**Chemical Reaction Engineering—Spring 2020**
**Homework 4 Solutions**

## PROBLEM #1

$$r_{O_3} = -k_1[Cl_2][O_3] - k_2[ClO_2][O_3] - k_3[ClO_3][O_3]$$

NEED TO FIND $[ClO_2]$ AND $[ClO_3]$

$$r_{ClO_2} = 0 = k_1[Cl_2][O_3] - k_2[ClO_2][O_3] + k_3[ClO_3][O_3] \qquad \text{PSSH}$$

$$k_2[ClO_2][O_3] = k_1[Cl_2][O_3] + k_3[ClO_3][O_3]$$

$$[ClO_2] = \frac{k_1[Cl_2]\cancel{[O_3]} + k_3[ClO_3]\cancel{[O_3]}}{k_2\cancel{[O_3]}}$$

$$[ClO_2] = \frac{k_1[Cl_2] + k_3[ClO_3]}{k_2}$$

$$r_{ClO_3} = 0 = k_2[ClO_2][O_3] - k_3[ClO_3][O_3] - 2k_4[ClO_3]^2$$

$$r_{ClO_3} + r_{ClO_2} = 0$$

$$0 = k_1[Cl_2][O_3] - \cancel{k_2[ClO_2][O_3]} + \cancel{k_3[ClO_3][O_3]} + \cancel{k_2[ClO_2][O_3]} - \cancel{k_3[ClO_3][O_3]} - 2k_4[ClO_3]^2$$

$$0 = k_1[Cl_2][O_3] - 2k_4[ClO_3]^2$$

$$[ClO_3] = \left(\frac{k_1[Cl_2][O_3]}{2k_4}\right)^{0.5}$$

$$[ClO_2] = \frac{k_1[Cl_2]}{k_2} + \frac{k_3\left(\frac{k_1[Cl_2][O_3]}{2k_4}\right)^{0.5}}{k_2}$$

$$r_{O_3} = -k_1[Cl_2][O_3] - k_2\left(\frac{k_1}{k_2}[Cl_2] + \frac{k_3}{k_2}\sqrt{\frac{k_1[Cl_2][O_3]}{2k_4}}\right)[O_3]$$

$$- k_3\sqrt{\frac{k_1[Cl_2][O_3]}{2k_4}}[O_3]$$

$$\boxed{r_{O_3} = 2\left(-k_1[Cl_2][O_3] - k_3\sqrt{\frac{k_1[Cl_2][O_3]}{2k_4}}[O_3]\right)}$$

$$\boxed{r_{O_3} = 2[O_3]\left(-k_1[Cl_2] - k_3\sqrt{\frac{k_1[Cl_2][O_3]}{2k_4}}\right)}$$

PROBLEM #2

a)

$$A + B \underset{-1}{\overset{1}{\rightleftharpoons}} I$$

$$A + I \xrightarrow{2} 2C$$

<u>PSSH ON (I)</u>

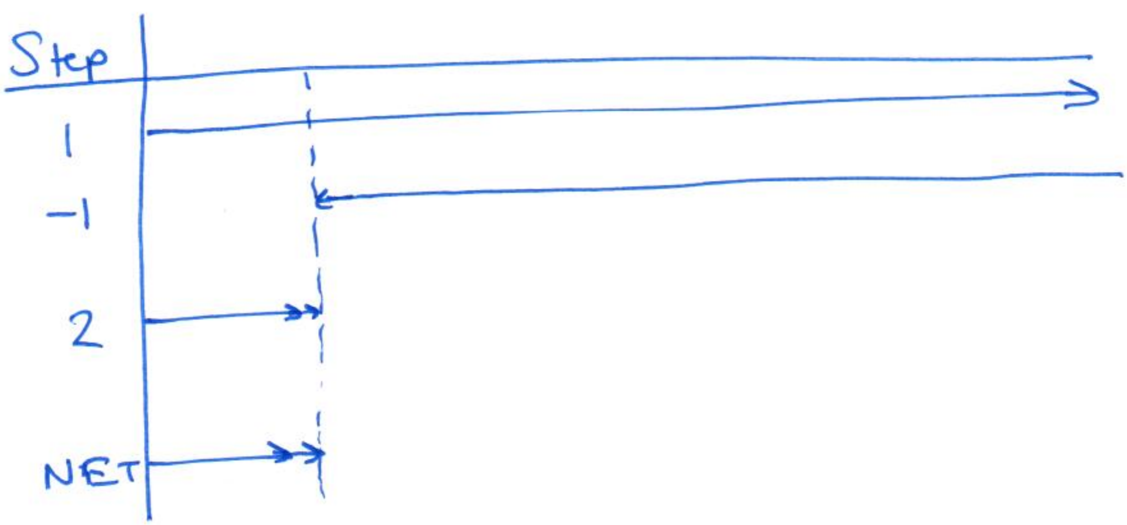
$$\frac{d(I)}{dt} = 0 = k_1(A)(B) - k_{-1}(I) - k_2(A)(I)$$

$$(I) = \frac{k_1(A)(B)}{k_{-1} + k_2(A)}$$

$$r_{NET} = r_2$$

$$r_2 = \frac{r_A}{\nu_2} \longrightarrow -r_A = 2r_2 = \boxed{\frac{2k_2k_1(A)^2(B)}{k_{-1} + k_2(A)}}$$

b.



c) QE ON STEP #1

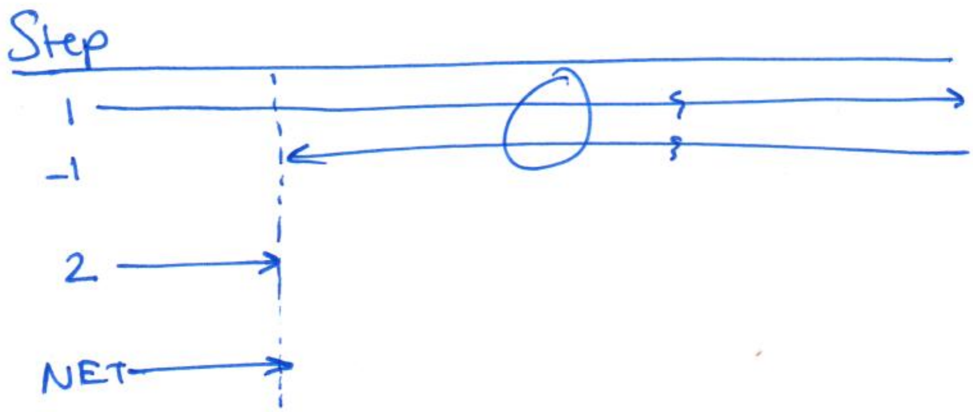
$$r_1 \approx r_{-1}$$

$$k_1 (A)(B) = k_{-1} (I)$$

$$K_1 = \frac{k_1}{k_{-1}} = \frac{(I)}{(A)(B)}$$

$$(I) = K_1 (A)(B)$$

$$-r_A = 2r_2 = 2k_2 (A)(I) = \boxed{2k_2 K_1 (A)^2 (B)}$$




d) $\boxed{k_{-1} \gg k_2 (A)}$

PROBLEM #3

$$\begin{array}{llll} A & \underset{-1}{\overset{1}{\rightleftharpoons}} & Y + B & \sigma_i \\ & & & 3 \\ A + Y & \xrightarrow{2} & 2Z & 1 \\ Y + Z & \xrightarrow{3} & C & 2 \end{array}$$

a. $$\boxed{r = \frac{r_3}{\sigma_3} = \frac{r_3}{2}}$$

b. PSSH ON (Z)

$$\frac{d(Z)}{dt} = 0 = 2k_2(A)(Y) - k_3(Y)(Z)$$

$$(Z) = \frac{2k_2(A)}{k_3}$$

PSSH ON (Y)

$$\frac{d(Y)}{dt} = k_1(A) - k_{-1}(Y)(B) - k_2(A)(Y) - k_3(Y)(Z)$$

$$\frac{k_1(A)}{k_{-1}(B) + k_2(A) + k_3(Z)} = (Y)$$

$$\frac{k_1(A)}{+k_1(B) + 3k_2(A)} = (Y)$$

$$r = \frac{r_3}{2} = \frac{k_3(Y)(Z)}{2} = \frac{\cancel{k_3}\, k_1(A)}{\cancel{2}(k_{-1}(B) + 3k_2(A))} \; \frac{\cancel{2} k_2(A)}{\cancel{k_3}}$$

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

c) $k_{-1}(B) \gg 3k_2(A)$

d) i) $\dfrac{d(Y)}{dt} = 0 = k_1(A) - k_2(A)(Y) - k_3(Y)(Z)$

$$(Y) = \frac{k_1(A)}{k_2 + k_3(Z)}$$

$\dfrac{d(Z)}{dt} = 0$ SAME EXPRESSION AS BEFORE

$$(Z) = \frac{2k_2(A)}{k_3}$$

$$(Y) = \frac{k_1(A)}{3k_2(A)} = \frac{k_1}{3k_2}$$

$$r = \frac{r_3}{\sigma_3} = \frac{r_3}{2} = \frac{k_3}{2}(Y)(Z) = \frac{k_3}{2}\left(\frac{k_1}{3k_2}\right)\left(\frac{2k_2(A)}{k_3}\right)$$

$$r = \frac{k_1(A)}{3}$$

ii) QE ON STEP 1 MEANS : $\frac{1}{3}(\cancel{Y})(B)k_{-1} \gg k_2(\cancel{Y})(A)$

$$k_{-1}(B) \gg 3k_2(A)$$

PART B REDUCES TO : $r = \dfrac{k_1 k_2 (A)^2}{k_{-1}(B)}$

# PROBLEM #4

$$\overset{AC}{CH_3CHO} \xrightarrow{k_1} CH_3\cdot + CHO\cdot$$

$$CH_3\cdot + \overset{AC}{CH_3CHO} \xrightarrow{k_2} CH_3\cdot + CO + CH_4$$

$$CHO\cdot + \overset{AC}{CH_3CHO} \xrightarrow{k_3} CH_3\cdot + 2CO + H_2$$

$$2CH_3\cdot \xrightarrow{k_4} C_2H_6$$

$$-r_{AC} = -r_1 - r_2 - r_3 = k_1(AC) + k_2(CH_3\cdot)(AC) + k_3(CHO\cdot)(AC)$$

$$-r_{AC} = (AC)\Big(k_1 + k_2(CH_3\cdot) + k_3(CHO\cdot)\Big)$$

ASSUME $CH_3\cdot$ + $CHO\cdot$ ARE REACTIVE INTERMEDIATES.

$$\frac{d(CHO\cdot)}{dt} = k_1(AC) - k_3(CHO\cdot)(AC) = 0$$

$$k_1\cancel{(AC)} = k_3(CHO\cdot)\cancel{(AC)}$$

$$\frac{k_1}{k_3} = (CHO\cdot)$$

$$\frac{d(CH_3\cdot)}{dt} = 0 = k_1(AC) + k_3(CHO\cdot)(AC) - 2k_4(CH_3\cdot)^2$$

$$2k_4(CH_3\cdot)^2 = k_1(AC) + k_3(CHO\cdot)(AC)$$

$$2k_4(CH_3\cdot)^2 = k_1(AC) + k_3\left(\frac{k_1}{k_3}\right)(AC)$$

$$\cancel{2}k_4(CH_3\cdot)^2 = \cancel{2}k_1(AC)$$

$$(CH_3\cdot) = \sqrt{\frac{k_1(AC)}{k_4}}$$

$$-r_{AC} = (AC)\left[k_1 + k_2\sqrt{\frac{k_1(AC)}{k_4}} + k_3\left(\frac{k_1}{k_5}\right)\right]$$

$$\boxed{-r_{AC} = (AC)\left[2k_1 + k_2\sqrt{\frac{k_1(AC)}{k_4}}\right]}$$

c) $-r_{C_2H_6} = -r_4 = -k_4(CH_3\cdot)^2 = -\frac{\cancel{k_4}\,k_1(AC)}{\cancel{k_4}} = -k_1(AC)$

$$-r_{AC} = (AC)\left[2k_1 + k_2\sqrt{\frac{k_1(AC)}{k_4}}\right]$$

$$-r_{CH_4} = -r_2 = -k_2(CH_3\cdot)(AC)$$

$$\frac{d(CH_4)}{dt} = k_2\sqrt{\frac{k_1(AC)}{k_4}}\,(AC)$$

$$-r_{CO} = -r_2 - 2r_3 = -k_2(AC)(CH_3\cdot) - 2(CHO\cdot)(AC)$$

$$\frac{d(CO)}{dt} = (AC)\left[k_2\sqrt{\frac{k_1(AC)}{k_4}} + 2k_1\right]$$

PROBLEM # 5

$$2A \underset{-1}{\overset{1}{\rightleftharpoons}} B$$

$$A + B \underset{-2}{\overset{2}{\rightleftharpoons}} 2C$$

a. $\sigma_1 = 1 \qquad \sigma_2 = 1$

b. B IS A REACTIVE INTERMEDIATE.

$$\frac{d(B)}{dt} = 0 = k_1 (A)^2 - k_{-1}(B) - k_2(A)(B) + k_{-2}(C)^2$$

$$\frac{k_1 (A)^2 + k_{-2}(C)^2}{k_{-1} + k_2 (A)} = (B)$$

$$\frac{d(C)}{dt} = 2k_2 (A)(B) - 2k_{-2}(C)^2$$

$$\frac{d(C)}{dt} = 2k_2 (A)\left(\frac{k_1 (A)^2 + k_{-2}(C)^2}{k_{-1} + k_2 (A)}\right) - 2k_{-2}(C)^2$$

c. STEP #1 is QE

$$k_1 (A)^2 = k_{-1}(B)$$

$$\frac{k_1 (A)^2}{k_{-1}} = (B) = K_1 (A)^2$$

$$\frac{d(C)}{dt} = 2k_2 K_1 (A)^3 - 2k_{-2}(C)^2$$