Chemistry 271 – 23XX **Your Name:** ______________________________

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University of Maryland, College Park **Your SID #:** ______________________________

General Chemistry and Energetics

Final Exam (200 points total) **Your Section # or time:** ______________________________

May 13, 2016

You have 120 minutes for this exam.

Explanations should be concise and clear. 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:

$K_a = [H^+][A^-]/[HA]$ $pH = -\log([H^+])$ $K_b = [HA][HO^-]/[A^-]$

$K_w = [H^+][HO^-]$ $pH = pK_a + \log [A^-]/[HA]$ $\Delta G° = -RT\ln K_{eq}$

$R = 0.08206$ L·atm/mole K $k_B = 1.38 \times 10^{-23}$ J/K $\ln K_{eq} = (-\Delta H°/R)(1/T) + \Delta S°/R$

$\Delta S = q/T$ R = 8.314 J/mole K = 1.987 cal/mole K = $N_A k_B$

$S = k_B \ln W$ $\Delta G = \Delta H - T\Delta S$ $\Delta G = \Delta G° + RT\ln Q$

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

°C = °K – 273.15 $P(v)dv = Cv^2 \exp(-mv^2/2kT)$ $E = E° - 2.303(RT/n\mathcal{F})\log_{10}Q$

$2.303RT/\mathcal{F} = 0.0592$ Volts at 25 °C $\mathcal{F} = 96500$ C(oulomb)/mole

$\Delta G° = -n\mathcal{F}E°_{cell}$ $\ln k = (-E_a/RT) + \ln A$ 1 Volt = 1 Joule/Coulomb

$[A] = [A]_0 - kt$ $\ln[A] = \ln[A]_0 - kt$ $1/[A] = 1/[A]_0 + 2kt$

Standard hydrogen electrode: $2\,H^+(aq, 1\,M) + 2\,e^- \rightarrow H_2\,(g)$ $E°_{red} = 0.000$ 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. (50 pts) Fundamental thermodynamics

ΔG is the change in free energy, but as we have discussed, free energy isn't exactly an energy, and it's also not obvious what is free about it. Other than that, the name is perfectly sensible: G stands for "Gibbs."

(a; 8 pts) There are two meanings for "free": (1) as in liberated, "Born Free," or "Free at last," (2) as in no-cost, "There ain't no such thing as a free lunch." Identify which meaning applies to G and what the "free" means in "free energy." Explain how this relates to the equation $\Delta G = -nFE_{cell}$.

(b; 2 pts) The idea that free energy is minimized when a system reaches equilibrium is really a statement of the (circle one): 1st 2nd or 3rd Law of Thermodynamics.

(c; 2 pts) The First law of Thermodynamics says that __________________________ is conserved.

(d; 8 pts) If you memorized the equation $G = G° + RT \ln P$, but forgot the sign, how could you figure out whether **+** or **–** is logically correct? Also, what does the superscript ° in G° stand for?

(e; 20 pts; 2 pts each) Consider the reaction $A(aq) \rightleftharpoons B(aq)$, with the standard state molar free energy of A = $G°_A$ = –3 kJ/mole at 298 K and the molar free energy of B = $G°_B$ = 1 kJ/mole at 298 K.

Circle or write in correct answers in the table below:

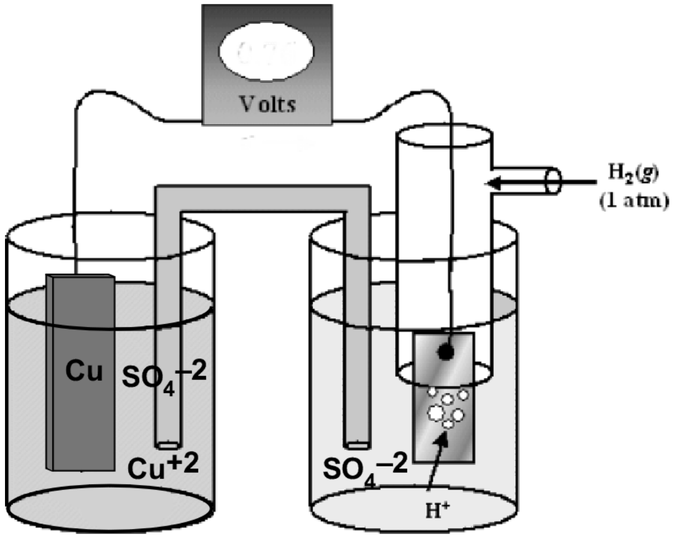
The equilibrium constant expression in terms of [A] and [B] is	K_c =		
The standard state free energy change for A → B, $\Delta G°_{rxn}$, is	$\Delta G°_{rxn}$ = ____________kJ/mole		
The observed ΔG_{rxn} at equal concentrations of A and B is	ΔG_{rxn} = _____________kJ/mole		
The observed free energy change ΔG_{rxn} at 2.4 M A and 0.5 M B is	ΔG_{rxn} = _____________kJ/mole		
The numerical value of K_c at 298 K is	K_c =		
The total free energy of an equilibrium mixture of A and B is (circle one):	Less than -3 kJ/mole	Between +1 and -3 kJ/mole	Cannot be determined
To answer the question above I would need to know (circle one):	The exact concentrations of A and B	I answered it already	There is no way to answer
K_{eq} at 400 K is (circle one):	Cannot be determined	Greater than K_{eq} at 298 K	Less than K_{eq} at 298 K
To answer the question above I would need to know (circle one):	Both ΔH° and ΔS° values (assuming they are constant)	Only the sign of ΔH° (assumed constant)	Already answered
ΔG_{rxn} at equilibrium is	ΔG_{rxn} = ____________kJ/mole		

(f; 10 pts) Sketch the graph for total free energy of an A+B mixture as a function of the percent found as B (i.e. the *x*-axis ranges from 0% to 100% B), given a total concentration [A]+[B] of 1 M, at 298 K.

Score for the page____________

2. Electrochemistry (40 pts)

Consider the electrochemical cell below. On the left is a $Cu(s)|Cu^{+2}(aq)$ half-cell, with 1M $Cu^{+2}(aq)$, $E°_{red} = 0.3402$ V. On the right there is a standard hydrogen ($H_2(g)|H^+$) electrode ($E°_{red} = 0.000$ V by definition), except someone has replaced the solution with H_2SO_4 of unknown concentration, making it a "non-standard hydrogen electrode" (NSHE). The SO_4^{2-} ion is an inert spectator. **The measured cell voltage is 0.3175 V, with the Cu electrode acting as the cathode.** (Recall that what happens at the cathode is due to the fact that both words start with a consonant.)



Adapted from http://www.mikeblaber.org/oldwine/chm1046/notes/Electro/CellEMF/CellEMF.htm

(a; 6 pts) Write down the balanced reduction half-reactions for each half-cell.

(b; 4 pts) Write down the balanced overall redox reaction and calculate $E°_{cell}$.

(c; 3 pts) On the diagram, draw in the direction of electron flow in the external circuit and the direction of sulfate ion flow through the salt bridge.

(d; 3 pts) How could you tell just visually, after a while, that the copper electrode is the cathode?

(e; 6 pts) Calculate ΔG° and the equilibrium constant for the reaction.

Score for the page____________

(f; 6 pts) Qualitatively, why would it be difficult to measure this equilibrium constant directly, for example by sealing off the system and measuring $[Cu^{+2}]$ and P_{H2} when everything has come to equilibrium?

(g; 6 pts) Write down the Nernst equation. Plug in the values for E_{cell}, $E°_{cell}$ and the appropriate expression for Q.

(h; 6 pts) Calculate the $[H^+]$ and the pH in the NSHE.

Score for the page____________

3. van't Hoff (25 pts)

We know that $\Delta G = \Delta H - T\Delta S$ in general, and $\Delta G° = -RT \ln K_{eq}$ for chemical equilibrium.

(a; 8 pts) Use these two equations to derive the van't Hoff equation.

(b; 9 pts) Sketch a van't Hoff plot for an endothermic disordering reaction. Label the axes. Indicate on your plot the temperature range over which the reaction would be spontaneous.

(c; 2 pts) Give an example of an endothermic disordering reaction.

Score for the page_____________

(c; 6 pts) What does LeChatelier's principle predict for the effect of heating up an endothermic disordering reaction, and why? What particular aspect of the van't Hoff plot puts this idea on a quantitative basis?

4. Applications (45 pts)

DNA hybridization, single-stranded W + single-stranded C ⇌ W•C duplex, is an exothermic ordering reaction. The exothermicity comes from forming noncovalent hydrogen bonds and base stacking interactions.

(a; 4 pts) What are the signs of $\Delta H°$ and $\Delta S°$ for hybridization?

(b; 6 pts) Give two different molecular explanations that contribute to the sign of $\Delta S°$.

Score for the page____________

The melting temperature Tm is defined as the temperature at which half of the DNA strands are in single-stranded form and half of them are in double stranded form. If we start with equal concentrations of W and C, this means that [W•C] = [W] = [C] at Tm.

(c; 9 pts) For starting concentrations of 3×10^{-6} M each W and C, what are [W], [C], and [W•C] at equilibrium at Tm (noting that the concentration of W•C is given in terms of double-stranded DNA helices)? What is the numerical value of K? What is the numerical value of $\Delta G°$?

(d; 4 pts) At what concentrations of W, C, and W•C would $\Delta G°$ equal zero at Tm, corresponding to K = 1? DNA has a density of about 1.7 g/cm^3, and a 12-mer oligonucleotide has a molecular weight of about 4000 g/mole. What is the molar concentration of DNA in an aqueous "solution" that is 50 % DNA by volume?

Score for the page____________

(e; 10 pts) Sketch a UV absorbance melting curve for DNA, labeling the axes and the Tm.

(f; 3 pts) What is the function of Photosystem I (the one on the right hand side of the Z scheme)?

(g; 3 pts) What is the function of Photosystem II? What is its by-product?

(h; 6 pts) Assuming that the early Earth was a reducing environment (in other words, there were lots of reducing agents like $H_2S(aq)$ or $Fe(s)$ lying around), which photosystem probably evolved first, and why?

Score for the page____________

5. More about why thermodynamics works the way it does (40 pts).

(a; 6 pts) State the Third Law of Thermodynamics.

(b; 6 pts) We have noted that there is no absolute energy scale. In contrast, tabulated entropy values S° (entropy at 1 atm and 298 K) are given as absolute numbers. Explain how it is possible to obtain absolute entropies, by describing qualitatively how the numbers are obtained.

(c; 8 pts) Sketch a curve for S vs. T, for T from 0 to 400K, for a substance that melts at 250 K and boils at 325K.

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Trouton's rule states that for the vaporization of many substances (methane, CO_2, O_2, and others) the heat of vaporization divided by the boiling temperature, **$\Delta H°_{vap}/T_b$, is about 80 J/K**, independent of the identity of the substance.

(d; 8 pts) Considering the definition of free energy and the value of the free energy of vaporization at the boiling point, what does Trouton's rule tell us about the entropy of vaporization, $\Delta S°_{vap}$?

(e; 6 pts) Rationalize why $\Delta S°_{vap}$ is nearly the same for the set of molecules above (and many others).

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(f; 6 pts) Finally, based on what you know about H-bonding in water, rationalize why Trouton's rule fails for water, and predict whether $\Delta H^\circ_{vap}/T_b$ for water is larger or smaller than the value predicted by Trouton's rule.

Page	**Score**
2	/20
3	/30
4	/22
5	/18
6	/19
7	/16
8	/13
9	/22
10	/20
11	/14
12	/6
Total	**/200**

Score for the page____________