CBE 142: Chemical Kinetics & Reaction Engineering

Midterm #1 October 5th 2017

This exam is worth 100 points and 25% of your course grade. You have 80 minutes to complete this exam, so please manage time wisely. Please read through the questions carefully before giving your response. Make sure to SHOW ALL YOUR WORK and BOX your final answers! Answers without a clear and legible thought process will receive no credit.

Name:	
Student ID:	The Early State of the State of
Section (Day/GSI) that you attend:	1 10 lat 1 2 and 2

You are allowed one 8.5"x11" sheet of paper (front and back) and a calculator for this exam. Any additional paper you wish to be graded must have your <u>NAME</u> and <u>STUDENT ID</u> written on each page.

Problem	Max Points	Points Earned
1	5	2011 1 - 1 1 1 2 2 1 1 1 2 2 1 1 1 1 2 2 2 1 1 1 1 2 2 2 1 1 1 1 2 2 2 2 1 1 1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2
2 .	5	
3	15	
4	20	
5	25	
6	30	

TOTAL	/ 100
	/ LVV

Problem # 1. Short Answer: Basic Concepts in Reactor Design [5 pts]

Suppose that the *liquid-phase* reaction $A \to B$ occurs with rate $-r_A = kC_A{}^{\alpha}$, where α is some constant.

For the following questions, there is a BSTR, a PFR, and a CSTR, all of which are isothermal and isobaric and the flow reactors are operating at steady state.

(a) [4 pts] You are told that the total volume of each reactor is equivalent $V_{CSTR} = V_{PFR} = V_{BSTR} = 10 \text{ L}$. The feeds of the flow reactors are pure A at a molar flowrate of $F_{A0} = 1 \text{ mol s}^{-1}$ and volumetric flowrate 1 L s⁻¹. The batch reactor is initially charged with pure A and has an initial $N_{A0} = 10 \text{ mol of species A}$. At time $\tau = 10 \text{ s}$, the conversion of the BSTR is measured and compared with the conversion in the CSTR and PFR. The following relation is found:

$$X_{CSTR} > X_{PFR} = X_{BSTR}$$

Is α positive, negative, or zero? Justify physically in a single sentence why X_{CSTR} is higher. Answers without correct justification receive no credit.

w is negative: Xcorr is higher because a CSTR dilutes reactants upon entry. For a negative-order reaction, this bicreases the rate, which increases the conversion.

+4 FOR all correct, no partial credit

(b) [1 pts] The same conditions as part (a) apply. At time $\tau = 10$ s, the conversion of the BSTR is measured and compared with the conversion in the CSTR and PFR. The following relation is found:

$$X_{CSTR} = X_{PFR} = X_{BSTR}$$

Is α positive, negative, or zero? Justify physically in a single sentence why. Answers without correct justification receive no credit.

a is zero. If all 3 conversions are the same, then divition doesn't affect the rate, which is only the case if concentration doesn't affect the rate.

8 to 5 Day 15 my of 20 months and Angel 21 to

+ 1 all correct, no partial credit

Problem # 2. Short Answer: Basic Concepts in Reactor Design [5 pts]

You are an engineer at a chemical company tasked with manufacturing compound P via the elementary reaction $2 A + B \stackrel{k_1}{\to} P$, which has a rate r_1 .

Unfortunately, an elementary side reaction also occurs, producing the worthless compound W. The side reaction is $A + 2B \xrightarrow{k_2} W$, which has a rate r_2 .

All reactions are in the liquid-phase and your goal is to maximize the selectivity to compound P. The selectivity to P is defined as: $S = \frac{r_1}{r_2}$

Select one of the options below that should be used to maximize the selectivity to P. You must include a brief justification for your answer. Answers without correct justification will receive no credit.

- (a) BSTR
- (b) PFR
- (c) CSTR
- (d) Semibatch reactor initially containing pure A, into which B is fed slowly
- (e) Semibatch reactor initially containing pure B, into which A is fed slowly
- (f) Reactive distillation where P evaporates immediately upon formation
- (g) Both (a) and (b)

Problem #3. Short Answer: Basic Concepts in Reactor Design [15 Points]

A semi-bath reactor is initially charged with some amount of element D at a concentration of C_{D0} at volume V_0 . Entering is an **unreactive** element, C, at molar flow rate F_{C0} and a volumetric flow rate of v_0 . Write the expressions for C_C and C_D as a function of time.

From

$$v_0$$

+1 for mod bad on $C = D$
 $4/5$ for solving mod bad

 $\frac{OR}{5/5}$
 $5/5$ for $V(t) = V_0 + v_$

Problem #4. PSSH and QE [20 pts]

Consider the following mechanism:

$$B + hv \xrightarrow{k_1} B^*$$

$$B^* + AH_2 \xrightarrow{k_2} \cdot BH + \cdot AH$$

$$2 \cdot BH \xrightarrow{k_3} (BH)_2$$

$$2 \cdot AH \xrightarrow{k_4} A + (AH)_2$$

The overall reaction is: $2 B + AH_2 + hv \rightarrow (BH)_2 + A$. The reactive intermediates are B^* , $\cdot AH$, and $\cdot BH$.

(a) [7 pts] Derive the rate of (BH)₂ formation in terms of the concentrations of stable species.

Solution 1: Using 13

i)
$$r_{net} = \frac{r_2}{2} = \frac{r_3}{7}$$
 and $r_{BH2} = r_3$

$$0 = k_1(8) - k_1(8*) - k_2(8*)(A+2)$$

Solve for 8*:

(8*) =
$$\frac{k_1(8)}{k_{-1} + k_2(HH_2)}$$

$$\Gamma_{BH2} = \frac{1}{2} k_2 \left(\frac{k_1(B)}{k_{-1} + k_2(AH_2)} (AH_2) \right)$$

$$\Gamma_{BH2} = \frac{1}{2} \frac{k_2 k_1(B)(AH_2)}{k_{-1} + k_2(AH_2)}$$

Pactial credit:

- no fartial credit on individual step for which points are awarded
- However, errors that propagate
 will not have points deducted more
 than once. i.e, writing TBH2 = T2
 will lose you 3, but you will get
 Tor correctly plugging in T2=k2(B**(AH2))
 and getting TBH2 = k2(B*)(AH2)

solution 2: Using 13

$$0 = k_2(8*X^{RH2}) - 2k_3(\cdot 8H)^2$$
Solving for $(\cdot 8H)^2$;
$$(\cdot 8H)^2 = \frac{1}{2} \frac{k_2}{k_2} (8*)(8H2)$$

(84) =
$$\frac{k_1(8)}{k_{-1} + k_2(AH_2)}$$

$$(\cdot BH)^2 = \frac{1}{2} \frac{k_3}{k_3} \left(\frac{k_1(B)}{k-1 + k_2(AH_2)} \right) (AH_2)$$

solution 3: using n-ry

(B*) =
$$\frac{k_1(B)}{k_{-1} + k_2(BH_2)}$$

(FI) for
$$1 \frac{\Gamma_{BH_2} = \frac{1}{2} \left(k_1(B) - \frac{k_{-1} k_2(BH_2)}{k_{-1} + k_2(BH_2)} \right)}{\Gamma_{BH_2} = \frac{1}{2} \frac{k_2 k_1(B \chi_{BH_2})}{k_{-1} + k_2(BH_2)}$$

Solution 4: using cy

(8*) =
$$\frac{k_1(8)}{k_{-1} + k_2(RH_2)}$$

enidono (iii)

(+1)
$$\Gamma_{8H_2} = \frac{1}{2} \frac{\kappa_2 \kappa_1 (8 \chi_{RH_2})}{\kappa_{-1} + \kappa_2 (RH_2)}$$

other deductions:

- -1 for (hy) in rate jaw
- terms from 1 line to the next

(b) [3 pts] Assume that step 1 is quasi-equilibrated. Now, derive the rate of BH₂ formation in terms of the concentrations of stable species.

Solution:

combine with rate law from part (a):

partial credit:

- no partial credit for (B*) = k1(B)
- 1 awarded for correctly plugging in whatever expression For (B*) you get into whatever rate law you had in part (a)

(c) [5 pts] Under what conditions does the PSSH solution collapse to the QEA solution i.e. what is the rigorous justification?

saution:

QEA rate: (BHz = 1 R2 K1(B)(AH2)

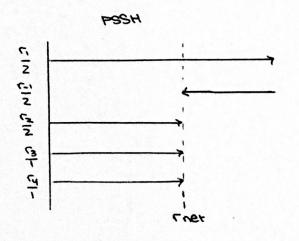
comparing 1994 and QEA: if k-1 >> k2(AH2), solution collapses to QEA

(5) \$ k-1 >> k2(AH2)

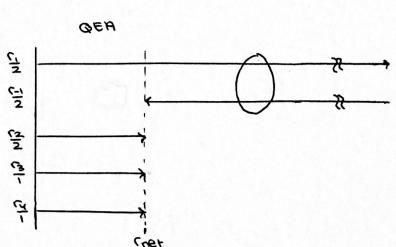
Partial credit:

- Full credit for a solution that 1800s post rate From (a) [whatever it may be] to collapse to QEH som from (b) [whatever that rate may be]
- Et included kall in justification - (3) if missing a concentration term from justification (e.g. have k-1 >> k2) and this is the only errors +3 for a similar error as well.
- F3 if Imaquality is flipped
- D FOC 6, OC 6-1 23 ES
- no credit otherwise

(d) [5 pts] Draw rate-arrow diagrams for the case where step 1 is not quasi-equilibrated from part (a) and for the case where step 1 is quasi-equilibrated from part (b). Make sure to clearly label rnet as the net rate of reaction with a vertical dashed line and include numerical values for sigma.



For all 6 values correct



- For net rate of each step divided by & = rnet. rnet should be labeled, all Forward & reverse reactions should be shown.
- (1) For arrows in 1934 are same order of magnitude.
- For clearly showing 1 8 1 17 12, 13, 14 in QEH. Doesn't need to 10 have circle over amous, but they should obviously be large.

Problem #5. Gas phase reactions [25 pts]

Announced!

Consider the elementary gas phase reaction

$$3A + B \rightarrow 3C + 2D$$

taking place in a batch reactor at constant pressure.

- There is two times the initial amount of N in the batch reactor such that $2N_{A0}=N_{B0}$
- The reactor is operating isobarically, $P_{total} = 10$ atm
- The reactor is operating isothermally, T=300K
- The rate law is $-r_A = k_1 C_A$ where $k_1 = 0.3$ Kg sec⁻¹ $R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$ $3 \text{ S}^{-1} : \text{Announced}$

Base your conversion on the limiting reactant.

(a) [2 pts] What is the limiting reactant?

(b) [11 pts] Complete the stoichiometric table for all species with respect to the limiting reactant.

+1/box

Species	Initial	Change	Final
A	N _{A0}	- NAUZA	Mao (1-24)
В	2N _{A0}	- 13 NAOXA	NaloB - 3x
C	0	+ NAO XA	NoxA
D	0	+ 3 NAO 2/A	3 Mao 2/4
Total	$N_{T0} = 3N_{AC} \times_A$	+ 3 No 24	$N_T = M_A (3 + \frac{1}{3})$

(c) [7 pts] At what time t does the reaction reach 80% conversion?

if project about
$$V \leftarrow \frac{dN_A}{v_A V} = dt = t + 7$$
in $v_A V - 2$, but

calculate rest the name $N_{AO} = \frac{dx_A}{h_C A V} = t$

$$\frac{dx_A}{dx_A} = \frac{M_{AO}(1-x)}{V} = \frac{M_{AO}(1-x)}{V} = \frac{M_{AO}(1-x)}{V_O(1+\frac{1}{3}x)}$$

$$\frac{dx_A}{dx_{AO}} = t$$

$$\frac{N_{\infty}}{k_{1}}\frac{dx}{\sqrt{(1-x)}} = t$$

$$(-2)\frac{1}{h_1}\int_0^{\infty}\frac{1}{1-x_A}dx=t$$

(d) [5 pts] In just a few sentences, explain what the residence time would be in a constant pressure PFR, compare it to the batch reactor in part (c), and explain physically why that is. Answers without correct justification receive no credit.

The residence time in a constant pressure PFR would be
the same as the clock time in a BSTR keeper the
thestance a volume element travels in a PFR is analogour
ter that same time in a BSTR. Thus 2=t

+3 for solution of mathematical just

+5 for solution of physical justification

Problem #6. Operating a CSTR in real time [30 pts]

The isothermal, liquid phase, 1st order reaction of A \rightarrow B is occurring in a CSTR with rate constant k = 0.3 hr⁻¹. The inlet and outlet volumetric flowrates are $v_0 = v = 25$ L hr⁻¹, and the feed is pure A with a concentration of 1 mol L⁻¹.

The current amount of liquid in the reactor is 500 L. The density of the liquid is always a constant.

(a) [4 pts] What is the conversion of species A if this reactor is being operated at steady state?

Fro-FA +
$$\Gamma_AV = 0$$

Fro-FA - $KCAV = 0$

Fro-FA - $KCAV = 0$

Fro-FA - $KCAV = 0$
 $C_{AO} - C_{AO}(1-x) - KC_{AO}(1-x)V = 0$
 $X - KV + KVX = 0$
 $X - KV + KVX = 0$
 $X = \frac{KV}{V} = \frac{V}{V} = \frac{500L}{25 Uhr} = 20 hr$
 $X = \frac{0.3.20}{1+0.3.20} = \frac{6}{7}$

Fro-FA + $\Gamma_AV = 0$
 $X = \frac{0.3.20}{1+0.3.20} = \frac{6}{7}$

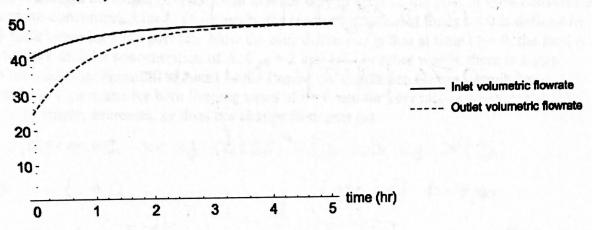
(b) [8 pts] Now, a new regulation is imposed on product stream such that X_A must now be at least 90%. Then a colleague suggests that this be accomplished by adding the following time-dependent terms to the original volumetric flow rates ($v_0 = 25 \text{ L hr}^{-1}$):

Inlet volumetric flowrate: $v_0'(t) = 25(1 - \exp[-(t+1)]) + v_0$ for all $t \ge 0$

Outlet volumetric flowrate: $v'(t) = 25(1 - \exp[-t]) + v_0$ for all $t \ge 0$

Hence for all $t \ge 0$, the inlet and outlet volumetric flow rates are $v'_o(t)$ and v'(t), respectively. At t < 0, the reactor is defined by the steady state behavior described in part (a). For your visual convenience, these flow rate functions are plotted below:

Volumetric flowrate (L/hr)



After a sufficiently long time, what would be the expected conversion for the reactor if you implemented this change to the volumetric flowrates? Was your colleague correct and would you achieve the desired conversion of A of 90%?

[+1PT] Mass bol:
$$\frac{dV}{dt} = \% - V$$

$$\frac{dV}{dt} = 25 - 25 \exp[-(t+1)] + \% - 25 + 25 \exp(-t) - \%$$

$$\frac{dV}{dt} = -25 \exp(-t) e^{-1} + 25 \exp(-t)$$

$$\frac{dV}{dt} = 25 \exp(-t) (1 - \frac{1}{e})$$
[+1PT] int. bounds: $\int_{V_0}^{V_0} dV = \int_{0}^{\infty} 25 \exp(-t) (1 - \frac{1}{e})$

$$V_{\omega} - V_{o} = -(25 \exp(-t)(1-t))^{\infty} = -(0-25(1-t))$$

. At sufficiently long time we have reached SS W/V=V00

$$x = \frac{k \frac{V_{0}}{V_{0,t \to \infty}}}{1 + k \frac{V_{\infty}}{V_{0,t \to \infty}}}$$

$$x = \frac{0.3 \frac{515.1}{50}}{1 + 6.3 \cdot \frac{515.8}{50}} + 1 \text{ PT for } \tau_{\infty} = \frac{V_{\infty}}{V_{0,100}}$$

the first the same of the

(c) [2 pts] Explain physically in one sentence why the conversion found in part (b) went up, down, or stayed the same from your answer in part (a).

-2 pts/

The new steady-state residence time in part (b) decreased from the residence time in part (b), leading to a lower conversion.

(d) [10 pts] A second colleague proposes that another way to achieve the goal of 90% conversion is to use a more concentrated feed. Once again, the reactor operation at times t < 0 is defined by the steady state behavior from part (a). Now the *only* difference is that at time t >= 0, the feed is switched to have an inlet concentration of A, $C_{A0} = 2 \text{ mol } L^{-1}$. In other words, there is a step change to the inlet concentration of A at t >= 0. Derive the expression for the instantaneous conversion X(t). Determine for both limiting cases of t = 0 and for very large t whether the conversion increases, decreases, or does not change from part (a).

*Can determine limiting cases w/o solving x(t):

TIPT Chi =
$$C_A(t=0) = C_A$$
, part A

$$\frac{C_{A,i}}{C_{AO,PATTA}} = [- \times part A]$$

$$C_{A,i} = 1 \frac{mol}{L} (1-0.857)$$

$$C_{A,i} = 0.143 \frac{mol}{L}$$

$$(t \rightarrow 0) = 1 - \frac{0.143}{2}$$
 $(t \rightarrow 0) = 0.93$

$$\frac{dNA}{dt} = F_{AO} - F_{A} + r_{A}V$$

$$\frac{d(A)}{dt} = \frac{CAO}{T} - \frac{CA}{T} - kCA = \frac{CAO}{T} - (1+kT)\frac{CA}{T}$$

$$T \frac{dCA}{dt} = CAO - (1+kT)CA$$

$$\int_{C_{A_{i}}}^{C_{A(i)}} \frac{1c_{A}}{C_{A_{i}}} = \int_{0}^{t} \frac{1}{t} \frac{$$

(e) [6 pts] A third colleague proposes to achieve a conversion of 90% via the following. From 0 < t < N, the outlet volumetric flowrate will be 0 and at t = N will return to 25 L hr⁻¹. Once again, the reactor operation at times t < 0 is defined by the steady state behavior of part (a). Now calculate the value of N which will ensure that the conversion of A will eventually reach exactly 90% after a sufficiently long time t.