

Chemistry 271

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 14, 2012

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:

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$$

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

$$K_b = [\text{HA}][\text{HO}^-]/[\text{A}^-]$$

$$K_w = [\text{H}^+][\text{HO}^-]$$

$$\text{pH} = \text{p}K_a + \log [\text{A}^-]/[\text{HA}]$$

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mole K}$$

$$k_B = 1.38 \times 10^{-23} \text{ J/K}$$

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

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

$$R = 8.314 \text{ J/mole K} = 1.987 \text{ cal/mole K} = N_A k_B$$

$$S = k_B \ln W$$

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

$$E = \sum n_i \varepsilon_i$$

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

$$n_i/n_0 = \exp[-(\varepsilon_i - \varepsilon_0)/kT]$$

$$N = \sum n_i$$

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

$$^\circ\text{C} = ^\circ\text{K} - 273.15$$

$$P(v)dv = Cv^2 \exp(-mv^2/2kT)$$

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

$$2.303RT/\mathcal{F} = 0.0592 \text{ Volts at } 25^\circ\text{C}$$

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

$$\Delta G^\circ = -n\mathcal{F}E^\circ_{\text{cell}}$$

$$\ln k = (-E_a/RT) + \ln A$$

$$1 \text{ Volt} = 1 \text{ Joule/Coulomb}$$

$$[\text{A}] = [\text{A}]_0 - kt$$

$$\ln[\text{A}] = \ln[\text{A}]_0 - kt$$

$$1/[\text{A}] = 1/[\text{A}]_0 + 2kt$$

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

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

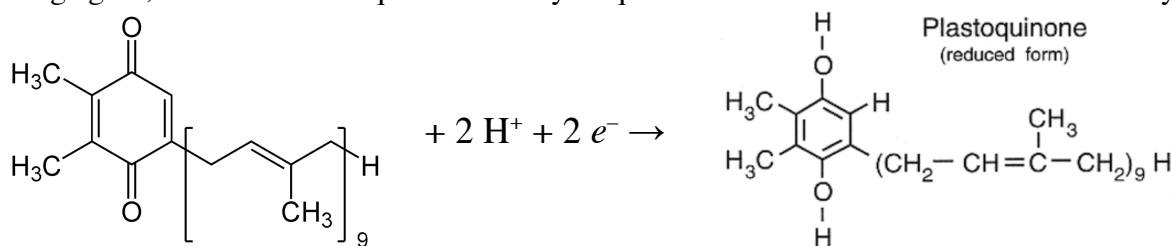
"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

1. Short Answer (27 pts)

(a; 3 pts) One word to explain why it is that sometimes the electrochemical reaction that one observes is not the one that one would think should be thermodynamically favorable:_____

(b; 6 pts) Eyring (transition state) theory and the Maxwell-Boltzmann distribution both predict a similar functional form for the temperature dependence of the rate constant. The resulting (name of Swedish physical chemist here_____) equation is:_____.

(c; 8 pts) The excited state chlorophyll chromophore (P680*) of Photosystem II is a reasonably strong reducing agent, able to reduce a quinone to a hydroquinone via intermediates we will not worry about:



What is the function of the reduced form of the plastoquinone (= hydroquinone)? What is the function of the P680⁺ cation that is the other reaction product?

(d; 6 pts) How does increased CO₂ in the atmosphere lead to global warming?

(e; 4 pts) Why is burning natural gas (CH₄) less bad than burning even the cleanest coal (C) in terms of global warming?

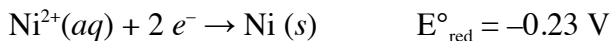
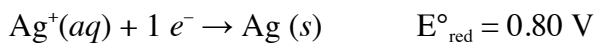
2. Electrochemistry (60 pts)

(a; 13 pts) If you hook up the two half cells below, what balanced spontaneous (voltaic) redox reaction occurs? What would you see visually as the reaction proceeded? Calculate E°_{cell} . What balanced electrolytic reaction would occur if you added in a battery that forces electrons in the opposite direction?

Half cell #1: Ag (s) electrode / 1 M $\text{Ag}^+(\text{aq})$ with 1 M inert spectator anion NO_3^-

Half cell #2: Ni (s) electrode / 1 M $\text{Ni}^{2+}(\text{aq})$ with 2 M inert spectator anion Cl^-

Reduction potentials:

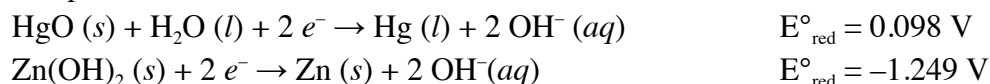


(b; 14 pts) Write down balanced half-reactions for (1) the reduction of protons to give dihydrogen (H_2), and (2) the oxidation of water to give dioxygen (O_2) in acidic solution. We talked about leveling in the context of acid-base chemistry, the idea that no acid stronger than hydronium is stable in water, and no base stronger than hydroxide is stable in water. What is the corresponding idea for electrochemistry in aqueous solution?

(c; 8 pts) Calculate $E'_{\text{red}}(\text{H}^+)$, i.e. the cell voltage that one would observe for the standard hydrogen electrode (SHE) operated at the biochemical standard state pH 7 instead of pH 0, coupled to a SHE run at the usual chemical standard state.

(d; 20 pts) The reduction of mercuric oxide (HgO) is the basis of the mercuric oxide battery, coupled with Zn oxidation to give zinc hydroxide, all under basic conditions.. The battery was banned due to toxicity concerns.

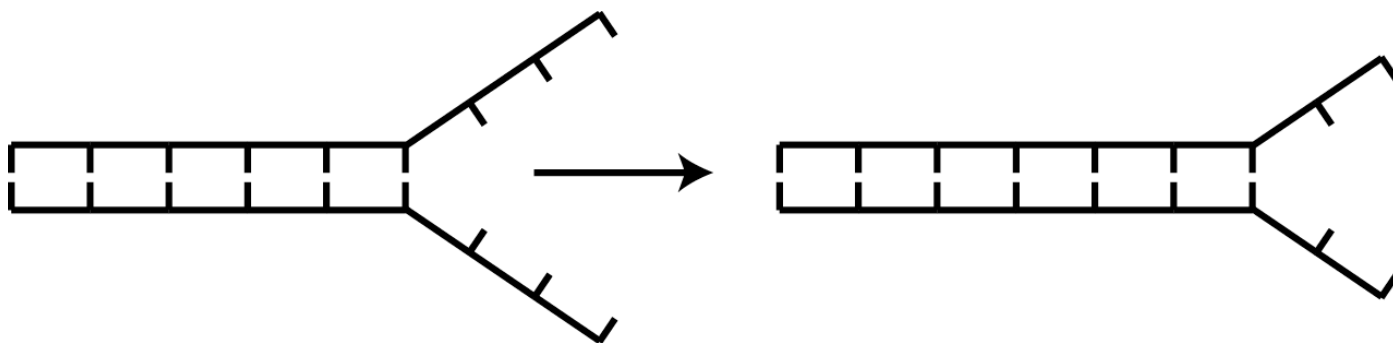
Reduction potentials:



Write the balanced voltaic redox reaction. Calculate E°_{cell} . Calculate the standard state free energy change per mole of HgO and the equilibrium constant for the reaction. Calculate E_{cell} at pH 8.5 but otherwise standard conditions.

(e; 5 pts) In a battery it is often desirable for both the reactants and the products to be solids (in the mercuric oxide battery the HgO/Hg is embedded in graphite for safety and conductivity). Give a reason having to do with voltage.

3. DNA Thermodynamics (24 pts)



(a; 8 pts) The enthalpy change for formation of a base pair in DNA, as in the sketch above, is negative. Why? The entropy change is also negative. Why?

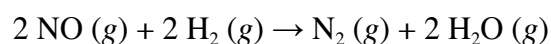
(b; 6 pts) The free energy turns out to be negative for temperatures below about 95 °C. How can DNA ever melt at temperatures below 95 °C, i.e. what important entropy consideration must also be considered? Why do shorter DNA molecules melt at lower temperatures than longer molecules?

(c; 5 pts) Longer PCR primers hybridize more tightly to their target sequences. Why don't we always just make PCR primers as long as we can in order to make the reaction work better?

(d; 5 pts) Give an opinion and very brief reasoning on whether a future pre-natal test that predicts a child's IQ should be available to prospective parents. Assume that the test actually works (whether IQ means anything is a separate issue that we are not concerned with here).

4. Kinetics (60 pts)

Nitric oxide reacts with hydrogen at elevated temperature according to the following chemical equation (from Oxtoby):



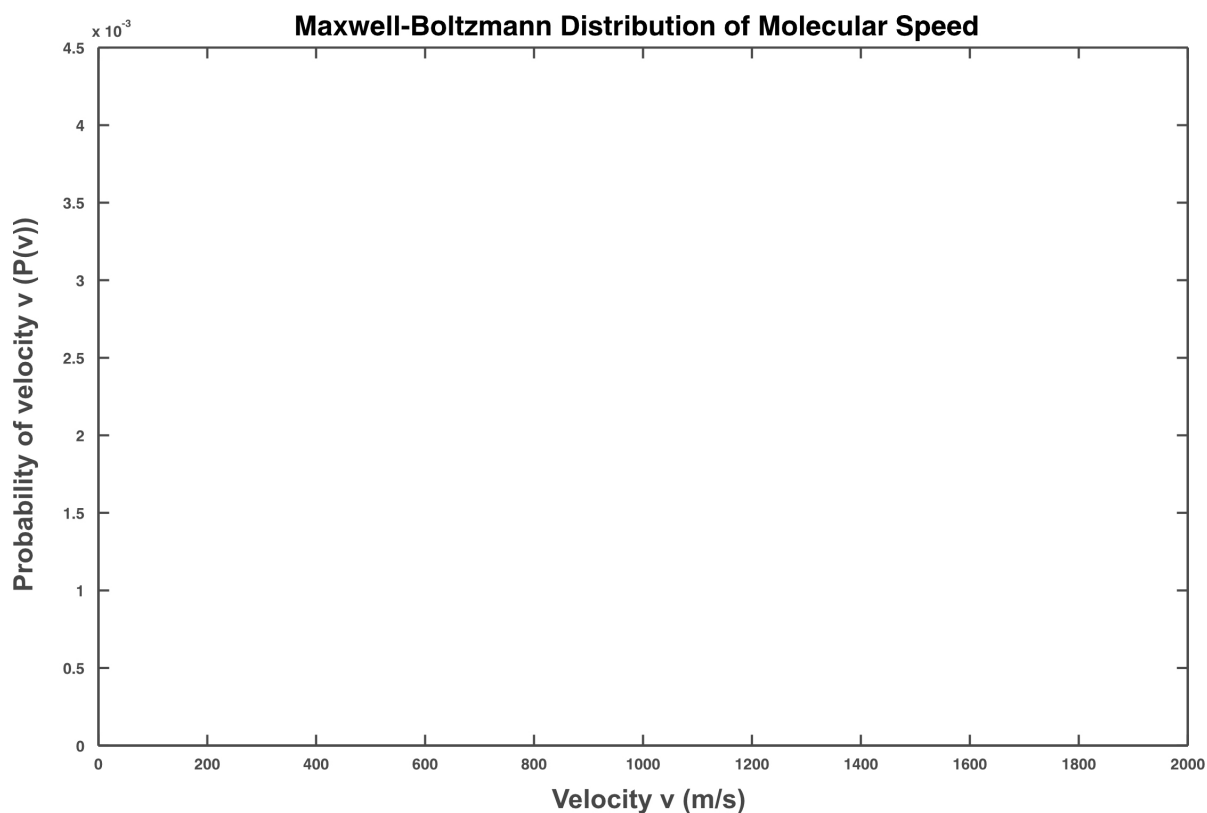
(a; 8 pts) It is observed that when the concentration of H_2 is cut in half, the reaction rate is also cut in half. What is the order of the reaction with respect to H_2 ? When the concentration of NO is increased by a factor of 5, the reaction rate increases by a factor of 25. What is the order of reaction with respect to NO? Write down the differential rate law.

(b; 7 pts) How does the observed rate law tell us that the $\text{NO} + \text{H}_2$ reaction cannot possibly be proceeding through a single elementary step under these conditions? Why would we have guessed *a priori* that this reaction would be very unlikely to be elementary?

(c; 20 pts) Sketch the concentration of reactant A as a function of time for the elementary reactions $\text{A} \rightarrow \text{B}$ and $\text{A} + \text{A} \rightarrow \text{C}$, on one graph, assuming that each reaction has a half-life of 5 minutes. It might be hard to tell the curves apart experimentally. What experiment could you do to determine whether the reaction was first-order or second-order? Sketch the expected result for the concentration of A as a function of time for your proposed experiment.

(d; 7 pts) Explain why the half-life of a zero-order reaction is proportional to reactant concentration. Don't explicate the equation: give a physical rationale.

(e; 18 pts) On the axes below, sketch the Maxwell-Boltzmann distribution for the speed of gas molecules at two different temperatures (for the same gas). Identify which is the hotter and which is the cooler temperature. Explain the shape of the curve (why it goes up, why it goes down).



Score for the page _____

5. Free energy reaction coordinate diagrams (29 pts)

Draw and label free energy reaction coordinate diagrams for the following situations:

(a; 7 pts) A converts to intermediate B slowly, and then B converts to C more rapidly than it (B) goes back to A, and the final product C is more stable than A.

(b; 10 pts) Reactant A can convert to either B or C, both of which are thermodynamically more stable than A. B is thermodynamically more stable than C, but C forms faster than B. This is kinetic vs. thermodynamic control.

(c; 12 pts) $A+B$ converts to P in one slow step. On the same diagram, with the free energy of $A+B+E$ set equal to $A+B$, $A+B+E$ converts to intermediate Q much more rapidly than $A+B \rightarrow P$, and Q converts to $P+E$ at the same rate with which it goes back to $A+B+E$. What do we call E ?

Page	Score
2	/27
3	/27
4	/28
5	/19
6	/18
7	/27
8	/25
9	/17
10	/12
Total	/200

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