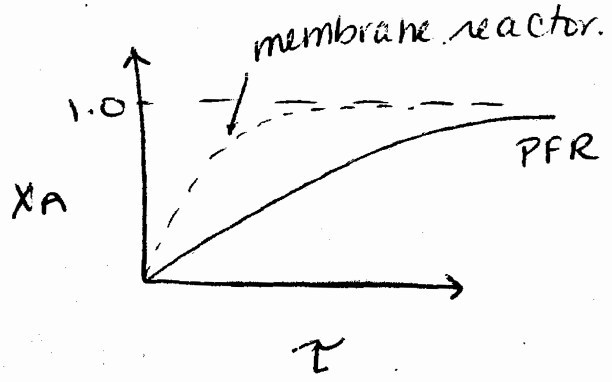


In a CSTR, we "dilute" the concentration of the reactants to the final (outlet) concentration; to increase the conversion in a negative order reaction, we desire dilute concentrations.

NAME ______________________________

c. Consider a second-order irreversible reaction (A + B → C + D) that occurs in a tubular, ideal gas-phase reactor that is operated at both isothermal and isobaric conditions. Qualitatively sketch the conversion of A as a function of residence time for (i) an irreversible reaction in a PFR and (ii) an irreversible reaction in a membrane reactor in which product C is removed, both on the same plot.

5 points max



1. Show faster conversion in a membrane reactor. (concentrate the reactants).

NAME ______________________________

Problem 2. (20 points)

Methyl azide decomposes irreversibly in an isothermal and isobaric, gas-phase, PFR reactor. The elementary reaction is $H_3CNNN \rightarrow N_2 + H_2 + HCN$. The rate constant at 300 K is 5.03×10^{-8} s^{-1} (concentration basis) and has an activation barrier of 54 kJ mol^{-1}. What residence time is needed to achieve 50% conversion at 500 K?

20 points max

$$H_3CNNN \xrightarrow{k_f} N_2 + H_2 + HCN$$

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

$k(300K) = 5.03\times10^{-8}\ s^{-1}$

$E_A = 54\ kJ/mol^{-}$

$\tau = ?$ to achieve $X = 0.5$

Design : PFR

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

Rate $= -r_A = k_f C_A$

Stoich. Table

Species	Initial	Change	Final	Conc.
A	F_{A0}	$-F_{A0}X$	$F_{A0}(1-X)$	$C_A = \frac{F_{A0}(1-X)}{v}$
B	0	$+F_{A0}X$	$F_{A0}X$	$C_B = \frac{F_{A0}(X)}{v}$ =
C	0	$+F_{A0}X$	$F_{A0}X$	$C_C = \frac{F_{A0}X}{v}$
D	0	$+F_{A0}X$	$F_{A0}X$	$C_D = \frac{F_{A0}X}{v}$

$$v = v_0(1+\varepsilon X)\underbrace{\cancel{\left(\frac{P_0}{P}\right)}}_{1}\underbrace{\cancel{\left(\frac{T}{T_0}\right)}}_{1}$$

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

$$v = v_0(1+2X)$$

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

$$C_B = C_C = C_D = \frac{C_{A0}X}{1+2X}$$

Rate: $-r_A = k_f C_A = k_f \frac{C_{A0}(1-X)}{(1+2X)}$

Design: $\frac{dX}{dV} = \frac{k_f C_{A0}(1-X)}{F_{A0}(1+2X)} = \frac{k_f(1-X)}{v_0(1+2X)}$

$$\int_0^X \frac{(1+2X)}{(1-X)}\,dX = \frac{k_f}{v_0}\int_0^V dV$$

$$= \frac{(2)X}{-1} + \frac{(1)(-1)-(2)(1)}{(-1)^2}\ln(-X+1)\Big|_0^X$$

$$= -2X - 3\ln(1-X)\Big|_0^X = -2X - 3\ln(1-X) - (-3\overset{0}{\cancel{\ln(1)}})$$

$$= 3\ln\left(\frac{1}{1-X}\right) - 2X = \frac{k_f}{v_0}V = k_f\tau$$

$$\tau = \frac{3}{k_f}\ln\left(\frac{1}{1-X}\right) - \frac{2X}{k_f} = \tau$$

Arrhenius :

$$k(T) = k(T_{ref})\exp\left(\frac{-E_A}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)$$

$$k(500K) = 5.03\times10^{-8}\,s^{-1}\exp\left(\frac{-54}{0.008314}\left(\frac{1}{500} - \frac{1}{300}\right)\right)$$

$$= 2.9\times10^{-4}\ s^{-1}$$

$$\tau = \frac{3}{2.9\times10^{-4}}\ln\left(\frac{1}{1-0.5}\right) - \frac{2(0.5)}{2.9\times10^{-4}}$$

$$\boxed{\tau = 3720\ s = 1.03\ hrs}$$

NAME ______________________

Problem 3. (20 points)

The reaction between A and B to form P is proposed to follow the set of elementary steps below, which involve the reactive intermediate I_1. The overall reaction is $3A + 2B \rightarrow P$.

		σ_i
1. $A + B \leftrightarrow I_1$	k_1, k_{-1}	2
2. $2A + I_1 \rightarrow 2P$	k_2	0.5

a. Derive a rate expression for the rate of consumption of A. 8 points max

PSSH on reactive intermediate I_1:

$$0 = k_1[A][B] - k_{-1}[I_1] - k_2[A]^2[I_1]$$

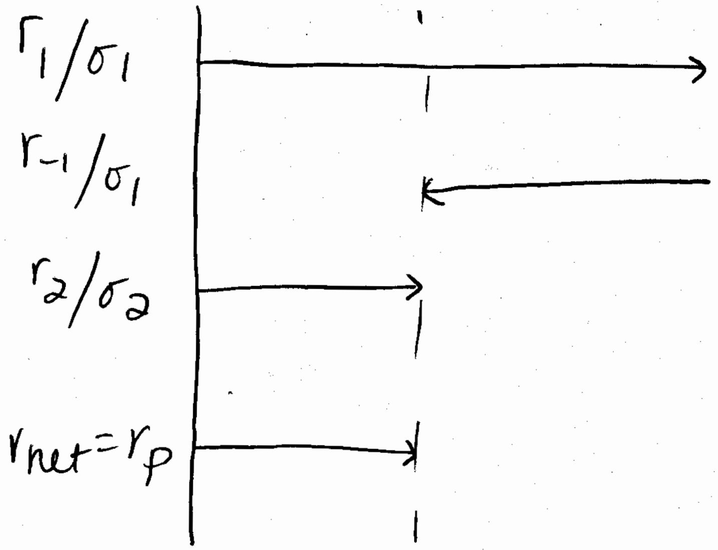
$$[I_1] = \frac{k_1[A][B]}{k_{-1} + k_2[A]^2}$$

$$r_p = 2k_2[A]^2[I_1] = \frac{2k_2k_1[A]^3[B]}{k_{-1} + k_2[A]^2}$$

By stoichiometry:

$$\frac{r_P}{1} = \frac{r_A}{-3} \Rightarrow r_A = -\frac{6k_2k_1[A]^3[B]}{k_{-1} + k_2[A]^2}$$

b. Draw a rate-arrow diagram for the mechanism proposed in part (a). Clearly relate the rates of each relevant step (r_1, r_{-1}, r_2) to the rate of the net reaction (r_{net}). 2 points max



NAME ______________________________

c. Assume step one is in quasi-equilibrium. Derive the rate of consumption of A.

Quasi- equilibrium assumption: 6 points max

$k_{-1}[I] = k_1[A][B]$

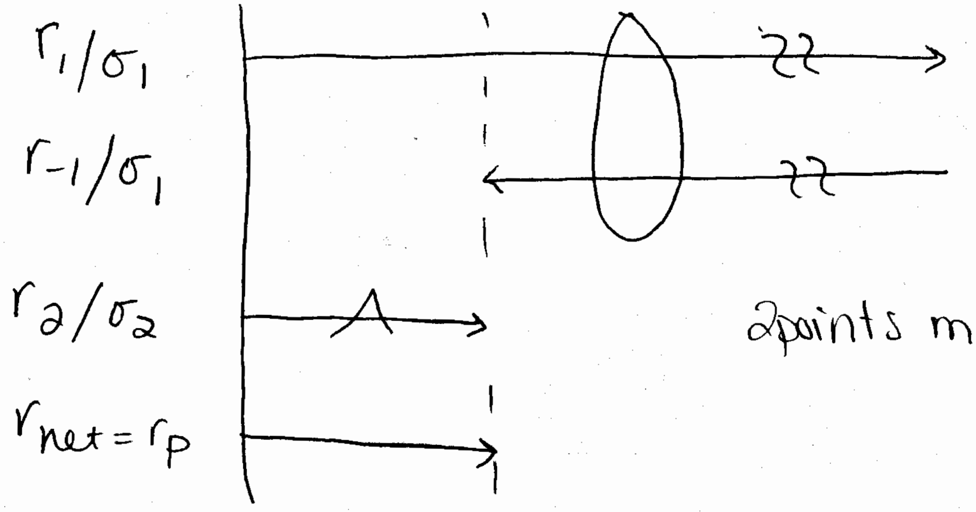
$[I] = K_1[A][B]$

$r_p = 2k_2[A]^2[I]$

$r_p = 2k_2K_1[A]^3[B]$

$r_A = -3r_p = -6k_2K_1[A]^3[B]$

d. Draw a rate-arrow diagram for the mechanism proposed in part (c). Clearly relate the rates of each relevant step (r_1, r_{-1}, r_2) to the rate of the net reaction (r_{net}).



2points max

e. Provide the rigorous justification for collapsing the quasi-equilibrium result to the pseudo-steady state result.

If $k_{-1} >> k_2[A]^2$, reduces to QE result.

This makes physical sense => the first step is now in equilibrium. 2 points max

NAME ________________________________

Problem 4. (25 points)

The gas-phase reaction 2HI ↔ $H_2 + I_2$ is elementary and reversible. The feed to an isothermal PFR is an equimolar mixture of only HI and H_2 at 1000 K and 1 atm total pressure. The total volumetric flow rate of the feed is 32.8 $dm^3\ s^{-1}$. Under these conditions, the measured equilibrium conversion was 14%. The rate constant for the forward reaction, k_f, is 14.5 dm^3/mol/sec. An isothermal CSTR is operated at the same temperature and with the same inlet stream as the PFR above. What volume is required to reach 10% conversion in this CSTR?

$$2HI \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_2 + I_2$$

25 points max

$$2A \rightleftharpoons B + C$$

$T = 1000\ K$

$P = 1\ atm$

$F_{A0} = F_{B0}$

$X_{equi} = 0.14$

$k_f = 14.5 \frac{dm^3}{mol\, s}$

Rate: $-r_A = 2k_f C_A^2 - 2k_r C_B C_C$

$$= 2k_f \left(C_A^2 - \frac{C_B C_C}{K_e}\right)$$

Stoich Table:

Species	Initial	Change	Final	Conc.
A	F_{A0}	$-F_{A0}X$	$F_{A0}(1-X)$	$C_A = \frac{F_{A0}(1-X)}{v}$
B	F_{B0}	$\frac{1}{2}F_{A0}X$	$F_{A0}(1+\frac{1}{2}X)$	$C_B = \frac{F_{A0}(1+\frac{1}{2}X)}{v}$
C	0	$\frac{1}{2}F_{A0}X$	$\frac{1}{2}F_{A0}X$	$C_C = \frac{\frac{1}{2}F_{A0}X}{v}$

$v = v_0 (1 + \varepsilon X)$

$\varepsilon = y_{A0} \delta = (\frac{1}{2})(0)$

$v = v_0$

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

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

$C_C = \frac{1}{2} C_{A0} X$

Rate: $-r_A = 2k_f \left(C_{A0}^2 (1-X)^2 - \frac{\frac{1}{2} C_{A0}^2 X (1 + \frac{1}{2}X)}{K_C} \right)$

@ equi $r_A = 0$

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

$$K_C = \frac{\frac{1}{2} X (1 + \frac{1}{2}X)}{(1-X)^2} = \frac{\frac{1}{2}(0.14)(1 + \frac{1}{2}(0.14))}{(1-0.14)^2} = 0.101$$

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

Need F_{A0} . . . .

$P v = F_{T0} R T$

$$\frac{(1\text{ atm})(32.8 \frac{dm^3}{s})}{(0.08206)(1000K)} = F_{T0} = 0.4 \frac{mol}{s}$$

$F_{A0} = 0.2$ mol/s

$$C_{A0} = \frac{F_{A0}}{v_0} = \frac{0.2\,\text{mol/s}}{32.8\,\text{dm}^3/\text{s}} = 0.0061\ \frac{\text{mol}}{\text{dm}^3}$$

$$-r_A = 2(14.5)(0.0061)^2\left[0.9^2 - \frac{1}{2}\,\frac{(0.1)(1+\frac{1}{2}(0.1))}{.101}\right]$$

$$= 3.13\times10^{-4}\,\frac{\text{mol}}{\text{dm}^3\,\text{s}} \quad @\ X = 0.1$$

$$V = \frac{0.2\,\frac{\text{mol}}{\text{s}}\,(0.1)}{3.13\times10^{-4}\,\frac{\text{mol}}{\text{dm}^3\text{-s}}} = \boxed{63.9\,\text{dm}^3}$$

NAME ______________________________

Problem 5. (20 points)

You have a stirred tank that is initially filled with red dye in water at an initial uniform concentration of 2 mol dm^{-3}. At time t = 0 min, a stream of water with red dye at a concentration of 0.3 mol dm^{-3} enters the tank at a flow rate of 2 dm^3 min^{-1}. Assume the tank volume is constant and all liquids are incompressible and have the same density.

a. What do you expect the limiting concentrations of red dye to be at very short and long times? Justify your answer in one sentence. 2points max

At t=0 the concentration is the initial conc. (2 mol dm3) & as t → ∞ the concentration is that of the entering stream (0.3 mol/dm^3).

b. What is the concentration of the red dye at a time, t = the reactor residence time τ.

10points max

Mole balance on red-dye:

Accu = Gen + In − Out

$$\frac{dN_A}{dt} = 0 + F_{A0} - F_A$$

$$\frac{d(C_A V)}{dt} = v_0 C_{A0} - v_0 C_A = C_A \cancelto{0}{\frac{dV}{dt}} + V\frac{dC_A}{dt}$$

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

$$\int_{C_{Ai}}^{C_A} \frac{dC_A}{C_{A0} - C_A} = \frac{1}{\tau}\int_0^t dt$$

$$\left.\frac{\ln|-C_A + C_{A0}|}{-1}\right|_{C_{Ai}}^{C_A} = -\ln|C_{A0} - C_A| + \ln|C_{A0} - C_{Ai}| = \frac{t}{\tau}$$

$$\ln\left(\frac{C_{A0}-C_{Ai}}{C_{A0}-C_A}\right)=\frac{t}{\tau}$$

$$C_{A0}-C_{Ai}=(C_{A0}-C_A)\exp(t/\tau)$$

$$\boxed{C_A=C_{A0}-(C_{A0}-C_{Ai})\exp(-t/\tau)}$$

When $t=\tau$

$$C_A=C_{A0}-(C_{A0}-C_{Ai})\exp(-1)$$

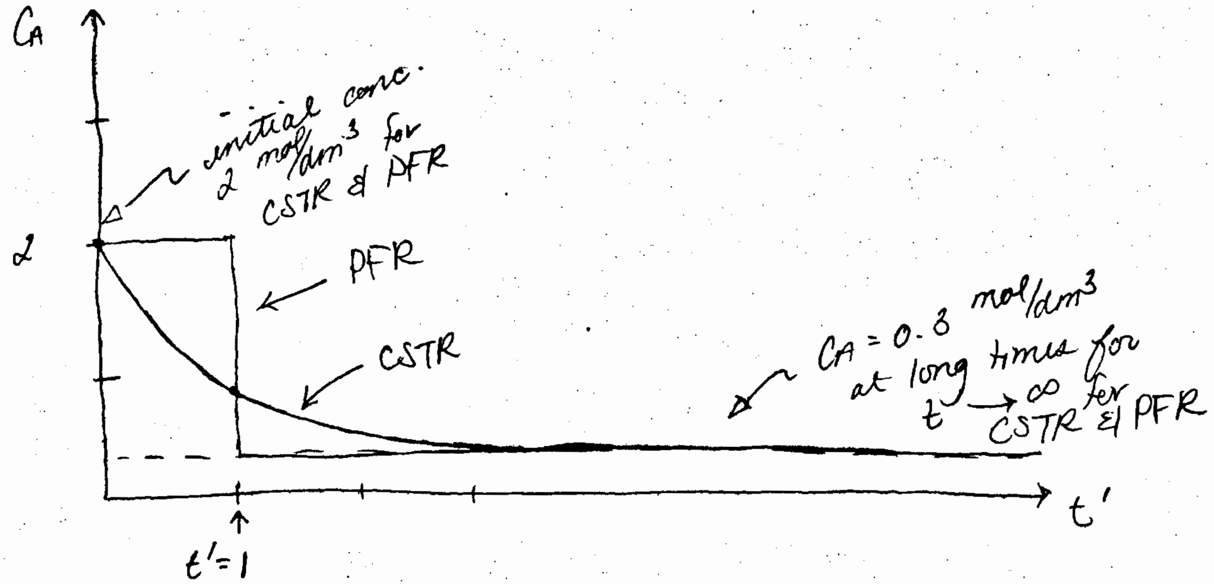
$$=0.3-(0.3-2)\exp(-1)$$

$$\boxed{C_A=0.925\ \text{mol}/\text{dm}^3}$$

NAME ______________________

c. Sketch the concentration of red dye as a function of t' = t/τ (where t is the timer and τ is the residence time). Clearly label the concentration at t' = 0 and its asymptotic value at very long times.

4 points max



d. On the same plot as **part c**, sketch the concentration exiting a PFR as a function of t'. You may assume the PFR has the same residence time and the same initial and inlet concentrations of dye. Again, clearly label the concentration at t' = 0 and its value at very long times. Also label on the plot for the PFR where t'= 1.

see above.

4 points max