

Physical Chemistry II - Homework 9

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1. Using the following data for the reaction $A + B \xrightarrow{k_r} C$, determine the order of the reaction with respect to A and B, and the rate constant for the reaction.

Exp	[A] (M)	[B] (M)	Initial Rate (v) (Ms ⁻¹)	ln[A]	ln[B]	ln[v]
1	2.30E-04	3.10E-05	5.25E-04	-8.37743125	-10.3815234	-7.5521123
2	4.60E-04	6.20E-05	4.20E-03	-7.68428407	-9.68837617	-5.4726708
3	9.20E-04	6.20E-05	1.70E-02	-6.99113689	-9.68837617	-4.0745419

$$\ln v = \ln k_r + \alpha \ln(A) + \beta \ln(B)$$

To calculate α , use [A] and v from exp 1 and exp 2 since [B] are equal in these experiments.

$$\ln \frac{1.7 \times 10^{-2}}{4.2 \times 10^{-3}} = \alpha \ln \frac{9.2 \times 10^{-4}}{4.6 \times 10^{-4}} \rightarrow \alpha = \boxed{2}$$

Use [B], [A], and v values from exp 1 and 2 and $\alpha = 2$ to calculate β

$$\ln \frac{4.2 \times 10^{-3}}{5.25 \times 10^{-4}} = 2 \times \ln \frac{4.6 \times 10^{-4}}{2.3 \times 10^{-4}} + \beta \ln \frac{6.2 \times 10^{-5}}{3.1 \times 10^{-5}} \rightarrow \beta = \boxed{1}$$

Use $[A] = 2.3 \times 10^{-4}$, $[B] = 3.1 \times 10^{-5}$, $\alpha = 2$, $\beta = 1$, and $v = 5.25 \times 10^{-4}$ to calculate k_r .

$$v = k_r[A]^\alpha[B]^\beta \rightarrow k_r = \boxed{3.20 \times 10^8 M^2 s^{-1}}$$

2. The decomposition of N_2O_5 is an important process in tropospheric chemistry. The half-life of the first-order decomposition of this compound is 2.05×10^4 s . How long will it take for a sample of N_2O_5 to decay to 60% of its initial value?

$$t_{1/2} = \frac{\ln 2}{k_r} = 2.05 \times 10^4 \rightarrow k_r = 3.38 \times 10^{-5} M s^{-1}$$

$$\ln \frac{[A]}{[A_0]} = -k_r t \rightarrow t = \frac{1}{k_r} \ln \frac{[A_0]}{[A]} = \frac{1}{3.38 \times 10^{-5}} \ln \frac{1}{0.6} = \boxed{15107s}$$

3. For the reaction $A + B \rightarrow \text{products}$, with equal initial concentrations, a graph of $\frac{1}{[A]^{1/2}}$ is found to be linear. What is the overall order of the reaction?

$$v = k_r[A]^\alpha[B]^\beta$$

$$\frac{1}{[A]^{1/2}} \rightarrow \text{unit } M^{-1/2}$$

$$\rightarrow k_r = M^{-1/2}s^{-1}$$

$$-1/2 + \alpha + \beta = 1 \rightarrow \alpha + \beta = \boxed{3/2}$$

4. The reaction $NO + H_2 \rightarrow H_2O + 1/2 N_2$ has been studied in the gas phase at $826^\circ C$ by the method of initial rates. The initial rate was monitored by the measuring of the total pressure of the system and these data were obtained:

(a) Find the order wrt each reactant and find the value of the rate constant. Use partial pressures in the same way as concentrations are used, since concentrations are proportional to partial pressures in an ideal gas mixture. (Hint: take the average from all four runs to determine k).

(b) For $P_{H_2}(\text{initial})=100 \text{ kPa}$ and $P_{NO}(\text{initial})=100 \text{ kPa}$, find the initial rate.

(c) For the initial pressures of part (b), find the pressure of each substance 100 s after the start of the reaction.

(d) For $P_{NO}(\text{initial})=200 \text{ kPa}$ and $P_{H_2}(\text{initial})=5 \text{ kPa}$, find the time for half the hydrogen to react.

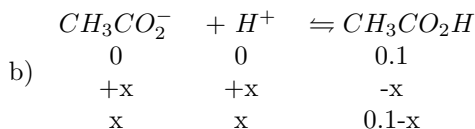
(e) for $P_{NO}(\text{initial})=5 \text{ kPa}$ and $P_{H_2}(\text{initial})=200 \text{ kPa}$, find the time for half the NO to react.

Exp	P H ₂ (initial), kPa	PNO (initial), kPa	-dP / dt, kPa s ⁻¹	ln [H ₂]	ln [NO]	ln R				
1	53.3	40	0.137	3.975936	3.688879	-1.987774	ln R ₂ - ln R ₁	-1.423473	ln[NO] ₂ - ln[NO] ₁	-0.678259
2	53.3	20.3	0.033	3.975936	3.010621	-3.411248				
3	38.5	53.3	0.213	3.650658	3.975936	-1.546463	ln R ₄ - ln R ₃	-0.707332	ln[H ₂] ₄ - ln[H ₂] ₃	-0.675129
4	19.6	53.3	0.105	2.97553	3.975936	-2.253795				
	r = k[A] ^α [B] ^β = k[H ₂] ¹ [NO] ²						ln R ₂ - ln R ₁ = β (ln[NO] ₂ - ln[NO] ₁) → β = 2			
Exp	k						ln R ₄ - ln R ₃ = α (ln[H ₂] ₄ - ln[H ₂] ₃) → α = 1			
1	1.60647E-06									
2	1.50243E-06									
3	1.94744E-06									
4	1.88573E-06									
average	1.73552E-06	kPa ⁻² s ⁻¹								
b) rate = (100kPa) ² (100kPa)(1.7x10 ⁻⁶ kPa ⁻² s ⁻¹) = 1.7kPa.s ⁻¹										
c) $\frac{d[H_2]}{dt} = -k[H_2]^3 \rightarrow \frac{dH_2}{H_2^3} = -k dt \rightarrow \int_{100}^{H_{2f}} \frac{d[H_2]}{[H_2]^3} = \int_0^{100} -k dt \rightarrow \frac{1}{2[H_2]^2} \Big _{100}^{H_{2f}} = -kt \Big _0^{100} \rightarrow \frac{1}{2[H_2]^2} - \frac{1}{100^2} = -(1.735 \times 10^{-6} kPa^{-2} s^{-1})(100s) = 1.735 \times 10^{-4} kPa^{-2}$										
$\rightarrow [H_{2f}] = 47 kPa$							Because NO has the same initial pressure as for hydrogen gas, the answer for NO is the same			
$R = \frac{d[P]}{dt} = -k[H_2][NO]^2 \rightarrow \frac{dH_2}{[H_2]} = -k[NO]^2 dt$ and $\frac{dNO}{[NO]^2} = -k[H_2] dt \rightarrow \ln P(H_2) \Big _{H_{2i}}^{H_{2f}} = -k(P(NO))^2 t_1$ and $(-1/P(NO)) \Big _{NOi}^{NO_f} = -k(P(H_2))^2 t_1$										
for d) P(NO)=200kPa, P(H ₂) _i = ln($\frac{1}{2}$), and k = 1.7x 10 ⁻⁶ → t _{1/2} = 9.98s										
for e) P(H ₂)=200kPa and P(NO)=5kPa, $(-1/P(NO)) \Big _{NOi}^{NO_f} = -(2/5 \cdot 1/5)$ and k = 1.7x10 ⁻⁶ → t _{1/2} = 576s										

5. For the reaction at 298 K, $CH_3CO_2^- + H^+ \rightleftharpoons CH_3CO_2H$, $k_f = 4.5 \times 10^{10} M^{-1} s^{-1}$, and $k_r = 8.0 \times 10^5 s^{-1}$. A solution is made from 0.100 mol of acetic acid and enough water to make 1.000 L. (a) Find the value of the equilibrium constant for the reaction at 298 K (assuming ideal solution). (b) Find the equilibrium concentrations of all three solutes at 298 K. (c) Find the relaxation time if a small perturbation is imposed on the solution such that the final temperatures is 298 K.

a)

$$K_{eq} = \frac{\text{products}}{\text{reactants}} = \frac{K_f}{K_r} = \frac{4.5 \times 10^{10} M^{-1} s^{-1}}{8.0 \times 10^5 s^{-1}} = 5.63 \times 10^4 M^{-1}$$



$$K_{eq} = \frac{0.1 - x}{x^2} = 5.63 \times 10^4 M^{-1} \longrightarrow x = 1.32 \times 10^{-3} M$$

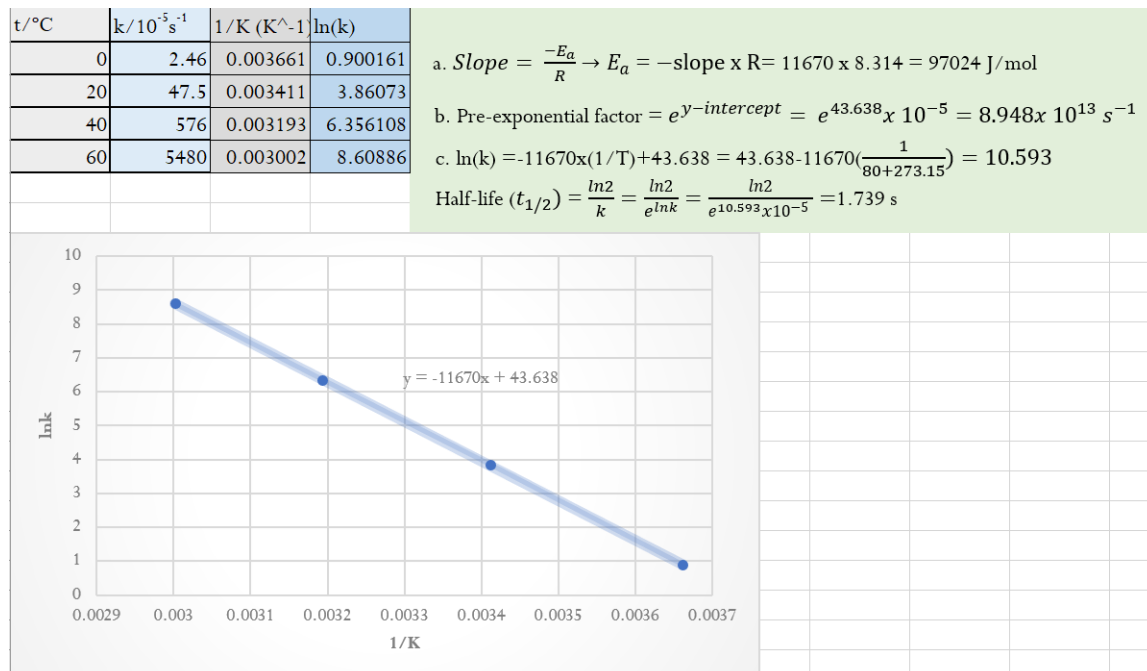
$$[CH_3CO_2^-] = [H^+] = 1.32 \times 10^{-3} M, \text{ and } [CH_3CO_2H] = 0.1 - x = 0.0986 M$$

c)

$$\tau = [k_r + k_f([A][B])]^{-1} = [8 \times 10^5 s^{-1} + 4.5 \times 10^{10} (M.s)^{-1} \times (2 \times 1.329 \times 10^{-3} M)]^{-1}$$

$$= 8.36 \times 10^{-9} s$$

6. The following rate constants were obtained for the first-order decomposition of acetone dicarboxylic acid in aqueous solution. (a) Calculate the energy of activation. (b) Calculate the pre-exponential factor A. (c) What is the half-life of this reaction at 80°C?



7. Suppose that $A \xrightarrow{k_1} B \xrightarrow{k_2} C \rightarrow \dots$ and you are interested in isolating the largest possible amount of B. Derive an equation for the time that the concentration of B goes through a maximum. For a given value of k_2 , would you wait a longer time for B to go through its maximum if A reacts more rapidly than B or if B reacts more rapidly than A?

The equation above is a consecutive elementary reaction. The rate of formation of the intermediate B is:

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

Assume that the initial concentration of A is $[A]_0$ and this is a first-order reaction, the rate formation of B can be written as:

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[B]$$

The solution for the differential equation above is a time-dependent function of [I]:

$$[B] = \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) [A]_0$$

The maximum concentration of B can be found as follow:

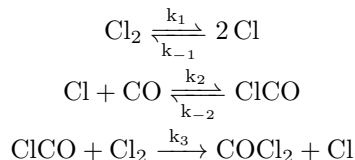
$$\begin{aligned} \frac{d[B]}{dt} &= d\left[\frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) [A]_0\right] \\ &= [A]_0 \frac{k_1}{k_2 - k_1} (k_2 e^{-k_2 t} - k_1 e^{-k_1 t}) = 0 \end{aligned}$$

Since $[A]_0$, k_1 , and k_2 cannot be zeros, the equation above is true only when:

$$\begin{aligned} k_2 e^{-k_2 t} - k_1 e^{-k_1 t} &= 0 \\ \Leftrightarrow \frac{k_2}{k_1} &= e^{-(k_1 - k_2)t} \\ \Leftrightarrow \ln \frac{k_2}{k_1} &= (k_1 - k_2)t_{max} \\ \Leftrightarrow t_{max} &= \frac{1}{(k_1 - k_2)} \ln \frac{k_1}{k_2} \end{aligned}$$

From the function of t_{max} , if A reacts more rapidly than B or $k_1 > k_2$, t_{max} will be smaller than when $k_2 > k_1$

8. The formation of phosgene by the reaction $CO + Cl_2 \rightleftharpoons COCl_2$ appears to follow the following mechanism. Assuming that the intermediate Cl and COCl are in a steady state, what is the rate law for this reaction?



Assuming that the intermediate Cl and COCl are in a steady state, what is the rate law for this reaction?

The rate law for the formation of phosgene is:

$$\frac{d[COCl_2]}{dt} = k_3[COCl][Cl_2]$$

The rate of reactions for each individual reaction are:

$$\begin{aligned} v_1 &= k_1[Cl_2], & v_{-1} &= k_{-1}[Cl]^2 \\ v_2 &= k_2[Cl][CO], & v_{-2} &= k_{-2}[COCl] \\ v_3 &= k_3[ClCO][Cl_2] \end{aligned}$$

The rate of reactions of the two intermediate reactions are all zeros if the steady-state approximation is applied. Therefore,

$$\frac{d[Cl]}{dt} = \frac{d[COCl]}{dt} = 0$$

or

$$\frac{d[Cl]}{dt} = v_1 - v_{-1} - v_2 + v_{-2} + v_3 = \frac{d[COCl]}{dt} = v_2 - v_{-2} - v_3 = 0$$

$$\longrightarrow v_1 = v_{-1} \text{ or } k_1[Cl_2] = k_{-1}[Cl]^2$$

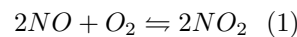
$$\text{and } v_2 = v_{-2} + v_3 \text{ or } k_2[Cl][CO] = k_{-2}[COCl] + k_3[ClCO][Cl_2]$$

$$\longrightarrow [Cl] = \left(\frac{k_1[Cl_2]}{k_{-1}}\right)^{1/2} \text{ and } [COCl] = \frac{k_2[Cl][CO]}{k_{-2} + k_3[Cl_2]} = \frac{k_2\left(\frac{k_1[Cl_2]}{k_{-1}}\right)^{1/2}[CO]}{k_{-2} + k_3[Cl_2]}$$

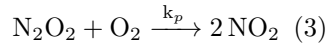
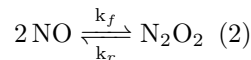
Apply [COCl] to the rate law for the formation of phosgene:

$$\frac{d[COCl_2]}{dt} = k_3 \frac{k_2\left(\frac{k_1[Cl_2]}{k_{-1}}\right)^{1/2}[CO]}{k_{-2} + k_3[Cl_2]} [Cl_2]$$

9. The atmospheric reaction of NO and O₂ to form NO₂ is given by



A proposed reaction mechanism is as follow. Use the pre-equilibrium approximation to propose a rate law.



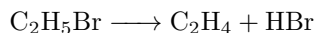
Apply the steady-state and the pre-equilibrium approximation:

$$\frac{[N_2O_2]}{[NO]^2} = \frac{k_f}{k_r} \text{ and } [N_2O_2] = \frac{k_f}{k_r} [NO]^2$$

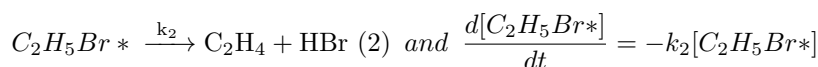
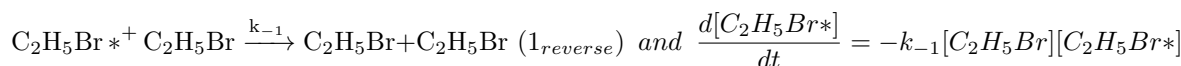
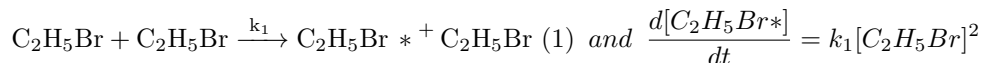
The rate law of the reaction can be written as

$$v_3 = k_p[N_2O_2][O_2] = \boxed{k_p \frac{k_f}{k_r} [NO]^2 [O_2]}$$

10. The decomposition of ethyl bromide, C_2H_5Br , in the gas phase is observed to be a first-order reaction mechanism. Write the steps of the mechanism, assuming the Lindemann mechanism applies. The products are ethane, C_2H_4 , and hydrogen bromide, HBr . What must be the case for the first-order rate law to be observed?



Applying the Lindemann-Hinshelwood mechanism:



$$\frac{d[C_2H_5Br^*]}{dt} = k_1[C_2H_5Br]^2 - k_{-1}[C_2H_5Br][C_2H_5Br^*] - k_2[C_2H_5Br^*]$$

Applying the steady-state approximation:

$$\frac{d[C_2H_5Br^*]}{dt} = 0 \rightarrow k_1[C_2H_5Br]^2 = k_{-1}[C_2H_5Br][C_2H_5Br^*] + k_2[C_2H_5Br^*]$$

$$\rightarrow [C_2H_5Br^*] = \frac{k_1[C_2H_5Br]^2}{k_{-1}[C_2H_5Br] + k_2}$$

The rate law for the product C_2H_4 from the chemical reaction (2) is:

$$\frac{d[C_2H_4]}{dt} = k_2[C_2H_5Br^*] = \boxed{\frac{k_1 k_2 [C_2H_5Br]^2}{k_{-1}[C_2H_5Br] + k_2}}$$

The first-order rate law occurs when $k_2 \gg k_1$.

11. a) Estimate the average number of units in a polymer produced by a chain mechanism in which termination occurs by combination of radicals.

(b) What is the average polymer length when the termination mechanism is a disproportionation reaction of the form $\cdot M + \cdot M \rightarrow M + :M$.

(c) Finally, derive the expression for the growth with time of the degree of polymerization $\langle N \rangle$ of a polymer formed by a step-wise process in terms of the concentration of the initial concentration of $[A]_0$ groups that react in the polymerization reaction and the rate constant k_r of the condensation reaction.

(a)

Rate of production of radicals: $2fk_i[In]$

Rate of depletion of radicals: $-2k_t[\cdot M]^2$

where f is the fraction of radicals, k_i is the rate of initiation step, k_t is the rate of termination step.

Applying steady-state approximation:

$$2fk_i[In] - 2k_t[\cdot M]^2 \longrightarrow [\cdot M] = \left(\frac{fk_i[In]}{k_t}\right)^{1/2}$$

Rate of propagation is $v_p = k_p[M][\cdot M] = k_p[M](\frac{fk_i[In]}{k_t})^{1/2}$

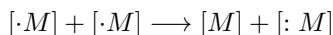
This is the rate of polymerization $\lambda = k_r[In]^{1/2}[M]$ with $k_r = k_p(\frac{fk_i}{k_t})^{1/2}$

In this case, the average number of units in the polymer produced is 2λ since 1 initiator produces 2 radicals. Therefore:

$$\langle N \rangle = 2k_r[M][In]^{1/2}$$

(b)

For disproportion polymerization:



Rate law is

$$\frac{d[\cdot M]}{dt} = k_d[\cdot M]^2$$

chain length $= \langle N \rangle$. For disproportion polymerization, radical chains don't combine.

Therefore, chain length $= k_r[M][In]^{-1/2}$

(c)

Step-wise polymerization: let $OH-R-COOH = B-R-A$

$$\frac{d[A]}{dt} = -k_r[B][A] = -k_r[A]^2$$

Integrate $\frac{1}{[A]}$ from $[A]_0$ to $[A]$:

$$\left[\frac{1}{[A]} - \frac{1}{[A]_0} \right] = k_r t \longrightarrow \frac{1}{[A]} = k_r t + \frac{1}{[A]_0} \longrightarrow [A] = \frac{[A]_0}{k_t[A]_0 + 1}$$

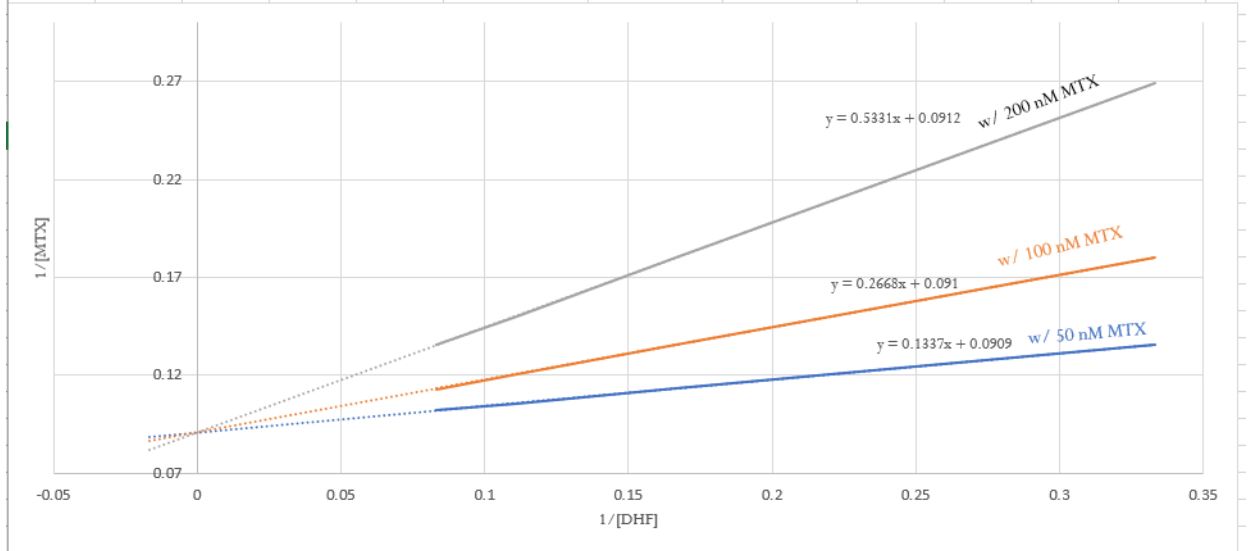
Fraction of condensed group:

$$p = \frac{[A]_0 - [A]}{[A]_0} = \frac{k_r t [A]_0}{1 + k_r t [A]_0}$$

$$\langle N \rangle = \frac{[A]}{[A]_0} = \frac{1}{1 - p} = \frac{1}{1 - \frac{[A]_0 - [A]}{[A]_0}} = \frac{k_r t [A]_0}{1 + k_r t [A]_0} = 1 + k_r t [A]_0$$

12. Dihydrofolate reductase (DHFR) is an enzyme that reduces 7,8-dihydrofolate (DHF) to 6,5,7,8-tetrahydrofolate, a step in the biosynthesis of thymidine. Methotrexate (MTX) inhibits the enzyme. MTX has been used in cancer therapies because the inhibition of DHFR restriction the thymidine production required for cell division. In the absence of thymidine, the cancerous cells cannot multiply. Using the following data of DHFR activity in the presence of MTX, determine the inhibition mechanism of MTX and the maximum reaction rate. Finally, if K_m for DHFR is $0.100 \mu M$, what is K_i ?

[DHF] mM	Rate w/ 50 nM MTX (mMs ⁻¹)	Rate w/ 100 nM MTX (mMs ⁻¹)	Rate with 200 nM MTX (mMs ⁻¹)	1/[DHF]	1/[w/ 50 MTX]	1/[w/ 100 MTX]	1/[w/ 200 MTX]
3	7.38	5.56	3.72	0.3333333	0.135501355	0.179856115	0.268817204
6	8.84	7.38	5.55	0.1666667	0.113122172	0.135501355	0.18018018
9	9.46	8.29	6.65	0.1111111	0.105708245	0.120627262	0.15037594
12	9.79	8.84	7.38	0.0833333	0.102145046	0.113122172	0.135501355



a) competitive (because the slopes are different but the y intercept is the same)

b) slope = $1/v_{max}$ $v_{max} = 1/ y\text{-intercept} \rightarrow v_{max} = 1/0.091 = 11 \text{ mMs}$

c)

$$1 + \frac{[I]}{K_i} = \frac{K'_m}{K_m} = \frac{v_{max}m}{K_m} = \frac{11 \times 0.1337 \text{ mM}}{100 \text{ nM}} = 14707$$

$$\rightarrow K_i = \frac{50 \text{ nM}}{14707 - 1} = 0.00340 \text{ nM}$$