Josh Whitehead 16 Feb 2022

# HW 4

1) Find $r_{O_3}((O_2),(Cl_2),(O_3))$

assume:
~~[scribble]~~ $\theta_{all}=1$

$r_{O_3}=-r_1-r_2-r_3$

$=-k_1(Cl_2)(O_3)-k_2(ClO_2)(O_3)-k_3(ClO_3)(O_3)$

- need $(ClO_2)$, $(ClO_3)$ because they are intermediates

assume PSSH for $(ClO_2)$:

$r_{ClO_2}\approx 0\approx r_1-r_2+r_3$

$=k_1(Cl_2)(O_3)-k_2(ClO_2)(O_3)+k_3(ClO_3)(O_3)$

PSSH for $(ClO_3)$:

$r_{ClO_3}\approx 0\approx r_2-r_3-r_4$

$=k_2(ClO_2)(O_3)-k_3(ClO_3)(O_3)-k_4(ClO_3)^2=0$

rearrange $r_{ClO_2}$: $k_2(ClO_2)(O_3)-k_3(ClO_3)(O_3)=k_1(Cl_2)(O_3)$

rearrange $r_{ClO_3}$: $k_2(ClO_2)(O_3)-k_3(ClO_3)(O_3)=k_4(ClO_3)^2$

$\therefore\ k_4(ClO_3)^2=k_1(Cl_2)(O_3)\rightarrow ClO_3=\left(\frac{k_1}{k_4}(Cl_2)(O_3)\right)^{1/2}$

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$$(ClO_2) = \frac{k_1}{k_2}(Cl_2) + \frac{k_3}{k_2}(ClO_3)$$

$$(ClO_3) = \left[\frac{k_1}{k_4}(Cl_2)(O_3)\right]^{1/2}$$

$$\therefore (ClO_2) = \frac{k_1}{k_2}(Cl_2) + \frac{k_3}{k_2}\left[\frac{k_1}{k_4}(Cl_2)(O_3)\right]^{1/2}$$

$$r_{O_3} = -k_1(O_3)(Cl_2) - \cancel{k_2}\left[\frac{k_1}{\cancel{k_2}}(Cl_2) + \frac{k_3}{\cancel{k_2}}\left[\frac{k_1}{k_4}(Cl_2)(O_3)\right]^{1/2}\right](O_3)$$
$$-k_3\left[\frac{k_1}{k_4}(Cl_2)(O_3)\right]^{1/2}(O_3)$$

$$= (O_3)\left[-k_1(Cl_2) - k_1(Cl_2) - k_3\left[\frac{k_1}{k_4}(Cl_2)(O_3)\right]^{1/2} - k_3\left[\frac{k_1}{k_4}(Cl_2)(O_3)\right]^{1/2}\right]$$

$$\boxed{\therefore -r_{O_3} = (O_3)\left(+2k_1(Cl_2) + 2k_3\left[\frac{k_1}{k_4}(Cl_2)(O_3)\right]^{1/2}\right)}$$

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2) $A + B \longleftrightarrow I \qquad k_1, k_{-1}$

$A + I \longrightarrow 2C \qquad k_2$

a.) find $r_A$:

$$r_A = -r_1 - r_2 + r_{-1} = -k_1(A)(B) + k_{-1}(I) - k_2(A)(I)$$

PSSH:

$$r_I \approx 0 \approx r_1 - r_{-1} - r_2 = k_1(A)(B) - k_{-1}(I) - k_2(A)(I)$$

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

$$\therefore \cancel{r_A = -k_1(A)(B) + k_{-1}\left(\frac{k_1(A)(B)}{k_{-1}+k_2(A)}\right) - k_2(A)\left(\frac{k_1(A)(B)}{k_{-1}+k_2 A}\right)}$$

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

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

$$r_A = \cancel{-k_{-1}(I)} - k_2(A)(I) + \cancel{k_{-1}(I)} - k_2(A)(I)$$

$$-r_A = +k_2(A)(I) + k_2(A)(I) = \boxed{+2k_2(A)\left(\frac{k_1(A)(B)}{k_{-1}+k_2(A)}\right)}$$

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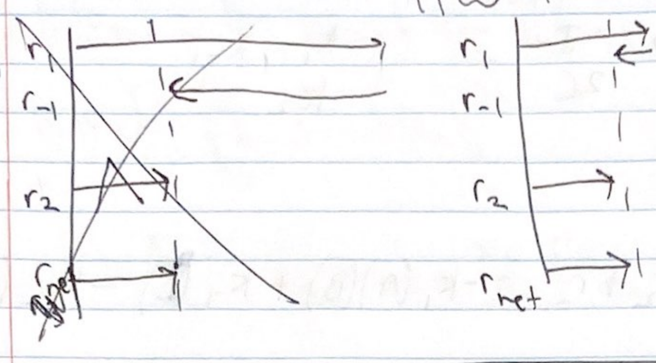
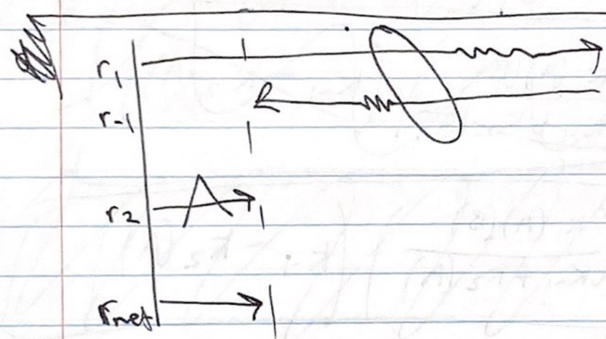
2) b)



c) assume QE: $r_1 = r_{-1}$

$$k_1(A)(B) = k_{-1}(I) \rightarrow (I) = \bar{K}_1 (A)(B)$$

$$r = \frac{r_2}{-2} = k_2 (A)(I) \quad \boxed{= 2k_2 \bar{K}_1 (A)^2 (B)}$$



d) The PSSH would reduce to QE if $\boxed{k_{-1} \gg k_2}$

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3) a) $A \underset{}{\overset{k_1, k_{-1}}{\rightleftarrows}} Y + B$ $\quad \sigma_1 = 3$

$A + Y \xrightarrow{k_2} 2Z$ $\quad \sigma_2 = 1$

$Y + Z \xrightarrow{k_3} C$ $\quad \sigma_3 = 2$

For $4A \rightarrow 3B + 2C$

$$r = \frac{r_1}{\sigma_1} = \frac{r_3}{\sigma_2} = \boxed{\frac{r_3}{2} = r}$$

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b) ~~$r = \frac{r_A}{2} = \frac{r_A}{4} = k_A$~~

$$r = \frac{r_3}{2} = 0.5\, k_3 (Y)(Z)$$

PSSH on Y

$$r_Y = 0 = k_1(A) - k_{-1}(Y)(B) - k_2(A)(Y) - k_3(Y)(Z)$$

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

PSSH on Z

$$r_Z = 0 = k_2(A)\cancel{(Y)} - k_3\cancel{(Y)}(Z)$$

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

$$\therefore r = 0.5\,\cancel{k_3}\left(\frac{k_1(A)}{k_{-1}(B) + k_2(A) + k_3\left(\frac{k_2(A)}{k_3}\right)}\right)\frac{k_2(A)}{\cancel{k_3}}$$

$$\boxed{= 0.5 k_2 (A)\left(\frac{k_1(A)}{k_{-1}(B) + 2k_2(A)}\right)}$$

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3)c) for $r = \alpha \frac{(A)^2}{(B)}$

$\boxed{k_{-1} >> 2k_2}$ OR if $\boxed{QE}$

$\rightarrow \frac{0.5\, k_2 (A)\ k_1 (A)}{k_{-1}(B) + \cancel{2k_2(A)}}$

$= 0.5\, k_2\, \bar{K}_1 \frac{(A)^2}{(B)}$ and $\alpha = 0.5 k_2 \bar{K}_1$

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d)i) if step 1 is irreversible:

$r = \frac{0.5\, k_2 k_1 (A)^2}{\cancel{k_{-1}(B)} + 2(k_2(A)} = \frac{0.5\, \cancel{k_2} k_1 (A)^{\cancel{2}}}{2\cancel{k_2}\cancel{(A)}}$

$\boxed{r = 0.25\, k_1 (A)}$

ii) if step 1 is QE:

$k_1 (A) = k_{-1} (Y)(B) \longrightarrow (Y) = \bar{K}_1 \frac{(A)}{(B)}$

$r = 0.5\, k_3 \bar{K}_1 \frac{(A)}{(B)} (Z) = 0.5\, \cancel{k_3} \bar{K}_1 \frac{(A)}{(B)} \frac{k_2 (A)}{\cancel{k_3}}$

$\boxed{r = 0.5\, k_2 \bar{K}_1 \frac{(A)^2}{(B)}}$

also, QE means $\underline{k_{-1} >> k_2}$

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4) a)

$$A \rightarrow B + C \qquad k_1$$
$$A + B \rightarrow B + D + E \qquad k_2$$
$$A + C \rightarrow B + 2D + F \qquad k_3$$
$$2B \rightarrow G \qquad k_4$$

B, C = reactive intermediates

D, E, F, G = products

$$r_A = -k_1(A) - k_2(A)(B) - k_3(A)(C)$$

PSSH on (B)

$$r_B = 0 = k_1(A) + k_3(A)(C) - k_4(B)^2$$
$$\rightarrow (B) = \left(\frac{k_1(A) + k_3(A)(C)}{k_4}\right)^{1/2}$$

PSSH on (C)

$$r_C = k_1\cancel{(A)} - k_3\cancel{(A)}(C) = 0 \rightarrow \underline{(C) = \frac{k_1}{k_3}}$$

$$\therefore (B) = \left(\frac{2k_1(A)}{k_4}\right)^{1/2}$$

$$-r_A = (A)\left[k_1 + k_2\left(\frac{2k_1(A)}{k_4}\right)^{1/2} + \cancel{k_3}\frac{k_1}{\cancel{k_3}}\right]$$
$$\boxed{= (A)\left[2k_1 + k_2\left(\frac{2k_1(A)}{k_4}\right)^{1/2}\right]}$$

where $(A) = (CH_3CHO)$

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4) b) $-r_{AC}$ reduces to $K_2(AC)\sqrt{\frac{K_1(AC)}{K_4}}$

$\boxed{\text{when } K_1 << K_2, K_3 \therefore}$

PSSH on (C):

$(C) = \frac{K_1}{K_3}$

PSSH on (B):

$$(B) = \left(\frac{K_1(A) + K_3(A)(C)}{K_4}\right)^{1/2}$$

* if $K_1 << K_3$ : $(C) \simeq 0$

$$\therefore (B) = \left(\frac{K_1(A)}{K_4}\right)^{1/2}$$

and

$$-r_A = K_1(A) + K_2(A)(B) + \cancel{K_3(A)(C)}$$

$$= K_1(A) + K_2(A)\left(\frac{K_1(A)}{K_4}\right)^{1/2}$$

* if $K_1 << K_2$ then

$$= K_2(A)\left(\frac{K_1(A)}{K_4}\right)^{1/2} = K_2\sqrt{\frac{K_1}{K_4}}(A)^{3/2}$$

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4)c) overall rxn:

$$2CH_3CHO + 4CH_3 + 2CHO \longrightarrow 4CO + H_2 + 2CH_4 + 2C_2H_6$$

$$\therefore \frac{r_{Ac}}{-2} = \frac{r_{CO}}{4} = \frac{r_{CH_4}}{2} = \frac{r_{C_2H_6}}{2}$$

$$r_{Ac} = \boxed{\frac{d(Ac)}{dt} = -(A)\left[2k_1 + k_2\left(\frac{2k_1(A)}{k_4}\right)^{1/2}\right]}$$

$$-2r_{Ac} = r_{CO} \quad , \quad -r_{Ac} = r_{CH_4} \quad , \quad -r_{Ac} = r_{C_2H_6}$$

$$\therefore \boxed{\frac{d(CO)}{dt} = 2(A)\left[2k_1 + k_2\left(\frac{2k_1(A)}{k_4}\right)^{1/2}\right]}$$

$$\boxed{\frac{d(CH_4)}{dt} = (A)\left[2k_1 + k_2\left(\frac{2k_1(A)}{k_4}\right)^{1/2}\right]}$$

$$\boxed{\frac{d(C_2H_6)}{dt} = (A)\left[2k_1 + k_2\left(\frac{2k_1(A)}{k_4}\right)^{1/2}\right]}$$

where $(A) = (CH_3CHO)$

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5) a) $2A \leftrightarrow B \quad k_1, k_{-1}$ Overall: $3A \leftrightarrow 2C$

$A + B \leftrightarrow 2C \quad k_2, k_{-2}$

$$\boxed{\sigma_2 = 1, \quad \sigma_1 = 1}$$

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

PSSH on (B)

$r_B = 0 = k_1 (A)^2 - k_{-1}(B) - k_2 (A)(B) + k_{-2}(C)^2$

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

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

c) if step 1 = QE:

$r_1 = r_{-1} \Rightarrow k_1 (A)^2 = k_{-1}(B) \rightarrow (B) = \underline{K}_1 (A)^2$

$r = \frac{r_2}{1} = \frac{r_c}{2} \rightarrow r_c = 2 r_2$

$r_2 = k_2 (A)(B) = k_2 (A)^3 \underline{K}_1$

$$\boxed{\frac{d(C)}{dt} = 2 k_2 \underline{K}_1 (A)^3}$$