Chemistry 1B, Spring 2015

April 13, 2015
(50 min., closed book)

Name: KEY

GSI: ________

SID: ________

Section: ________

Write your name and that of your GSI on all 10 pages of the exam. There is one additional sheet for scratch paper. Equations, constants, data and a periodic table are on this page. Please ask your GSI for additional scratch paper.

For credit:
Show your work for calculations. Round to the appropriate number of significant figures and don't forget units!

Write your answers in the boxes – anything outside of the boxes will not be graded.
Please keep your responses succinct.

You may use a **non-graphing** scientific calculator. Both pen and pencil are acceptable.

DO NOT OPEN THIS EXAM UNTIL TOLD TO DO SO.

GOOD LUCK!

Section	Page	Points	Score
1. Oxidation of Iron	2-3	9	
2. PES	4-5	14	
3. Enzymes	6-7	17	
4. Clock Reaction	8-9	21	
5. Short Answer and Problem	10	9	
Total		70	

Useful Equations and Constants

$R = 8.314\ \text{J} / (\text{mol K})$

$^\circ\text{C} + 273.15 = \text{K}$

$\Delta G^\circ = -RT \ln K$

$$\ln\frac{[A]_t}{[A]_0} = -kt$$

$$\frac{1}{[B]_t} - \frac{1}{[B]_0} = kt$$

$$k = Ae^{-E_a/RT}$$

$$\ln k = \left(-\frac{E_{act}}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

$$v_0 = \frac{V_{\max}[S]}{K_M + [S]}$$

$$\frac{1}{V_0} = \frac{K_M + [S]}{V_{max}[S]}$$

$$= \frac{K_M}{V_{max}}\frac{1}{[S]} + \frac{1}{V_{max}}$$

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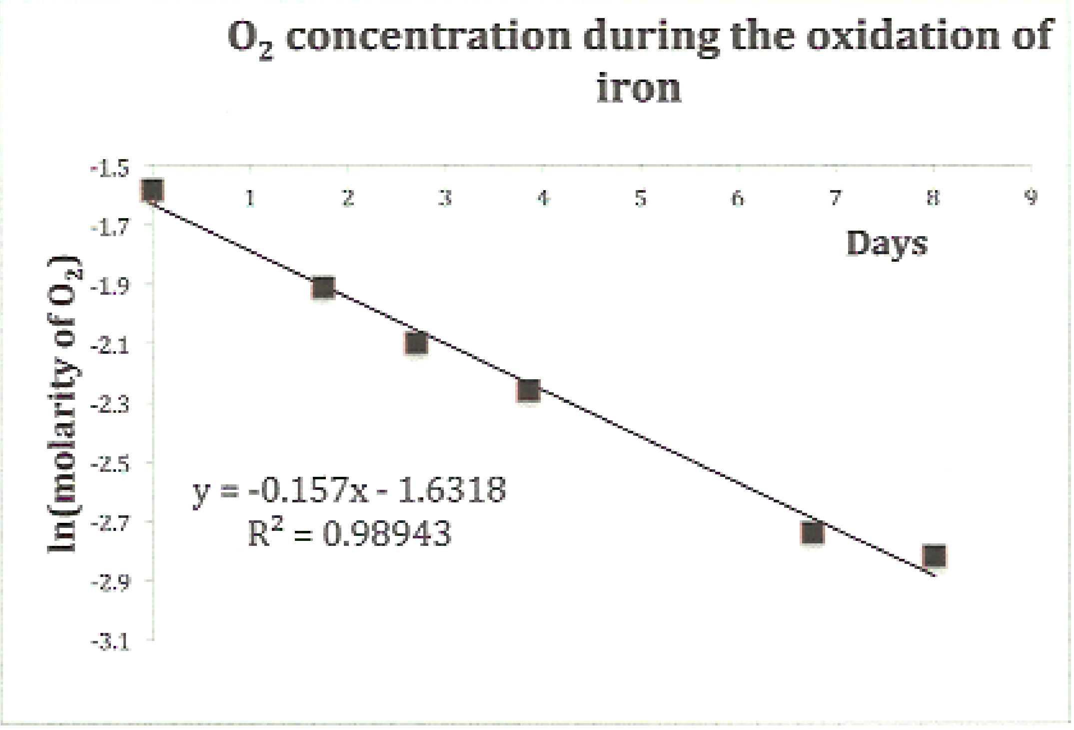
Section 1: Oxidation of Iron

Steel wool (solid iron) is oxidized in a closed buret with oxygen (O_2) in air. The expected rate law for this reaction is:

Rate = $k [O_2]^x$

x is the reaction order for oxygen.



1) a. Based on the available information, what is the value of x? Explain your reasoning.

x = 1

There is a linear relationship between ln(concentration) and time, which is characteristic of the first-order integrated rate law.

Name ____________________ GSI ______________________

(Section 1, cont.)

1) b. Calculate the half-life of the reaction to two decimal places.

half-life = 4.41 days

For 1st order

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

At ½ life, $[A]_t = \frac{1}{2}[A]_0$

$$\ln \frac{\frac{1}{2}\cancel{[A]_0}}{\cancel{[A]_0}} = -kt_{1/2}$$

$$-\frac{\ln 1/2}{k} = t_{1/2}$$

$$\frac{\ln 2}{k} = t_{1/2}$$

For 1st order

$k = -\text{slope}$

$= 0{,}157 \text{ days}^{-1}$

$$t_{1/2} = \frac{\ln 2}{0{,}157 \text{ days}^{-1}}$$

$= 4.41495\ldots$ days

$t_{1/2} = 4.41$ days

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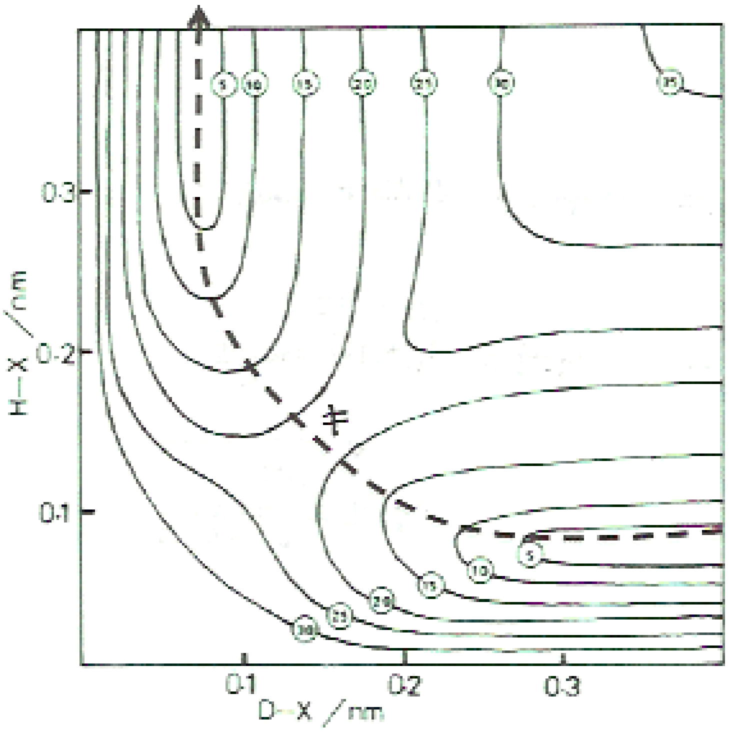
Section 2: Potential Energy Surfaces

The potential energy surface for the reaction of HX + D· → XD + H· is shown below. (X is a halogen and D is deuterium, ^2H)



The energies (kJ/mol) appear as circled numbers on the contours. The reaction path is labeled with the dashed line.

1) a. On the diagram, label the location of the activated complex using the following symbol: ‡

   b. To the best of your ability, approximate the activation energy (E_a) for this reaction:

E_a = 20 - 25 kJ/mol

~22 kJ/mol − 0 kJ/mol = 22 kJ/mol

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(Section 2, cont.)

2) To the best of your ability, approximate the bond length of DX to the second decimal place:

Bond length = ~0.075 nm

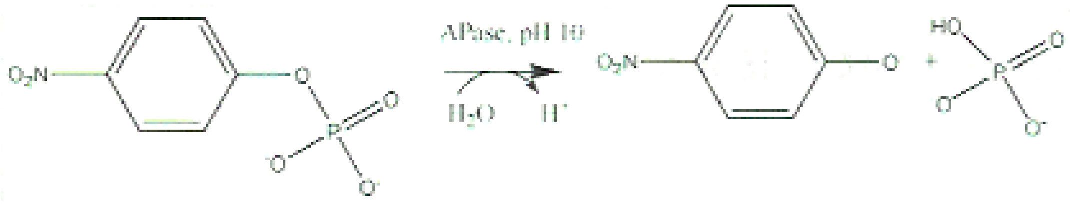
3) Draw molecular structures of D-X, H-X and the transition state below.

Reactants	Activated Complex	Products
H-X $D^\bullet$	H····X···D	H X-D

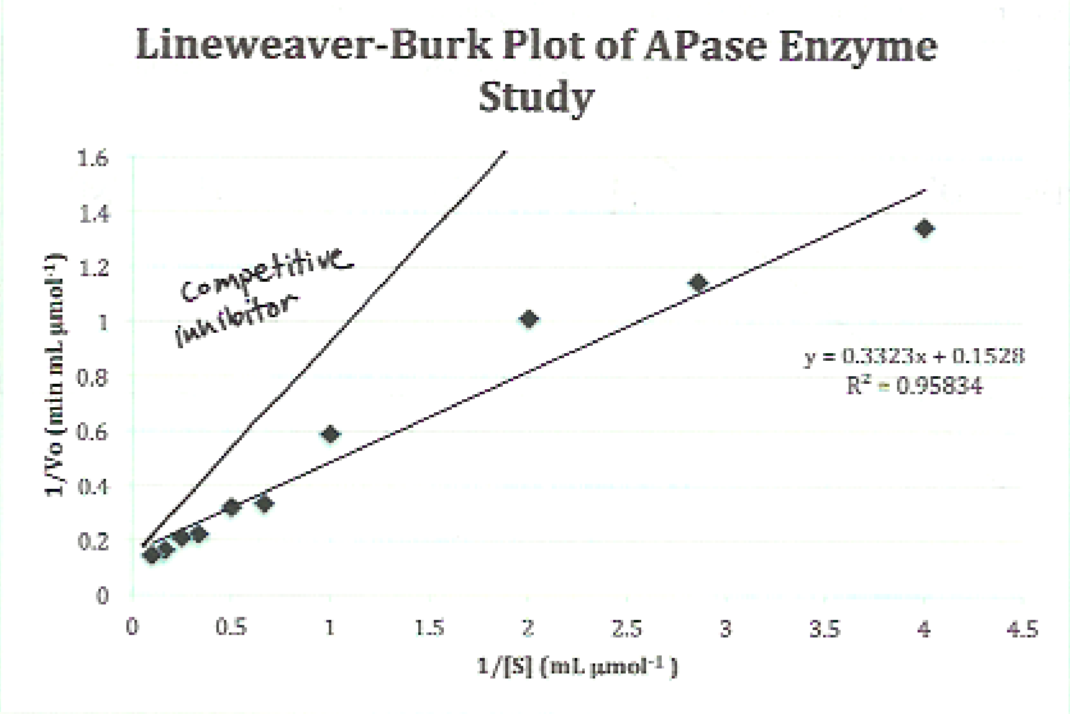
Name ______________________ GSI ______________________

Section 3: Enzymes

Alkaline phosphatase (APase) is an enzyme for the following reaction with p-nitrophenylphosphate as the substrate:



The Lineweaver-Burk plot for this reaction is the following:



1) Calculate V_{max}.

V_{max} = $6.545 \frac{\mu mol}{min \cdot mL}$

$$V_{max} = \frac{1}{y\text{-int}} = \frac{1}{0.1528 \frac{min \cdot mL}{\mu mol}} = 6.5445\ldots \frac{\mu mol}{min \cdot mL}$$

$$\hookrightarrow 6.545 \frac{\mu mol}{min \cdot mL}$$

Name ____________________ GSI ______________________

(Section 3, cont.)

2) Calculate K_m.

K_m = 2.175 μmol / mL

$$\text{slope} = \frac{K_M}{V_{MAX}}$$

$$K_M = \text{slope} \cdot V_{MAX}$$

$$K_M = 0.3323 \cdot 6,545$$

$$K_M = 2.175 \ \mu mol/mL$$

3) A phosphate inhibitor is competitive.

a) Sketch the expected plot for this inhibitor on the previous Lineweaver-Burk plot.
b) Describe how a competitive inhibition affects V_{max} and K_m.

A competitive inhibitor blocks the substrate from binding with the enzyme. At high concentrations of S (in comparison to I), the reaction exhibits the behavior modeled by Michaelis-Menten, so VMAX does not change. However, due to the presence of the I, we will need more S to reach 1/2 Vmax, so KM increases.

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Section 4: Clock Reaction

The following reaction was studied using the iodine clock reaction set-up:

$$H_2O_2 + 2\,I^- + 2H^+ \rightarrow I_2 + 2H_2O$$

The following data was obtained at room temperature. Except for flask #4, all experiments were conducted at 25.0°C.

Flask #	$[H_2O_2]_i$ (M)	$[I^-]_i$ (M)	Initial rate of I_2 formation (M/s)
1	0.012	0.015	1.71×10^{-6}
2	0.02	0.015	2.91×10^{-6}
3	0.02	0.006	1.16×10^{-6}
4 (1.00°C)	0.012	0.015	3.37×10^{-7}

1) a. Calculate the reaction orders for H_2O_2 and I^-. Round reaction orders to whole numbers. Assuming that the reaction order for H^+ is zero, write out the rate law.

$d[I_2]/dt =$ $k[H_2O_2][I^-]$

Flask 1:2

$$\frac{Rate_1}{Rate_2} = \left(\frac{[H_2O_2]_1}{[H_2O_2]_2}\right)^x$$

$$\frac{1.71 \times 10^{-6}}{2.91 \times 10^{-6}} = \left(\frac{0.012}{0.02}\right)^x$$

$$x = \frac{\ln(0.588)}{\ln(0.6)}$$

$$x = 1.04\ldots \rightarrow \textcircled{1}$$

Flask 2:3

$$\frac{Rate_2}{Rate_3} = \left(\frac{[I^-]_2}{[I^-]_3}\right)^y$$

$$\frac{2.91 \times 10^{-6}}{1.16 \times 10^{-6}} = \left(\frac{0.015}{0.006}\right)^y$$

$$y = \frac{\ln(2.51)}{\ln(2.5)} \qquad y = 1.004\ldots \rightarrow \textcircled{1}$$

Name ____________________ GSI ____________________

(Section 4, cont.)

1) b. Calculate the reaction rate constant, k, at 25.0°C

k = $9.5 \times 10^{-3} \frac{1}{M \cdot S}$ (number will vary if flask 2,3 data is used.)

$$Rate_1 = k[H_2O_2]_1[I^-]_1$$

$$k = \frac{1.71 \times 10^{-6} \frac{M}{S}}{0.012M \cdot 0.015M}$$

$$k = 9.5 \times 10^{-3} \frac{1}{M \cdot S}$$

2) Calculate the activation energy (E_a, kJ/mol) for this reaction.

E_a = 46 kJ/mol

$$\frac{k_1}{k_4} = \frac{Ae^{-EA/RT_1}}{Ae^{-EA/RT_4}}$$

$$\frac{\frac{Rate_1}{\cancel{[I^-]_1[H_2O_2]_1}}}{\frac{Rate_4}{\cancel{[I^-]_4[H_2O_2]_4}}} = e^{-\frac{EA}{RT_1} + \frac{EA}{RT_4}}$$

$$\ln \frac{Rate_1}{Rate_4} = \frac{EA}{R}\left(\frac{1}{T_4} - \frac{1}{T_1}\right)$$

$T_1 = 298.15\,K$

$T_4 = 274.15\,K$

$$E_A = \frac{\ln \frac{Rate_1}{Rate_4} \cdot R}{\left(\frac{1}{T_4} - \frac{1}{T_1}\right)}$$

$E_A = 45988.8\ldots$ J/mol

↓

46 kJ/mol

3) How would you expect the rate of the reaction to change as the temperature was increased? Explain your reasoning.

The rate would increase with temperature. At higher temperatures, more molecules have enough energy to overcome the activation energy. (Boltzmann's Distribution).

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Section 5: Short Answer and Problem

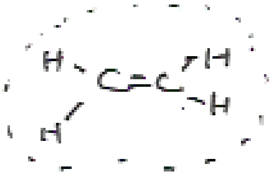
Please keep responses within the box. You may use figures to illustrate your reasoning.

1) Approximate whether the steric factor (p) for the following reaction is greater than, equal to, or less than 1. (Circle one in the box.) Explain your reasoning.

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

[✓ Less than 1] Equal to 1 Greater than 1

Collision theory assumes all molecules/atoms are small hard spheres. C_2H_4 is a larger, linear(-like) molecule, so its actual shape is smaller than the spherical approximation.



2) For the following mechanism:
   a. Identify the intermediate(s).
   b. Derive an expression for the rate law for the overall reaction using steady-state approximation. k_2 is significantly smaller than k_1 and k_{-1}.

$$MoCl_6^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MoCl_5^- + Cl^-$$

$$NO_3^- + MoCl_5^- \xrightarrow{k_2} OMoCl_5^- + NO_2^-$$

Intermediate(s): $MoCl_5^-$

Rate = $k \dfrac{[NO_3^-][MoCl_6^{2-}]}{[Cl^-]}$

$Rate = k_2[NO_3^-][MoCl_5^-]$

steady state approx. for $MoCl_5^-$

$$\frac{d[MoCl_5^-]}{dt} = 0 = k_1[MoCl_6^{2-}] - k_{-1}[MoCl_5^-][Cl^-] - \underbrace{\cancel{k_2[NO_3^-][MoCl_5^-]}}_{} \rightarrow 0$$

$$[MoCl_5^-] = \frac{k_1[MoCl_6^{2-}]}{k_{-1}[Cl^-]}$$

$$Rate = k_2[NO_3^-] \cdot \frac{k_1}{k_{-1}} \frac{[MoCl_6^{2-}]}{[Cl^-]} = k_{obs} \frac{[NO_3^-][MoCl_6^{2-}]}{[Cl^-]}$$