Chemistry 220 • Lab Test #1 • Spring 2015 Name: _____

Directions: Answer the following questions in the spaces provided. Show all work and units to receive credit.

1. Consider the reaction: $Cu^{2+}_{(aq)} + 4\ NH_{3(aq)} \Leftrightarrow Cu(NH_3)_4^{2+}{}_{(aq)}$ (dark blue)

A series of standards with varying copper (II) tetraammonia complex concentrations were prepared by using an excess of copper (II) ion to push the reaction to completion. The absorbance (at 610 nm) was taken for the standards and a plot of the Absorbance (y-axis) vs. $[Cu(NH_3)_4^{2+}]$ was made and the resulting line had the equation:

$[Cu(NH_3)_4^{2+}]_{eq} = \frac{0.202 - 0.009}{341\ M^{-1}} = 5.66 \times 10^{-4}$ $\quad y = 341\,x + 0.009$

Equilibrium mixtures were then prepared. The volumes of stock solutions used, as well as the absorbance of the equilibrium mixture are listed for one trial in the table below.

Volume (mL) of 0.010 *M* stock $Cu(NO_3)_2$	Volume (mL) of 0.010 *M* stock NH_3	Total Volume (mL) of Equilibrium mixture	$[Cu^{2+}]_0$ in *M*	$[NH_3]_0$ in *M*	Absorbance (at 610 nm)
1.00	5.00	15.0	6.7×10^{-4}	3.3×10^{-3}	~~0.247~~ 0.202

A) Calculate the initial concentrations for the two reactants in the solution described above.

$[Cu^{2+}]_0 = \frac{(0.010\ M)(1.00\ mL)}{15.0\ mL} = 6.7 \times 10^{-4}\ M$ (6.67×10^{-4})

$[NH_3]_0 = \frac{(0.010M)(5.00\ mL)}{(15.0\ mL)} = 3.3 \times 10^{-3}\ M$ (3.33×10^{-3})

B) Determine K_{eq} for the reaction.

	Cu^{2+}	+	$4\ NH_3$	$\rightleftharpoons$	$Cu(NH_3)_4^{2+}$
i	$0.000667\ M$		$0.00333\ M$		∅
c	-0.000566		$-4(0.000566\ M)$		$+0.000566$
e	$0.000101\ M$		$1.066\times10^{-3}\ M$		$0.000566\ M$

$K = \frac{(0.000566)}{(0.000101)(0.001066)^4} = \boxed{4.3 \times 10^{12}}$

2. (4 points) Consider the following reaction: $Fe^{3+}_{(aq)} + 2\ CN^-_{(aq)} \Leftrightarrow Fe(CN)_2^+{}_{(aq)}$

(light yellow) (clear) (dark red-purple)

At equilibrium at 25°C, the reaction solution is a deep red-purple. When the reaction flask is placed in an ice bath at 2°C, the solution turns a much *lighter* color.

Is the reaction endothermic or exothermic? *Explain briefly.*

Endothermic. Removing heat causes a shift to left, indicating heat was acting like a reactant.

Will K_{eq} for the reaction INCREASE, DECREASE, or remain CONSTANT?

DECREASE (more reactants → smaller K)

3. (4 points) Consider the reaction: $Cu^{2+}_{(aq)} + 4\ NH_{3(aq)} \Leftrightarrow Cu(NH_3)_4^{2+}{}_{(aq)}$

(dark blue)

The reaction above is at equilibrium at 25°C. The solution is diluted by adding deionized water at 25°C.

Will the reaction shift RIGHT, shift LEFT, or remain UNCHANGED?

LEFT

Will K_{eq} for the reaction INCREASE, DECREASE, or remain CONSTANT?

CONSTANT

4. (4 points) The equilibrium constant for a chemical reaction is known to be **K = 135 000**
In the lab, a student performs the evaluation of K six times and calculates the following values:

Trial	Experimental K
1	12 600
2	13 200
3	12 700
4	13 100
5	12 900
6	12 800

Average = 12 900
Standard Deviation = 230

Comment on the precision & accuracy of the student's data.

Be specific – provide a quantitative justification for your reasoning.

NOT ACCURATE

12,900 is off by an order of magnitude from 135,000.

PRECISE

$\sigma = 230$ is small compared to 12,900 (< 2%)

5. (8 points) Consider the esterification / hydrolysis system described below:

$$CH_3CH_2CO_2H + CH_3OH \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} CH_3CH_2CO_2CH_3 + H_2O$$

Week 1 & Week 2 data are tabulated below for titrations of 3.00-mL samples of the reaction mixture. The initial amounts of the three species initially present are listed below. None of the propanoic acid ($CH_3CH_2CO_2H$) is present initially. The reaction mixture has a total volume of close to 30 mL. Each test aliquot is 3.00 mL and will be assumed to be exactly 1/10 of the overall solution. All titration data and the ICQ table are for a 3.00-mL aliquot. Note that water is not acting as the solvent, and therefore must appear in the reaction quotient expression. Because $\Delta n = 0$, work in moles rather than mol/L.

Complete the titration data table, the ICQ table, and calculate Q for week 2.

HYDROLYSIS DATA:

$M_m = 88.1$

Mass of ester ($CH_3CH_2CO_2CH_3$): 3.12 g

$\frac{3.12\,g}{88.1\,g/mol} = 0.0354 \times \frac{1}{10} = 0.00354$ mol est

Volume of H_2O: 15.0 mL $M_m = 18.02$

Density of water: 1.0 g/mL

Volume of Methanol (CH_3OH): 15.0 mL

$M_m = 32.04$

Density of Methanol (CH_3OH): 0.79 g/mL

Titrations data	***H_2SO_4 correction:*** Week 1	Week 2
Final Burette Reading (mL)	26.29	17.49
Initial Burette Reading (mL)	22.55	5.67
Volume NaOH (mL)	3.74	11.82
Mole NaOH	0.000374	0.001182
	Moles H+ from catalyst: 0.000374	Moles acetic acid: 0.000808

Concentration of NaOH solution:

0.100 *M*

initial mol H_2O

$\frac{15\,mL}{1} \left| \frac{1\,g}{1\,mL} \right| \frac{mol}{18.02\,g} = 0.832 \times \frac{1}{10} = 0.0832$

initial mol CH_3OH

$\frac{15\,mL}{1} \left| \frac{0.79\,g}{1\,mL} \right| \frac{1\,mol}{32.04\,g} = 0.370 \times 1/10 = 0.037$

I-C-Q table $CH_3CH_2CO_2H + CH_3OH \Leftrightarrow CH_3CH_2CO_2CH_3 + H_2O$

Initial (moles)	(zero)	0.0370	0.00354	0.0832	$\times \frac{1}{10}$
Change (moles)	+0.000808	+0.000808	−0.000808	−0.000808	
Current reaction conditions (moles)	0.000808	0.0378	0.00273	0.0824	

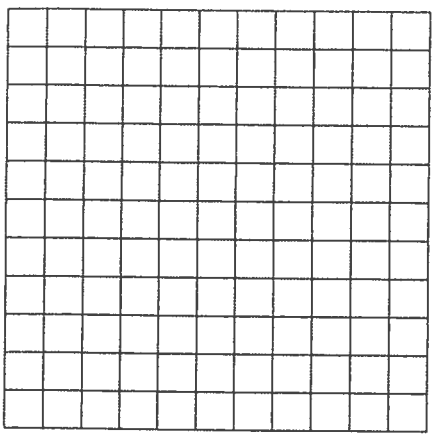
$$Q = \frac{(0.00273)(0.0824)}{(0.000808)(0.0378)} = \boxed{7.4}$$

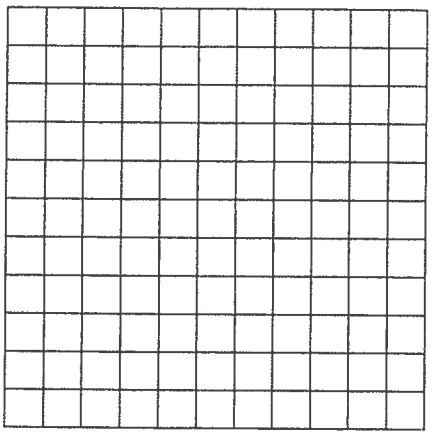
6 (11 points) For the decomposition of dicyclohexadiene, $C_{12}H_{16\,(l)}$, the data below were collected for the reaction.

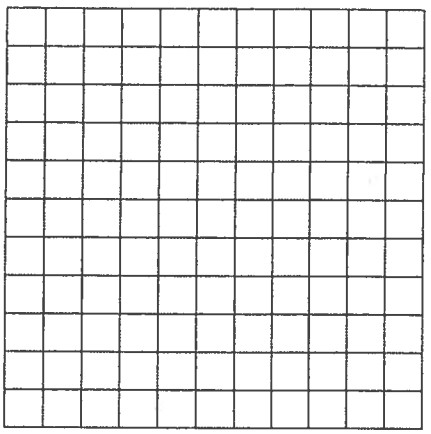
$$C_{12}H_{16\,(l)} \rightarrow 2\,C_6H_{8\,(l)}$$

t (minutes)	$[C_{12}H_{16}]$ (mol/L)		
0	0.50		
10.0	0.29		
20.0	0.17		
30.0	0.098		
40.0	0.057		
50.0	0.033		

See next page







A) Using the above information, determine the order of the reaction for $C_{12}H_{16\,(l)}$ by graphical means. Show ALL work above. The order will be 0,1, or 2. You must graphically confirm which it is, and which it is not. Follow all the rules of good graphing. Order = 1 (one)

B) Calculate k for this reaction (include units) ***by the best means possible*** from the data and/or your graphs above. You may ***not*** use a calculator statistics function to make the determination.

See next page

C) What will be the rate of the reaction at time = 25 min?

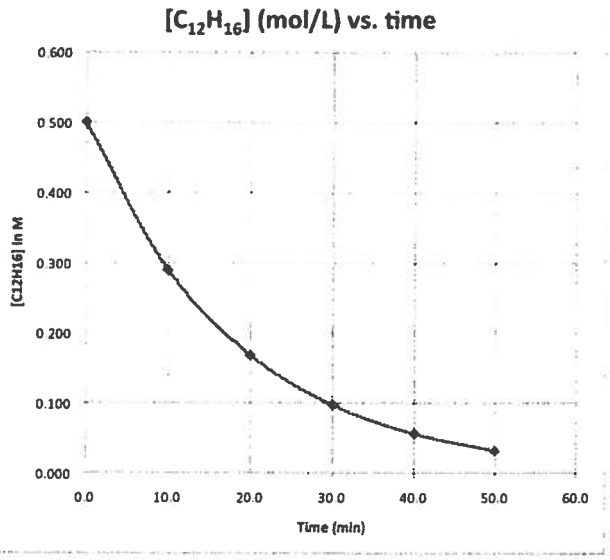
At 25 min: $\ln[C_{12}H_{16}] = -(0.0544\ min^{-1})(25\ min) + \ln(0.50\ M)$

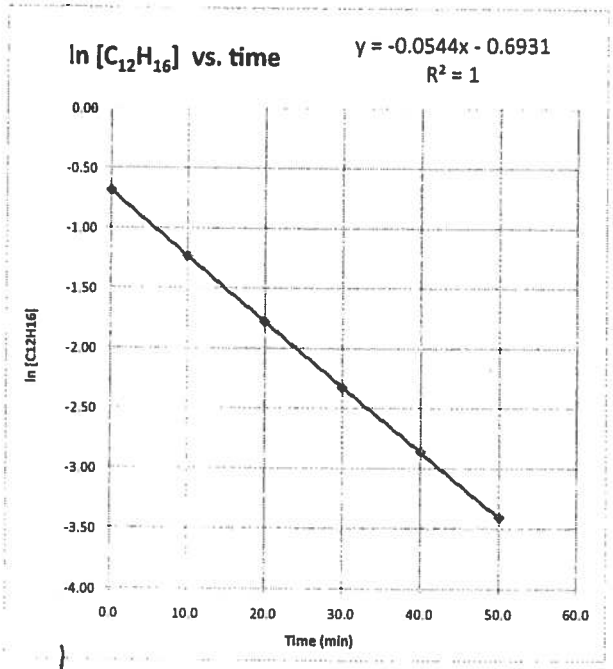
$[C_{12}H_{16}] = 0.128\ M$

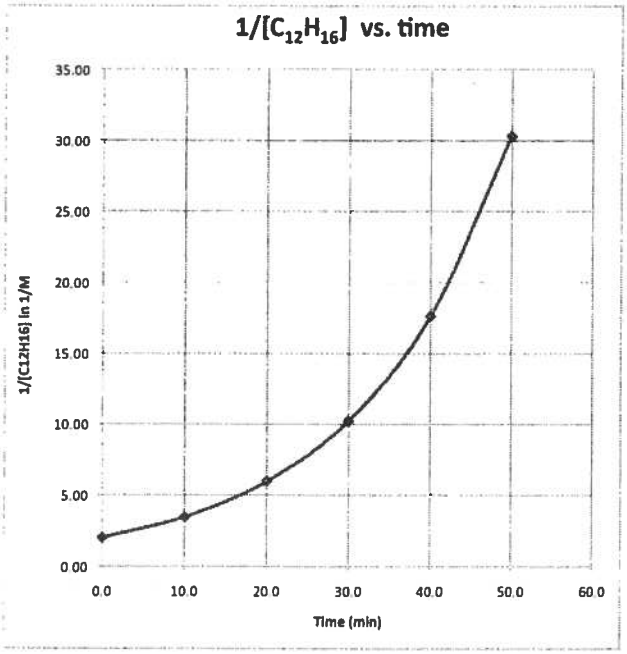
$rate = k[C_{12}H_{16}] = (0.0544\ min^{-1})(0.128\ M)$

rate = 0.0070 M/min

t (minutes)	$[C_{12}H_{16}]$ (mol/L)	ln	1/[]
0.0	0.500	-0.69	2.00
10.0	0.290	-1.24	3.45
20.0	0.168	-1.78	5.94
30.0	0.098	-2.33	10.23
40.0	0.057	-2.87	17.62
50.0	0.033	-3.41	30.36







↳ indicates 1st order

$$k = -\text{slope} = -\left(\frac{\Delta \ln [C_{12}H_{16}]}{\Delta t}\right)$$

$$= -\left(\frac{(-3.41) - (-0.69)}{50.0\ \text{min} - 0\ \text{min}}\right)$$

$$= 0.0544\ \text{min}^{-1}$$ (matches linear regression)

7. (9 points) Consider the reaction: $6\ Br^-_{(aq)} + 2\ MnO_4^-{}_{(aq)} + 4\ H_2O_{(l)} \rightarrow 3\ Br_{2(aq)} + 2\ MnO_{2(s)} + 8\ OH^-_{(aq)}$

Based on the following information, determine the order of the reaction for Br^-, the rate constant, and write the rate law expression.

In a separate set of experiments, the order of the reaction for MnO_4^- was determined to be 1 (one). Because water is the solvent, we will ignore its affect on the rate of the reaction.

Solutions with the following initial concentrations were prepared. Rates for the reaction were also determined and are tabulated here. Empty columns are for additional values you will need for graphing.

Trial #	$[Br^-]$ (*M*)	log $[Br^-]$	$[MnO_4^-]$ (*M*)	not needed	Rate (mol Br_2 / min)	log rate
1	0.024	−1.62	0.0080		0.00010	−4.00
2	0.048	−1.32	0.0080		0.00039	−3.41
3	0.072	−1.14	0.0080		0.00089	−3.05
4	0.096	−1.02	0.0080		0.00160	−2.80

Consider the relationship: **log(rate) = n log[reactant] + (y-intercept)** where n = order for the particular reactant studied.

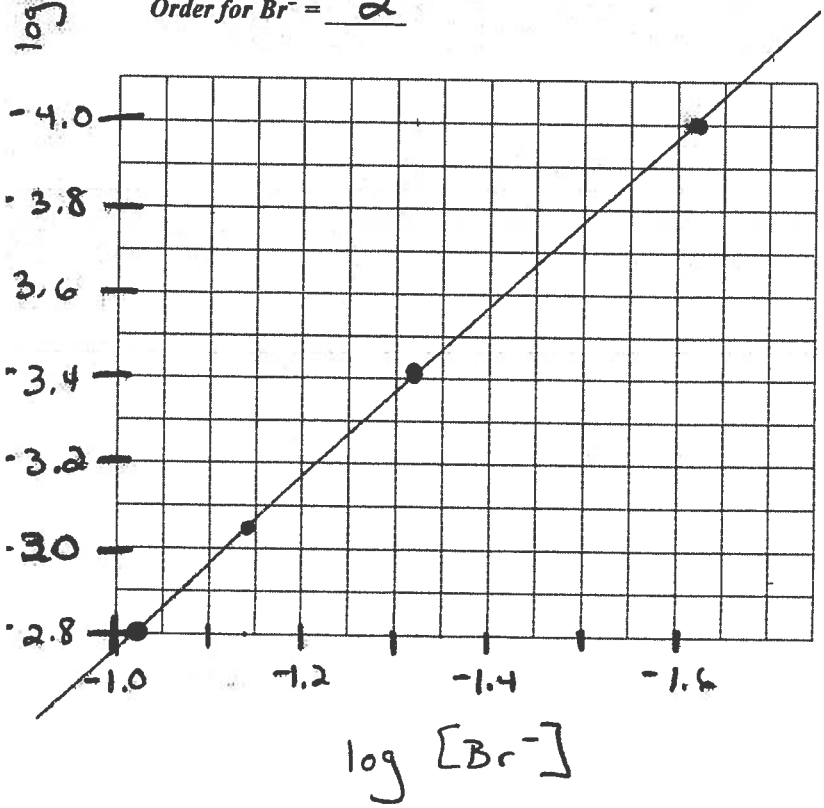
Using the data above, and the necessary manipulations of that data (extra room in the table to tabulate – you may or may not need all of the extra columns), plot the appropriate values to graphically determine the order of the reaction for each reactant. Determine the SLOPE of the line. Show work!

Order for MnO_4^- = 1 (from a separate experiment)

Order for H_2O = ignored – can be considered zero (in actuality, it is incorporated into k)

Order for Br^- = 2

6



$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{(-4.00) - (-2.80)}{(-1.62) - (-1.20)}$$

$$= 2 = \text{order for } [Br^-]$$

Continued on the next page.

7. (continued)

Write the differential rate law.

Calculate k (including units). You may base it on a single trial. Show work.

using trial 1:

$$\text{rate} = k[Br^-]^2[MnO_4^-]^1$$

$$k = \frac{(0.00010)}{(0.024)^2(0.0080)} = 21.7$$

$$= 22 \left(\frac{\text{mol } Br_2}{L^3 \cdot \text{min}}\right)$$

$$= \left(\frac{L^3}{\text{mol}^2 \cdot \text{min}}\right)$$