Chemical Kinetics and Reaction Engineering

MIDTERM EXAMINATION I
Wednesday, February 25, 2009

The exam is 110 points total and 20% of the course grade.

Please read through the questions carefully before giving your response.

*Only answers written in the **blue book** will be graded.*

Question Number	Your Points	Possible Points
1		35
2		40
3		35
Total		110

Name:____

SID:____

Problem 1 (35 points)

Please provide concise answers (and explanations) to these three unrelated (to each other) questions:

(i) A_2 reacts in an elementary gas-phase dissociation reaction to form 2 molecules of A in a plug-flow reactor held at constant temperature (T) and constant pressure (P). The standard free energy of the reaction is ΔG^o. Derive an implicit equation for the equilibrium conversion (X_{eq}), in terms of P, T, and ΔG^o, when the feed is an equimolar mixture of A_2 and an inert I. Would removing the inert while maintaining the same inlet A_2 pressure increase or decrease X_{eq}? Why? (15 points)

(ii) Explain (in <200 words and perhaps a couple of useful equations) the meaning, implementation, validity and usefulness of the pseudo steady-state and quasi-equilibrium assumptions in deriving rate equations from sequences of elementary steps. (10 points)

(iii) You are given two CSTRs of equal volume to carry out a liquid phase reaction ($A \rightarrow B$) with a rate equation ($r = k(A)^2/(1 + K(A))$). Would you arrange them in parallel or in series to reach the highest exit conversion of A? Why? (10 points) (Explain in <200 words and perhaps some useful equations)

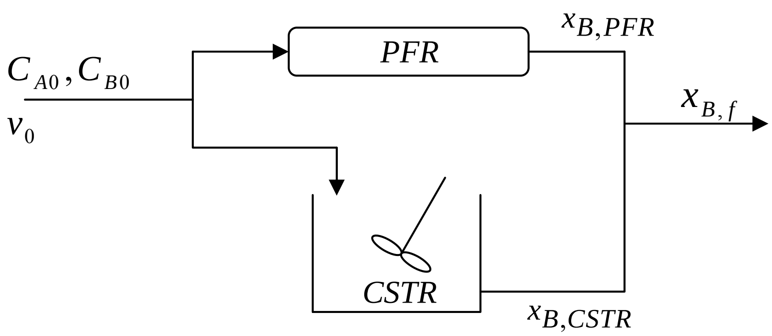
Problem 2 (40 points)

An inlet gas stream (v_0 = 10 dm^3 min^{-1} and C_{T0} = 10 mol dm^{-3}), composed of 20% A / 20% B / 60% inert, 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.

$$2A + B \rightleftarrows C + D$$

$$r = k_1 C_B - k_{-1} C_D$$

$$k_1 = 3 \text{ min}^{-1},\ k_{-1} = 0.8 \text{ min}^{-1}$$



(a) When the reaction is <u>irreversible</u> and goes to completion, which species is the limiting reactant? (5 points)

(b) Starting from a general mole balance on a differential volume element, derive the steady-state design equation (in integral form) for the volume of the PFR, V_{PFR}, expressed solely in terms of the conversion of B, $x_{B,PFR}$. Do not solve. (10 points)

(c) Starting from a general mole balance, derive the steady-state design equation for the CSTR and calculate the volume of the CSTR, V_{CSTR}, if the conversion of B leaving the reactor ($x_{B,CSTR}$) is 0.4. (10 points)

(d) If the conversion of B leaving the PFR is 0.48, calculate the conversion of B in the combined exit stream, $x_{B,f}$. (5 points)

(e) Suppose that the walls of the CSTR have been coated with an excess of material that selectively removes D irreversibly and instantaneously from the gas phase.

  (i) Calculate the new CSTR volume required to reach an exit conversion of B ($x_{B,CSTR}$) of 0.4. (5 points)

  (ii) Explain (in <100 words and perhaps some useful equations) why the reactor volume did or did not change compared to part (c). (5 points)

Problem 3 (35 points)

The gas-phase reaction

$$4A \rightarrow 3B + 2C$$

occurs via the following sequence of elementary steps:

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

$$A + I_1 \xrightarrow{k_2} 2I_2$$

$$I_1 + I_2 \xrightarrow{k_3} C$$

(a) Obtain an expression for the reaction rate, r, in terms of the reaction rate for step 3, r_3. (5 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 ***only*** PSSH. (8 points)

(c) Experimentally, at some conditions, the reaction rate exhibits the following dependence on the concentration of A and B:

$$r = \alpha \frac{[A]^2}{[B]}$$

What approximations are required in the rate expression obtained in part (b) to explain this dependence? What is the name of the "chemical" assumption for which these approximations are valid, and to which elementary step(s) does this assumption apply? (4 points)

(d) For the general case, simplify the rate expression obtained in part (b) assuming that:

(i) step 1 is irreversible (4 points)
(ii) step 1 is quasi-equilibrated (4 points)

For each case, identify the specific inequalities that must be satisfied for each assumption to hold.

(e) Assume that step 1 is quasi-equilibrated, but that I_1 can also form a toxic undesired byproduct, U, in a slow reaction pathway given by the following elementary step:

$$I_1 \xrightarrow{k_4} U$$

A selectivity, S, is defined as the ratio of production rates of desired *(C)* to undesired *(U)* product:

$$S = \frac{r_C}{r_U}$$

Would using a CSTR or a PFR (operated at the same exit conversion) result in a higher selectivity? Explain in <100 words (and perhaps some useful equations). (10 points)