ChE 142 February 23, 2005

Midterm I Key

(Closed Book and notes, one 8.5”x11” sheet of notes is allowed)

Printed Name ____

By signing this sheet, you agree to adhere to the U.C. Berkeley Honor Code

Signed Name____

1) **5** /5

2) **5** /5

3) **5** /5

4) **10** /10

5) **15** /15

6) **10** /10

Total: **50** /50

1. **(5 Pts.) Describe four characteristics of an elementary reaction.**

   a) Takes place as a single irreducible (no intermediates) molecular process

   b) The rate law is directly related to the stoichiometry.

   c) A sequence of elementary reactions combine to form the mechanism of the overall reaction.

   d) Microscopic reversibility: at equilibrium the forward and reverse rates must be equal.

   e) The molecularity of the reaction must be less than or equal to 3

2. **(5 Pts.) Ramon and Mary-Jane, two young chemical engineers, are having a discussion about which order to place a CSTR and PFR available in their plant in order to obtain the highest conversion for a reaction that is known to follow first order kinetics with respect to the reactant. Ramon says that the CSTR should go first, but Mary-Jane says that the PFR should go first. Assuming that the volume of the PFR and CSTR are equal who is right and why?**

They are both correct. For a 1st order reaction, it does not matter which reactor is placed first the conversion will be the same.

3. **(5 Pts.) The reaction 2A + B → C occurs in the gas phase in a PFR. The feed contains 50% A and 50% B. Please answer the following questions.**

   (i) **What are the values of δ and ε?**

Since A is the limiting reagent we will write

$$\delta = -\sum_j \frac{\nu_i}{\nu_A} = -\left(\frac{\nu_C}{\nu_A} + \frac{\nu_B}{\nu_A} + \frac{\nu_A}{\nu_A}\right) = -\left(\frac{1}{-2} + \frac{-1}{-2} + \frac{-2}{-2}\right) = -1$$

$$\varepsilon = y_{A0}\delta = 0.5 * -1 = -0.5$$

(ii) Write rate expressions for the consumption of A and the appearance of C in terms of the conversion of the limiting reagent. You can assume that the reaction as written is an elementary process.

We know $\frac{r_A}{\nu_A} = \frac{r_B}{\nu_B} = \frac{r_C}{\nu_C}$ then $r_A = \frac{\nu_A}{\nu_C} r_C = \frac{-2}{1} r_C = -2r_C$ or $\boxed{-r_A = 2r_C}$

Assuming an elementary reaction $r_C = kC_B C_A^2$

From stoichiometry table: $C_j = \dfrac{C_{A0}\left(\Theta_j - \frac{\nu_j}{\nu_A} X_A\right)}{(1+\varepsilon X_A)}$ where $\Theta_j = \dfrac{C_{j0}}{C_{A0}}$

then $C_A = \dfrac{C_{A0}(1-X_A)}{(1-0.5*X_A)}$ and $C_B = \dfrac{C_{A0}\left(1-\frac{1}{2}X_A\right)}{(1-0.5*X_A)}$

Finally, $\boxed{r_C = \dfrac{kC_{A0}^3\left(1-\frac{1}{2}X_A\right)(1-X_A)^2}{(1-0.5X_A)^3}}$ and $\boxed{-r_A = \dfrac{2kC_{A0}^3\left(1-\frac{1}{2}X_A\right)(1-X_A)^2}{(1-0.5X_A)^3}}$

4. **(10 Pts.) Chemical vapor deposition is used in the semiconductor industry to decompose a volatile precursor in order to deposit a thin film of metal on a hot surface. Suppose that this reaction can be represented by $P_{(g)} \rightarrow M_{(s)}$ and that this process takes place in a PFR. The metal, M, is deposited on the walls of the reactor. Pure P is fed to the reactor and the temperature and pressure are constant along the reactor.**

   (i) **The rate of reaction is first order in P. What, if anything, should be done to assure that the rate of metal deposition is uniform along the reactor? Be sure to explain whatever you propose.**

We would like the deposition rate to be constant (ie. $-r_P = kC_p = \text{constant}$). Let us find how the reaction rate varies with conversion. We have a gas phase reaction so we must calculate the contraction/expansion factor

$$\delta = -\sum_j \frac{\nu_i}{\nu_P} = -\left(\frac{\nu_P}{\nu_P}\right) = -1 \text{ and } \varepsilon = y_{P0}\delta = 1*-1 = -1$$

calculating the concentration of P as a function of conversion

$$C_P = \frac{C_{P0}\left(\Theta_P - \frac{\nu_P}{\nu_P}X_P\right)}{(1+\varepsilon X_P)} = \frac{C_{P0}(1-X_A)}{(1-X_A)} = C_{P0}$$

The reaction rate then can be written as

$$-r_P = kC_p = kC_{p0} = \text{constant}$$

We can see that the concentration within the reactor is constant; therefore we don't need to do anything to insure that we get a uniform deposition! The concentration remains constant, because the flow rate decreases along the reactor (due to the increasing conversion). $\upsilon = \upsilon_0(1-X_P)$

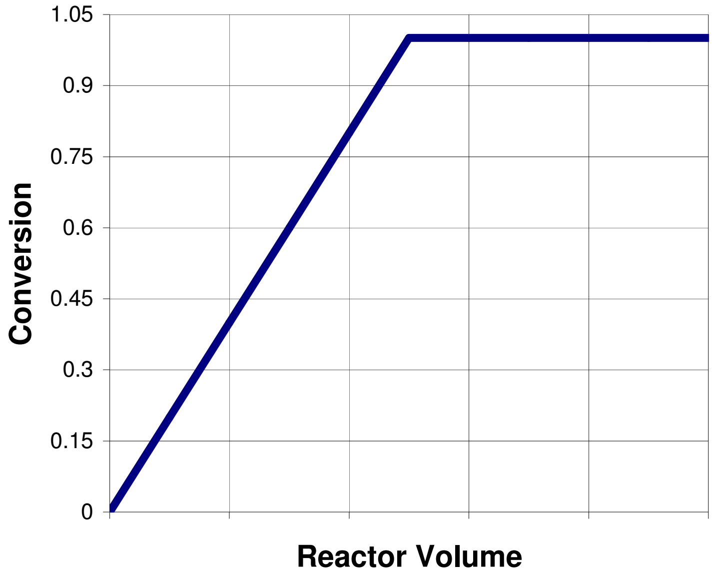
(ii) Sketch a profile of precursor conversion as function of reactor length or volume and indicate the point at which X_P = 1.0. Is there anything unusual about the profile that you have sketched?

Design equation for a PFR

$$\frac{dF_P}{dV} = r_P$$

$$\text{====>}\quad V = F_{P0}\int_0^{X_P}\frac{dX}{-r_P} = F_{P0}\int_0^{X_P}\frac{dX}{kC_{P0}} = \frac{F_{P0}X_P}{kC_{P0}}$$

$$\text{====>}\quad \boxed{X_P = \frac{kC_{P0}V}{F_{P0}} = \frac{kV}{\upsilon_0}}$$



Notice that the conversion increases linearly with reactor volume with a slope of kC_{P0}/F_{P0} until we reach a point when the conversion is equal to 1 and a discontinuity forms.

5. (15 pts.) The following reaction occurs irreversibly:

$$\mathbf{2\,D + E \rightarrow 3\,S + T}$$

(a) The 100 L/h liquid feed is 60% D and 40% E on a molar basis. The rate of reaction is first order in E, i.e. $r = k\,C_E$, and the rate constant has a value of $0.136\ \text{min}^{-1}$. Calculate the conversion that can be achieved in a $10\ \text{dm}^3$ CSTR.

From the CSTR design equation: $V = \dfrac{F_{D0}\,X}{-r_D}$

We are given the rate expression: $r = k\,C_E$

Species D is the limiting reagent., so it will be the basis for our calculations.

$$C_E = C_{D0}\left(\Theta_E - \frac{\nu_E}{\nu_D}X\right) = C_{D0}\left(\frac{2}{3} - \frac{1}{2}X\right)$$

$$r = \frac{r_D}{-2} \ \text{ so } \ -r_D = 2\,r = 2\,k\,C_{D0}\left(\frac{2}{3} - \frac{1}{2}X\right)$$

Therefore, $V = \dfrac{F_{D0}\,X}{2\,k\,C_{D0}\left(\frac{2}{3} - \frac{1}{2}X\right)}$ and since $\dfrac{F_{D0}}{C_{D0}} = \nu_0$, $V = \dfrac{\nu_0\,X}{2\,k\left(\frac{2}{3} - \frac{1}{2}X\right)}$

Solving for conversion, $X = \dfrac{\alpha\,\Theta_E}{1+0.5\,\alpha}$ where $\alpha = \dfrac{V2k}{v_0} = \dfrac{10\text{L}}{100\text{L/h}}\left|\dfrac{2}{}\right|\dfrac{0.136}{\text{min}}\left|\dfrac{60\text{min}}{\text{h}}\right. = 1.632$

$$\boxed{X = \frac{(1.632)(2/3)}{1+0.5\,(1.632)} = 0.599}$$

(b) Given that the reactor was operated at 373 K in part (a) and the activation energy of the reaction is 72.3 kJ/mol, what is the conversion of this CSTR if the reaction temperature is raised to 383 K? (R = 8.314 J/mol·K)

$$k = A\exp(-E/RT)$$

$$k_2 = k_1 \exp\left[-\frac{E}{RT}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right] = \frac{0.136}{\text{min}}\exp\left[-\frac{72300\,\text{J}}{\text{mol}}\left|\frac{\text{mol K}}{8.314\,\text{J}}\right.\left(\frac{1}{383\,\text{K}}-\frac{1}{373\,\text{K}}\right)\right] = 0.250$$

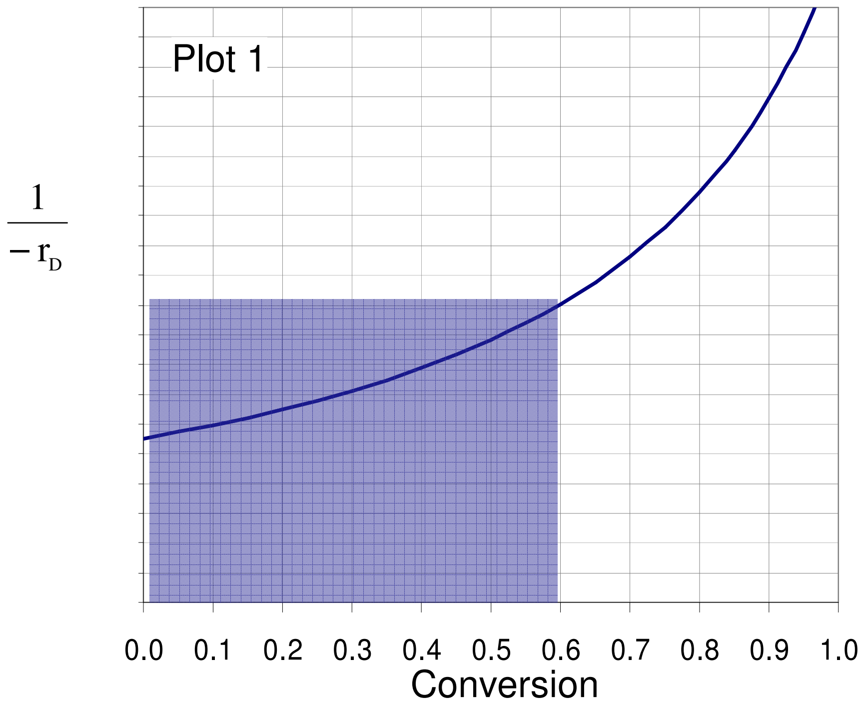
$$\alpha = \frac{V2k}{v_0} = \frac{10\text{L}}{100\text{L/h}}\left|\frac{2}{}\right|\frac{0.25}{\text{min}}\left|\frac{60\text{min}}{\text{h}}\right. = 3.0$$

$$\boxed{X = \frac{\alpha\,\Theta_E}{1+0.5\,\alpha} = \frac{(3.0)(2/3)}{1+0.5\,(3.0)} = 0.80}$$

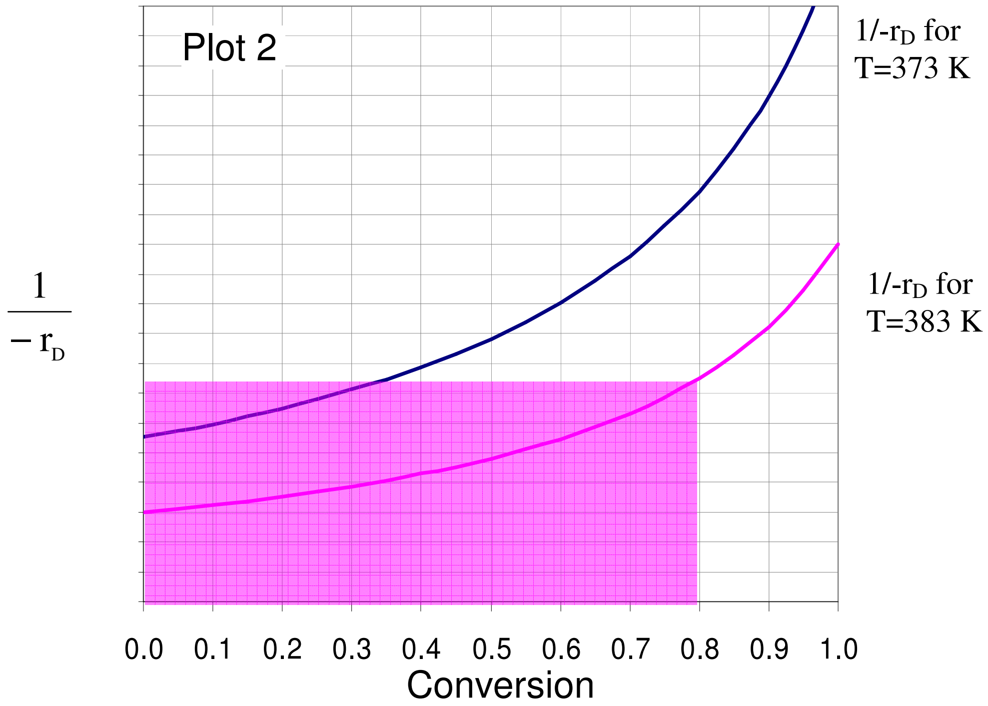
(c) **The Levenspiel plot for the reaction in part (a) is given below.**

(i) **On plot 1, shade the area which when multiplied by the molar flow rate yields the volume of the CSTR.**

(ii) **On plot 2, draw a similar sketch that illustrates how a different conversion is achieved under the conditions given in part (b). Note that the line on plot 2 corresponds to the reaction rate at 373 K.**



The area of the shaded box is 60 boxes or 0.6*10 arb. units = 6.



At T=383 K, the conversion is 0.8 and the CSTR has the same volume, so the area of the box must be the same. Thus, 6 = 0.8* Y arb. units. Y = 6/0.8 = 7.5 arb. units on the y-axis. This defines a point on the $1/\text{-}r_D$ curve and the rest of the curve can then be sketched. Since at a higher temperature, the rate is higher, we expect the $1/\text{-}r_D$ curve at T=383 K to be lower than the curve for T=373 K.

6. **(10 pts.) The decomposition of ozone is believed to proceed via the following three-step mechanism:**

$$\textbf{1.}\quad M + O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O\cdot + O_2 + M$$

$$\textbf{2.}\quad O\cdot + O_3 \xrightarrow{k_2} 2\,O_2$$

(a) **Assuming that O· (atomic oxygen) is a very reactive intermediate, derive an overall rate expression for the rate of ozone decomposition.**

Applying the pseudo-steady state hypothesis

$$r_{O*} = k_1[O_3][M] - k_{-1}[M][O_2][O*] - k_2[O_3][O*] = 0$$

$$k_1[O_3][M] + [O*]\left(-k_{-1}[M][O_2] - k_2[O_3]\right) = 0$$

$$[O*] = \frac{k_1[O_3][M]}{k_{-1}[M][O_2] + k_2[O_3]}$$

Writing net rate of disappearance of ozone

$$-r_{O3} = k_1[O_3][M] - k_{-1}[M][O_2][O*] + k_2[O_3][O*] = k_1[O_3][M] - [O*]\left(-k_{-1}[M][O_2] + k_2[O_3]\right)$$

substitution of [O*] yields

$$-r_{O3} = k_1[O_3][M] - \frac{k_1[O_3][M]\left(-k_{-1}[M][O_2] + k_2[O_3]\right)}{k_{-1}[M][O_2] + k_2[O_3]}$$

or

$$-r_{O3} = k_1[O_3][M]\left(1 - \frac{\left(-k_{-1}[M][O_2] + k_2[O_3]\right)}{k_{-1}[M][O_2] + k_2[O_3]}\right)$$

expanding terms

$$-r_{O3} = \frac{k_1[O_3][M]\left(k_{-1}[M][O_2] + k_2[O_3]\right) - k_1[O_3][M]\left(-k_{-1}[M][O_2] + k_2[O_3]\right)}{k_{-1}[M][O_2] + k_2[O_3]}$$

$$-r_{O3} = \frac{k_1k_{-1}[O_3][O_2][M]^2 + k_1k_2[M][O_3]^2 + k_1k_{-1}[O_3][O_2][M]^2 - k_1k_2[M][O_3]^2}{k_{-1}[M][O_2] + k_2[O_3]}$$

this can be reduced to the following

$$\boxed{-r_{O3} = \frac{2k_1k_2[M][O_3]^2}{k_{-1}[M][O_2]+k_2[O_3]} = \frac{k[M][O_3]^2}{[M][O_2]+k^{i}[O_3]}} \qquad \text{where } \boxed{k = \frac{2k_1k_2}{k_{-1}}} \;\; \& \;\; \boxed{k^{l} = \frac{k_2}{k_{-1}}}$$

(b) How does the rate expression derived in part (a) change if reaction 2 is assumed to be rate limiting?

If reaction 2 is rate limiting then reaction 1 can be assumed to be in quasi-equilibrium and the rate of disappearance of ozone is determined reaction 2

$$-r_{O3} = k_2[O_3][O*]$$

If reaction 1 is in quasi-equilibrium we can write

$$k_1[O_3][M] = k_{-1}[M][O_2][O*]$$

$$K = \frac{k_1}{k_{-1}} = \frac{[M][O_2][O*]}{[O_3][M]} = \frac{[O_2][O*]}{[O_3]} \qquad \text{then} \quad [O*] = \frac{K[O_3]}{[O_2]}$$

so the rate of disappearance of ozone then becomes

$$\boxed{-r_{O3} = \frac{k_2K[O_3][O_3]}{[O_2]} = \frac{k_1k_2}{k_{-1}}\frac{[O_3]^2}{[O_2]}}$$