

**Chemistry 271, Section 23xx  
General Chemistry and Energetics  
Final Exam (200 points total)**

**University of Maryland, College Park  
Prof. Jason Kahn  
December 14, 2010**

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: Friday, December 17, 11-2 Chemistry 1110-1111**

**Useful Equations:**

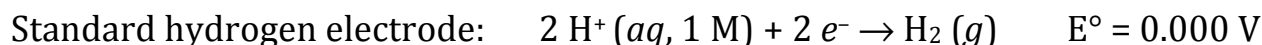
$$\Delta S - q/T \geq 0$$

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

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

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

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



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

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

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

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

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

$$n_i/n_o = \exp[-(\epsilon_i - \epsilon_o)/kT]$$

$$R = 8.314 \text{ J/mole K}$$

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

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

$$dS = (c_p/T) dT$$

$$S = k \ln W$$

$$PV = nRT$$

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

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

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

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

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

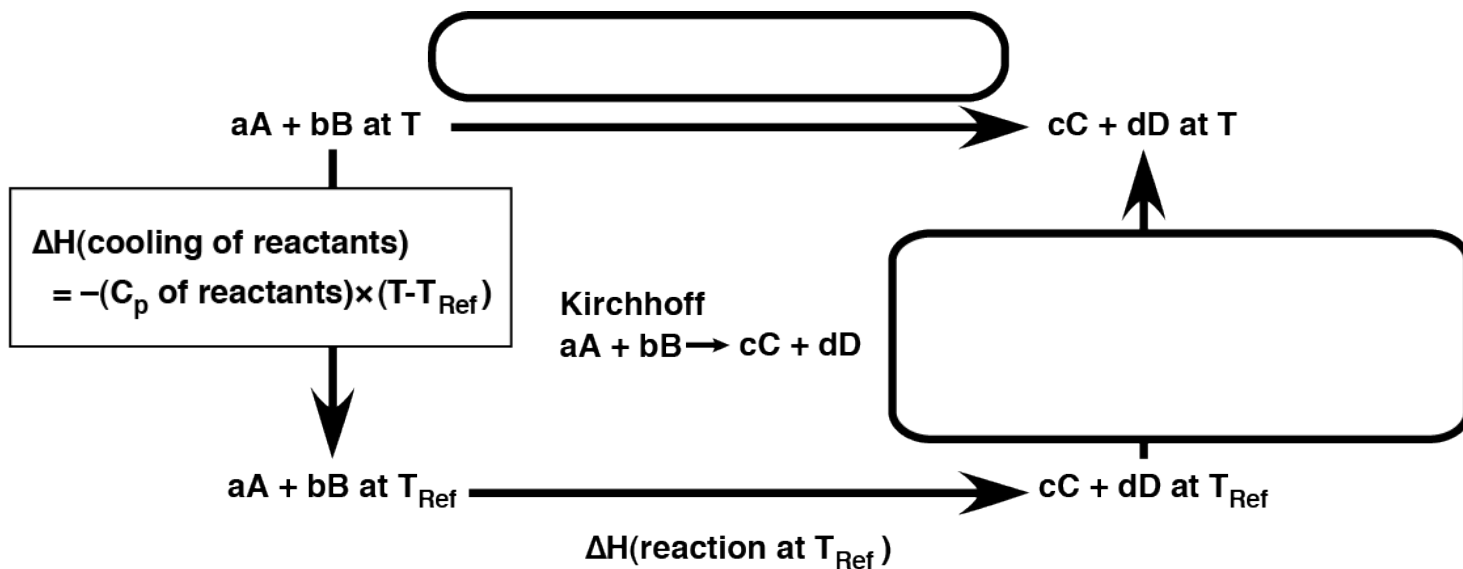
$$c_p = q_p/dT = dH/dT$$

**1. Multiple Choice (24 pts)**

- (i, 4 pts) The Third Law of Thermodynamics gives us a reference state of zero entropy. What else is necessary for measuring absolute entropies of pure substances at non-zero temperature?
- (a) The First Law of Thermodynamics.
  - (b) Measurements of heat capacity as a function of temperature.
  - (c) Calculation of the free energy of formation from tabulated data.
  - (d) Enumeration of microstates.
  - (e) We cannot measure absolute entropy, only changes in entropy.
- (ii, 4 pts) A second-order rate constant
- (a) has units of  $\text{time}^{-1}$ .
  - (b) changes during the course of the reaction as the reactant is depleted.
  - (c) can almost never be faster than diffusion-controlled.
  - (d) has units of  $\text{M}^{-1}\text{s}^{-1}$ .
  - (e) (c) and (d).
- (iii, 4 pts) The Steady State Approximation
- (a) is not useful in enzyme kinetics because substrate concentration is constantly changing.
  - (b) can be applied only to reactions of the type  $\text{A} \rightarrow \text{B} \rightarrow \text{C}$ .
  - (c) holds only at equilibrium, when the state of the system is steady.
  - (d) includes rapid pre-equilibrium as a special case.
  - (e) is applicable to the product of any rapid reaction.
- (iv, 4 pts) The half life  $t_{1/2}$  of a second order reaction  $\text{A} + \text{A} \rightarrow \text{B}$
- (a)  $= (\ln 2)/k$
  - (b)  $= 1/\{k([\text{A}]_0)^2\}$
  - (c)  $= [\text{A}]_0/k$
  - (d) is always shorter than the half life of a first-order reaction.
  - (e) none of the above
- (v, 4 pts) The function of Photosystem I in plants is to
- (a) use light energy to reduce  $\text{NADP}^+$  to  $\text{NADPH}$ .
  - (b) collect light energy and deliver it to Photosystem II.
  - (c) oxidize water to provide light.
  - (d) re-reduce the reaction center of Photosystem II.
  - (e) reduce water to maintain a basic pH.
- (vi, 4 pts) Assimilation is defined as
- (a) using a substance as a terminal electron acceptor and making no further use of the product.
  - (b) converting (typically through reduction) inorganic material into biomass.
  - (c) nitrogen fixation and all other processes that split diatomic molecules.
  - (d) absorption of enemies by an oppressive regime.
  - (e) none of the above.

**2. Heat Capacity (20 pts)**

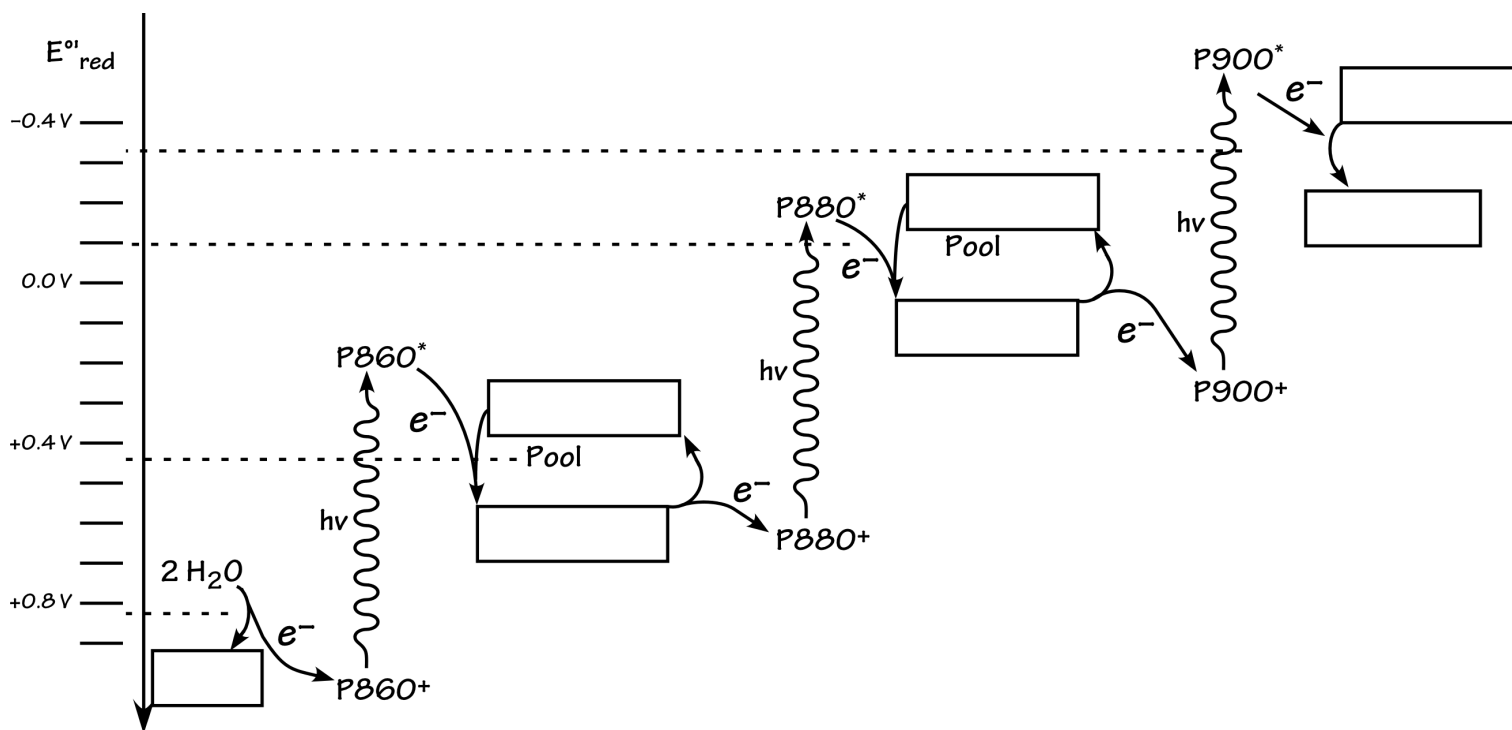
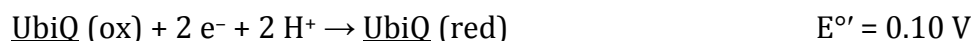
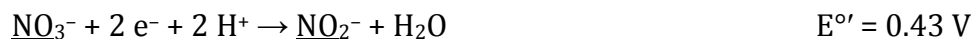
(a; 12 pts) Fill in the boxes in the Kirchhoff cycle below that illustrates why a change in heat capacity ( $\Delta C_p$ ) in going from reactants to products implies a temperature-dependent value for the  $\Delta H$  of the reaction. Derive the expression for  $\Delta H$  at temperature  $T > T_{\text{ref}}$  given that we know  $\Delta H$  at  $T_{\text{ref}}$  and the relevant heat capacities.



(b; 8 pts) In the example we gave in discussion of calculating the equilibrium constant of the Haber process as a function of temperature, the calculated  $K_{eq}$  using the full heat capacity treatment was actually quite close to the  $K_{eq}$  calculated with constant  $\Delta H^\circ$  and  $\Delta S^\circ$ , even though the  $\Delta H^\circ$  changed substantially. Qualitatively, how is this possible?

**3. Photosynthesis and atmospheric chemistry (40 pts)**

(a; 21 pts) Imagine a world orbiting a star that emits in the infra-red region of the spectrum. The plants on this world are found to have three photosystems (P860, P880, and P900) rather than two. P860 oxidizes water and P900 reduces NADP<sup>+</sup> to NADPH as on Earth. The two intermediate electron pools are nitrate/nitrite and ubiquinone/ubiquinol, with standard reduction potentials at the biochemical standard state shown below. Complete the “ZZ” scheme below by entering each one of the underlined species below in one box in the diagram.



(b; 6 pts) Why do these plants need three photosystems to do what our plants do with two?

(c; 4 pts) Two possible failure pathways for photosynthesis are \_\_\_\_\_, if the electron is not transferred away from the excited state fast enough, or \_\_\_\_\_, if the electron is not removed from the immediate vicinity fast enough.

(d; 9 pts) How does increased atmospheric CO<sub>2</sub> cause global warming?

#### **4. Kinetics and Thermodynamics (45 pts)**

(a; 7 pts) The Maxwell-Boltzmann distribution and Arrhenius equation state that the rate of an elementary reaction always increases with increasing temperature. So how is it possible for the equilibrium constant of a reaction  $A \rightleftharpoons B$  to decrease as temperature increases? Would the reaction be (circle one) exothermic or endothermic?

(b; 24 pts) Fill in the blanks. A catalyst can change the \_\_\_\_\_ and/or the \_\_\_\_\_ of a reaction but not its \_\_\_\_\_ constant.

The underlined " $v^2$ " factor in the Maxwell-Boltzmann distribution  $C \underline{v^2} (\exp(-mv^2/2kT))$  arises because of the  $\omega(\epsilon)$  factor in the Boltzmann distribution, the \_\_\_\_\_, which is the number of ways in which a particle can have \_\_\_\_\_. The underlined  $v^2$  comes from the \_\_\_\_\_ of a sphere of radius  $v$ .

A rate law can be determined by inspection only for a(n) \_\_\_\_\_ reaction.

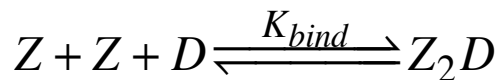
The "2" in  $S_N2$  comes from the fact that \_\_\_\_\_.

(c; 8 pts) Sketch the Arrhenius plot used to measure activation energy  $E_a$  and the preexponential factor  $A$ . Label the axes. What is the molecular meaning of  $E_a$  according to collision theory for gas phase reactions?

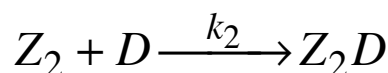
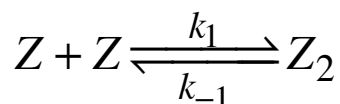
(d; 6 pts) In discussing gas-phase reactions we frequently discussed the need for a collision gas  $M$  to catalyze either dissociation or recombination reactions. It is easy to understand that the collision gas can deliver energy to break apart molecules (think of any parking lot). Why is the collision gas needed to allow atoms/molecules to recombine?

**5. Kinetics and the Steady State Approximation (35 pts)**

Leucine zipper proteins (Z) are monomeric in solution by themselves but they bind to DNA (D) as dimers, with the overall reaction being



There has been debate about the reaction mechanism. One possibility is that a monomer Z must dimerize to form an unstable intermediate  $Z_2$  that either readily falls apart or else binds to DNA. The proposed mechanism is as follows, where we ignore the reverse of the second step (this is reasonable if the complex is very stable):



(a; 5 pts) Write down the differential rate law for the appearance of  $Z_2D$ . It includes the unknown  $[Z_2]$ .

(b; 12 pts) Apply the Steady State Approximation to the unstable  $Z_2$  intermediate to determine its steady state concentration during the binding reaction.

(c; 4 pts) Substitute your answer for (b) into your answer for (a) to get the rate of production of  $Z_2D$ .

(d; 5 pts) If the  $Z_2$  intermediate is so unstable that it almost always falls apart rather than binding a molecule of D, then the differential rate equation reduces to the expression below. We can also rationalize the form of the rate law below based on the idea that the  $Z_2$  intermediate becomes kinetically irrelevant if it never accumulates or goes on to product: What form would you expect for an overall binding reaction with no intermediates?

$$\frac{d[Z_2D]}{dt} = k_2 (k_1 / k_{-1}) [Z]^2 [D]$$

(e; 9 pts) From your answer to (c), what is the reaction order with respect to D if the binding of  $Z_2$  dimer to DNA is fast and the DNA is at high concentration? Physically, explain this initially surprising result.



**4. Miscellaneous Electrochemistry (36 pts)**

A couple of years ago "Blood Falls" in Antarctica had its 15 minutes of fame. Organisms in an anoxic (no  $O_2$ ) lake under a glacier live by transferring electrons from organic carbon that was buried with them to  $Fe^{+3}$  mobilized when the glacier scrapes rust ( $Fe_2O_3/Fe(OH)_3$ ) from rocks, reducing the ferric iron to  $Fe^{+2}$ . The "blood" in Blood Falls comes about because every once in a while the glacier moves and squeezes out some of the contents of the under-ice lake, and when the dissolved  $Fe^{+2}$  hits the air and re-oxidizes.

We will take ethanol as a model for reduced organic carbon food, although presumably being buried in the dark for two million years has made these microbes into a pretty sober bunch.

Some  $E^\circ$  values:

Acetaldehyde reduction:  $E^\circ = -0.197\text{ V}$

Acetate reduction to acetaldehyde:  $E^\circ = -0.581\text{ V}$

Reduction of ferric iron:  $E^\circ = +0.770\text{ V}$

Reduction of  $O_2$ :  $O_2 + 4 e^- + 4 H^+ \rightarrow 2 H_2O$   $E^\circ = +0.815\text{ V}$  (pH 7)

(a; 12 pts) Write the two half-reactions and the overall balanced chemical reaction for the oxidation of  $CH_3CH_2OH$  to  $CH_3CHO$  (acetaldehyde) and the reduction of  $Fe^{+3}$  to  $Fe^{+2}$  and determine " $n$ ." Calculate  $E^\circ$  for this reaction.

(b; 5 pts) Based on the Nernst equation, explain why, for a typical battery, the voltage does not drop substantially until the battery is nearly entirely dead.

(c; 9 pts) When the lead-acid storage battery is recharged by the alternator of the car, the reduction half-reaction is  $\text{PbSO}_4(s) + \text{H}^+(aq) + 2 e^- \rightarrow \text{Pb}(s) + \text{HSO}_4^-(aq)$   $E^\circ_{\text{red}} = -0.356 \text{ V}$

We usually just accept this, but on second thought it is surprising that it works given that protons are present in the reaction. What redox reaction, which occurs in the standard hydrogen electrode, might be expected to occur instead of the reduction of  $\text{PbSO}_4$ , and why? (The \_\_\_\_\_ explains why the other redox reactions do not occur readily: for complicated reasons, it requires a much higher voltage to actually get them to go. This is one reason that platinum, the metal used for the SHE electrode, is not used in car batteries. Another reason is that a pound of platinum would cost about as much as the rest of the car.)

(d; 10 pts) Fill in the blanks. Strong reductants are found at the \_\_\_\_\_ of the typical table of \_\_\_\_\_,

Fat is a denser store of energy than carbohydrate because it has more \_\_\_\_\_ per carbon.

The pH of the biochemical standard state is \_\_\_\_\_ whereas the pH of the chemical standard state can be either \_\_\_\_\_ or \_\_\_\_\_ depending on the reaction in question.

Page	Score
2	/24
3	/20
4	/27
5	/20
6	/38
7	/17
8	/18
9	/17
10	/19
<b>Total</b>	<b>/200</b>

Score for the page \_\_\_\_\_