

## Problem 1

Part (i)

$$\cancel{F_{A0}} - F_A + \int_V r_A dV = \frac{dN_A}{dt}$$

↓ well-mixed

$$r_A V = \frac{dN_A}{dt}, \quad \text{let } N_A = N_{A0}(1-X_A) \Rightarrow \frac{dN_A}{dt} = N_{A0} \left( -\frac{dX_A}{dt} \right)$$

$$\text{Now } (-r_A)V = N_{A0} \frac{dX_A}{dt}, \quad V = V_0 \Rightarrow (-r_A) = \frac{N_{A0}}{V_0} \frac{dX_A}{dt} = C_{A0} \frac{dX_A}{dt}$$

Rate Law

$$(-r_A) = k C_A C_B^2$$

Stoichiometry

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X_A)}{V_0} = C_{A0}(1-X_A)$$

$$C_B = \frac{N_B}{V} = \frac{N_{A0}}{V_0} \left( \theta_B - \frac{b}{a} X_A \right)$$

$$C_B = C_{A0}(1-2X_A)$$

$$\text{Now } (-r_A) = k C_A C_B^2 = k [C_{A0}(1-X_A)] [C_{A0}(1-2X_A)]^2$$

$$(-r_A) = k C_{A0}^3 (1-X_A)(1-2X_A)^2$$

Part (ii)

$$T = 303 \text{ K}$$

$$P_0 = 300 \text{ kPa}$$

$$K_{303} = K_{273} \exp \left[ \frac{\Delta E}{R} \left( \frac{1}{273 \text{ K}} - \frac{1}{303 \text{ K}} \right) \right]$$

$$= (0.45 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}) \exp \left[ \frac{50000 \text{ J mol}^{-1}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{273 \text{ K}} - \frac{1}{303 \text{ K}} \right) \right]$$

$$K_{303} = 3.98 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

$$C_{A0} = \frac{y_{A0} P_0}{RT_0} = \frac{(0.5)(300 \text{ kPa})}{(8.3145 \frac{\text{L kPa}}{\text{mol K}})(303 \text{ K})}; \quad C_{A0} = 0.059 \text{ mol L}^{-1}$$

Part (ii) continued

$$(-r_A) = C_{A0} \frac{dX_A}{dt}$$

$$K C_{A0}^3 (1-X_A)(1-2X_A)^2 = C_{A0} \frac{dX_A}{dt} \Rightarrow \int_0^{t'} dt = \frac{C_{A0}}{K C_{A0}^3} \int_0^X \frac{dX_A}{(1-X_A)(1-2X_A)^2}$$

$$t = \frac{1}{K C_{A0}^2} \left[ -\left(\frac{1}{2X-1}\right) + \ln(1-2X) - \ln(2-2X) \right] \Big|_0^X$$

$X = 0.25$   
 $t = 42.9 \text{ min}$

Part (iii)

Considering A as the limiting reactant (which it is not, but points were still given...)

$$V_0 = 1L$$

$$V = 0.6P \rightarrow V = V_0 (1 + \epsilon X_A) \frac{P_0}{P}$$

$$V = V_0 (1 + \epsilon X_A) \frac{0.6V_0}{0.6V}$$

$$V^2 = V_0^2 (1 + \epsilon X_A)$$

$$V = V_0 (1 - X_A)^{1/2}$$

$$\epsilon = \gamma_{A0} \delta = (0.5)(1-2-1)$$

$$\epsilon = -1$$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X_A)}{V_0(1-X_A)^{1/2}} ; C_A = C_{A0} (1-X_A)^{1/2}$$

$$C_B = \frac{N_B}{V} = \frac{N_{B0}(1-2X_A)}{V_0(1-X_A)^{1/2}} ; C_B = C_{A0} \frac{(1-2X_A)}{(1-X_A)^{1/2}}$$

Considering B as the limiting reactant...

$$V = V_0 (1 + \epsilon X_B)^{1/2}$$

$$\epsilon = \gamma_{B0} \delta = (0.5)\left(\frac{1}{2} - 1 - \frac{1}{2}\right)$$

$$V = V_0 (1 - 0.5X_B)^{1/2}$$

$$\epsilon = -0.5$$

$$C_A = \frac{N_A}{V} = \frac{N_{B0}(1-0.5X_B)}{V_0(1-0.5X_B)^{1/2}} ; C_A = C_{B0} (1-0.5X_B)^{1/2}$$

$$C_B = \frac{N_B}{V} = \frac{N_{B0}(1-X_B)}{V_0(1-0.5X_B)^{1/2}} ; C_B = C_{B0} \frac{(1-X_B)}{(1-0.5X_B)^{1/2}}$$

Part (iv)

$$(-r_A) = k C_A C_B^2$$

Again, using A as the limiting reactant

$$(-r_A) = k \left[ C_{A0} (1-X_A)^{1/2} \right] \left[ \frac{C_{A0} (1-2X_A)}{(1-X_A)^{1/2}} \right]^2$$

$$(-r_A) = \frac{k C_{A0}^3 (1-2X_A)^2}{(1-X_A)^{1/2}}$$

$$C_{A0} = \frac{N_{A0}}{V_0} = \frac{Y_{A0} P_0 V_0}{R T_0 V_0} = \frac{0.5 \left( \frac{V_0}{0.6} \right) V_0 / RT}{V_0}$$

$$C_{A0} = \frac{(0.5/0.6)(1.0L)(kPa)}{(8.3145 \frac{kJ}{mol \cdot K})(303K)} \cdot \frac{1.0L}{1.0L}$$

$$C_{A0} = 3.3 \times 10^{-4} \text{ mol L}^{-1}$$

$$(-r_A) = (3.98 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}) (3.3 \times 10^{-4} \text{ mol L}^{-1})^3 \left[ \frac{(1-2X_A)^2}{(1-X_A)^{1/2}} \right]$$

$$(-r_A) = 1.43 \times 10^{-10} \text{ mol L}^{-1} \text{ min}^{-1} \frac{(1-2X_A)^2}{(1-X_A)^{1/2}}$$

Using B as limiting reactant,  $C_{B0} = 3.3 \times 10^{-4} \text{ mol L}^{-1}$

$$(-r_B) = 2k C_A C_B^2$$

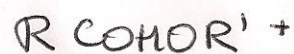
$$= 2k C_{B0}^3 \frac{(1-X_B)^2}{(1-0.5X_B)^{1/2}} ; (-r_B) = 7.86 \times 10^{-10} \text{ mol L}^{-1} \text{ min}^{-1} \frac{(1-X_B)^2}{(1-0.5X_B)^{1/2}}$$

## Problem 2

(i) We need an expression for the overall reaction rate

$$\Rightarrow r = \frac{d[R'OH]}{dt} = r_{R'OH}$$

Intermediates:  $R'^+$  &



$\Rightarrow$  we can use PSSM in this species

$$\frac{d[R'OH]}{dt} = k_3 [H_2O] [R'^+] \quad \text{(need this)} \quad \textcircled{1}$$

$$\frac{d[R'^+]}{dt} \stackrel{\text{PSSM}}{=} 0 = k_2 [RCOOR'^+] - k_3 [R'^+] [H_2O]$$

$$\Rightarrow [R'^+] = \frac{k_2 [RCOOR'^+]}{k_3 [H_2O]} \quad \text{now need this} \quad \textcircled{2}$$

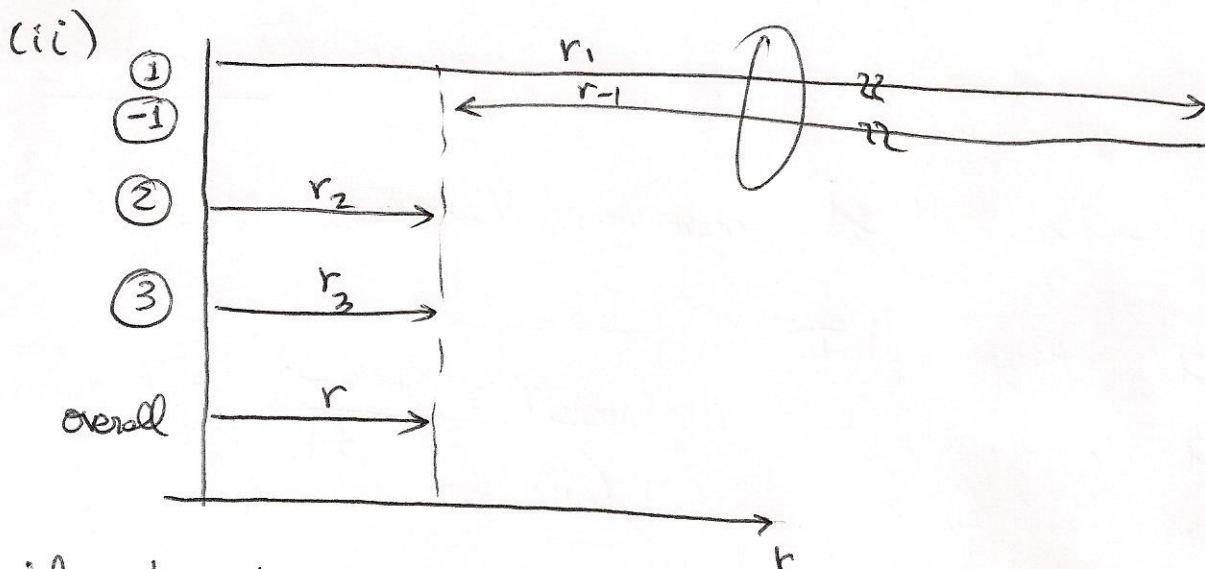
$$\frac{d[RCOOR'^+]}{dt} \stackrel{\text{PSSM}}{=} 0 = k_1 [RCOOR'] [H^+] - (k_{-1} + k_2) [RCOOR'^+]$$

$$\Rightarrow [RCOOR'^+] = \frac{k_1 [RCOOR'] [H^+]}{(k_{-1} + k_2)} \quad \textcircled{3}$$

$\textcircled{3}$  into  $\textcircled{2}$ , and then  $\textcircled{2}$  into  $\textcircled{1}$

$$\frac{d[R'OH]}{dt} = k_3 [H_2O] \cdot \frac{k_2}{k_3 [H_2O]} \cdot \frac{k_1 [RCOOR'] [H^+]}{(k_{-1} + k_2)}$$

$$\boxed{\frac{d[R'OH]}{dt} = \frac{k_2 k_1 [RCOOR'] [H^+]}{(k_{-1} + k_2)}}$$



if step 1 is PE:  $r_1 \approx r_{-1}$

$$k_1 [R'COOR'] [H^+] = k_{-1} [R'COHOR'^+]$$

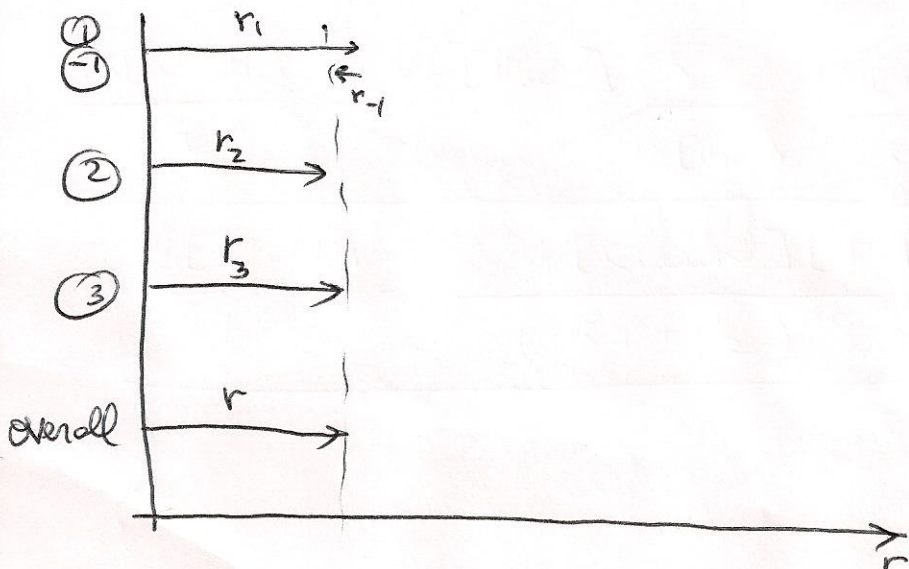
$$\Rightarrow [R'COHOR'^+] = \frac{k_1 [R'COOR'] [H^+]}{k_{-1}}$$

$$[R'^+] = \frac{k_2 [R'COHOR'^+]}{k_3 [H_2O]} = \frac{k_2 k_1 [R'COOR'] [H^+]}{k_{-1} k_3 [H_2O]}$$

$$\frac{d[R'OH]}{dt} = \frac{k_2 k_1}{k_{-1}} [R'COOR'] [H^+]$$

(iii) If the only constant was  $k_1 \Rightarrow k_{-1} \ll k_2$

$$\Rightarrow \frac{d[R'OH]}{dt} = k_1 [R'COOR'] [H^+]$$



(iv)

$$\frac{d[R'COOR']}{dt} = - \frac{d[R'OH]}{dt} = - \frac{k_1 k_2 [R'COOR'] [H^+]}{(k_{-1} + k_2)}$$

We know that

$$\frac{d[H^+]}{dt} = 0 \quad \left( \begin{array}{l} \text{not generated or} \\ \text{consumed during reaction} \end{array} \right) \Rightarrow [H^+] = \text{constant}$$

⇒ Integrating at 90% conversion,  $C = 0.1 C_0$

$$\int_{C_0}^{0.1 C_0} \frac{d[R'COOR']}{[R'COOR']} = - \frac{k_1 k_2 [H^+]}{(k_{-1} + k_2)} t_{90\%}$$

$$\Rightarrow \ln \left( \frac{0.1 C_0}{C_0} \right) = - \frac{k_1 k_2 [H^+]}{(k_{-1} + k_2)} t_{90\%}$$

$$t_{90\%} = - \frac{\ln(0.1) \cdot (k_{-1} + k_2)}{k_1 k_2 [H^+]} = \frac{-\ln(0.1) \cdot (0.15 \text{ s}^{-1})}{1 \text{ L/mol} \cdot 0.05 \text{ s}^{-1} \cdot 10^{-3} \text{ mol/L}}$$

$$t_{90\%} = 6908 \text{ sec}$$

(v) The reaction would require a higher residence time, because the feed is diluted to the outlet concentration and so the reaction rate is slower.