CHME 312, Reaction Engineering, 2011 Spring

Exam III, Open Text (H. Scott Fogler, *Elements of Chemical Reaction Engineering*)

Note: For partial credit, please write your answer clearly and legibly.
For better credit, do all algebra and substitute digits, and check final figures carefully.

1. An irreversible reaction was studied to find out its kinetics.

$$A + B \rightarrow AB$$

They found the production rate was expressed as $r_{AB} = kC_B^2$, almost independent of the C_A. Assuming that intermediates consist of association of reactants and the reaction has no chain reaction, suggest the **reaction mechanism** including such conditions which satisfy the expression found. (50)

Sol)

- If this reaction is elementary, then $r_{AB} = kC_AC_B$ ☜ the result is different from this assumption.

- Let's try with some non-elementary mechanisms

1) Assuming 2 step reactions with intermediate A_2*

$$2A \Leftrightarrow A_2*$$

$$A_2* + B \Leftrightarrow A + AB$$

This reactions can be rearrange to give 4 elementary reactions

$$2A \xrightarrow{k_1} A_2* \quad (1)$$

$$A_2* \xrightarrow{k_2} 2A \quad (2)$$

$$A_2* + B \xrightarrow{k_3} A + AB \quad (3)$$

$$A + AB \xrightarrow{k_4} A_2* + B \quad (4)$$

- The production rate of AB is, by equation (3) and (4)

$$r_{AB} = k_3C_{A_2*}C_B - k_4C_AC_{AB} \quad (5)$$

- Since C_{A2*} is extremely small and we cannot measure it, we need to express C_{A2*} in terms of measurable quantities, C_A, C_B, or C_{AB}.

$$r_{A_2*} = \frac{1}{2}k_1 C_A^2 - k_2 C_{A_2*} - k_3 C_{A2*} C_B + k_4 C_A C_{AB}$$

- C_{A_2*} is very small and r_{A_2*} is considered as 0 ☜ PSSH

$$C_{A_2*} = \frac{\frac{1}{2}k_1 C_A^2 + k_4 C_A C_{AB}}{k_2 + k_3 C_B}$$

$$r_{AB} = \frac{\frac{1}{2}k_1 k_3 C_A^2 C_B - k_2 k_4 C_A C_{AB}}{k_2 + k_3 C_B} \qquad (6)$$

- If k_2 is very small, equation (6) can be simplified as

$$r_{AB} = \frac{1}{2}k_1 C_A^2 \qquad (7)$$

☜ This is a symmetry case of A with B observed.

- If k_4 is very small, equation (6) can be simplified as

$$r_{AB} = \frac{(k_1 k_3 / 2k_2) C_A^2 C_B}{1 + (k_3/k_2) C_B}$$ ☜ If C_B is small it can be expressed as $r_{AB} = \frac{k_1 k_3}{2k_2} C_A^2$

☜ This is a symmetry case of A with B observed.

2) Assuming 2 step reactions with intermediate B_2*

$$2B \xrightarrow{k_1} B_2* \qquad (1)$$

$$B_2* \xrightarrow{k_2} 2B \qquad (2)$$

$$B_2* + A \xrightarrow{k_3} B + AB \qquad (3)$$

$$B + AB \xrightarrow{k_4} B_2* + B \qquad (4)$$

- The production rate of AB is, by equation (3) and (4)

$$r_{AB} = k_3 C_{B_2*} C_A - k_4 C_B C_{AB} \qquad (5)$$

- Since C_{B_2*} is extremely small and we cannot measure it, we need to express C_{B_2*} in terms of measurable quantities, C_A, C_B, or C_{AB}.

$$r_{B_2*} = \frac{1}{2}k_1 C_B^2 - k_2 C_{B_2*} - k_3 C_{B_2*} C_A + k_4 C_B C_{AB}$$

- C_{B_2*} is very small and r_{B_2*} is considered as 0 ☜ PSSH

$$C_{B_2*} = \frac{\frac{1}{2}k_1 C_B^2 + k_4 C_B C_{AB}}{k_2 + k_3 C_A}$$

$$r_{AB} = \frac{\frac{1}{2}k_1 k_3 C_B^2 C_A - k_2 k_4 C_B C_{AB}}{k_2 + k_3 C_A} \qquad (6)$$

- If ***k*₂ is very small**, equation (6) can be simplified as

$r_{AB} = \frac{1}{2}k_1 C_B^2$ ☜ This satisfies the observation given in the statement.

- If ***k*₄ is very small**, equation (6) can be simplified as

$r_{AB} = \dfrac{(k_1 k_3 / 2k_2) C_B^2 C_A}{1 + (k_3/k_4) C_A}$ ☜ If $\mathbf{C_A}$ **is small** it can be expressed as $r_{AB} = \dfrac{k_1 k_3}{2k_2} C_B^2$

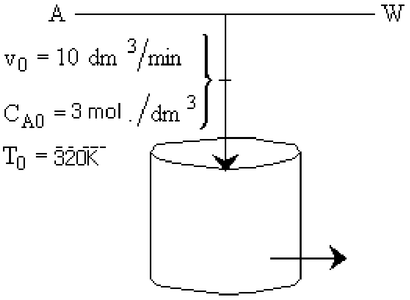
2. The acid-catalyzed irreversible liquid phase reaction is carried out adiabatically in a CSTR. The reaction is second order in A. The feed, which is equal molar in water (which contains the catalyst) and A, enters the reactor at a temperature of 47˚C and a total volumetric flow rate of 10 dm^3/min. The concentration of A entering the reactor is 3 mole.

   a) What is the reactor **volume** to achieve 80% conversion? (20)

   b) What **conversion** can be achieved in a 1000 dm^3 CSTR? What is the exit temperature? (30)

Additional information

ΔH_{Rx} = -3,100 cal/mol	C_{Pw} = 18 cal/mol•°C
C_{PA} = 15 cal/mol•°C	k = 0.005 at 25°C
C_{PB} = 15 cal/mol•°C	E = 15,000 cal/mol



(a) Mole Balance

$$V = \frac{F_{A0}X}{-r_A}$$

Energy Balance

$$X_{EB} = \Sigma\Theta_i C_{Pi}(T - T_0)/-\Delta H_{Rx}$$

$$X = \frac{(C_{P_A} + C_{P_W})(T - T_0)}{-\Delta H_{Rx}}$$

$$T = T_0 + \frac{(-\Delta H_{Rx})}{C_{P_A} + C_{P_W}} X$$

$$T = 320 + \frac{3100}{15+18} X = 320 + 93.9X$$

For 80% conversion T = 320 + (93.9)(0.8) = **395.1 K**

At 395.1 K

$$k = 0.005\exp\left[\frac{15000}{1.987}\left(\frac{1}{298} - \frac{1}{395.1}\right)\right] = (0.005)(505.6) = 2.528\frac{\text{dm}^3}{\text{mol}\cdot\text{s}}$$

$$V = \frac{1}{kC_{A0}}\left(\frac{X}{(1-X)^2}\right) = \frac{1}{(2.528)(3)}\left(\frac{0.8}{(1-0.8)^2}\right) = \mathbf{2.64dm^3}$$

(b) What conversion can be achieved in a 1000 dm^3 CSTR? What is the exit temperature?

$$-r_A = kC_A^2$$

$$C_A = C_{A0}(1-X) \quad , \quad F_{A0} = C_{A0}v_0 \quad , \quad \tau = \frac{V}{v_0}$$

$$V = \frac{F_{A0}X}{kC_{A0}^2(1-X)^2} \quad , \quad \tau = \frac{1}{kC_{A0}}\frac{X}{(1-X)^2}$$

$$\tau k C_{A0} = \frac{X}{(1-X)^2}$$

$$\tau k C_{A0} - 2\tau k C_{A0} X + \tau k C_{A0} X^2 = X$$

$$\tau k C_{A0} X^2 - (2\tau k C_{A0} + 1)X + \tau k C_{A0} = 0$$

$$X = \frac{(2\tau k C_{A0} + 1) - \sqrt{(2\tau k C_{A0} + 1)^2 + 4(\tau k C_{A0})^2}}{2\tau k C_{A0}}$$

$$X = \frac{2\tau k C_{A0} + 1 - \sqrt{4(\tau k C_{A0})^2 + 4\tau k C_{A0} + 1 - 4(\tau k C_{A0})^2}}{2\tau k C_{A0}}$$

Let

$$Da = \tau k C_{A0}$$

$$X_{MB} = \frac{(2\tau k C_{A0} + 1) - \sqrt{4\tau k C_{A0} + 1}}{2\tau k C_{A0}} = \frac{(2Da + 1) - \sqrt{4Da + 1}}{2Da}$$

$$X_{MB} = \frac{(2Da + 1) - \sqrt{4Da + 1}}{2Da}$$

where $Da = \tau k C_{A0} = C_{A0} k_1 \, e^{\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)}$

$$X_{EB} = T_o + \frac{(-\Delta H_{Rx})\mathrm{T}}{(C_{p_A} + C_{p_W})}$$

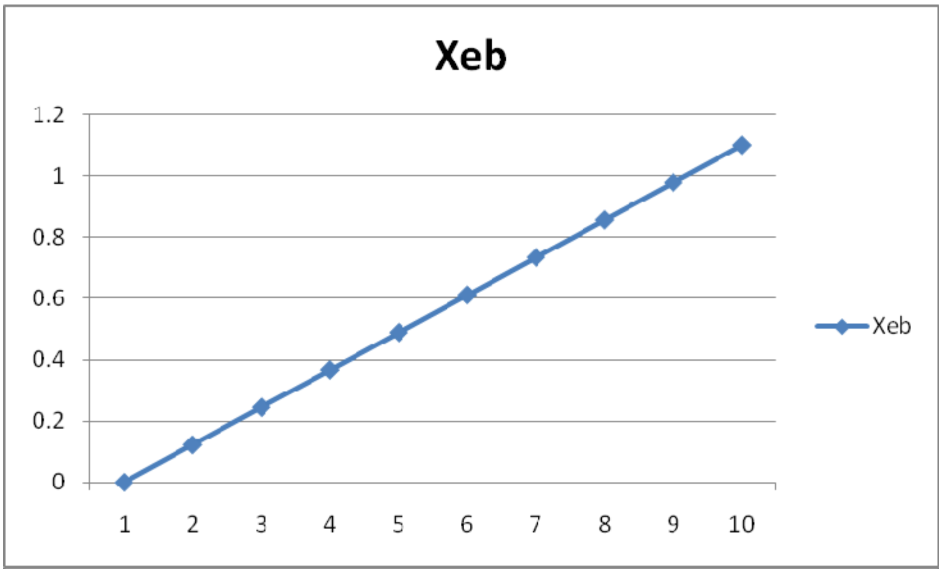
$X_{EB} = (T - 320)/93.9$

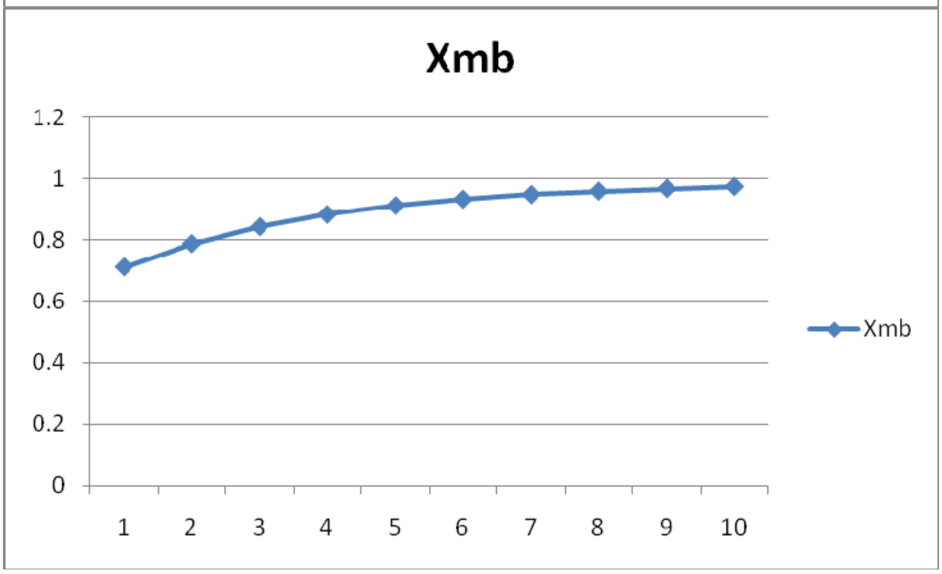
The exit temperature and conversion are determined from the intersection of X_{EB} and X_{MB}

At **411.6 K**

X_{EB} = (411.6 - 320)/93.9 = 0.976

X_{MB} = 0.976


Xeb
1.2
1
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
8
9
10
Xeb


Xmb
1.2
1
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
8
9
10
Xmb