Chemistry 271, Section 21xx	**Your Name:**____________________________
University of Maryland, College Park	**Your SID #:**____________________________
General Chemistry and Energetics	**Prof. Jason Kahn**
Exam II (100 points total)	**May 2, 2007**

You have 53 minutes for this exam.

Exams written in pencil or erasable ink will not be re-graded under any circumstances.

Explanations should be concise and clear. I have given you more space than you should need. 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.

Many useful equations are given on page 9.

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. DNA Thermodynamics (25 pts)

The formation of the double-stranded DNA 20-mer oligonucleotide below from the separated single strands has been measured to proceed with ΔH° = –128 kcal/mole and ΔS° = –346 cal/moleK. Assume a total strand concentration of 3 μM (1.5 μM for each strand).

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5'-TATTAAGCGACCACACATAA
   ATAATTCGCTGGTGTGTATT-5'
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(a; 7 pts) What is the T_m for this oligonucleotide? What is the value of ΔG° at the T_m?

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(b; 8 pts) Briefly explain why $\Delta H°$ and $\Delta S°$ are each negative for the hybridization reaction.

(c; 6 pts) Briefly and qualitatively explain how the nearest-neighbor rules for prediction of DNA melting thermodynamics are analogous to the bond-energy approximation used to estimate $\Delta H°_f$ for previously unknown organic compounds.

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(d; 4 pts) The DNA microarrays sold by Affymetrix typically use 25-mer DNA probes. One application is to detect the amount of a known mRNA sequence in a clinical sample. Each target mRNA (or fluorescently labeled copy of same) typically hybridizes to 20 or so different probe oligonucleotides on the array. Each of these perfect match probe oligos is accompanied by a "mismatch probe" on a nearby spot, with the idea being that the target mRNA will hybridize preferentially to the target probe over the mismatch probe. One doesn't want to operate these sensitive and expensive machines at very high temperatures. Why don't they use sequences much longer than 25 nucleotides long on the arrays?

2. Anaerobic Metabolism (25 pts)

The "Anammox" reaction (anaerobic ammonia oxidation) is carried out by bacteria in the Black Sea. The Anammox bacteria are chemolithoautotrophs, which is considered an advantage for their possible use in wastewater treatment because they don't have to be fed reduced carbon.

(a; 8 pts) The Anammox reaction is as follows: $NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$

Write down separate oxidative and reductive reactions for the individual conversions of ammonium and nitrite to elemental nitrogen. The beauty part is that the electrons and protons needed for Anammox are balanced.

(b; 4 pts) $\Delta G°' = -357$ kJ/mole for the Anammox reaction as written above. What is $E°'$?

(c; 2 pts) Is the Anammox reaction assimilative or dissimilative? (Circle one.)

(d; 8 pts) The source of nitrite (NO_2^-) for the Anammox reaction is other bugs who reduce nitrate to nitrite as follows:

$$NO_3^-(aq) + 2\ H^+(aq) + 2\ e^- \rightarrow NO_2^-(aq) + H_2O(l)$$

This is an example of syntrophy. Briefly define syntrophy. It is obvious what the recipient in a syntrophic relationship gains. What is the advantage to the donor?

(e; 3 pts) We have discussed the metabolism of methanogens, which transfer electrons from hydrogen to carbon dioxide to produce methane. They live on the edge of starvation, because the free energy available from this reaction is low. Why don't the methanogens just burn the methane that they make and live high on the hog?

Score for the page____________

3. Redox Reactions to Live By (12 pts)

The Breathalyzer works on the principle of oxidizing ethanol to acetic acid, with concurrent reduction of orange dichromate $Cr_2O_7^{2-}$ to green Cr^{3+}.

Standard reduction potentials:

$CH_3COOH(aq) + 4\ H^+(aq) + 4\ e^- \rightarrow CH_3CH_2OH(aq) + H_2O(l)$
E° = 0.058 V

$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$
E° = 1.33 V

(a; 4 pts) What is the balanced overall reaction?

(b; 2 pts) What is E° for the overall reaction?

(c; 6 pts) What is the actual cell voltage E, at 25 °C, if all reagents are in their chemical standard states (1 M everything) except that the pH is 4?

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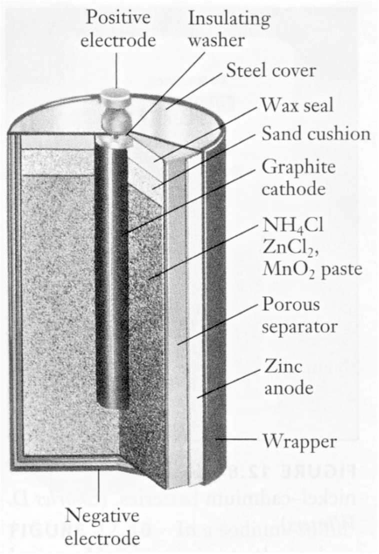
4. Electrochemistry (14 pts)

The Leclanché cell (misnamed the dry cell) shown at the right has a zinc anode (the negative terminal). The cathode is MnO_2 dispersed in graphite throughout the body of the cell, with the central graphite electrode acting to return the electrons from the external circuit. The chloride in the picture is a spectator ion.

(a; 10 pts) The anodic half-reaction for this galvanic cell is $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$. The cathodic half-reaction is

$$2\,MnO_2(s) + 2\,NH_4^+(aq) + n\,e^- \rightarrow Mn_2O_3(s) + 2\,NH_3(aq) + H_2O.$$

Who is being reduced here? Calculate *n* for the reduction half-reaction. Write down the overall net galvanic reaction.



(b; 4 pts) The Leclanché cell is headed for obsolescence, in part because its voltage drops off with time. It is being replaced by the alkaline cell with the overall reaction below, which uses the same redox couple. Why does the voltage of the Leclanché cell decline with use, whereas the voltage of the alkaline cell is constant until it is nearly dead (you need not calculate E°s)?

$$Zn(s) + 2\,MnO_2(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + Mn_2O_3(s)$$

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5. Kinetics (24 pts): NO CALCULUS REQUIRED

Kinetic partitioning describes the distribution of products for reactions under kinetic control, such as correct and incorrect base incorporation by DNA polymerases.

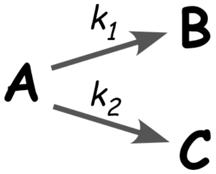
For the elementary reaction A -> B, the differential rate law is $-d[A]/dt = k[A]$.

(a; 3 pts) What is the integrated rate law for a the first-order reaction A -> B assuming that we start with 100 % A at concentration $[A]_0$ (not a trick question)?

(b; 3 pts) Given that all of the starting material that starts out as A can always be found as either A or B at any time during the reaction, derive an integrated rate law expression for the amount of B as a function of time.

(c; 6 pts) Now consider the scheme at the right, where A can be converted to either B or C.

What are the differential rate laws for loss of [A], gain of [B], and gain of [C]?



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(d; 3 pts) B and C are always produced at a constant ratio (in other words, for every mole of B we get x moles of C. From your answer to (c), what is [C]/[B] = x?

(e; 3 pts) By analogy with your answer in (a) for A -> B, what is the integrated rate law for the concentration of A as a function of time?

(f; 6 pts) The total concentration of products is given by $[B] + [C] = [A]_0 - [A]$ as in (b) above. Use your answers to (d) and (e) to derive the integrated rate law for the total amount of [B] as a function of time.

Page	Score
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Useful Equations:

$\Delta S - q/T \geq 0$

$S = k\ln W$

$K_a = [H^+][A^-]/[HA]$

$W = N!/(\prod n_i!)$

$°C = °K - 273.15$

$2.303RT/\mathcal{F} = 0.0592$ Volts at 25 °C

$\mathcal{F} = 96500$ C(oulomb)/mole

$pH = -\log([H^+])$

$\Delta G = \Delta H - T\Delta S$

$\Delta G° = -RT\ln K_{eq}$

$n_i/n_0 = \exp[-(E_i - E_0)/kT]$

$R = 1.987$ cal/mole K

$1\ V = 1\ J/C$

$E = mc^2$

$PV = nRT$

$e^{i\pi} + 1 = 0$

$T_m = \Delta H°/[\Delta S° + R\ln(C_t/4)]$

$E = E° - 2.303(RT/n\mathcal{F})\log_{10}Q$

$\Delta G = -n\mathcal{F}E$

$a^2 + b^2 - 2ab\cos C = c^2$

Chemical standard state: 1M solutes, pure liquids, 1 atm gases

Biochemical standard state: pH 7, all species in the ionic form found at pH 7

$\ln K_{eq} = (-\Delta H°/RT + \Delta S°/R)$

$[A] = [A]_0 - kt$

$\ln[A] = \ln[A]_0 - kt$

$1/[A] = 1/[A]_0 + 2kt$