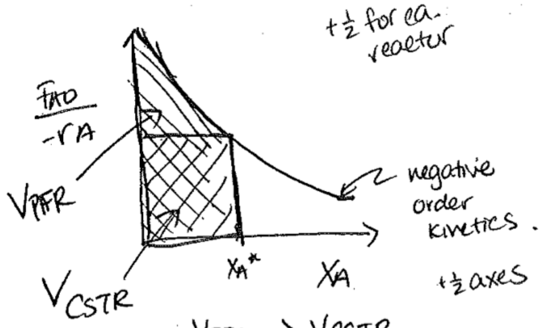
CBE 142 FALL 2012 MIDTERM 1 SOLUTIONS

## Problem 1:

a) CSTR vs PFR:



$V_{PFR} > V_{CSTR}$

For neg. order kinetics, the rate increases as conversion increases so a CSTR will ~~use~~ require less volume since it operates at the minimum concentration (diluted feed), which is desirable for negative ordered kinetics. +1.5 explanation

+0

$\boxed{V_{CSTR}!}$

b) Of all the options: $3A + I_2 \rightleftharpoons 2I_2$ is least likely to be an elementary rxn because # the forward reaction involves the collision of 4 molecules at the same time, which is highly unlikely.
+2 (4 molecs)

c) it's a reversible reaction, so at equilibrium:

+1

$$K_c = \frac{[C][D]}{[A]^2[B]} = \frac{\frac{N_C N_D}{V^2}}{\frac{N_A^2 N_B}{V^3}} \propto V \quad \text{or} \quad K_c = \frac{N_C N_D}{N_A^2 N_B} V$$

$$\text{or} \quad K_p = \frac{Y_C Y_D}{Y_A Y_B} \frac{1}{P_{TOT}}$$

case i) constant P will give us a higher equilibrium conversion because the volume will decrease as the reaction progresses, but will shift toward more product production to compensat
+0.5 +½

d) $P + Q \rightarrow 2R + S$.

There is an increase in the number of moles, leading to a volume increase, more dilution, for the constant pressure case – so a constant volume reactor is preferred.
+1 +1

e) True. 1st order elementary reactions obey Arrhenius equation: $K = Ae^{-\frac{E_a}{RT}}$. T↑, K↑.

+1

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mass balance

$$\frac{d\rho V}{dt} = \overset{in}{\rho_o v_o} - \overset{out}{\rho_i \frac{v_o}{a}} \qquad \rho = \rho_o = \rho_i$$

$$\frac{dV}{dt} = v_o\left(1 - \frac{1}{a}\right)$$

$$V(t) = V_i + v_o\left(1 - \frac{1}{a}\right)t$$

material balance

$$\frac{dN_A}{dt} = C_{Ao} v_o - C_A \frac{v_o}{a} \qquad \text{I.C.} \quad C_A(0) = \frac{C_{Ao}}{b}$$

$$\frac{d(C_A V)}{dt} = C_{Ao} v_o - C_A \frac{v_o}{a}$$

$$V(t)\frac{dC_A}{dt} + C_A \frac{dV}{dt} = C_{Ao} v_o - C_A \frac{v_o}{a}$$

$$\left[V_i + v_o\left(1 - \frac{1}{a}\right)t\right]\frac{dC_A}{dt} + \underbrace{C_A v_o\left(1 - \frac{1}{a}\right) = C_{Ao} v_o - C_A \frac{v_o}{a}}_{\text{cancel}}$$

$$\int_{C_{Ao}/b}^{C_A} \frac{dC_A}{C_{Ao} - C_A} = v_o \int_0^t \frac{dt}{V_i + v_o\left(1 - \frac{1}{a}\right)t}$$

$$-\ln\left(C_{Ao} - C_A\right)\Big|_{C_{Ao}/b}^{C_A} = \frac{v_o}{v_o\left(1 - \frac{1}{a}\right)}\left[\ln\left(V_i + v_o\left(1 - \frac{1}{a}\right)t\right)\right]\Big|_0^t$$

$$-\ln\left(\frac{C_{Ao} - C_A}{C_{Ao}(1 - 1/b)}\right) = \frac{1}{1 - \frac{1}{a}} \ln\left(\frac{V_i + v_o\left(1 - \frac{1}{a}\right)t}{V_i}\right)$$

$$\frac{1 - C_A/C_{Ao}}{1 - 1/b} = \left(1 + \frac{v_o}{V_i}\left(1 - \frac{1}{a}\right)t\right)^{1/\frac{1}{a}-1}$$

$$\boxed{\frac{C_A}{C_{Ao}} = 1 - (1 - 1/b)\left[1 + \frac{v_o}{V_i}(1 - 1/a)t\right]^{1/1/a-1}}$$

as $t \to 0$ $\quad \frac{C_A}{C_{Ao}} = 1 - (1 - 1/b)[1]^{1/1/a-1} \Rightarrow C_A = \frac{C_{Ao}}{b}$ ✓

as $t \to \infty$ $\quad \frac{C_A}{C_{Ao}} = 1 - (1 - 1/b)[1 - 1]^{1/1/a-1} \Rightarrow C_A = C_{Ao}$ ✓

b. $V(t) = 2V_i$

$V_i = v_o(1-1/a)*t$

100L=8 L/min (1-0.25)*t

t=16.67 min = 16 min 40 s

## #3: Reactive Distillation

$$A + B \rightleftharpoons C + D$$

$C_{B0}, v_0$ feed.

$F_C, F_B$ exits $\frac{\text{mol}}{\text{time}}$

a) mass balance on system:

$$+1 \quad \underset{(B)}{\text{mass in}} - \underset{(B+C)}{\text{mass out}} = \frac{dm}{dt} = \frac{d(\rho V)}{dt}$$

or $\rho_0 \cdot v_0$.

assume const $\rho$ in reactor volume: $\rho_0 = \rho$

$$\cancel{+2}\ +2 \quad \underset{\left(\frac{mol}{time}\right)}{C_{B0} v_0} \cdot \underset{\left(\frac{g}{mol}\right)}{MW_B} - (F_C MW_C + F_B MW_B) = \rho_0 \frac{dV}{dt}$$

$$+1\ \cancel{+2} \quad \frac{dV}{dt} = \frac{MW_B}{\rho}(F_{B0} - F_B) - \frac{MW_C}{\rho}(F_C)$$

b) mole balance on ea. species: $\frac{dN_j}{dt}$ :

moles accum = moles in − moles out + moles gen +1 (if nothing else)

A: $\frac{dN_A}{dt} = 0 - 0 + +r_A V(t)$ +2

B: $\frac{dN_B}{dt} = F_{B0} - F_B + r_A V(t)$. +2

C: $\frac{dN_C}{dt} = -F_C - r_A V(t)$ +2

D: $\frac{dN_D}{dt} = 0 + 0 - r_A V(t)$ +2

c) reversible, elementary rxn.

$$-r_A = k_f \left(\frac{N_A}{V}\right)\left(\frac{N_B}{V}\right) - k_r \left(\frac{N_C}{V}\right)\left(\frac{N_D}{V}\right)$$

$$\begin{array}{lc}
 & \sigma_i \\
A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_1 & \underline{1} \\
A + I_1 \xrightarrow{k_2} 2I_2 & \underline{1} \\
I_2 \xrightarrow{k_3} 2C & \underline{2} \\
\hline
2A + B \rightarrow 4C &
\end{array}$$

(a) $r = \frac{r_3}{\sigma_3} = \frac{r_3}{2}$

(b) $I_1$ : $0 = \frac{dI_1}{dt} = k_1[A][B] - k_{-1}[I_1] - k_2[A][I_1]$

$$\therefore [I_1] = \frac{k_1[A][B]}{k_{-1} + k_2[A]}$$

$I_2$ : $0 = \frac{dI_2}{dt} = 2k_2[A][I_1] - k_3[I_2]$

$$\therefore [I_2] = \frac{2k_2}{k_3}[A][I_1] = \frac{2k_2[A]}{k_3} \cdot \frac{k_1[A][B]}{k_{-1} + k_2[A]}$$

$$= \frac{2k_1k_2[A]^2[B]}{k_3(k_{-1} + k_2[A])}$$

$$\therefore \ r = \frac{r_3}{2} = \frac{1}{2} \cdot k_3[I_2] = \frac{k_1k_2[A]^2[B]}{k_{-1} + k_2[A]}$$

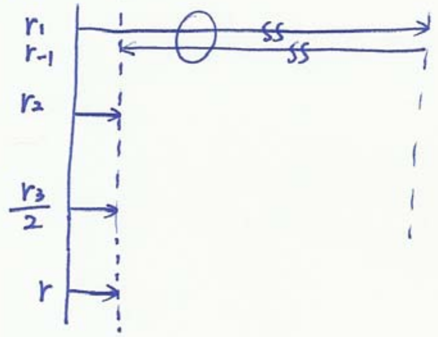
(c) QE on step 1: $r_1 = r_{-1}$

$$k_1[A][B] = k_{-1}[I_1]$$

$$\therefore [I_1] = K_1[A][B] \qquad \left(\text{or } \frac{k_1}{k_{-1}}[A][B]\right)$$

$$\therefore \ r = k_2[A][I_1] = k_2[A]\,K_1[A][B] = k_2K_1[A]^2[B]$$

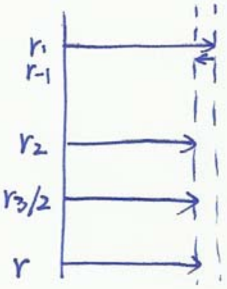
Arrow diagram



(d) $k_{-1} \gg k_2[A]$ ( $r_{-1} \gg r_2$ )

(e) step 1 is irreversible.

( $\because$ $k_{-1} \ll k_2[A]$ , $r_{(pssH)} = k_1[A][B]$ )



5. (a) B is limiting reactant

(b)

| | Initial | Change | Final |
|---|---|---|---|
| B | $F_{B0,CSTR}$ | $F_{B0,CSTR}X_B$ | $F_{B0,CSTR}(1-X_B)$ |
| A | $F_{A0,CSTR}=3F_{B0,CSTR}$ | $-2F_{B0,CSTR}X_B$ | $F_{B0,CSTR}(3-2X_B)$ |
| C | $F_{C0,CSTR}=0$ | $F_{B0,CSTR}X_B$ | $F_{B0,CSTR}X_B$ |
| D | $F_{D0,CSTR}=0$ | $F_{B0,CSTR}X_B$ | $F_{B0,CSTR}X_B$ |

($X_B$ here refers to $X_{B,CSTR}$)

$$v_{CSTR} = v_{0\,CSTR}(1+\varepsilon X_B) \quad , \quad \varepsilon = y_{B0}\,\delta = 0.2 \times (-1) = -0.2$$

$$\therefore\ v_{CSTR} = 0.4 v_0 (1-0.2X_B)$$

$$\therefore\ C_{B,CSTR} = \frac{F_{B0,CSTR}(1-X_B)}{v_{CSTR}} = \frac{0.4F_{B0}(1-X_B)}{0.4V_0(1-0.2X_B)} = C_{B0}\frac{(1-X_B)}{(1-0.2X_B)}$$

$$= 2\ (\text{mol/dm}^3)\ \frac{1-X_B}{1-0.2X_B} \quad (X_B = X_{B,CSTR})$$

$$C_{A,CSTR} = C_{B0}\frac{3-2X_B}{1-0.2X_B} = 2\ (\text{mol/dm}^3)\ \frac{3-2X_B}{1-0.2X_B}$$

$$C_{C,CSTR} = C_{B0}\frac{X_B}{1-0.2X_B} = 2\ (\text{mol/dm}^3)\ \frac{X_B}{1-0.2X_B}$$

$$C_{D,CSTR} = C_{B0}\frac{X_B}{1-0.2X_B} = 2\ (\text{mol/dm}^3)\ \frac{X_B}{1-0.2X_B}$$

c)
$$V_{CSTR} = \frac{F_{B,CSTR}\cdot X_{B,CSTR}}{-r_{B,CSTR}} = \frac{0.4F_{B0}\cdot X_{B,CSTR}}{k_1 C_{B,CSTR} - k_{-1}C_{D,CSTR}}$$

$$= \frac{0.4F_{B0}X_{B,CSTR}}{\underbrace{k_1 C_{B0}\frac{1-X_{B,CSTR}}{1-0.2X_{B,CSTR}}}_{C_{B,CSTR}=1.30\ \text{mol/dm}^3} - k_{-1}\underbrace{C_{B0}\frac{X_{B,CSTR}}{1-0.2X_{B,CSTR}}}_{C_{D,CSTR}=0.870\ \text{mol/dm}^3}}$$

$$= 1.0\,\text{dm}^3$$

(d) Overall conversion of B

PFR: $F_{B,PFR} = 0.6\, F_{B0}\,(1-x_{B,PFR}) = 6.24$ mol B/min

CSTR: $F_{B,CSTR} = 0.4\, F_{B0}\,(1-x_{B,CSTR}) = 4.8$ mol B/min

$0.4 \times 20 \times (1-0.4)$

$$x_{B,f} = \frac{F_{B0} - F_{B,CSTR} - F_{B,PFR}}{F_{B0}} = \frac{20 - 4.8 - 6.24}{20} = 0.45$$

Or: weighted average

$$x_{B,f} = 0.6 \times 0.48 + 0.4 \times 0.4 = 0.45$$

(e) The volume of CSTR required for a conversion of B of 0.4 when D is removed should decrease relative to CSTR in (c) because the reverse reaction will no longer occur and the concentration will be higher in the reactor because of the removal of D.

( $\varepsilon = 0.2 \times (1-3) = -0.4$ $C_B$ is higher, $C_D = 0$ )