Chemistry 134	Your Name:	
Prof. Jason Kahn		
University of Maryland, College Park	Your SID #:	
General Chemistry and Energetics		
<u>Final Exam (150 points total)</u>		<u>December 19, 2016</u>

You have 120 minutes for this exam.

Explanations should be <u>concise</u> and <u>clear</u>. There is extra space on the last page if you need it. You will need a calculator for this exam. No other study aids or materials are permitted. Generous partial credit will be given, *i.e.*, if you don't know, guess.

## **Useful Equations:**

$K_a = [\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{H}\mathrm{A}]$	$pH = -\log([H^+])$	$K_b = [\text{HA}][\text{HO}^-]/[\text{A}^-]$	
$K_w = [H^+][HO^-]$	$pH = pK_a + \log [A^-]/[HA]$	$\Delta G^{\circ} = - \mathrm{R}T \mathrm{ln}K_{eq}$	
$R = 0.08206 \text{ L} \cdot \text{atm/mole K}$	$k_B = 1.38 \text{ x } 10^{-23} \text{ J/K}$	$\ln K_{eq} = (-\Delta H^{\circ}/R)(1/T) + \Delta S^{\circ}/R$	
$\Delta S = q/T$	R = 8.314  J/mole K = 1.98	$37 \text{ cal/mole } \mathbf{K} = \mathbf{N}_A k_B$	
$S = k_B \ln W$	$\Delta G = \Delta H - T \Delta S$	$\Delta G = \Delta G^{\circ} + RT \ln Q$	
Chemical standard state: 1 M solutes, pure liquids, 1 atm gases			
Biochemical standard state: pH 7, all species in the ionic form found at pH 7			
$^{\circ}C = ^{\circ}K - 273.15$ P	$(v)dv = Cv^2 exp(-mv^2/2kT)$	$\mathbf{E} = \mathbf{E}^{\circ} - 2.303 (\mathbf{RT}/n\mathcal{F}) \log_{10} \mathbf{Q}$	
$2.303$ RT/ $\mathcal{F}$ = 0.0592 Volts at 25 °C		$\mathcal{F}$ = 96500 C(oulomb)/mole	
$\Delta G^{\circ} = -n\mathcal{F} E^{\circ}_{cell}$	$\ln k = (-E_a/RT) + \ln A$	1 Volt = 1 Joule/Coulomb	
$[\mathbf{A}] = [\mathbf{A}]_0 - kt$	$\ln[\mathbf{A}] = \ln[\mathbf{A}]_0 - kt$	$1/[A] = 1/[A]_0 + 2kt$	
Standard hydrogen electrode:	$2 \text{ H}^+(aq, 1 \text{ M}) + 2 e^- \rightarrow \text{H}_2$	(g) $E^{\circ}_{red} = 0.000 V$	

# Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:

"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

## 1. Organic Chemistry (46 pts)

(a; 6 pts) Why does carbon get a branch of chemistry to itself? Why not Si, or Al, or P, or some other deserving element? What makes carbon unique? Answer in two phrases or sentences.

(b; 10 pts) Draw two examples of a branched chain alcohol with molecular formula C<sub>5</sub>H<sub>12</sub>O. (There are at least 5 possible answers, not including stereochemistry.)

(c; 10 pts) Draw *trans*-3-*n*-heptene, C<sub>7</sub>H<sub>14</sub>. Draw one of the three possible products of oxidizing (i.e. removing 2 H's from) *trans*-3-*n*-heptene, to make a molecule with molecular formula C<sub>7</sub>H<sub>12</sub> containing two conjugated double bonds.

(d; 20 points) Identify the amine, aldehyde, ketone, and ester functional groups in the molecule below. How many hydrogens are attached at each of carbons 1, 2, and 3? Which one of those three carbons is a "stereocenter," meaning that changing the spatial arrangement of bonds at that carbon would give a different 3-dimemnsional structure?



#### 2. Acid-Base chemistry (36 pts)

(a; 8 pts) Calculate the pH of a 0.100 M solution of the weak monoprotic acid HCOOH, formic acid,  $pK_a$  3.62. Assume "*x*" is small.

- Consider the titration curve for the titration of 100 ml of 0.1 M formic acid with 0 to 150 ml of strong base, 0.1 M NaOH.
- (b; 12 pts) Write down the base dissociation equation for formate ion, HCOO<sup>-</sup>. Use it to calculate the pH at the equivalence point of the titration (100 ml of NaOH added). Again, assume "y" (not the same as "x") is small. Before you start, you know the pH is >7. Why?

(c; 10 pts) Sketch the titration curve described above. Label the buffer region and state the pH at the halfequivalence point (50 ml of NaOH added). (d; 6 pts) What is the approximate pH at the end of the titration, when we have added 150 ml of 0.1 M NaOH? Hint: I call the end of the titration "adding base to salt."

# 3. Electrochemistry (45 pts)

- Consider a  $Ag(s)/Ag^+(aq)$  half cell set up by one of your lab partners, hooked up to what your other lab partner told you is a Standard Hydrogen Electrode (SHE). Based on the standard reduction potential tables, the voltage should be +0.80 V for the reduction of  $Ag^+$  (causing it to plate out on the electrode), with accompanying oxidation of  $H_2$  to  $H^+$ .
- (a; 12 pts) Sketch the setup, including labeling the anode, cathode, and salt bridge and indicating the direction of electron flow through the external circuit.

(b; 8 pts) Write down each half-reaction and the balanced overall redox reaction.

- Instead of 0.80V, you measure 0.85 V. You suspect that one, but only one, of the aqueous components was prepared incorrectly, i.e. that either the Ag<sup>+</sup> concentration or the H<sup>+</sup> concentration is not at the standard state. [We ignore any possible overpotential or conductivity complications.]
- (c; 8 pts) Calculate the non-standard Ag<sup>+</sup> concentration that would be required for you to observe 0.85 V, assuming that the SHE was set up correctly.

(d; 6 pts) Calculate the pH of the non-standard hydrogen electrode (denoted the % @#\*&%\$-NSHE) that would be required to give 0.85 V, assuming that the Ag(*s*)/Ag<sup>+</sup>(*aq*) half-cell was set up correctly.

(e; 5 pts) Which half-cell is the likely culprit: explain your reasoning?

(f; 6 pts) Where does the energy released in combustion come from? In terms of redox, explain why burning natural gas provides about twice as more free energy per carbon atom released than burning coal or wood.

## 5. Chemical Equilibrium (23 pts)

The equilibrium constant for the endothermic reaction  $H_2(g) + I_2(s) \rightleftharpoons 2 HI(g)$  is  $K_p = 0.345$ , at 25 °C. (a; 5 pts) Gaseous H<sub>2</sub> is added to excess solid iodine and the equilibrium partial pressure of H<sub>2</sub> is found to be

 $P_{H2} = 0.87$  atm. What is the equilibrium partial pressure of HI at 25 °C?

(b; 10 pts) Excess solid I<sub>2</sub> is added to a container filled with 3.50 atm of H<sub>2</sub>, with the vessel maintained at constant volume and 25 °C. Set up but do not solve the quadratic equation that would give you the final partial pressure of HI. Will the final total pressure in the container be more or less than 3.50 atm (you do not need to do a calculation to answer)?

(c; 8 pts) If the volume of the container is increased at constant temperature, which way will the equilibrium shift, and why? If the temperature is increased, will the equilibrium constant increase or decrease?

Page	Score
2	/26
3	/28
4	/22
5	/18
6	/22
7	/11
8	/15
9	/8
Total	/150