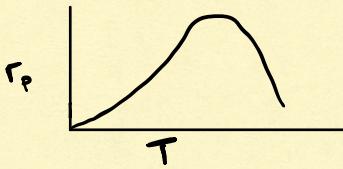
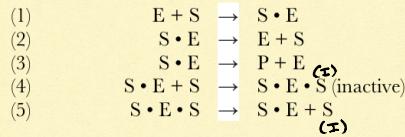


- 1) Consider the reaction of an enzyme, E , with a substrate, S , at 300K which forms a product P . The enzyme has two binding sites. Only one of these sites is active for S . Indicate the statements you agree with and justify your answer

run fast

	agree	disagree	justification
The enzyme E operates within an optimal temperature range, this range is the same for all enzymes.		X	This will change based on which kind of a system we are looking at we for example it would be different for mice and humans
If we change the type of substrate and raise the temperature the overall rate of formation of the product could increase.	X		Yes this is possible because 
If we add an inhibitor the rate of formation of the product as a function of C_S will be smaller but could go down as C_S is increased if the inhibitor is uncompetitive.		X	For substrate inhibition r_p will be smaller as C_S is increased.
If we add a competitive inhibitor but block the reverse reaction: $E \cdot I \rightarrow E + I$, we will form less product P within a fixed amount of time than if that path was not blocked.	X		if $(E \cdot I) \rightarrow E + I$ Then the enzyme will be inactive will not allow substrate to bind to active site.
The plot of $1/-r_S$ respect to $1/C_S$ shows that at time zero the intercept has changed respect to the standard Michaelis-Menten equation. Then the slope changes after 10min. This could be due to the presence of two inhibitors.	X		at time = 0 the change in intercept suggests that there is Uncompetitive inhibition a change in Slope at 10min would indicate the presence of a Competitive inhibition. This would suggest the presence of 2 inhibitors one that binds a different site (Uncompetitive) and one that binds to the same site (competitive) after 10 minutes

- 2) It has been observed that substrate inhibition occurs through the following enzymatic reaction mechanism:



You may assume that $K_M = 0.42 \text{ mmol/L}$, $V_{max} = 3.44 \text{ mmol/(L min)}$, and $K_I = 0.3 \text{ mmol/L}$, where $K_M = (k_2 + k_3)/k_1$, $V_{max} = k_3 E_t$, and $K_I = k_5/k_4$.

- Derive the rate law with respect to the substrate for this case of substrate inhibition.
- Using differentiation of the rate law (show your derivation), determine the concentration for which the rate of reaction is at a maximum, as well as the corresponding value of the rate of reaction [in mmol/L and mmol/(L min), respectively].
- If the reactivation pathway (5) is significantly slower than the deactivation pathway (4) (i.e., $k_5 \ll k_4$), what would the rate law derived in part (a) reduce to?

(Concentration will be denoted as Letters with (), instead of C_{letter})

$$r_p = k_3(E \cdot S)$$

$$(E \cdot S) = \frac{k_1(E)(S)}{k_2 + k_3} = \frac{(E)(S)}{K_M} ; K_M = k_1/k_2 + k_3 = (0.42 \text{ mmol/L})$$

$$r_p = k_3(E \cdot S) = k_3 \frac{(E)(S)}{K_M}$$

$$\begin{aligned}
 r_{E \cdot S} &= 0 = k_1(E)(S) - k_2(E \cdot S) - k_3(E \cdot S) - k_4(I)(E \cdot S) + k_5(E \cdot I \cdot S) \\
 r_{E \cdot S \cdot I} &= 0 = k_4(I)(E \cdot S) - k_5(E \cdot I \cdot S)
 \end{aligned}
 \quad] + \quad$$

$$O = k_1(E)(S) - k_2(E \cdot S) - k_3(E \cdot S)$$

$$(E \cdot S) = \frac{k_1(E)(S)}{k_2 + k_3} = \frac{(E)(S)}{K_M} \star ; K_M = \frac{k_2 + k_3}{k_1}$$

$$r_{E \cdot S \cdot I} = 0 = k_4(I)(E \cdot S) - k_5(E \cdot I \cdot S)$$

$$(E \cdot I \cdot S) = \frac{k_4(I)(E \cdot S)}{k_5} = \frac{k_4(I)}{k_5} \left(\frac{(E)(S)}{K_M} \right) = \frac{(I)(E)(S)}{(K_I)(K_M)} \star ; K_I = k_5/k_4 = (0.3 \text{ mmol})$$

$$E_t = (E) + (E \cdot S) + (I \cdot E \cdot S) = (E) \left[1 + \frac{(S)}{K_M} + \frac{(I)(S)}{K_M K_I} \right]$$

$$r_p = k_3(E \cdot S) = k_3 \frac{(E)(S)}{K_M} = \frac{k_3 E_t(S)}{K_M \left[1 + \frac{(S)}{K_M} + \frac{(I)(S)}{K_M K_I} \right]} = \frac{V_{max}(S)}{K_M + (S) \left(1 + \frac{(I)}{K_I} \right)} ; r_p = -r_s ; V_{max} = (3.44 \text{ mmol/L min})$$

A)

$$-r_s = \frac{V_{max}(S)}{K_M + (S) \left(1 + \frac{(I)}{K_I} \right)}$$

$$-r_s = \frac{V_{max}(s)}{K_m + (s)\left(1 + \frac{(s)}{K_I}\right)} \longrightarrow \left. \frac{d(-r_s)}{d(s)} \right|_{s=S_{max}} = 0$$

$(I) \rightarrow (s)$

$$-r_s = \frac{V_{max}(s)}{K_m + (s)\left(1 + \frac{(s)}{K_I}\right)}$$

$$0 = \frac{V_{max}(s)}{K_m + (s)\left(1 + \frac{(s)}{K_I}\right)} - \frac{1}{d(s)} \quad ; \quad (s) = (S_{max})$$

$$0 = \frac{(s)}{K_m + (s)\left(1 + \frac{(s)}{K_I}\right)} - \frac{1}{d(s)}$$

$$0 = \left(\frac{(s)}{K_m} + 1 + \frac{K_I}{(s)} \right) - \frac{1}{d(s)}$$

$$0 = \left(\frac{1}{K_m} + 0 + \frac{K_I}{-(s)^2} \right)$$

$$\frac{1}{K_m} = \frac{K_I}{(s)^2} \longrightarrow (s)^2 = K_m K_I \longrightarrow (S_{max}) = (K_m K_I)^{\frac{1}{2}}$$

$$(S_{max}) = (K_m K_I)^{\frac{1}{2}} = \left((0.42 \text{ mmol/L}) (0.3 \frac{\text{mmol}}{\text{L}}) \right)^{\frac{1}{2}} = 0.35490479$$

$\approx 0.35 \text{ mmol/L}$

$$(S_{max}) = (0.35 \text{ mmol/L})$$

$$\begin{aligned} -r_s &= \frac{V_{max}(s)}{K_m + (s)\left(1 + \frac{(s)}{K_I}\right)} = \frac{V_{max}(s)}{K_m + (s)\left(1 + \frac{(s)}{K_I}\right)} = \frac{(3.44 \text{ mmol/L} \cdot \text{min}) (0.35 \text{ mmol/L})}{(0.42 \text{ mmol/L}) + (0.35 \text{ mmol/L}) \left(1 + \frac{(0.35 \text{ mmol/L})}{(0.3 \frac{\text{mmol}}{\text{L}})} \right)} \\ &= 1.021782 \end{aligned}$$

B)

$$-r_{S_{max}} = 1.02 \frac{\text{mmol}}{\text{L} \cdot \text{min}}$$

$$k_I = k_5/k_4$$

(i.e., $k_5 \ll k_4$)

$$k_I \ll k_{I,\text{old}}$$

$$-r_s = \frac{V_{max}(s)}{k_m + (s) \left(1 + \frac{(I)}{k_z}\right)}$$

$$\frac{I}{k_{I,\text{new}}} \gg \frac{I_{\text{old}}}{k_{I,\text{old}}}$$

$$-r_s = \frac{V_{max}(s)}{k_m + (s) \left(1 + \frac{(I)}{k_{I,\text{new}}}\right)}$$

$$\frac{V_{max}(s)}{k_m} + V_{max} + \cancel{\frac{V_{max}(k_{I,\text{new}})}{(I)}}$$

c)

$$-r_s = \frac{V_{max}(s)}{k_m} + V_{max}$$

- 3)** You measure the rate of reaction for various concentrations of A. You then add an inhibitor I with a concentration of 0.1 mmol/L and repeat the rate measurements.

C_A (mmol/L)	1.00	1.29	1.67	2.15	2.78	3.59	4.64	5.99	7.74	10.00
$\frac{-r_A}{(x 10^{-3} \text{ mmol}} \text{ L} \cdot \text{min})$	2.85	3.58	4.37	5.33	6.22	7.45	8.80	10.1	11.2	12.8
$\frac{-r_{A,\text{inhib}}}{(x 10^{-3} \text{ mmol}} \text{ L} \cdot \text{min})$	1.41	1.77	2.18	2.65	3.19	3.74	4.34	5.00	5.62	6.26

- Determine the Michaelis-Menten parameters (K_M and V_{max}).
- Using Lineweaver-Burk plots, determine the type of inhibition occurring when the inhibitor I is added to the system.
- From the slope in your plot in part (b), determine the K_I value.

465 Homework 6

```
In [37]: import numpy as np
import matplotlib.pyplot as plt
```

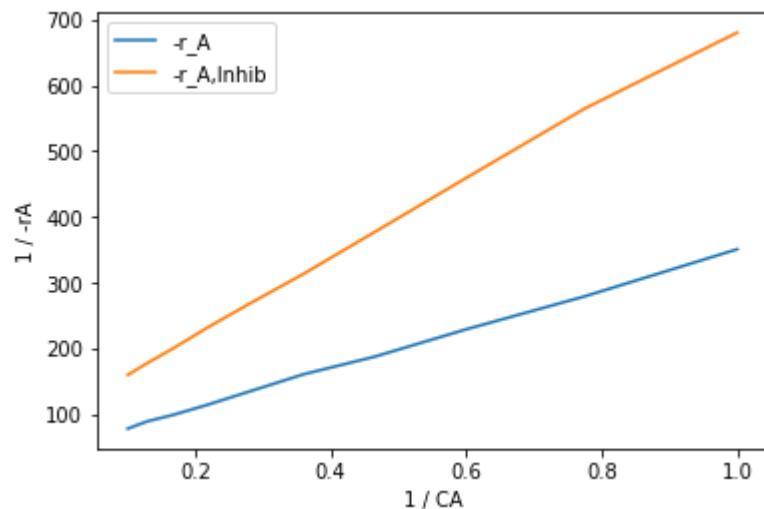
- 3) You measure the rate of reaction for various concentrations of A. You then add an inhibitor I with a concentration of 0.1 mmol/L and repeat the rate measurements.**

```
In [38]: CA= np.array([1,1.29,1.67,2.15,2.78,3.59,4.64,5.99,7.74,10]) #(mmol/L)
rA= np.array([2.85,3.58,4.37,5.33,6.22,7.45,8.8,10.1,11.2,12.8])#(10^-3 mmol /
L min ): negative rA
rAI= np.array([1.47,1.77,2.18,2.65,3.19,3.74,4.34,5,5.62,6.26]) #(10^-3 mmol /
L min ): negative rA
CA1 = 1/CA
rA1 = 1 / (rA * 10**-3)
rAI1 = 1 / (rAI * 10**-3)
```

A.) Determine the Michaelis-Menten parameters (KM and Vmax).

```
In [39]: plt.plot(CA1,rA1, label = '-r_A')
plt.plot(CA1,rAI1, label = '-r_A,Inhib')
plt.xlabel("1 / CA")
plt.ylabel("1 / -rA")
plt.legend()
```

Out[39]: <matplotlib.legend.Legend at 0x28527cc1608>



```
In [40]: slope, intercept = np.polyfit(CA1, rA1, 1)
print(slope, intercept)
slope, intercept = np.polyfit(CA1, rAI1, 1)
print(slope, intercept)
```

```
299.6755415586358 49.63294030675206
585.1620712673348 103.75227829019687
```

No inhib Slope, intercept. 299.6755415586358 49.63294030675206

Inhib Slope, intercept. 585.1620712673348 103.75227829019687

$1/v_{max} = 49.63294030675206$

$v_{max} = 0.020147909711163335$

$(K_M/V_{max}) = 299.6755415586358$

$K_M = 299.6755415586358 * 0.020147909711163335$

$K_M = 6.03783575396737$

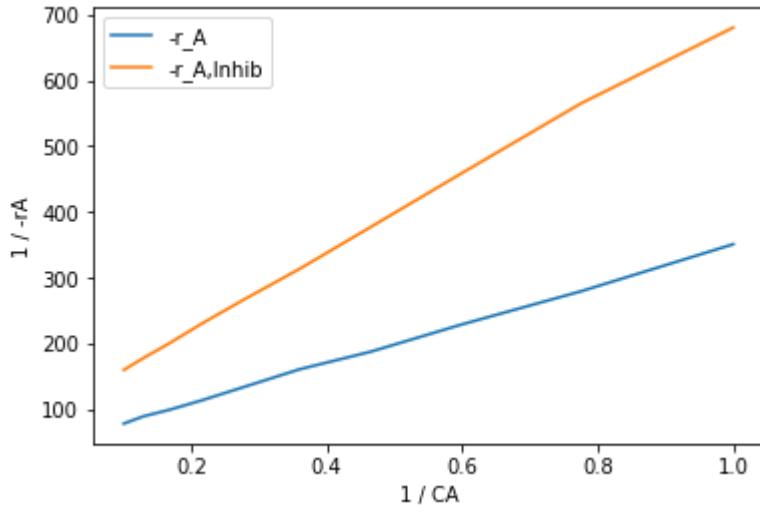
A) **$K_M = 6.04 \text{ mmol/L}$**

$V_{max} = 0.0201 \text{ mmol/L} \cdot \text{min}$

B.) Using Lineweaver-Burk plots, determine the type of inhibition occurring when the inhibitor I is added to the system.

```
In [41]: plt.plot(CA1,rA1, label = '-r_A')
plt.plot(CA1,rAI1, label = '-r_A,Inhib')
plt.xlabel("1 / CA")
plt.ylabel("1 / -rA")
plt.legend()
```

Out[41]: <matplotlib.legend.Legend at 0x28527d3a2c8>



b)

Because both the intercept has changed and the slope has changed we understand that this is a noncompetitive inhibition

C.) From the slope in your plot in part (b), determine the KI value.

$$\text{slope} = 585.1620712673348 = (\text{KM}/\text{Vmax})(1+(I)/\text{KI})$$

$$585.1620712673348 = (\text{KM}/\text{Vmax})(1+(I)/\text{KI})$$

$$585.1620712673348 = (6.037835753967369/0.020147909711163335)(1+(I)/\text{KI})$$

$$1.952652085731994 = (1+(I)/\text{KI})$$

$$0.952652085731994 = (I)/\text{KI}$$

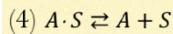
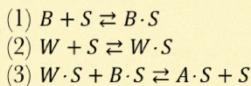
$$0.952652085731994 = (.1 \text{ mmol/L})/\text{KI}$$

$$0.10497011605570833 = \text{KI}$$

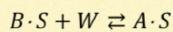
c)

$$\text{KI} = 0.105 \text{ mmol/L}^2 \text{min}^2$$

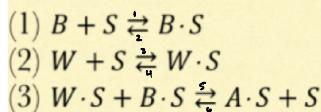
- 4) The catalytic hydration of liquid butene to form sec-butanol (A) is produced by a catalyzed reaction of butene (B) and water (W). The catalyst is solid Zeolite ZSM-5. The catalyst gets deactivated during the reaction, but we will ignore this for the purpose of this problem. A proposed reaction mechanism for the formation of sec-butanol is:



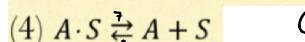
- a. Derive the rate law under the assumption that the surface reaction is the rate-limiting step.
- b. Derive the rate law under that assumption that the adsorption of B is the rate-limiting step.
- c. Derive the rate law under the assumption that the surface reaction is the rate-limiting step and the reaction follows Eley-Rideal kinetics, i.e.



- d. Derive the rate law under the assumption that the surface reaction is the rate-limiting step, and isobutene and water are adsorbed on two types of surface sites on the catalyst.



(Assume Elementary Rate Law)



(Concentration will be denoted as Letters with (), instead of C_{letter})

- a. Derive the rate law under the assumption that the surface reaction is the rate-limiting step.



$$r_s = \kappa_5 (W \cdot S) \cdot (B \cdot S) - \kappa_6 (A \cdot S)(S) \quad \kappa_5 = \kappa_s \quad \kappa_6 = \kappa_{-s}$$

$$\tilde{K}_{\kappa_s} = \frac{\kappa_s}{\kappa_6} = \frac{\kappa_s}{\kappa_{-s}}$$

$$\kappa_5 (W \cdot S) \cdot (B \cdot S) - \kappa_6 (A \cdot S)(S) = \kappa_s \left[(W \cdot S)(B \cdot S) - \frac{(A \cdot S)(S)}{\tilde{K}_{\kappa_s}} \right]$$

$\downarrow C_y$

$$\text{Total # of sites} = (\tau) = (S) + (B \cdot S) + (W \cdot S) + (A \cdot S)$$

When the Surface reaction is the rate-limiting step $\kappa_p \gg \kappa_s, \kappa_a \gg \kappa_s$ (From lecture notes)
Solve for $(W \cdot S), (B \cdot S), (A \cdot S)$

$$\begin{aligned}\kappa_1 &= \kappa_A \\ \kappa_2 &= \kappa_{-A} \\ \kappa_3 &= \kappa_{A_2} \\ \kappa_4 &= \kappa_{-A_2} \\ \kappa_5 &= \kappa_S \\ \kappa_6 &= \kappa_{-S} \\ \kappa_7 &= \kappa_D \\ \kappa_8 &= \kappa_{-D}\end{aligned}$$

$$\begin{aligned}\tilde{K}_{\kappa_A} &= \frac{\kappa_1}{\kappa_2} = \frac{\kappa_A}{\kappa_{-A}} \\ \tilde{K}_{\kappa_{A_2}} &= \frac{\kappa_3}{\kappa_4} = \frac{\kappa_{A_2}}{\kappa_{-A_2}} \\ \tilde{K}_S &= \frac{\kappa_5}{\kappa_6} = \frac{\kappa_S}{\kappa_{-S}} \\ \tilde{K}_D &= \frac{\kappa_7}{\kappa_8} = \frac{\kappa_D}{\kappa_{-D}}\end{aligned}$$

$$r_A = k_1(B)(S) - k_2(B \cdot S) = k_A \left[(B)(S) - \frac{(B \cdot S)}{k_A} \right] \quad k_A \gg r_A \text{ ; } \frac{r_A}{k_A} \approx 0$$

$$\left[(B)(S) - \frac{(B \cdot S)}{k_A} \right] \approx 0 \quad (B)(S) = \frac{(B \cdot S)}{k_A} \quad (B \cdot S) = k_A (B)(S)$$

$$r_{A_2} = k_3(W)(S) - k_4(W \cdot S) = k_{A_2} \left[(W)(S) - \frac{(W \cdot S)}{k_{A_2}} \right] \quad k_{A_2} \gg r_{A_2} \text{ ; } \frac{r_{A_2}}{k_{A_2}} \approx 0$$

$$\left[(W)(S) - \frac{(W \cdot S)}{k_{A_2}} \right] \approx 0 \quad (W)(S) = \frac{(W \cdot S)}{k_{A_2}} \quad (W \cdot S) = k_{A_2} (W)(S)$$

$$r_D = k_7(A \cdot S) - k_8(A)(S) = k_D \left[(A \cdot S) - \frac{(A)(S)}{k_D} \right] \quad k_D \gg r_D \text{ ; } \frac{r_D}{k_D} \approx 0$$

$$\left[(A \cdot S) - \frac{(A)(S)}{k_D} \right] \approx 0 \quad (A \cdot S) = \frac{(A)(S)}{k_D}$$

$$(T) = (S) + (B \cdot S) + (W \cdot S) + (A \cdot S) = (S) + k_A (B)(S) + k_{A_2} (W)(S) + \frac{(A)(S)}{k_D}$$

$$= (S) \left[1 + k_A (B) + k_{A_2} (W) + \frac{(A)}{k_D} \right] \quad (S) = (T) \left[1 + k_A (B) + k_{A_2} (W) + \frac{(A)}{k_D} \right]^{-1}$$

$$r_s = k_s \left[(W \cdot S)(B \cdot S) - \frac{(A \cdot S)(S)}{k_s} \right] = k_s \left[\left(k_{A_2} (W)(S) \right) \left(k_A (B)(S) \right) - \frac{\left(\frac{(A)(S)}{k_D} \right)(S)}{k_s} \right]$$

$$= k_s (S)^2 \left[\left(k_{A_2} (W) \right) \left(k_A (B) \right) - \frac{\left(\frac{(A)}{k_D} \right)}{k_s} \right]$$

A)

$$r_s = k_s (T)^2 \left[\left(k_{A_2} (W) \right) \left(k_A (B) \right) - \frac{\left(\frac{(A)}{k_D} \right)}{k_s} \right] \over \left[1 + k_A (B) + k_{A_2} (W) + \frac{(A)}{k_D} \right]^2$$

b. Derive the rate law under that assumption that the adsorption of B is the rate-limiting step.

$$r_A = k_1(B)(S) - k_2(A \cdot S) = k_A \left[(B)(S) - \frac{(A \cdot S)}{K_{A_2}} \right]$$

$$r_S = k_5(W \cdot S) + (B \cdot S) - k_6(A \cdot S)(S) = k_S \left[(W \cdot S)(B \cdot S) - \frac{(A \cdot S)(S)}{K_S} \right] \quad K_{A_2} \gg r_{A_2} ; \frac{r_{A_2}}{k_{A_2}} \approx 0$$

$$\left[(W \cdot S)(B \cdot S) - \frac{(A \cdot S)(S)}{K_S} \right] \approx 0 \quad (B \cdot S) = \frac{(A \cdot S)(S)}{K_S (W \cdot S)}$$

$$r_{A_2} = k_3(W)(S) - k_4(W \cdot S) = k_{A_2} \left[(W)(S) - \frac{(W \cdot S)}{K_{A_2}} \right] \quad K_{A_2} \gg r_{A_2} ; \frac{r_{A_2}}{k_{A_2}} \approx 0$$

$$\left[(W)(S) - \frac{(W \cdot S)}{K_{A_2}} \right] \approx 0 \quad (W)(S) = \frac{(W \cdot S)}{K_{A_2}} \quad (W \cdot S) = K_{A_2}(W)(S)$$

$$r_D = k_7(A \cdot S) - k_8(A)(S) = k_D \left[(A \cdot S) - \frac{(A)(S)}{K_D} \right] \quad K_D \gg r_D ; \frac{r_D}{k_D} \approx 0$$

$$\left[(A \cdot S) - \frac{(A)(S)}{K_D} \right] \approx 0 \quad (A \cdot S) = \frac{(A)(S)}{K_D}$$

$$(B \cdot S) = \frac{(A \cdot S)(S)}{K_S (W \cdot S)} = \frac{(A \cdot S)(S)}{K_S (W \cdot S)} = \frac{\left(\frac{(A)(S)}{K_D} \right) (S)}{\left(\frac{(W \cdot S)}{K_{A_2}} \right)} = \left(\frac{(A)(S)}{\left(\frac{(W \cdot S)}{K_{A_2}} \right) K_D} \right)$$

$$r_A = k_A \left[(B)(S) - \frac{(B \cdot S)}{K_A} \right] = k_A \left[(B)(S) - \left(\frac{\left(\frac{(A)(S)}{\left(\frac{(W \cdot S)}{K_{A_2}} \right) K_D} \right)}{K_A} \right) \right]$$

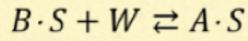
$$(T) = (S) + (B \cdot S) + (W \cdot S) + (A \cdot S) = (S) + \left(\frac{(A)(S)}{\left(\frac{(W \cdot S)}{K_{A_2}} \right) K_D} \right) + K_{A_2}(W)(S) + \frac{(A)(S)}{K_D}$$

$$= (S) \left[1 + \left(\frac{(A)}{\left(\frac{(W \cdot S)}{K_{A_2}} \right) K_D} \right) + K_{A_2}(W) + \frac{(A)}{K_D} \right] \quad (S) = (T) \left[1 + \left(\frac{(A)}{\left(\frac{(W \cdot S)}{K_{A_2}} \right) K_D} \right) + K_{A_2}(W) + \frac{(A)}{K_D} \right]^{-1}$$

$$r_A = k_A(S) \left[(B) - \left(\frac{(A)}{\left(\frac{(W \cdot S)}{K_{A_2}} \right) K_D} \right) \right] = \frac{k_A(T) \left[(B) - \left(\frac{(A)}{\left(\frac{(W \cdot S)}{K_{A_2}} \right) K_D} \right) \right]}{\left[1 + \left(\frac{(A)}{\left(\frac{(W \cdot S)}{K_{A_2}} \right) K_D} \right) + K_{A_2}(W) + \frac{(A)}{K_D} \right]}$$

$$B) \quad r_A = \frac{k_A(T) \left[(B) - \left(\frac{(A)}{\left(\frac{(W \cdot S)}{K_{A_2}} \right) K_D} \right) \right]}{\left[1 + \left(\frac{(A)}{\left(\frac{(W \cdot S)}{K_{A_2}} \right) K_D} \right) + K_{A_2}(W) + \frac{(A)}{K_D} \right]}$$

- c. Derive the rate law under the assumption that the surface reaction is the rate-limiting step and the reaction follows Eley-Rideal kinetics, i.e.



$$r_s = k_s (B \cdot S)(w) - k_{-s} (A \cdot S) = k_s \left[(B \cdot S)(w) - \frac{(A \cdot S)}{k_s} \right]$$

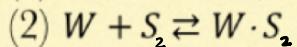
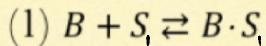
$$(B \cdot S) = K_A(B)(S) \quad (A \cdot S) = \frac{(A)(S)}{K_0}$$

$$r_s = k_s \left[K_A(B)(S)(w) - \frac{(A)(S)}{K_0 k_s} \right] = k_s (S) \left[K_A(B)(w) - \frac{(A)}{K_0 k_s} \right]$$

$$(S) = (\tau) \left[1 + K_A(B) + K_A(w) + \frac{(A)}{K_0} \right]^{-1}$$

$$\textcircled{c} \quad r_s = \frac{k_s (\tau) \left[K_A(B)(w) - \frac{(A)}{K_0 k_s} \right]}{\left[1 + K_A(B) + K_A(w) + \frac{(A)}{K_0} \right]}$$

- d. Derive the rate law under the assumption that the surface reaction is the rate-limiting step, and isobutene and water are adsorbed on two types of surface sites on the catalyst.



It seems there isn't enough information for problem 4d to be fully solved in Homework 6. The surface reaction will follow the form : $B \cdot S_1 + W \cdot S_2 \rightarrow A + S_1 + S_2$ (desorption along with reaction)

$$r_A = k_1(B)(S_1) - k_2(B \cdot S_1) = k_A \left[(B)(S_1) - \frac{(B \cdot S_1)}{K_{A_1}} \right] \quad k_A \gg r_A \quad ; \quad \frac{r_A}{k_A} \approx 0$$

$$\left[(B)(S_1) - \frac{(B \cdot S_1)}{K_{A_1}} \right] \approx 0 \quad (B)(S_1) = \frac{(B \cdot S_1)}{K_{A_1}} \quad (B \cdot S_1) = (K_{A_1}(B)(S_1))$$

$$r_{A_2} = k_3(W)(S_2) - k_4(W \cdot S_2) = k_{A_2} \left[(W)(S_2) - \frac{(W \cdot S_2)}{K_{A_2}} \right] \quad k_{A_2} \gg r_{A_2} \quad ; \quad \frac{r_{A_2}}{k_{A_2}} \approx 0$$

$$\left[(W)(S_2) - \frac{(W \cdot S_2)}{K_{A_2}} \right] \approx 0 \quad (W)(S_2) = \frac{(W \cdot S_2)}{K_{A_2}} \quad (W \cdot S_2) = (K_{A_2}(W)(S_2))$$

$$r_S = k_5(B \cdot S_1)(W \cdot S_2) - k_6(S_1)(S_2)(A) = k_S \left[(B \cdot S_1)(W \cdot S_2) - \frac{(S_1)(S_2)(A)}{K_S} \right]$$

$$= k_S \left[(K_{A_1}(B)(S_1))(K_{A_2}(W)(S_2)) - \frac{(S_1)(S_2)(A)}{K_S} \right] = k_S(S_1)(S_2) \left[(K_{A_1}(B))(K_{A_2}(W)) - \frac{(A)}{K_S} \right] \cancel{*}$$

$$(T_1) = (S_1) + (B \cdot S_1) = (K_{A_1}(B)(S_1)) = (S_1) \left(1 + (K_{A_1}(B)) \right)$$

$$(T_2) = (S_2) + (W \cdot S_2) = (S_2) + (K_{A_2}(W)(S_2)) = (S_2) \left(1 + (K_{A_2}(W)) \right)$$

$$(S_1) = (T_1) \left(1 + (K_{A_1}(B)) \right)^{-1} \quad (S_2) = (T_2) \left(1 + (K_{A_2}(W)) \right)^{-1}$$

$$r_S = k_S(S_1)(S_2) \left[(K_{A_1}(B))(K_{A_2}(W)) - \frac{(A)}{K_S} \right] = \frac{k_S(T_1)(T_2) \left[(K_{A_1}(B))(K_{A_2}(W)) - \frac{(A)}{K_S} \right]}{\left(1 + (K_{A_1}(B)) \right) \left(1 + (K_{A_2}(W)) \right)}$$

D)

$$r_S = \frac{k_S(T_1)(T_2) \left[(K_{A_1}(B))(K_{A_2}(W)) - \frac{(A)}{K_S} \right]}{\left(1 + (K_{A_1}(B)) \right) \left(1 + (K_{A_2}(W)) \right)}$$