Dr. Bolaños **CHEM 111 - Exam 1A** Spring 2016

Name:_____ **Date:** _____

There are 25 questions totaling 90 points (scored out of 100 pts with Internship Activity). PLEASE look over the entire examination (8 pages total) BEFORE you begin to ensure your packet is complete. REMEMBER: The best place to start your exam may not be at the beginning! You have 2 hours to complete this examination and may only use a basic scientific calculator, the resource sheet and the periodic table provided. When specified, all work must be shown for credit AND all answers must be expressed with the proper amount of significant figures. Please sign the honor code at the end of the document, when complete. A scratch sheet is provided; feel free to pull it off your exam NOW and restaple when you submit your exam. If you need further clarification, please speak with the instructor. ****** I certify that the work presented in this examination is my own and that the rules set-forth for this examination were followed.***

Signature: _____

PART 1: Multiple Choice, True/False, Fill-In and Short Answer

Directions: Please answer every question below (Q1-20). No partial credit here, so please answer carefully. No work has to be shown (unless implicitly stated); however it is a good idea to record work in organized manner on your scratch sheet. Each question is worth 2 pts for each blank, unless otherwise stated.

1. Butane, (C_4H_{10}), contains a four carbon backbone with all available carbons bonded to H. The main intermolecular force found between adjacent butane molecules is _____ (provide letter).

   a. dipole-dipole b. ion-dipole c. dispersion d. hydrogen bonding

2. Rank the following substances in order of increasing solubility in water. *Please use the letters (a-d) in the blanks below.*

   a. CH_3COCH_3 b. C_6H_6 c. $HOCH_2CH_2CH(OH)CH_2OH$ d. $CH_3CH_2CH_2CH_2COCH_3$

   _____ < _____ < _____ < _____

3. Which is more concentrated (**circle one.**): 14.0 ppm CO_2 **OR** 1400.0 ppb CO_2 ?

4. Which of the following reactions would you predict to have the ***smallest*** orientation factor? Answer: _____

   a. $NOCl_2 + NO \rightarrow 2\ NOCl$ b. $N_2 + O_2 \rightarrow 2\ NO$ c. $S + O_2 \rightarrow SO_2$

5. At 25°C , the rate constant for a reaction is determined to be $3.0 \times 10^9\ M^{-2}\ s^{-1}$. The overall order of the reaction is _____.

6. The reaction below was determined to be second order in $C_2O_4^{2-}$ and 1/3 order in $HgCl_2$. Provide the rate law below, right. If the concentration of $C_2O_4^{2-}$ is tripled and the concentration of $HgCl_2$ is halved, the rate of the reaction will increase by a factor of _____.

   $2\ HgCl_2\,(aq) + C_2O_4^{2-}(aq) \rightarrow 2\ Cl^-(aq) + 2\ CO_2\,(g) + Hg_2Cl_2\,(s)$ ***Rate*** = _____

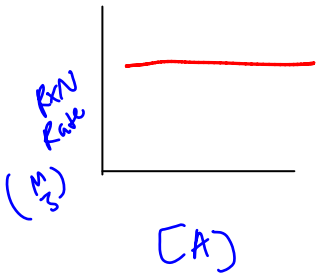
7. When a red blood cell is placed in a hypotonic solution, water flows ___b___ **(provide letter)** and is called ___hemolysis___ **(you provide formal process name).**

   a. out of the cell b. into the cell c. no net change

8. A solute dissolves endothermic in water. This means that $|\Delta H_{mix}|$ ___<___ $|\Delta H_{solvent + solute}|$.

9. For a solution with stronger than expected solute-solvent interactions, the experimental observed freezing point will be *higher than* ***OR*** *lowers than* ***OR*** *unchanged from* **(circle one)** the expected value.

10. You are asked to explain graphed kinetics data to a beginning student. Please provide the appropriate information below. Be sure to label axes, sketch curve, etc.

A → Products	**Reaction Rate vs. [A] yields this type of graph:**
Zero order	 **Significance of Plot:** The Rxn rate does not inc w/ increasing conc, and is therefore Rate is independent of conc in zero order

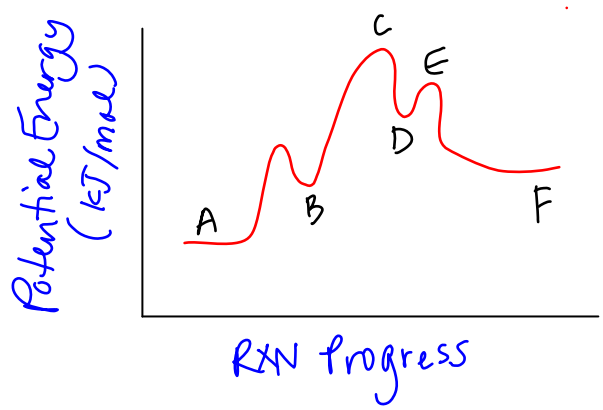
11. *Circle* aqueous solution below with the *lowest* boiling point. *Draw a rectangle around* the aqueous solution with the *highest boiling point*. These are all ideal, non-volatile solutions, each in 1.0 L solution.

0.275 *m* NaI 0.225 *m* K_3PO_4 0.100 *m* $Ba(NO_3)_2$ 0.200 *m* $HOCH_2CH_2OH$

12. Consider the graph below for A → F. There are ___3___ transitions states, and ___2___ number of intermediates labeled ___B, D___ on the graph (if any). Is the reaction exothermic? ___No___

Which reaction is fastest? ___D → F___ ***specify in same manner as reaction above.***

The reaction that determines the overall rate is: ___B → D___. ***Be careful, no partial credit here!***



PART 2: Computations - ***ALL work MUST be shown for CREDIT!*** *Point values are clearly labeled on each problem.*

13. Using the second order integrated rate law, derive the second order half life equation. *(5 pts.)*

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \qquad t_{1/2} = \frac{1}{k[A]_0}$$

At $t_{1/2}$, $[A]_t = \frac{1}{2}[A]_0$

$$\frac{1}{\frac{1}{2}[A]_0} = kt_{1/2} + \frac{1}{[A]_0} \rightarrow \frac{1}{[A]_0} = kt_{1/2}$$

14. Please consult the Solubility Table on the Resource Sheet (end of exam) to answer the following questions. A student adds 29.0 g of lead (II) nitrate to 41.0 g of water, heats the solution is heated to 50 °C and cools it to 30 °C. At 30 °C, 26.7 grams of lead(II) nitrate are dissolved in solution, while 2.3 grams of lead(II) nitrate are undissolved, at the bottom of container. ***If none, state 0 grams.***

At 30°C, $S_{Pb(NO_3)_2} = 65.0\ g$ in $100\ g\ H_2O$

$$\frac{65.0\ g\ Pb(NO_3)_2}{100.0\ g\ H_2O} = \frac{x}{41.0\ g\ H_2O}, \quad x = 26.65\ g\ Pb(NO_3)_2 = 26.7\ g\ Pb(NO_3)_2$$

$29.0 - 26.7 = 2.3\ g\ Pb(NO_3)_2$ (bottom) sat'd

15. Consider the kinetics data and the gas phase reaction of nitric monoxide and bromine at 273.15 K, below.

The rate law is : _____

$NO\ (g) + Br_2\ (g) \longrightarrow 2\ NOBr\ (g)$

Experiment	*$[I_2]$, M*	*[NO], M*	*Initial Rate (M/s)*
1	0.10	0.20	0.024
2	0.30 (>x3)	0.20	0.072 (x3<)
3	0.10	0.40	0.0389

I_2 is 1st Order

NO is 0.70 order

Rate = $k[NO][O_2]^{0.7}$

I_2 const:

$$\frac{0.0389}{0.024} = \left(\frac{0.40}{0.20}\right)^n$$

$1.6208 = 2^n$; $n = 0.6967 = 0.70$

$$\text{Rate} = 0.74\ s^{-1} M^{-0.7} [I_2][NO]^{0.7}$$

16. At 50.0 °C, the vapor pressure of pure water is 92.6 torr. After the addition of ethylene glycol (MW 62.07 g/mol), a 36.7 % (m/m) solution of ethylene glycol was prepared. The solute is non-volatile. Calculate the vapor pressure of the solution.

36.7 g EG → 0.59126 mol EG

100 g soln → 63.3 g solvent → 3.5127 m H_2O

$$X_{H_2O} = \frac{3.5127\ \text{mol}\ H_2O}{3.5127\ \text{mol} + 0.5912\ \text{mol}} = 0.855944$$

$$P_{soln} = X_{H_2O} P^\circ_{H_2O} = 0.85594 (92.6\ \text{torr}) = 79.26\ \text{torr}$$

17. A student is interested in preparing **150.0 g of a 1.200 m KCl** (FW = 74.55 g/mol) solution.

a. How would they prepare the solution? Need: 20.53 **g solute,** 229.4 **g solvent**

$\frac{1.200 \text{ mol KCl}}{1.0 \text{ kg } H_2O}$ $1.200 \text{ mol KCl} \times \frac{74.55 \text{ g KCl}}{1 \text{ mol KCl}} = 89.46 \text{ g KCl}$

$g_{soln} = 1000.0 \text{ g } H_2O + 89.46 \text{ g KCl} = 1089.46 \text{ g soln}$

$250.0 \text{ g soln} \times \frac{89.46 \text{ g KCl}}{1089.46 \text{ g soln}} = 20.53 \text{ g KCl}$

$g_{solvent} = 250.0 \text{ g} - 20.53 \text{ g} = 229.4 \text{ g } H_2O$

b. After the solution was made, the solution density was determined to be 1.025 g/mL. What is the molarity of the 1.200 m KCl solution.

$\frac{12.317 \text{ g KCl}}{150.0 \text{ g soln}} \times \frac{1 \text{ mol KCl}}{74.55 \text{ g KCl}} \times \frac{1.025 \text{ g soln}}{1 \text{ mL soln}} \times \frac{1 \text{ mL soln}}{1 \times 10^{-3} \text{ L soln}} = 1.1289 \text{ M KCl}$

$= 1.129 \text{ M KCl}$

18. Ammonia is formed via the Born-Haber cycle according the reaction:

$$N_{2\,(g)} + 3H_{2\,(g)} \longrightarrow 2\,NH_3$$

A 1.0 L solution containing 2.33 M of N_2 and 1.85 M H_2 is prepared, and the progress of the reaction is monitored and shown in the table below. The reaction studied is:

Time (s)	0.0	54.0	107.0	215.0	430.0
[H_2] (M)	1.85	1.58	1.36	1.02	0.580

a. What is the rate of change of NH_3 between 0.0 and 107.0 seconds?

$$-\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

$$\frac{\Delta[NH_3]}{\Delta t} = -\frac{2}{3}\frac{\Delta[H_2]}{\Delta t} = -\frac{2}{3}\frac{(1.36 - 1.85)\,M}{107.0\ sec} = 3.05\times10^{-3}\,\frac{M}{s}$$

b. What is the average reaction rate if the reaction between 0.0 and 107.0 seconds?

$$\text{Rate} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = -\frac{1}{3}\left(\frac{1.36 - 1.85}{107.0\ sec}\right)M = 1.53\times10^{-3}\,\frac{M}{s}$$

c. The concentration of N_2 **remaining** at 107 s is _____ M.

$$\text{Rate} = \frac{1.53\times10^{-3}\,M}{s} = \frac{-1}{1}\frac{\Delta[N_2]}{\Delta t}$$

$$-\frac{1.53\times10^{-3}\,M}{s}(107.0\,s) = \Delta[N_2] = \text{amt } N_2 \text{ reacted}$$

$$= 0.16371\ M\ N_2$$

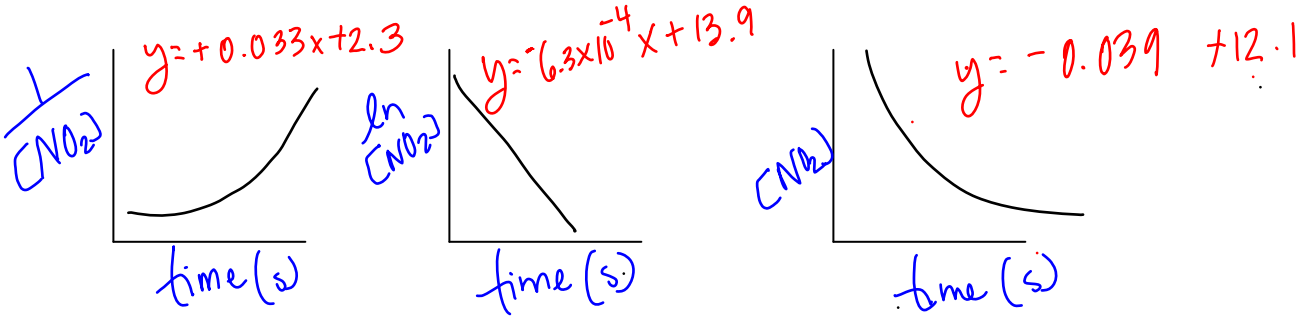
Since 1L

$$\text{Leftover } N_2 = 2.33\ \frac{mol\ N_2}{} - 0.1637\ \frac{mol\ N_2}{} = \frac{2.16629\ mol\ N_2}{1\ L}$$

$$= 2.17\ M\ N_2$$

19. A following plots were graphed for the reaction below at 500 K, with NO_2 initially at 0.900 M. Separate experiments determined the frequency factor of the reaction to be 8.05×10^{10} (same units as k).

$2\ NO_2 \longrightarrow 2\ NO + O_2$



a. The complete rate law of the reaction is $\text{Rate} = 6.3 \times 10^{-4}[NO_2]$

b. The amount of NO_2 after 2.5 min is 0.819 grams. Be careful here .

$\ln[A]_t = -(150s)(6.3 \times 10^{-4}) + \ln(0.900)$

$-0.09445 \quad -0.10536$

$\ln[A]_t = -0.19982$

$[A]_t = 0.8188\ g$

c. What amount of the formed O_2 (in grams) is present after the reaction has been proceeding for 2.5 minutes ?

$0.900\ g\ NO_2 - 0.8188\ g\ NO_2 = 0.08120\ g\ NO_2$ reacted

$0.08120\ g\ NO_2 \times \frac{1\ mol\ NO_2}{46.005\ g\ NO_2} \times \frac{1\ mol\ O_2}{2\ mol\ NO_2} \times \frac{32.00\ g\ O_2}{1\ mol\ O_2} = 2.824 \times 10^{-2}\ g\ O_2$

d. The activation energy for the reaction is _____ kJ/mol.

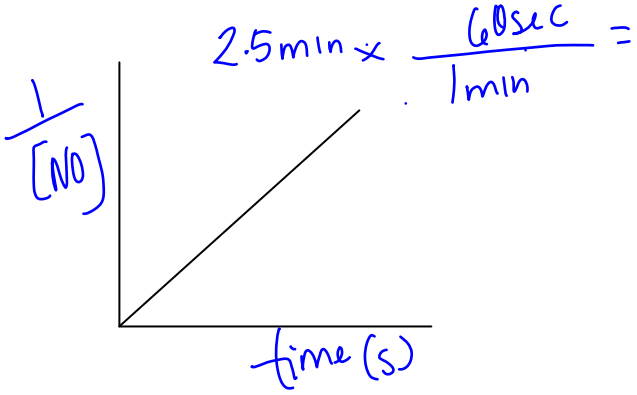
$\frac{k}{A} = e^{-\frac{E_a}{RT}}$; $\ln k - \ln A = -\frac{E_a}{RT}$

$-RT(\ln k - \ln A) = E_a$

$E_a = -8.314\frac{J}{mol\ K}(500K)(\ln 6.3 \times 10^{-4} - \ln 8.05 \times 10^{10})$

$E_a = 135{,}018.49\ J/mol = 135\ \frac{kJ}{mol}$

20. The reaction $2\ NO_{(g)} + Cl_{2\ (g)} \rightarrow 2\ NOCl_{(g)}$ was performed and the following data was obtained under constant $[Cl_2]$:



a. Is the following mechanism consistent with the data? Why or why not? Support your answer!

$NO_{(g)} + Cl_{2\ (g)} \rightleftharpoons NOCl_{2\ (g)}$ (Fast)

$NOCl_{2\ (g)} + NO_{(g)} \rightarrow NOCl_{(g)}$ (Slow) ← Rate limiting step

Rate = $k[NOCl_2][NO]$ ← intermed. Rate limiting

Fast: $k_f[NO][Cl_2] = k'_{rev}[NOCl_2]$

$[NOCl_2] = \frac{k_f}{k_{rev}}[NO][Cl_2]$ ← Sub

Rate = $k\frac{k_f}{k_r}[NO][Cl_2][NO]$

shows $[NO]^2$ — this confirms 2nd order in NO (as indicated by data above) but not Cl_2 (no data)

b. Does the above ~~linear plot~~ guarantee the overall rate law of the reaction? Why or why not? Support your answer.

No! This only confirms [NO] order, not (Cl_2).

No guarantee w/o additional data showing effect on Rate w/ $[Cl_2]$ conc. Can't assume it is zero order - need validation.

Reference Sheet

NAME_____

$R = 8.314\ J/mol^* K$

$R = 0.08206\ L * atm /mol*K$

$S_{gas} = k_H P_{gas}$

$P_{soln} = X_{solvent} P^o_{solvent}$

$P_a = X_a P^o_a$

$P_b = X_b P^o_b$

$P_{total} = P_a + P_b$

$\Delta T_f = mK_f$

$\Delta T_b = mK_b$

$\Pi = iMRT$ (R = 0.08206 L * atm /mol*K)

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

$\ln k = -Ea/R + \ln A$

$\ln (k_2/k_1) = Ea/R\ (1/T_1 - 1/T_2)$

$k = pze^{-Ea/RT}$

$[A]_t = -kt + [A]_o$

$1/[A]_t = kt + 1/[A]_o$

$\ln [A]_t = -kt + \ln A]_o$

$t_{1/2} = 0.693/k$

$t_{1/2} = [A]_o /2k$

$t_{1/2} = 1/k[A]_o$