In the first assignment you were asked to describe the goals of the course in terms of critical thinking, creative thinking, and a fundamental understanding of CRE. How well do you feel you made progress towards each of these goals?

1) I feel my critical thinking skills were increased
   Significantly Not at All
   5 4 3 2 1

2) I feel my creative thinking skills were increased
   Significantly Not at All
   5 4 3 2 1

3) I feel I learned how to ask critical questions
   Significantly Not at All
   5 4 3 2 1

4) I expect to use the techniques discussed in creative thinking (e.g. vertical thinking, lateral thinking, ideas from Barkers videos.
   Often Never
   5 4 3 2 1

5) I feel I met the goal of obtaining a fundamental understanding of CRE topics covered in the course.
   Definitely Not at All
   5 4 3 2 1

Name (optional)___________________________
ChE 344
Chemical Reaction Engineering
Winter 2000

Final Exam

Open Book, Notes, and Web

Name ______________________

SOLUTION

Honor Code ____________________________________________________________

_____________________________________________________________________

_____________________________________________________________________

_____________________________________________________________________

Signed ___________________________________________

1) ____/10 pts
2) ____/15 pts
3) ____/20 pts
4) ____/20 pts
5) ____/15 pts
6) ____/15 pts
7) ____/ 5 pts

Total 100 pts
1) The gas phase reaction

\[ 2A + B \rightarrow 2C \]

is carried out isothermally and isobarically. The reaction is first order in B and first order in A. The feed is equal molar in A and B and the entering concentration of A is 0.5 mol/dm\(^3\). The specific reaction rate is \( k = 4.0 \text{ dm}^3/\text{mol} \cdot \text{s} \).

(8%) a) Write the rate of reaction, \(-r_A\), solely as a function of conversion, evaluating all parameters.

\[ \begin{align*}
2A + B &\rightarrow 2C \quad \Rightarrow \quad A + \frac{1}{2}B \rightarrow C \\
-r_A &= kC_A C_B \\
C_A &= \frac{C_{Ao}(1-X)}{(1+\varepsilon X)} \\
C_B &= \frac{C_{Ao}(1-0.5*X)}{(1+\varepsilon X)} \\
\varepsilon &= \frac{y_{Ao}}{\delta} = 0.5 \times (1-1-0.5) = -0.25
\end{align*} \]

\[ -r_A = \frac{kC_{Ao}(1-X)C_{Ao}(1-0.5*X)}{(1+\varepsilon X)^2} = \frac{\left(4.0 \ \frac{\text{dm}^3}{\text{mol} \cdot \text{s}}\right)\left(0.5 \ \frac{\text{mol}}{\text{dm}^3}\right)^2(1-X)(1-0.5*X)}{(1-0.25*X)^2} \]

\[ -r_A = \frac{(1-X)(1-0.5*X)}{(1-0.25*X)^2} \ \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}} \]

(2%) b) Write an in-depth question related to CRE that requires critical thinking and explain why it requires critical thinking. Be sure to be as specific as you can.

Must be related to Chemical Reaction Engineering and require critical thinking.
(15%) 2) The gas phase irreversible reaction is carried out isothermally in a PBR.

\[ A \rightarrow B \]

The reaction is zero order. The entering temperature is 400 K, and the entering pressure is 10 atm. The flow is turbulent. For a 10 kg PBR with a pressure drop parameter \( \alpha = 0.01 \, \text{kg}^{-1} \), the exit conversion was found to be 0.4.

a) What catalyst weight of the PBR will you require if you need an exit conversion of 0.8, assuming that the particle diameter is decreased by a factor of 2 so that the pressure drop parameter is now increased to 0.02? Assume all other operating conditions are the same as for the base case (i.e. \( W = 10 \, \text{kg} \)).

Mole Balance: \( \frac{dX}{dW} = -\frac{r_A}{F_{Ao}} \)

Rate Law: \( -r_A = k \)

Combine: \( \frac{dX}{dW} = \frac{k}{F_{Ao}} \)

Find \( \frac{k}{F_{Ao}} \) using the initial case

\[
W = 20 \, \text{kg}
\]

\[
\int_{0}^{0.4} dX = k \int_{0}^{10} dW \Rightarrow 0.4 = 10 \frac{k}{F_{Ao}} \Rightarrow \frac{k}{F_{Ao}} = 0.04
\]

Now Find the new weight

\[
\int_{0}^{0.8} dX = 0.04 \int_{0}^{W} dW \Rightarrow 0.8 = 0.04W \Rightarrow W = 20 \, \text{kg}
\]

b) For the fixed inlet pressure of 10 atm, will the volumetric flow rate \( v \) (dm\(^3\)/s), be greater, smaller, or remain the same when the particle diameter is decreased by a factor of 2?

\begin{tabular}{c c c}
Increased & Decreased & Remain the Same \\
\hline
\end{tabular}

\[
v = \nu_0 \left( \frac{P}{P_o} \right) \left[ 1 + \varepsilon X \right] \left( \frac{T}{T_o} \right), \text{ isothermal so } \left( \frac{T}{T_o} \right) = 1
\]

\[
v \sim \frac{P}{P_o} \sim (1 - \alpha W)^{-0.5} \text{ because } \varepsilon \text{ is zero}
\]

\[
v_1 \sim (1 - 0.01 \, W)^{-0.5} \sim (1 - 0.01)^{-0.5} \sim (0.99)^{-0.5} \sim 1.005
\]

\[
v_2 \sim (1 - 0.02 \, W)^{-0.5} \sim (1 - 0.02)^{-0.5} \sim (0.98)^{-0.5} \sim 1.010
\]

\[ \therefore \quad v_2 > v_1 \]
The gas phase reactions

\[ \text{(1)} \quad \text{A} \longrightarrow \text{B} + 2\text{C} \quad -r'_{1\text{A}} = k_{1\text{A}} C_{\text{A}}^2 , \quad \Delta H_{\text{Rx1A}} = -\frac{50 \text{kJ}}{\text{mol A}} \]

\[ \text{(2)} \quad \text{C} + 3\text{A} \longrightarrow 2\text{D} \quad -r'_{2\text{C}} = k_{2\text{C}} C_{\text{A}} C_{\text{C}} , \quad \Delta H_{\text{Rx2A}} = +\frac{20 \text{kJ}}{\text{mol A}} \]

\[ \text{(3)} \quad \text{E} \longrightarrow \text{G} \quad -r'_{3\text{E}} = k_{3\text{E}} C_{\text{E}}^2 , \quad \Delta H_{\text{Rx3E}} = -\frac{80 \text{kJ}}{\text{mol}} \]

occur in a PBR with a heat exchanger. The PBR contains 500 kg of catalyst. The entering concentration of A is 0.8 mole/dm$^3$ and the entering concentration of E is 0.2 mol/dm$^3$. The entering volumetric flow rate is 10 dm$^3$/s at a temperature of 300K. It was found that the rate reaction for reactions (1) and (2) doubles for a 10 K increase from 300 to 310 in temperature while the rate of reaction (3) doubles for a 10 K increase from 500 K to 510 K. The entering pressure is 24.6 atm.

**Additional Information**

\[ C_{P\text{A}} = 60 \text{ J/mol K} \quad k_{1\text{A}} = 0.7 \text{ dm}^3/\text{mol} \cdot \text{s @300 K} \]

\[ C_{P\text{B}} = 20 \text{ J/mol K} \quad k_{2\text{C}} = 3.8 \text{ dm}^3/\text{mol} \cdot \text{s @300 K} \]

\[ C_{P\text{C}} = 20 \text{ J/mol K} \quad k_{3\text{E}} = 0.9 \text{ dm}^3/\text{mol} \cdot \text{s @500 K} \]

\[ C_{P\text{D}} = 100 \text{ J/mol K} \quad \alpha = 0.0001 \text{ kg}^{-1} \]

\[ C_{P\text{E}} = 50 \text{ J/mol K} \quad C_{T\text{o}} = 1.0 \text{ mol/dm}^3 \]

\[ C_{P\text{G}} = 50 \text{ J/mol K} \quad T_{\text{o}} = 300 K \]

\[ T_{\text{a}} = 350 K , \quad \frac{U_{\text{a}}}{\rho_{\text{b}}} = 20 \frac{\text{kJ}}{\text{s kg cat}} \]

Write a complete Polymath program to plot the temperature and species concentration as a function of catalyst weight. Including initial conditions.
\[
\begin{align*}
\frac{dF_A}{dw} &= -r_{1A} - 3r_{2C} \\
\frac{dF_B}{dw} &= r_{1A} \\
\frac{dF_C}{dw} &= 2r_{1A} - r_{2C} \\
\frac{dF_D}{dw} &= 2r_{2C}E \\
\frac{dF_E}{dw} &= -r_{3E} \\
\frac{dF_F}{dw} &= r_{3E} \\
\end{align*}
\]

\[
r_{1A} = k_{1A} C_A^2 \\
r_{2C} = k_{2C} C_A C_E \\
r_{3E} = k_{3E} C_E^2 \\
\]

\[
\frac{dT}{dw} = \frac{20,000 \left(T_0 - T\right) + \left[r_{1A}(50) + r_{2C}(80) + 3 + r_{3E}(80)\right] \times 1000}{20 F_A + 20 F_B + 20 F_C + 100 F_D + 50 F_E + 50 F_F} \quad T_0 = 300 \\
\]

\[
\frac{dP}{dw} = -\frac{d}{2} \left(\frac{T}{T_0}\right) \left(\frac{P_e}{P}\right) \left(\frac{F_T}{F_{T_0}}\right) \\
P_e = 2.96 \\
T_0 = 300 \\
d = 0.0001 \\
\]

\[
F_T = F_A + F_B + F_C + F_D + F_E + F_F \\
F_{T_0} = 10 \times (0.8 + 0.2) \\
C_A = \left(\frac{F_A}{F_T}\right) \left(\frac{P}{RT}\right) \\
C_C = \left(\frac{F_C}{F_T}\right) \left(\frac{P}{RT}\right) \quad \text{or} \quad C_C = C_{T_0} \frac{F_I}{F_T} \frac{P}{P_0} \frac{T}{T_0} \\
C_E = \left(\frac{F_E}{F_T}\right) \left(\frac{P}{RT}\right) \quad \text{while } C_{T_0} = 1.0 \\
\]

344/W'00 Final Exam
\[ k_{1a} = 0.7 \exp \left[ 6446 \left( \frac{1}{300} - \frac{1}{510} \right) \right] \]
\[ k_{2c} = 3.8 \exp \left[ 6446 \left( \frac{1}{300} - \frac{1}{510} \right) \right] \]
\[ K_{3E} = 0.9 \exp \left[ 17675 \left( \frac{1}{500} - \frac{1}{510} \right) \right] \]

Obtain \( \frac{E}{R} \) values

For \( k_{1a} \) and \( k_{2c} \)
\[ k_{1a}(310) = k(300) \exp \left[ \frac{E}{R} \left( \frac{1}{300} - \frac{1}{310} \right) \right] \]
\[ 2 = \exp \left[ \frac{E}{R} \left( \frac{1}{300} - \frac{1}{310} \right) \right] \]
\[ \frac{E}{R} = \frac{\ln 2}{\left( \frac{1}{300} - \frac{1}{310} \right)} = 6446 \]

For \( K_{3E} \)
\[ \frac{E}{R} = \frac{\ln 2}{\left( \frac{1}{500} - \frac{1}{510} \right)} = 17675 \]
(20%) 4) The following reversible, elementary, liquid phase reaction occurs in a PFR:

\[ \text{A} \xleftrightarrow{\text{B}} \]

The entering flow rate is 10 dm\(^3\)/s with an entering concentration of 2 M of A and the feed temperature is 310 K.

a) What is the reactor volume necessary to achieve 90% of the adiabatic equilibrium conversion in one PFR operated adiabatically? \( V \sim 12.34 \text{ dm}^3 \) (see below)

b) Now consider a series of reactors with interstage cooling so that the temperature is cooled to 300 K in each interstage cooler. How many reactors are necessary to achieve 95% conversion assuming 99.9% of the equilibrium conversion is achieved in each reactor? \( 3 \text{ Reactors (see Xequil. vs. T graph below)} \)

Hint: Recall Chapter 2 and/or appendix A.4 and make a rough estimate.

Additional information:

\[ \text{C}_p_A = \text{C}_p_B = 50 \text{ cal/mol/K} \]
\[ \Delta H^\circ_{\text{rxn}} = -10,000 \text{ cal/mol A} \]

Answer (for solution see table and graphs below): \( V_{\text{PFR}} \sim \frac{12.34}{12.34} \text{ dm}^3 \)

continued on next page
Problem 4 continued

\[ X_{EB} = \frac{\Delta H_{\text{rxn}}(T_{a})}{-\Delta H_{\text{rxn}}(T_{a})} = \frac{50(T-310)}{10000} - 0.005(T-310) \]

\[ T = 310, \ X_{EB} = 0 \]

\[ T = 410, \ X_{EB} = 0.5 \]

<table>
<thead>
<tr>
<th>X</th>
<th>T</th>
<th>Kc</th>
<th>k</th>
<th>(-r_a)</th>
<th>(-\frac{1}{r_a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>310</td>
<td>50</td>
<td>0.1</td>
<td>0.2</td>
<td>5</td>
</tr>
<tr>
<td>0.1</td>
<td>330</td>
<td>20</td>
<td>0.5</td>
<td>0.895</td>
<td>1.12</td>
</tr>
<tr>
<td>0.2</td>
<td>350</td>
<td>8</td>
<td>0.8</td>
<td>1.24</td>
<td>0.8</td>
</tr>
<tr>
<td>0.3</td>
<td>370</td>
<td>3</td>
<td>1.2</td>
<td>1.44</td>
<td>0.69</td>
</tr>
<tr>
<td>0.4</td>
<td>390</td>
<td>2</td>
<td>2</td>
<td>1.60</td>
<td>0.625</td>
</tr>
<tr>
<td>0.5</td>
<td>410</td>
<td>1</td>
<td>3</td>
<td>0.27</td>
<td>3.7</td>
</tr>
</tbody>
</table>

\[ A \xrightleftharpoons{\text{liquid phase, elementary}} B \]

\[ -r_a = kC_{A_0} \left[ \left(1-X\right) - \frac{X}{K_c} \right] \]

\[ C_{A_0} = 2 \text{ M} \]

\[ \frac{\Delta n_{A_0}}{m_{A_0}} = \frac{2 \text{ mol}}{10 \text{ dm}^3} = \frac{20 \text{ mol}}{5} \]

\[ \text{Su pg. 453} \]

\[ -7 \text{ for not varying } k, K_c \]
3 Reactors are needed to achieve 95% conversion
(15%) 5) The chemical vapor deposition of silica from TEOS (tetrethyl othosilicate)

\[
\text{OC}_2\text{H}_5
\]

\[
\text{C}_2\text{H}_5\text{O–Si–OC}_2\text{H}_5 \rightarrow \text{Si} + 4\text{CH}_2 = \text{CHOH} + 2\text{H}_2
\]

\[
\text{OC}_2\text{H}_5
\]

is carried out in a batch from the gas phase. The following data were obtained.

<table>
<thead>
<tr>
<th>(r_{\text{Dep}}) Rate (nm/s)</th>
<th>(P_{\text{TEOS}}) (atm)</th>
<th>(P_{\text{H}_2}) (atm)</th>
<th>(P_{\text{CH}_2 = \text{CHOH}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1</td>
<td>.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>.4</td>
<td>.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.5</td>
<td>.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9.1</td>
<td>1</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>9.1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>10</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>500</td>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4167</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>9091</td>
<td>100</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>19048</td>
<td>200</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>39024</td>
<td>400</td>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>99010</td>
<td>1000</td>
<td>100</td>
<td>50</td>
</tr>
</tbody>
</table>

a) Suggest a rate law from the above data.

\(r_{\text{Dep}} \neq \text{function}(P_{\text{H}_2})\)

\(r_{\text{Dep}} \neq \text{function}(P_{\text{CH}_2 = \text{CHOH}})\)

\(r_{\text{Dep}} = \text{function}(P_{\text{TEOS}})\)

Initially,

\[
\frac{r_2}{r_1} = \frac{0.4}{0.1} = \left(\frac{0.2}{0.1}\right)^2 = \left(\frac{P_2}{P_1}\right)^2 \Rightarrow r_{\text{Dep}} \sim P_{\text{TEOS}}^2
\]

Finally,

\[
\frac{r_2}{r_1} = \frac{99010}{39024} = 2.5 = \left(\frac{P_2}{P_1}\right) \Rightarrow r_{\text{Dep}} \sim P_{\text{TEOS}}
\]

Combining,

\[
r_{\text{Dep}} = \frac{kP_{\text{TEOS}}^2}{1 + K_rP_{\text{TEOS}}}
\]
b) Suggest a mechanism and rate limiting step consistent with the rate law.

Eley -Rideal Mechanism:
TEOS+ Si ⇌ TEOS• Si
TEOS•Si +TEOS ⇌ Si•Si+ 4CH₂ = CHOH +2H₂
The above is the rate limiting step
Si•Si ⇌ Si+Si (could add this step if stated weakly adsorbed)
(15%) 6) A number of irreversible elementary series reactions (e.g. \(X \rightarrow Y \rightarrow Z, D \rightarrow E \rightarrow F\)) all follow the sequence

\[A \rightarrow B \rightarrow C\]

were carried out adiabatically in a PBR. The following plots were obtained for the different reactions. (E.g. Case A represents the reaction \(X \rightarrow Y \rightarrow Z\), Case B represents \(D \rightarrow E \rightarrow F\), etc.)

\[\text{(A)}\]

\[\text{(B)}\]

\[\text{(C)}\]

\[\text{(D)}\]

\[\text{(E)}\]

continued on next page
a) Which case or cases could represent a reaction in which the second reaction in series (B → C) has a very very low frequency factor and a very very high activation energy when compared to the first (A → B)?

       Ans. B and C

       Explain B because the reaction stops (only first reaction occurs due to low frequency factor and high activation energy)  C because high activation energy will cause the second reaction to be very temperature sensitive

b) Which case or cases could represent a situation where both reactions are exothermic?

       Ans. C and D

       Explain The temperature goes up for both reactions (formation of B and destruction of B to form C)

       Explain The temperature goes up for both reactions (formation of B and destruction of B to form C)


c) Which case could represent a situation in which the first reaction is endothermic and the second is exothermic?

       Ans. A

       Explain The temperature goes down for the first reaction (formation of B) and goes up for the second reaction (formation of C from B)

       Explain The temperature goes down for the first reaction (formation of B) and goes up for the second reaction (formation of C from B)


d) Which case could represent a situation in which the first reaction is exothermic and the second is endothermic?

       Ans. E

       Explain The temperature goes up for the first reaction (formation of B) and goes down for the second reaction (formation of C from B)

       Explain The temperature goes up for the first reaction (formation of B) and goes down for the second reaction (formation of C from B)


e) Which case could represent a situation in which absolute value of the heat of reaction of the second reaction is greater than the first?

       Ans. C

       Explain The rate temperature increase for the second reaction is greater than that for the first reaction (indicative of a more exothermic heat of reaction for the second reaction)

       Explain The rate temperature increase for the second reaction is greater than that for the first reaction (indicative of a more exothermic heat of reaction for the second reaction)
(5%) 7) The following sequence is believed to occur for the decomposition of ethane

\[ C_2H_6 \xrightarrow{k_1} 2CH_3\cdot \]
\[ C_2H_6 + CH_3\cdot \xrightarrow{k_2} C_3H_8 + H\cdot \]
\[ H\cdot + H\cdot \xrightarrow{k_3} H_2 \]

Develop a rate law for the rate of formation of propylene in terms of the concentration of ethane.

Note: there was a typo in the exam. The chemical formula for propylene is \( C_3H_6 \), not \( C_3H_8 \) as given above.

\[ r_{\text{prop}} = k_2 [C_2H_6][CH_3\cdot] \]

Apply the PSSA to \( CH_3\cdot \)

\[ r_{CH_3\cdot} \equiv 0 = -k_2 [C_2H_6][CH_3\cdot] + k_1 [C_2H_6] \]

\[ k_2 [C_2H_6][CH_3\cdot] = k_1 [C_2H_6] \]

\[ [CH_3\cdot] = \frac{k_1}{k_2} \]

Now substitute back into \( r_{\text{prop}} \)

\[ r_{\text{prop}} = k_2 [C_2H_6] \frac{k_1}{k_2} \]

\[ r_{\text{prop}} = k_1 [C_2H_6] \]