Chemistry 271, Section 21xx **University of Maryland, College Park**
General Chemistry and Energetics **Prof. Jason Kahn**
Final Exam (200 points total) **May 15, 2009**

You have 120 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.

Partial credit will be given, *i.e.*, if you don't know, guess.

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."

Your Name: ______________________________

Your SID #: ______________________________

Viewing: Monday, May 18, 9:30-10:30 a.m., Chemistry 1346 (Wing 3)

Useful Equations:

$\Delta S - q/T \geq 0$ $\mathrm{pH} = -\log([\mathrm{H}^+])$ $S = k\ln W$

$\Delta G^\circ = -RT\ln K_{eq}$ $\Delta G = \Delta H - T\Delta S$ $PV = nRT$

$K_a = [\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}]$ $n_i/n_0 = \exp[-(E_i\text{-}E_0)/kT]$ $\Delta \mathrm{G} = -n\mathcal{F}\mathrm{E}$

${}^\circ\mathrm{C} = {}^\circ\mathrm{K} - 273.15$ $\mathrm{R} = 8.314$ J/mole K $\mathrm{E} = \mathrm{E}^\circ - 2.303(\mathrm{RT}/n\mathcal{F})\log_{10}\mathrm{Q}$

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

Standard hydrogen electrode: $2\ \mathrm{H}^+ (aq,\ 1\ \mathrm{M}) + 2\ e^- \rightarrow \mathrm{H}_2\ (g)$ $\mathrm{E}^\circ = 0.000$ V

$\ln K_{eq} = (-\Delta\mathrm{H}^\circ/\mathrm{RT} + \Delta\mathrm{S}^\circ/\mathrm{R})$ $\ln k = (-\mathrm{Ea}/\mathrm{RT}) + \ln \mathrm{A}$ 1 Volt = 1 Joule/Coulomb

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

1. Thermodynamics and Kinetics (40 pts)

(a; 6 pts) What is the second law of thermodynamics?

(b; 26 pts = 2 pts each) Circle True or False:

Exothermic reactions are always spontaneous	T	F
Thermodynamics provides no constraints on rates of reaction.	T	F
Catalysts can be developed to accelerate the same reaction in either the forward or the reverse direction selectively, without accelerating the reverse reaction.	T	F
Free energy minimization reflects the decreasing entropy of the universe.	T	F
Endothermic reactions are never spontaneous.	T	F
The steady-state approximation (SSA) is useful for elementary (single-step) reactions.	T	F
The steady-state approximation is that reactant concentration is constant.	T	F
The SSA applies to intermediates for which there is a rapid breakdown path.	T	F
The rate limiting step of a reaction is the one with the largest free energy of activation.	T	F
Catalysts can change the mechanism of a reaction	T	F
There are no fundamental limits on reaction rates	T	F
The biochemical standard state is referenced to 1 M/1 atm everything.	T	F
"There ain't no such thing as a free lunch" is Heinlein's restatement of the First Law of Thermodynamics.	T	F

(c; 8 pts) Why is burning oil better than burning coal as far as global warming is concerned? (I am looking for a fundamental answer; don't worry about contaminants etc.) Why is coal a better fuel for a steam engine locomotive than wood?

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2. First and Second Order Kinetics (50 pts)

(a; 6 pts) What is the half-life of a first order reaction, in terms of the rate constant for the reaction? Why is the half-life of a first-order reaction independent of the initial concentration of the reactant? Give a reason, not a recitation of the equation.

(b; 6 pts) What is the integrated rate law for a second-order reaction? Does the instantaneous rate of the reaction normalized to the amount of reactant (i.e. $(-(1/2)(d[A]/dt)/[A])$, increase or decrease as the reaction progresses? (Circle one.)

(c; 10 pts) What is the law of microscopic reversibility? Sketch a free energy reaction coordinate diagram to illustrate your answer.

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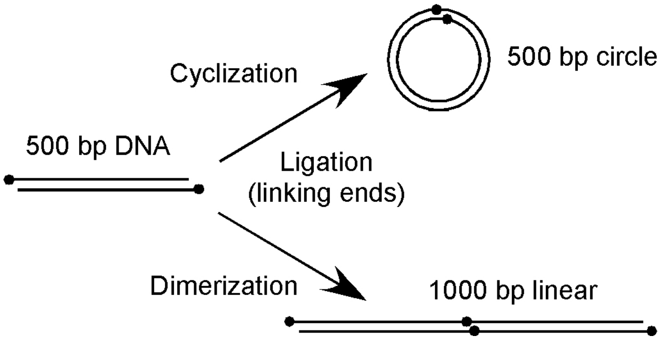
(d; 28 pts) Consider the pair of competing reactions sketched below: the first-order cyclization of linear DNA fragments to circular products, competing with second-order ligation of the same fragment to give dimeric linear products.

Assume that at a starting DNA concentration of 10 nM, in a 100 μl reaction mixture, after 10 minutes of reaction, you observe a 50:50 mixture of circular and dimeric DNA products as well as unreacted monomeric DNA.



For the following four different situations, state whether the ratio of circular to dimeric products is > 1, = 1, or < 1, and briefly explain your reasoning. (7 pts each)

(1) The same reaction mixture as above, but after 60 minutes of reaction, when it has gone mostly to completion.

(2) A second reaction performed at 20 nM starting [DNA] but otherwise identical, after 10 minutes.

(3) A 20 µL aliquot of the same reaction mixture, otherwise identical, after 10 minutes. (Not a trick question.)

(4) A longer piece of DNA, for which ΔS° for cyclization is much more negative than for the shorter piece of DNA shown, but ΔH° is unchanged, otherwise identical conditions, after 10 minutes

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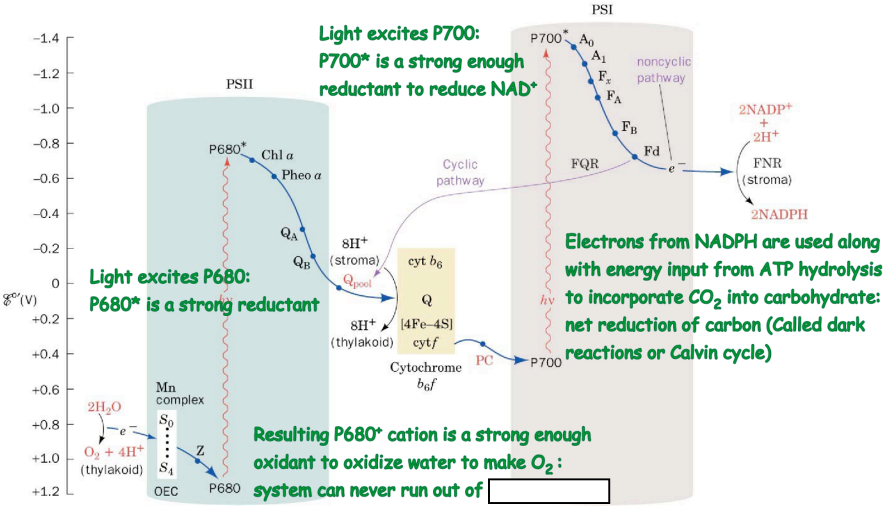
3. Redox Reactions to Live By (75 pts)

(a; 4 pts) We suggested a rationale for the sequential transfer of electrons through several intermediate electron acceptors on the way from NADH to O_2 in the electron transport system. Why not just transfer the electron directly and harvest the liberated free energy in one step?

(b; 4 pts) Two photosystems in photosynthesis might seem like one too many. What evolutionary advantage accrued to plants with the development of PSII? (Hint: the word that was in the box in the picture.)



Light excites P700: P700* is a strong enough reductant to reduce NAD^+

Light excites P680: P680* is a strong reductant

Resulting $P680^+$ cation is a strong enough oxidant to oxidize water to make O_2: system can never run out of ☐

Electrons from NADPH are used along with energy input from ATP hydrolysis to incorporate CO_2 into carbohydrate: net reduction of carbon (Called dark reactions or Calvin cycle)

We discussed the idea that microbes are usually on the edge of starvation. Anaerobic metabolism (other than fermentation) is based on living off the downhill flow of electrons. Microbes need both a source of electrons and a place to dump them. So do we.

(c; 3 pts) What do we call the final destination of the electrons?

(d; 3 pts) What particularly unappealing source of electrons for humans did we discuss in regards to the Siege of Leningrad? (In class I misidentified the city as Stalingrad.)

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The oxidation of acetic acid shown below has a small but positive standard-state free energy change:

$$CH_3COOH + 2\ H_2O \rightarrow 2\ CO_2 + 4\ H_2 \qquad \Delta G°' = +\ 95\ kJ/mol;\ \ n = 8$$

(e, 10 pts) Write the two half-reactions that make up the above reaction, one for the oxidation of acetic acid and one for the reduction of protons. Balance with water or protons as needed.

(f; 6 pts) Calculate E°' for this reaction. Why does the reaction initially seem like a poor choice on which to base a metabolism?

(g; 12 pts) Calculate E at 100 mM CH_3COOH, 0.0004 atm CO_2, 0.0001 atm H_2. Thus, how is it that the bug (*Geobacter*) can actually survive by using this reaction to make energy?

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(h; 8 pts) *Geobacter* may also be useful in bioremediation of uranium contamination in groundwater. *Geobacter* can oxidize the acetic acid and pass the electrons to soluble U^{+6}, converting it to U^{+4}, which then precipitates out of the water and can be removed as solid waste. This process is carried out by injecting acetate into the water table to support *Geobacter* growth. Why is it important to maintain anoxic conditions when this is done? How is this related to the observed stratification of nitrate-reducers and sulfate-reducers in sediments or the water column?

(i; 10 pts) We discussed the idea that stable biochemical oxidants cannot be stronger than oxygen, because if they were they would eventually rip electrons out of water. Write down the redox reaction that expresses this idea, given "$\text{SuperOx}^{+2} + 2\ e^{-} \rightarrow \text{SuperOx}$," with large and positive E, as one half-reaction. A different redox reaction limits the strength of stable aqueous reducing agents. Write down the redox reaction that would be carried out by the two-electron reductant "SuperRed."

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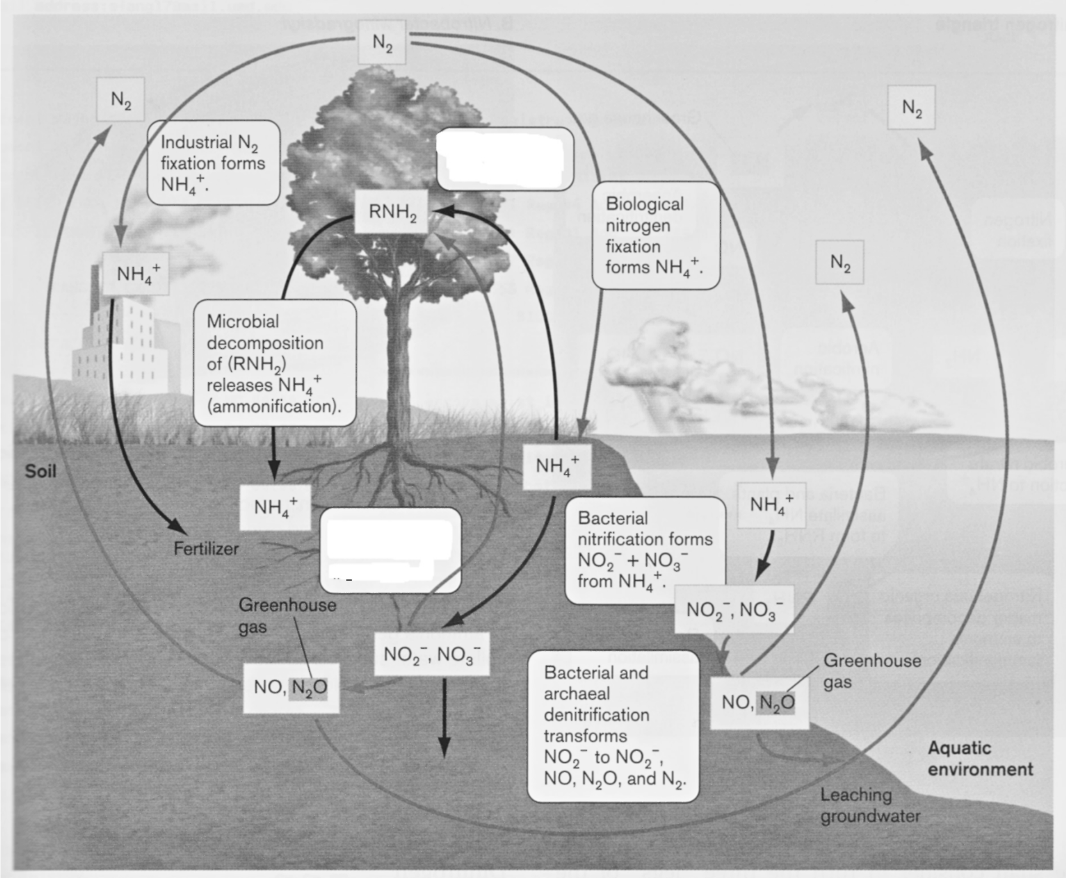
Biogeochemistry: The picture shows the nitrogen cycle in the atmosphere (from Slonczewski and Foster):



(j; 4 pts) Identify a dissimilatory reduction of a nitrogen compound.

(k; 4 pts) Identify an assimilatory reduction of a nitrogen compound.

(l; 7 pts) Where is the Haber process in the picture? Growing corn requires nitrogen fertilizer; why is the use of ethanol from corn not really helpful from the standpoint of ameliorating global climate change?

4. Steady State approximation (35 pts)

The thermal decomposition of gaseous N_2O_5 to form NO_2 and O_2 is a classic reaction which we oversimplify here. The equation is

$$2\ N_2O_5 \longrightarrow 4\ NO_2 + O_2$$

The observed rate law is

$$\text{Rate} \equiv d[O_2]/dt = k[N_2O_5]$$

where k is an empirically observed first-order rate constant.

(a; 5 pts) This rate law immediately tells us that the reaction is not a single elementary step as was initially believed 90 years ago. Why?

Ogg's proposed mechanism (1947) in terms of a set of elementary steps is as follows:

$$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{k_2} NO + NO_2 + O_2$$

$$NO + NO_3 \xrightarrow{k_3} 2NO_2$$

We can apply the SSA to both of the reactive intermediates NO_3 and NO. First we work with NO_3. The rate of production of NO_3 is

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5]$$

(b; 10 pts) What is the rate of decay of NO_3? You do not need to solve for [NO].

Applying the SSA to NO gives a steady state concentration of $[NO] = (k_2/k_3)[NO_2]$. Setting the rates of production and decay of NO_3 equal and substituting this value of [NO], we obtain

$$[NO_3] = \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + 2k_2[NO_2]}$$

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and again…

$$[\mathrm{NO_3}] = \frac{k_1[\mathrm{N_2O_5}]}{k_{-1}[\mathrm{NO_2}] + 2k_2[\mathrm{NO_2}]}$$

(c; 15 pts) Show that this expression for $[NO_3]$ along with the reaction mechanism above gives us the observed overall rate law for the production of O_2, and write an expression for the overall empirical rate constant *k* in terms of the rate constants for elementary steps.

(d; 5 pts) Why do we say that a proposed mechanism can be disproved but never proven?

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