Chemistry 271 – 22XX **Your Name:** ______________________________

Prof. Jason Kahn

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

General Chemistry and Energetics

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

December 18, 2013

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

$\Delta S - q/T \geq 0$ 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° = 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. Short Answer (40 pts)

(a; 6 pts) Photosystem II in plants uses light energy to create a P680$^+$ cation that is a strong enough ____to remove electrons from ________________, the product of which is the ____________________that we use to metabolize food we get from plants.

(b; 6 pts) ______________________________electrochemical cells use chemical energy to make electrical energy, whereas ____________________________________cells use an external voltage to drive a/an _______________________________ chemical change.

(c; 6 pts) Termolecular reactions in the gas phase are found when an inert collision gas is needed to ____________________________________ from a pair of reacting partners that are ___________________ a bond, which is (circle one) an exothermic/endothermic process.

(d; 6 pts) The Steady State Approximation applies to (circle one) reactants/intermediates/products that (circle all correct answers):

(a) accumulate to a high level during a reaction so that we can measure a steady concentration.

(b) are highly reactive so that they decay rapidly.

(c) are always present at vanishingly low concentrations.

(d) are created and destroyed at the same rate.

(e; 10 pts) True/False

Statement	**T/F**
Elementary reactions always get faster as temperature increases.	
Equilibrium constants always increase as temperature increases	
Rate laws can be written down by inspection if you know the equilibrium constant for a reaction	
For a reaction A $\rightleftharpoons$ B where the molar free energies of A and B differ such that $\overline{G^o}_A < \overline{G^o}_B$, the minimum free energy state is a pure solution of A.	
The minimum free energy state of the system corresponds to the minimum enthalpy state of the universe.	

(f; 6 pts) An oxidizing agent with a standard reduction potential more positive than that of O_2 is thermodynamically unstable in the standard state because____________________________________. A reducing agent with E_{ox} more positive than that of H_2 is thermodynamically unstable because ____.

Score for the page____________

2. Explanations (45 pts)

(a; 15 pts) Derive the Nernst equation using some of the equations on the front of the exam (equations that aren't the Nernst equation!). Conceptually explain why the sign must be negative in the Nernst equation.

(b; 15 pts) Briefly explain how increasing CO_2 levels in the atmosphere cause global warming, and mention one way in which society could attempt to return the atmosphere to 350 ppm.

Score for the page____________

(15 pts) Explain why DNA hybridization reactions are typically carried out not far below the melting temperature of the desired double-stranded DNA product. In your answer, define the DNA melting temperature, mention mismatch thermodynamics, and speculate on hybridization kinetics.

3. Electrochemistry and thermodynamics (55 pts)

There are several parts to this problem. They can frequently be answered even if you have not completed earlier parts.

Hydrogen peroxide, H_2O_2, is a moderately strong oxidizing agent. A H_2O_2 in aqueous solution is unstable, eventually decaying to give water and O_2 as follows:

$$H_2O_2\ (aq) \rightarrow H_2O\ (l) + O_2\ (g)\quad [\underline{\text{not balanced}}]$$

(a; 15 pts) Given the standard reduction potentials below, calculate $E°_{cell}$ for the reaction above in acidic solution, and give the balanced equation for the overall reaction.

$H_2O_2\ (aq) + 2\ H^+\ (aq) + 2\ e^- \rightarrow 2\ H_2O\ (l)$ $E°_{red} = 1.76$ V
$O_2\ (g) + 4\ H^+\ (aq) + 4\ e^- \rightarrow 2\ H_2O\ (l)$ $E°_{red} = 1.23$ V

Score for the page____________

(b; 10 pts) Without doing a calculation, give $E°'_{cell}$ = the potential at pH 7 and also $E°_{cell}$ under basic conditions, and explain your reasoning.

(c; 30 pts) Calculate the standard state free energy change $\Delta G°$ for the H_2O_2 decay reaction under acidic conditions, at 298 K. Calculate the equilibrium constant for the reaction at 298 K. What would the concentration of H_2O_2 be at equilibrium with the air at $PO_2 = 0.21$ atm? Why is a measurement of $E°_{cell}$ a better way to measure this K_{eq} than attempting to measure the K_{eq} directly? Speculate on the sign of $\Delta S°$. Does this tell you whether the equilibrium constant will go up or down as temperature increases?

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4. Kinetics and Mechanism (60 pts)

The uncatalyzed breakdown of H_2O_2 is difficult to study, because the reaction is catalyzed in a wide variety of ways. The uncatalyzed reaction in the gas phase at high temperature is believed to occur through a series of steps, with the first step being a rate limiting unimolecular homolytic cleavage to give hydroxyl radical:

$$\begin{array}{ll} H_2O_2\,(g) \rightarrow 2\,HO\bullet\,(g) & \text{r.l.s.} \\ HO\bullet\,(g) + H_2O_2\,(g) \rightarrow H_2O\,(g) + HO_2\bullet & \text{fast} \\ \vdots & \end{array}$$

(a; 10 pts) Give the expected observed rate law for the breakdown of H_2O_2. Also, explain how it is possible to ask you to do this even though I have not shown the rest of the mechanism.

(b; 15 pts) The observed rate constant for this reaction has a preexponential factor of 10^{13} s^{-1} and an activation energy of 201000 J/mole. Calculate the rate constant at 400 °C and at 100 °C. What would the half-life be at 100°C for H_2O_2 at a concentration of 0.010 M?

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You can buy hydrogen peroxide in aqueous solution, and it is reasonably stable on storage. However, there are many ways to catalyze the disproportionation. One example is the reaction with bromide ion under acidic conditions given by the proposed mechanism (= series of elementary reactions) below. The multiple arrows in the third step indicate fast steps that are kinetically invisible after an elementary S_N2 attack on HOBr (hypobromous acid) by H_2O_2.

$$H_2O_2 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_3O_2^+ \qquad \text{fast equilibrium}$$

$$H_3O_2^+ + Br^- \xrightarrow{k_2} HOBr + H_2O \qquad \text{slow}$$

$$HOBr + H_2O_2 \xrightarrow{k_3} \to\to H_2O + H^+ + Br^- + O_2 \qquad \text{fast}$$

(c; 4 pts) Write down the rate of appearance of O_2 just according to the third line of the mechanism above. To move further we will need the concentration of the reactive intermediate HOBr.

(d; 8 pts) Write down the expression for the rate of change of [HOBr] based on the 2nd and 3rd lines, and set the rate of change equal to zero (the SSA). Calculate the concentration of [HOBr]. Now you need to know the concentration of $H_3O_2^+$.

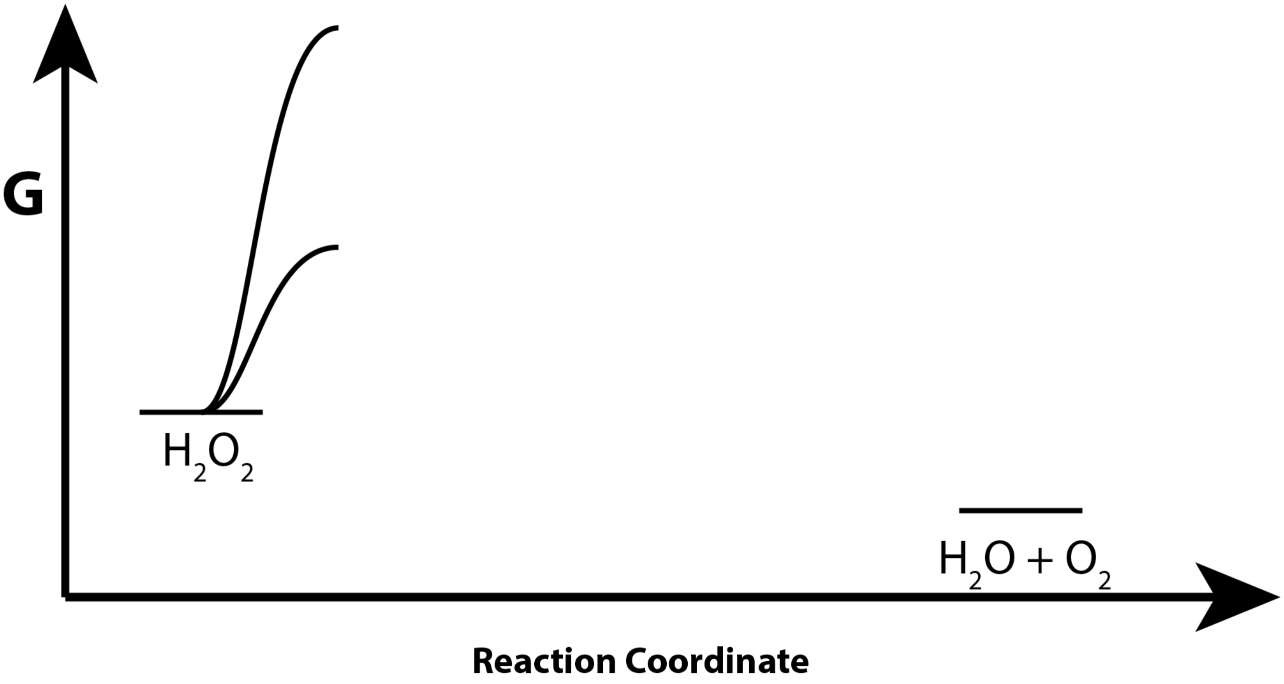
Score for the page____________

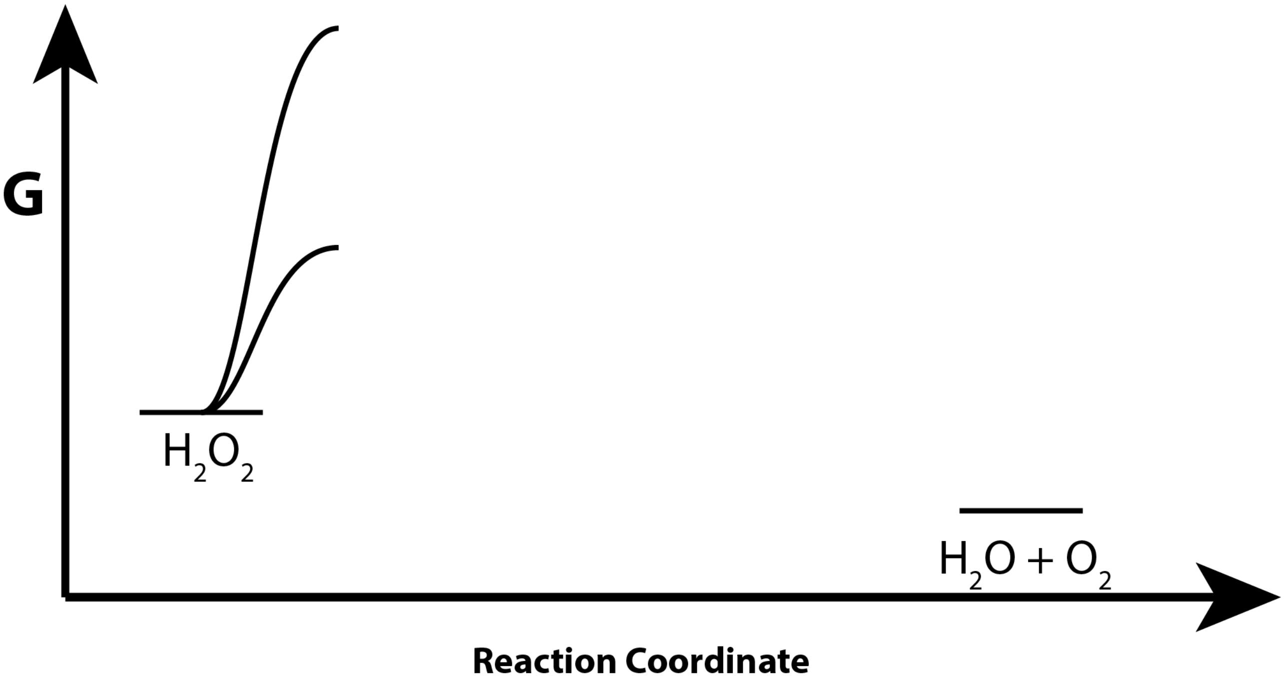
(e; 6 pts) Calculate [$H_3O_2^+$] in terms of [H_2O_2] and [H^+] from the first line of the mechanism, assuming that $H_3O_2^+$ and H_2O_2 are in rapid equilibrium. Based on your knowledge of chemistry, why is this a reasonable assumption?

(f; 7 pts) Write down the overall differential rate law for the production of O_2 according to the mechanism given. Briefly, how could you test experimentally whether this rate law is correct? [You can answer the second part even if you didn't get the rate law].

Score for the page____________

(g; 10 pts) Finally, complete the free energy reaction coordinate diagram comparing the uncatalyzed reaction (with its slow and rate-limiting first step) and the Br⁻-catalyzed reaction. The graph is repeated in case you want to clean up your diagram. Indicate which one you want graded.





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Extra work space. If you give an answer on this page make sure you write a clear note in the body of the exam telling us to look here.

Page	**Score**
2	/40
3	/30
4	/30
5	/40
6	/25
7	/12
8	/13
9	/10
Total	**/200**

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