Chemical Kinetics and Reactor Engineering

Exam 1
Tuesday, October 2, 2012

This exam is 100 points and worth 20% of the course grade. Please read through the questions carefully before giving your response. **Make sure you show all of your work and BOX your final answers!**

Name: ________________________________

SID: __________________________________

Section (day/person) you attend: ____________________

You are allowed one 8.5"x11" sheet of paper and a calculator for this exam.

Problem	Maximum Points	Points Earned
1	10	
2	18	
3	14	
4	28	
5	30	

PROBLEM 1. (10 points) Short Answers. Please be CONCISE and use 1 sentence for each written explanation.

a) For a liquid-phase reaction exhibiting negative-order kinetics, given a conversion and flow rate, which reactor will require a smaller volume, CSTR or PFR? Explain both graphically using a Levenspiel plot for CSTR and PFR, and explain why physically, in words. Clearly label axes and volumes of each reactor type. (3 points)

b) Which of the following is least likely to be an elementary reaction? Why? (2 points)

$$A+B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I_1$$

$$3A+I_1 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2I_2$$

$$I_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C$$

c) We have a reversible gas-phase reaction, $2A + B \leftrightarrow C + D$, occurring in a

i) constant volume BSTR

ii) constant pressure BSTR

which type of reactor will give us a higher equilibrium conversion? Justify your answer with an equation and 1 sentence. (2 points)

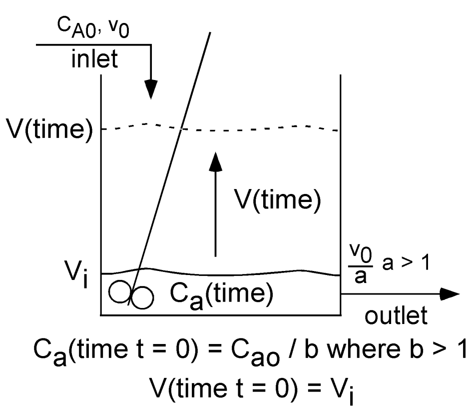
d) We have an irreversible gas phase reaction, $P + Q \rightarrow 2R + S$, occurring in
   i) constant volume BSTR
   ii) constant pressure BSTR

   which type of reactor will give us a higher rate of reactant consumption at a certain conversion, assuming positive-order kinetics? Explain why using an equation (2 points)

e) TRUE OR FALSE: For elementary reactions, the reaction rate always increases with increasing temperature. (1 point)

PROBLEM 2. (18 points) Consider the start-up of an ideal isothermal CSTR reactor. The vessel initially contains a dye solution having a dye concentration C_{a0}/b where b is a constant that is greater than 1, and a volume V_i. At time $t = 0$, both inlet and outlet ports are turned on. The inlet port flows with a volumetric flowrate v_0 and a concentration C_{a0} i.e. the inlet is more concentrated than the initial solution in the reactor. The outlet port flows with a volumetric flowrate v_0/a, where a is a constant that is greater than 1 i.e. the outlet volumetric flowrate is lower than the inlet volumetric flowrate. Assume that there is no chemical reaction occurring in the reactor, and all liquid solutions have the same density. Further assume that the reactor vessel is large enough that it does not overflow for the purposes of this problem.

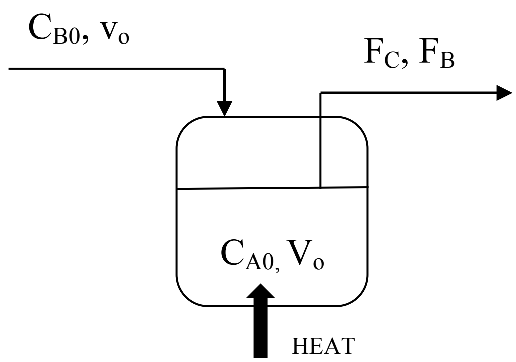
a) Derive an expression that can be solved for the concentration C_a(time) within the reactor. Show all work. Answers without equations and a logical progression of reasoning receive no credit. (Hint: Most of the credit for this problem will be awarded for setting up the required equation involving integrals with limits – evaluating the actual integrals and solving yields very few points.) Integral: $\int \frac{1}{ax+b}dx = \frac{1}{a}\ln|ax+b|$ (15 points)



b. Calculate the time needed for the volume to double if a=4, b=3, C_{A0} = 1 mol/L, V_i=100 L and v_o = 8 L/min. (3 points)

PROBLEM 3. (14 points) Your first project in a wastewater treatment plant is to propose a method for removing acetic acid from wastewater. The acetic acid is to be removed by an elementary reaction with methanol in a liquid-phase reactive distillation process, where the product, methyl acetate, and methanol exit the reactor in gaseous form.

$$\underset{A}{CH_3COOH} + \underset{B}{CH_3OH} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \underset{C}{CH_3COOHCH_3} + \underset{D}{H_2O}$$



The reactor is initially charged with wastewater at a concentration of acetic acid C_{A0}, and initial volume $V_{0.}$ A stream containing methanol ($C_{B,}$ v_0) is fed to the reactor starting at $t = 0$. Both methanol and methyl acetate are continuously vaporized and exit the reactor with an evaporation rate of F_C and F_B (mol/min), respectively. You **do not** need to write any equations in order to determine F_C and F_B – please assume them to be known and given to you at each point in time (in actuality they can be calculated based on the vapor pressure of the exiting species and equilibrium between gas and liquid phases). Further assume all liquids to be incompressible with a density of ρ_0.

Set up – but please do not solve – the system of differential equations that will allow you to solve the problem by doing the following.

a) Perform an overall mass balance on the system to obtain an expression for $\frac{dV}{dt}$. (4 points)

b) Perform a mole balance on each species to obtain an expression for $\frac{dN_j}{dt}$. Leave each expression in terms of $-r_a$. (8 points)

c) Express $-r_a$ for the reversible reaction above in terms of the number of moles of each species, N_j and reactor volume V. (2 points).

PROBLEM 4. (28 points) The gas-phase reaction

$$2A + B \rightarrow 4C$$

occurs via the following sequence of elementary steps:

		σ_i
$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_1$		___
$A + I_1 \xrightarrow{k_2} 2I_2$		___
$I_2 \xrightarrow{k_3} 2C$		___

(a) Obtain an expression for the reaction rate, r, in terms of the reaction rate for step 3, r_3. Justify your result by filling the stoichiometric numbers in the blank. (2 points)

(b) Using your answer from part (a), obtain an expression for the reaction rate, r, in terms of rate constants and concentrations of reactants and products, using PSSH on all intermediates. (8 points)

(c) Assume that step 1 is quasi-equilibrated. Derive the expression for the reaction rate, *r*, in terms of rate constants and concentrations of reactants and products. Draw the rate-arrow diagram. Clearly related the rates of each relevant step (r_1, r_{-1}, r_2, r_3) to the rate of the reaction *r*. (10 points)

(d) Provide the rigorous justification (what approximations are required) for collapsing the pseudo-steady state result to the quasi-equilibrium result. (3 points)

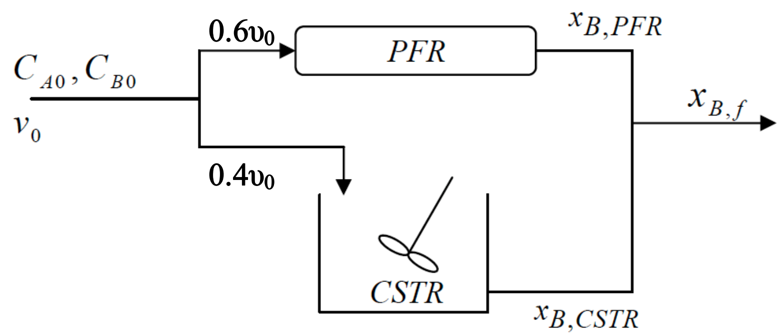
(e) Experimentally, at some conditions, the reaction rate exhibits first order dependence on the concentration of A and first order dependence of B. Compare your expression with the one in part b). What can we learn from step 1? Draw the rate-arrow diagram. Clearly related the rates of each relevant step (r_1, r_{-1}, r_2, r_3) to the rate of the reaction *r*. (5 points)

PROBLEM 5. (30 points)

An inlet gas stream ($v_0 = 10$ dm3 min-1 and $C_{T0} = 10$ mol dm-3), composed of 60% A / 20% B / 20% inert – all mole %, enters the system shown below. A splitter sends 60% of the volumetric flow to the PFR and 40% to the CSTR. Both reactors are isothermal and isobaric.

$$2A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

The reaction rate $r = k_1 C_B - k_{-1} C_D$, with $k_1 = 3\ \text{min}^{-1}$, $k_{-1} = 0.8\ \text{min}^{-1}$.



(a) When the reaction is irreversible and goes to completion, which species is the limiting reactant? (2 points)

(b) For the CSTR reactor, set up a stoichiometric table based on molar flow rates. Express the volumetric flow rate in terms of conversion of B leaving CSTR, $x_{B,CSTR}$, which is defined as: $x_{B,CSTR} = (F_{B0,\,CSTR} - F_{B,\,CSTR})/ F_{B0,\,CSTR}$ where $F_{B0,\,CSTR}$ represents the molar flow rate entering the CSTR and $F_{B,\,CSTR}$ represents the molar flow rate exiting the CSTR. Then express $C_{A,\,CSTR}$, $C_{B,\,CSTR}$, $C_{C,\,CSTR}$ and $C_{D,\,CSTR}$ in terms of $x_{B,CSTR}$. (15 points)

(c) Calculate the volume of the CSTR, V_{CSTR}, if the conversion of B leaving the reactor ($x_{B,CSTR}$) is 0.4. (6 points)

(d) If the conversion of B leaving the PFR is 0.48, and the conversion of B leaving CSTR is 0.4, calculate the conversion of B in the combined exit stream, $x_{B,f}$. Here, $x_{B,f}$ is defined as: $x_{B,f}$= (F_{B0}- $F_{B, CSTR}$- $F_{B, PFR}$)/ F_{B0} where F_{B0} is the molar flow rate of B to the entire process. (4 points)

(e) Suppose that the walls of the CSTR have been coated with a material that allows D to be selectively removed irreversibly and instantaneously from the gas phase of the reactor. Does the new CSTR volume required to reach an exit conversion of B ($x_{B,CSTR}$) of 0.4 change compared to part c)? Explain why in 1-2 sentences. Answers alone without clear explanation will receive no credit. (3 points)