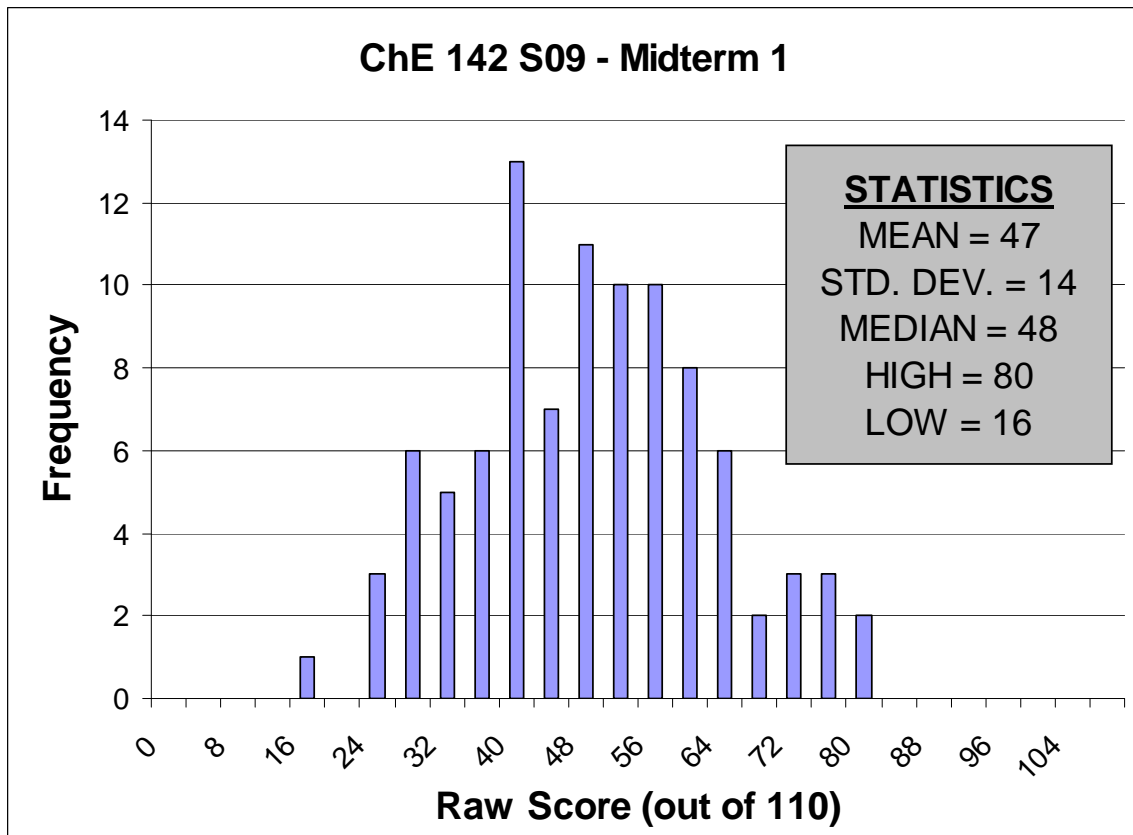


# Chemical Kinetics and Reaction Engineering

ChE 142 – Spring 2009

## MIDTERM EXAMINATION I SOLUTIONS



# Problem 1

i) elementary  $A_2(g) \rightarrow 2A(g)$   $P, R, T, P$  constant  
 $V, \nu$  must change

$$K_p = e^{-\Delta G^\circ/RT} = \frac{P_A^2}{P_{A_2}} = RT \frac{C_A^2}{C_{A_2}} \quad (1)$$

need  $C_j = f(X)$   $X \equiv X_{A_2, eq.}$

Method 1  $C_j = \frac{C_0 (\theta_j - \nu_j X)}{(1 + \delta Y_{A_0} X)}$   $\delta = +1$   
 $Y_{A_0} = 0.5$

$$C_{A_2} = \frac{C_0(1-X)}{1+0.5X} \quad C_A = \frac{2C_0 X}{1+0.5X}$$

or Method 2 : Stoichiometric Table

$A_2$	$F_0$	$-F_0 X_A$	$F_0(1-X_A)$	$\frac{C_0(1-X)}{1+0.5X}$
$A$	0	$2F_0 X_A$	$2F_0 X_A$	$\frac{2C_0 X}{1+0.5X}$
$I$	$F_0$	0	$F_0$	$\frac{C_0}{1+0.5X}$
			$2F_0 + F_0 X_A$	
			$F_0(2+X_A)$	
			$\nu = \nu_0(1+0.5X_A)$	

Substitute into (1)

$$e^{-\Delta G^\circ/RT} = \frac{\overset{P_0 \text{ of } A_2}{(RT C_0)} (4 X^2)}{(1+0.5X)(1-X)}$$

if  $Y_{A_0} = 1$  by  $P_0$  is still the same  
 $(1+0.5X) \rightarrow (1+X)$  in denominator.  
 and  $X$  is higher ( $A_2$  is diluted more by  $A$  and this helps equilibrium)

## Problem 1

- ii) PSSH - an assumption about intermediates (defined as species not in overall reaction but in elementary steps)

$$\left| \frac{dC_I}{dt} \right| \ll \left| \frac{dC_j}{dt} \right| \quad j = \text{reactants/products}$$

allows  $C_I$  to be represented in terms of  $C_j \rightarrow$  good since if reactive  $C_I$  difficult to measure

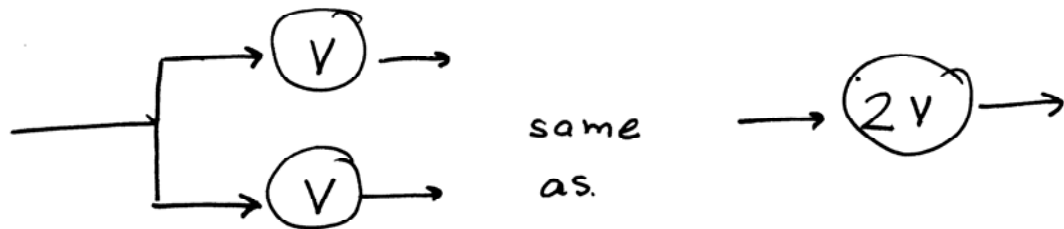
- for any species  $I$ , we add the rates of its formation in all steps involving  $I$  and set their sum equal to zero

QE - an assumption about a step, for which  $t_i$  and  $t_{-i}$  (not  $k_i, k_{-i}$ ) are both much larger than the net rate of the overall reaction

- requires "permission" to apply
- implemented by assuming  $t_i \approx t_{-i}$
- used to simplify algebra by removing additive terms in  $\frac{dC_I}{dt} = 0$ . (PSSA)

# Problem 1

iii).  $r = \frac{k(A)^2}{1 + K(A)}$        $n \geq 1$  for all (A)



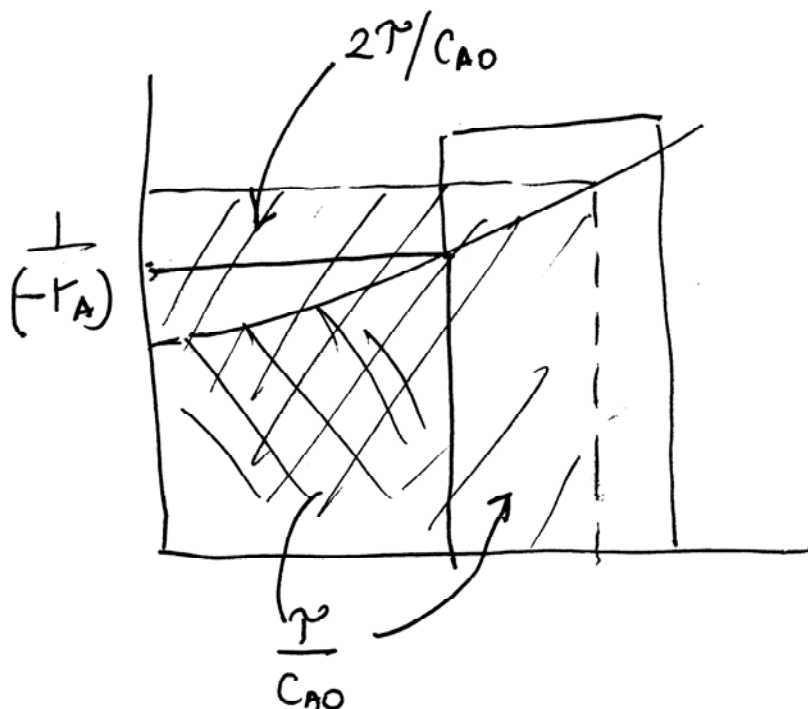
for a given  $F_{A0}$

$$2V = \frac{F_{A0} \cdot X_A}{(-r_A)} \longrightarrow V = \frac{\frac{F_{A0} \cdot X_A}{2}}{(-r_A)}$$

one reactor

two parallel reactors

so serial arrangement breaks up a CSTR with  $(2V)$  into two CSTR's of volume  $V$  in series  $\longrightarrow$  this helps for any  $n > 0$



## Problem 2

(a) Species A is the limiting reactant. We can show this by assuming all of A reacts to determine if any B remains.

$$F_{A0} = C_{A0} * v_0 = 0.20 * C_T * v_0 = 20 \text{ mol A min}^{-1}$$

$$\frac{20 \text{ mol A}}{\text{min}} * \frac{1 \text{ mol B}}{2 \text{ mol A}} = 10 \text{ mol B min}^{-1} \therefore 10 \text{ mol B min}^{-1} \text{ remain}$$

(b) PFR Balance In – Out + Gen = Acc

$$F_B|_V - F_B|_{V+\Delta V} + r_B \Delta V = 0$$

$$r_B = \frac{F_B|_{V+\Delta V} - F_B|_V}{\Delta V}$$

$$\lim_{\Delta V \rightarrow 0} r_B = \frac{dF_B}{dV}$$

$$F_B = 0.6 * F_{B0} (1 - x_B) \text{ Because 60\% of the flow is going to the PFR}$$

$$V = F_{B0} \int_0^{x_B^*} \frac{dx_B}{-r_B} = F_{B0} \int_0^{x_B^*} \frac{dx_B}{k_1 C_B - k_{-1} C_D}$$

The equation is non-stoichiometric, so we write:

$$\varepsilon = y_{B0} \delta = 0.2 * (1 + 1 - 2 - 1) = -0.2$$

$$C_B = \frac{F_{B0} (1 - x_B)}{v_0 (1 + \varepsilon x_B)} = C_{B0} \frac{(1 - x_B)}{(1 - 0.2x_B)}$$

$$C_D = C_{B0} \frac{x_B}{(1 - 0.2x_B)}$$

$$V = 0.6 * F_{B0} \int_0^{x_{B,PFR1}} \frac{dx_B}{k_1 C_{B0} \frac{(1 - x_B)}{(1 - 0.2x_B)} - k_{-1} C_{B0} \frac{x_B}{(1 - 0.2x_B)}}$$

$$V = 0.6 * 20 \int_0^{x_{B,PFR1}} \frac{dx_B}{(3)(2) \frac{(1 - x_B)}{(1 - 0.2x_B)} - (0.8)(2) \frac{x_B}{(1 - 0.2x_B)}}$$

(c) CSTR Balance

$$F_{B0,CSTR} - F_{B,CSTR} + r_B V = 0$$

$$F_{B0,CSTR} = 0.4 * F_{B0}$$

$$0.4 F_{B0} - 0.4 F_{B0} (1 - x_B) + r_B V = 0$$

$$V = \frac{0.4 F_{B0} x_B}{-r_B} = \frac{0.4 F_{B0} x_B}{k_1 C_{B0} \frac{(1 - x_{B,CSTR1})}{(1 - 0.2x_{B,CSTR1})} - k_{-1} C_{B0} \frac{x_{B,CSTR1}}{(1 - 0.2x_{B,CSTR1})}}$$

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

(d) Overall conversion of B

PFR

$$F_{B,PFR} = 0.6 * F_{B0} (1 - x_{B,PFR}) = 6.24 \text{ mol B min}^{-1}$$

CSTR

$$F_{B,CSTR} = 0.4 F_{B0} (1 - x_{B,CSTR}) = 0.4(20)(1 - 0.4) = 4.8 \text{ mol B min}^{-1}$$

Overall

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

Or, we could do a weighted average of the conversions

$$x_B = 0.6 * 0.48 + 0.4 * 0.4 = 0.45$$

(e) (i) We can find the new conversion by recalculating the value for the concentrations

$$\varepsilon = y_{B0} \delta = 0.2 * (1 - 2 - 1) = -0.4$$

$$C_B = C_{B0} \frac{(1 - x_{B,CSTR})}{(1 + \varepsilon x_B)} = C_{B0} \frac{(1 - x_{B,CSTR})}{(1 - 0.4 x_B)}$$

$$C_D = 0$$

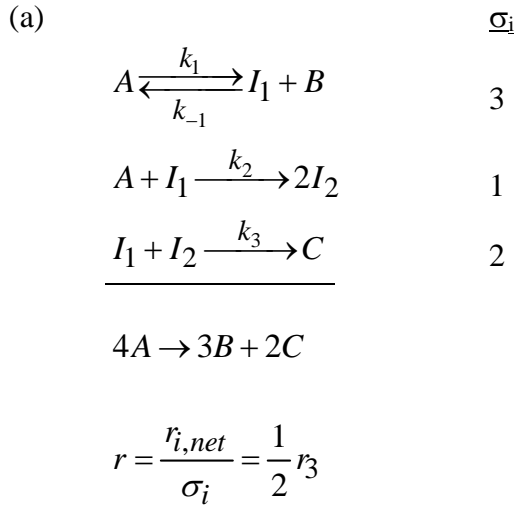
Substitute our new expressions for concentration into our rate expression from (c)

$$V = \frac{0.4 F_{B0} x_B}{-r_B} = \frac{0.4 F_{B0} x_B}{k_1 C_{B0} \frac{(1 - x_{B,CSTR1})}{(1 - 0.4 x_{B,CSTR1})} - k_{-1}(0)}$$

$$V = 0.75 \text{ dm}^3$$

(ii) The volume of CSTR1 required for a conversion of B of 0.4 when species D is removed should decrease relative to the 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.

Problem 3



(b)

$$r = \frac{1}{2} r_3 = \frac{k_3}{2} [I_1][I_2]$$

PSSH on  $I_2$ :

$$\frac{d[I_2]}{dt} = 2r_2 - r_3 = 2k_2[A][I_1] - k_3[I_1][I_2] = 0$$

$$[I_2] = \frac{2k_2[A]}{k_3}$$

PSSH on  $I_1$ :

$$\frac{d[I_1]}{dt} = r_1 - r_{-1} - r_2 - r_3 = 0$$

$$\frac{d[I_1]}{dt} = k_1[A] - k_{-1}[I_1][B] - k_2[A][I_1] - k_3[I_1][I_2] = 0$$

$$[I_1] = \frac{k_1[A]}{k_{-1}[B] + k_2[A] + k_3[I_2]} = \frac{k_1[A]}{k_{-1}[B] + 3k_2[A]}$$

Substitute expressions for  $[I_1]$  and  $[I_2]$  into rate expression and simplify:

$$r = \frac{k_1 k_2 [A]^2}{k_{-1}[B] + 3k_2[A]}$$

(c) The following approximation must be made:

$$k_{-1}[B] \gg 3k_2[A] \quad (r_{-1} \gg r_2)$$

which occurs when **step 1** is **quasi-equilibrated (QE)**.

(d) (i) If step 1 is irreversible:

$$r_{-1} \ll r_2 \quad k_{-1}[B] \ll k_2[A] \quad (k_{-1}[B] \ll 3k_2[A])$$

$$r = \frac{1}{3}k_1[A]$$

(ii) If step 1 is quasi-equilibrated:

$$r_{-1} \gg r_2 \quad k_{-1}[B] \gg k_2[A] \quad (k_{-1}[B] \gg 3k_2[A])$$

$$r = K_1k_2 \frac{[A]^2}{[B]}$$

(e) If step 1 is quasi-equilibrated, then:

$$r_C = 2r = 2K_1k_2 \frac{[A]^2}{[B]} \quad r_U = k_4[I_1] = K_1k_4 \frac{[A]}{[B]}$$

Determine the dependence of selectivity towards the desired product on the concentration of reactants and products:

$$S = \frac{r_C}{r_U} = \frac{2K_1k_2 \frac{[A]^2}{[B]}}{K_1k_4 \frac{[A]}{[B]}} = \frac{2k_2}{k_4}[A]$$

The selectivity has a first-order dependence on the concentration of A. Using a **PFR** will result in a higher selectivity than using a CSTR, because a PFR operates at the highest concentration of A possible (i.e. later dilution), while a CSTR operates at the exit concentration of A (i.e. earlier dilution).