ChE 344
Chemical Reaction Engineering
Winter 1999
Exam I
Part 1 (80%)

Solution
1) The trimerization

\[ 3A(g) \rightarrow A_3(g,l) \]

is carried out isothermally and without pressure drop in a PFR at 298 K and 2 atm. As the concentration of \( A_3 \) increases down the reactor and \( A_3 \) begins to condense. The vapor pressure of \( A_3 \) at 298 K is 0.5 atm. If an equal molar mixture of \( A \) and inert, \( I \), is fed to the reactor at what conversion of \( A \) will \( A_3 \) begin to condense?

\[ A(g) \rightarrow \frac{1}{3} A_3(g,l) \]

Condensation begins at

\[ y = \frac{P_v}{P_T} = \frac{0.5 \text{ atm}}{2 \text{ atm}} = 0.25 \]

<table>
<thead>
<tr>
<th>Species</th>
<th>Entering</th>
<th>Change</th>
<th>Before Cond.</th>
<th>After Cond.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A(g) )</td>
<td>( F_{A_0} )</td>
<td>( -F_{A_0}X )</td>
<td>( F_A = F_{A_0}(1-X) )</td>
<td>( F_A = F_{A_0}(1-X) )</td>
</tr>
<tr>
<td>( I(g) )</td>
<td>( F_{A_0} )</td>
<td>---</td>
<td>( F_I = F_{A_0} )</td>
<td>( F_I = F_{A_0} )</td>
</tr>
<tr>
<td>( A_3(g,l) )</td>
<td>---</td>
<td>( \frac{F_{A_0}X}{3} )</td>
<td>( F_{A_3} = \frac{F_{A_0}X}{3} )</td>
<td>( F_{A_3} = y_{A_3,e} F_T )</td>
</tr>
</tbody>
</table>

\[ F_T = F_{A_0} \left( 2 - \frac{2}{3}X \right) \]

\[ y_{A_3,e} = \frac{F_{A_3}}{F_T} = \frac{F_{A_0}X}{3} = 0.25 \]

\[ \frac{X}{6-2X} = \frac{1}{4} \]

\[ 4X = 6 - 2X \]

\[ 6X = 6 \]

\[ X = 1 \]
(30 pts) 2) In order to study the photochemical decay of aqueous bromine in bright sunlight, a small quantity of liquid bromine was dissolved in water contained in a glass battery jar and placed in direct sunlight. The following data were obtained:

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppm Br</td>
<td>2.45</td>
<td>1.74</td>
<td>1.23</td>
<td>0.88</td>
<td>0.62</td>
<td>0.44</td>
</tr>
</tbody>
</table>

a) Determine whether the reaction rate is zero-, first-, or second-order in bromine, and calculate the reaction rate constant in units of your choice.

b) Assuming identical exposure conditions, calculate the required hourly rate of injection of bromine (in pounds) into a sunlit body of water 25,000 gal in volume in order to maintain a sterilizing level of bromine of 1.0 ppm.

(Note: ppm parts of bromine per million parts brominated water by weight. In dilute aqueous solutions, 1 ppm=1 milligram per liter, molecular weight of Br = 80 Daltons.)

1 gal → 3.785 liters
1 lb → 454 gms

Rate law: 
\[ -r_A = k C_A^\alpha \]

Experiment MB: 
\[ \frac{dC_A}{dt} = r_A \text{ (batch)} \]

Experimental data provides \( C_A \) vs. time, thus \( \frac{dC_A}{dt} \) can be calculated

Combine:
\[ \frac{dC_A}{dt} = -k C_A^\alpha \]

\[ \ln \left( \frac{-dC_A}{dt} \right) = \ln k + \alpha \ln C_A \]

See plot for \( \frac{\Delta y}{\Delta x} \) vs. t

Pick 2 points: 2.45, –0.080 at random and 0.88, –0.029

\[ \alpha = \frac{\ln(+0.08) - \ln(+0.029)}{\ln(2.45) - \ln(0.08)} \]

\[ \alpha = 0.99 \approx 1 \]

pick 0.88, –0.029 \( \Rightarrow -3.54 = \ln k + (0.99)(-0.1278) \) \( \Rightarrow \ln k = -3.4134 \]

\[ k = 0.033 \text{ min}^{-1} \]
### Chart Estimate

<table>
<thead>
<tr>
<th>t</th>
<th>( (C_A) )</th>
<th>( X )</th>
<th>( y )</th>
<th>( \Delta y )</th>
<th>( \Delta x )</th>
<th>( \Delta y/\Delta x )</th>
<th>dy/dx</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.45</td>
<td></td>
<td></td>
<td>10</td>
<td>-0.71</td>
<td>-0.071</td>
<td>-0.080</td>
</tr>
<tr>
<td>20</td>
<td>1.74</td>
<td></td>
<td></td>
<td>10</td>
<td>-0.51</td>
<td>-0.051</td>
<td>-0.060</td>
</tr>
<tr>
<td>30</td>
<td>1.23</td>
<td></td>
<td></td>
<td>10</td>
<td>-0.35</td>
<td>-0.035</td>
<td>-0.042</td>
</tr>
<tr>
<td>40</td>
<td>0.88</td>
<td></td>
<td></td>
<td>10</td>
<td>-0.26</td>
<td>-0.026</td>
<td>-0.029</td>
</tr>
<tr>
<td>50</td>
<td>0.62</td>
<td></td>
<td></td>
<td>10</td>
<td>-0.18</td>
<td>-0.018</td>
<td>-0.020</td>
</tr>
<tr>
<td>60</td>
<td>0.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.015</td>
</tr>
</tbody>
</table>

### Problem 2, part b

[Diagram]

M.B.: rate in – rate out + gen. = accum

\[
\frac{dN_A}{dt} = F_A + r_A V
\]

since the Br concentration is constant at 1 ppm, a steady state assumption is valid.

so \[
\frac{dN_A}{dt} = 0 \Rightarrow -r_A V = F_A , \quad -r_A = kC_A
\]

\[
F_A = \frac{0.033 \text{ min}}{} \cdot (1 \text{ ppm}) \cdot 25,000 \text{ gal}
\]

\[
F_A = 825 \text{ ppm} \cdot \text{gal} \cdot \frac{60 \text{ min}}{1 \text{ hr}} \cdot \frac{3.785 \ell}{1 \text{ gal}} \cdot \frac{1g}{1000 \text{ mg}} \cdot \frac{lb}{454g}
\]

\[
F_A = 0.41 \text{ lb/hr}
\]
(20pts) 3) The irreversible elementary gas phase reaction

\[ 2A \rightarrow B + C \]

is currently carried out in a packed bed reactor containing 100 kg of catalyst. The entering pressure is 20 atm and the exit pressure is 4 atm. Currently 50% conversion is achieved. It is proposed to add a CSTR with 200 Kg of catalyst downstream of the PBR. There is no pressure drop in the CSTR. The flow rate and temperature remain unchanged.

a) What would be the overall conversion in such an arrangement?

b) Is there a better way to carry out the reaction, and if so what is it?

**Current**

\[
\begin{align*}
P_0 &= 20 \\
100 \text{ KG} \quad \longrightarrow \quad X &= 0.5 \\
P &= 4
\end{align*}
\]

**Proposed**

\[
\begin{align*}
P_0 &= 20 \\
100 \text{ KG} \quad \longrightarrow \quad X &= 0.5 \\
\text{200 KG} \quad \longrightarrow \quad X &= ?
\end{align*}
\]

a) CSTR: \( -r_A^{\text{out}} = \frac{F A_0 (X_{\text{out}} - X_{\text{in}})}{w} \)

MB

PBR: \( -r_A = F A_0 \frac{dX}{dw} \)

RL

\( -r_A = k C_A^2 \)

\[ A \rightarrow \frac{1}{2} B + \frac{1}{2} C \]

ST

\[ C_A = C_{A_0} \frac{(1 - X) P}{(1 + eX) P_0 \sqrt{T}} \]

Since \( \varepsilon = 0, \frac{P}{P_0} = (1 - \alpha w)^{1/2} \)

\[
\left( \frac{P}{P_0} \right)^2 = 1 - \alpha w
\]

\[
1 - \left( \frac{P}{P_0} \right)^2 = 1 - \left( \frac{4}{20} \right)^2
\]

\( \alpha = \frac{100}{w} \)

\( \alpha = 0.0096 \)

Combine: \( k C_A^2 (1 - X)^2 \left( \frac{P}{P_0} \right)^2 = F A_0 \frac{dX}{dw} \)
\[ \varepsilon = y_{A0} \delta , y_{A0} = 1 , \delta = 0 \]
\[ \varepsilon = 0 \]
\[ C_A = C_{A0} (1 - X) \frac{P}{P_0} \]
\[ \frac{kC_A^2}{F_{A0}} (1 - \alpha w) dw = \frac{dX}{(1 - X)^2} \]
Integrate
\[ \frac{kC_A^2}{F_{A0}} \left( w - \alpha \frac{w^2}{2} \right) \bigg|_0^{100} = \left. \frac{1}{(1 - X)^2} \right|_0^{0.5} \]
\[ \frac{kC_A^2}{F_{A0}} (100 - 48) = 2 - 1 \]
\[ \frac{kC_A^2}{F_{A0}} = \frac{1}{52} \]

For CSTR
\[ \frac{w kC_A^2}{F_{A0}} \left( \frac{P}{P_0} \right)^2 (1 - X_2) = (X_2 - 0.5) F_{A0}/w \]
\[ \frac{200}{52} \cdot (0.04)(1 - X_2)^2 = X_2 - 0.5 \]
\[ \frac{2}{13} \left( 1 - 2X_2 + X_2^2 \right) = X_2 - 0.5 \]
\[ \frac{2}{13} - \frac{4}{13} X_2 + \frac{2}{13} X_2^2 = X_2 - 0.5 \]
\[ \frac{2}{13} X_2^2 - \frac{17}{13} X_2 + \frac{17}{26} = 0 \]
\[ X_2 = \frac{17}{13} \pm \sqrt{\left( \frac{17}{13} \right)^2 - \frac{4}{13} \cdot \frac{17}{26}} = \frac{1.3077 \pm 1.1435}{0.3077} \]
\[ = 0.534 \text{ or } 7.96 \]

b) Want higher conversion
1) reduce pressure drop \( \rightarrow \) use larger pellets
increase temperature \( \rightarrow \) larger \( k \)
2) Use CSTR followed by PFR.
(10 pts) 4) The following reactions were found to occur while trying to make a desired product B

\[ \begin{align*}
(1) & \quad A \rightarrow B \quad -r_{A1} = k_{1A} C_A^2 \\
& \quad A \rightarrow X \quad -r_{A2} = k_{2A} C_A \\
& \quad A + X \rightarrow Y \quad -r_{A3} = k_{3A} C_A C_X
\end{align*} \]

Species X and Y are both foul pollutants

a) What is the instantaneous selectivity of B with respect to the foul pollutants X and Y?

b) How would you carry out this reaction to maximize the formation of B?

**Additional Information**

\[ \begin{align*}
& \quad k_{1A} = 0.5 e^{-10,000/T} \text{ min}^{-1}, \text{T in degrees Kelvin} \\
& \quad k_{2A} = 50 e^{-20,000/T} \text{ min}^{-1}, \text{T in degrees Kelvin} \\
& \quad k_{3A} = 100 e^{-5,000/T} \text{ min}^{-1}, \text{T in degrees Kelvin}
\end{align*} \]

a) \[ \begin{align*}
& \quad r_B = -r_{A1} \\
& \quad r_X = -r_{A2} + r_{A3} \\
& \quad r_Y = -r_{A3}
\end{align*} \]

Selectivity of B with respect to x and y
\[ S_{BXY} = \frac{r_B}{r_X + r_Y} = \frac{-r_{A1}}{-r_{A2}} = \frac{k_{1A}}{k_{2A}} C_A \]
\[ = 0.01 \exp\left[\frac{10,000}{T}\right] C_A \]

b) In order to maximize the formation of B, \( S_{BXY} \) should be maximized.
\[ \Rightarrow \text{High } C_A \rightarrow \text{use PFR} \]
\[ \Rightarrow \text{Low Temperature} \]
(10 pts) 5) The catalytic reaction

$$A \rightarrow B$$

to be carried out in a flow reaction system has the following rate law,

$$-r_A = \frac{kC_A}{(1 + K_A C_A)^2}$$

where

$$k = 1 \text{ min}^{-1}$$

$$K_A = 1 \text{ dm}^3/\text{mol}$$

The entering concentration of A is 2 mol/dm$^3$. What type of reactor or combination of reactors would have the smallest volume to

a) achieve 50% conversion?

b) achieve 80% conversion?

$$C_A = C_{A0}(1 - X)$$

$$-\frac{1}{r_A} = \frac{(1 + K_A C_A)^2}{kC_A} = \frac{[1 + 2(1 - X)]^2}{2(1 - X)}$$

a) CSTR
b) CSTR followed by a PFR

\[ \frac{-1}{R_A} \]