

**Chemistry 271, Section 22xx
General Chemistry and Energetics
Final Exam (200 points total)**

**University of Maryland, College Park
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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:

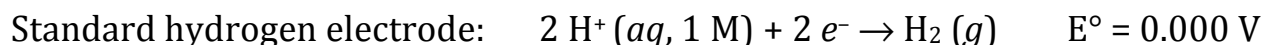
$$\Delta S - q/T \geq 0$$

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

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

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

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



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

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

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

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

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

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

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

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

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

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

$$S = k \ln W$$

$$PV = nRT$$

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

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

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

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

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

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

1. Multiple Choice (24 pts)

(i; 4 pts) The half life $t_{1/2}$ of a first order reaction $A \rightarrow B$

- (a) $= (\ln 2)/k$.
- (b) $= \{k([A]_0)^2\}^{-1}$.
- (c) $= [A]_0/k$.
- (d) is shorter than the half life of a second-order reaction.
- (e) none of the above

(ii; 4 pts) A first-order rate constant

- (a) has units of time^{-1} .
- (b) changes during the course of the reaction as the reactant is depleted.
- (c) cannot be faster than diffusion-controlled.
- (d) has units of $\text{M}^{-1}\text{s}^{-1}$.
- (e) none of the above.

(iii, 4 pts) The function of Photosystem II in plants is to

- (a) use light energy to reduce NADP^+ to NADPH .
- (b) collect light energy and deliver it to Photosystem I.
- (c) oxidize water to provide light.
- (d) re-reduce the reaction center of Photosystem I.
- (e) reduce water to maintain a basic pH.

(iv, 4 pts) Dissimilation is defined as

- (a) using a substance as a terminal electron acceptor and making no further use of the product.
- (b) reducing a substance in order to incorporate it into biomass.
- (c) nitrogen fixation and other processes that split diatomic molecules.
- (d) disguising (one's intentions, for example) under a feigned appearance.
- (e) none of the above.

(v, 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.

(vi, 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 $A \rightarrow B \rightarrow C$.
- (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.

2. Heat Capacity (20 pts)

The graph at the right shows the absolute entropy of benzene as a function of temperature.

(a; 6 pts) Label the boxes in the graph with the physical process that is occurring at the indicated vertical segments.

(b; 9 pts) For a given gas and temperature, think about what happens when the gas is heated at constant pressure vs. constant volume. Why is the heat capacity at constant pressure (C_p) greater than the heat capacity at constant volume (C_v)?

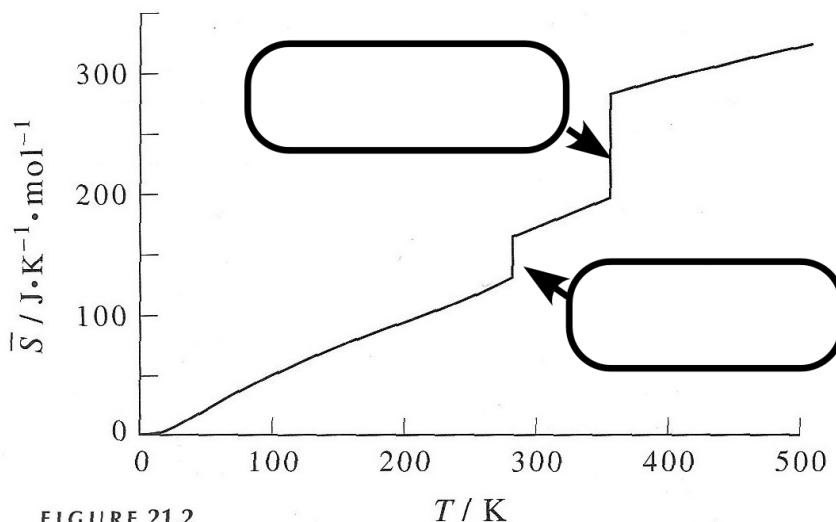


FIGURE 21.2

The molar entropy of benzene plotted against temperature from 0 K to 500 K.

(b; 5 pts) The enthalpy change for a reaction is usually obtained from the slope of a van't Hoff plot. How can we tell from a van't Hoff plot if a reaction has a non-zero ΔC_p ?

3. Photosynthesis and atmospheric chemistry (40 pts)

(a; 15 pts) Why have plants as well as our eyes evolved to be sensitive to the wavelengths that we have so egocentrically named "visible" light? Before the advent of photosynthesis, what was different about the spectrum of light reaching the earth, and why? Why was there no life on land at the time?

(b; 16 pts) Fill in the blanks

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. For an artificial solar cell to be useful, after charge separation the electrons must re-reduce the reductant only after traveling through the _____.

The excited state chromophore of Photosystem I is a very strong _____, whereas Photosystem II generates a(n) _____ that is strong enough to remove _____ from _____ and generate _____.

Score for the page _____

(c; 9 pts) How does increased atmospheric CO₂ 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 $Cv^2(\exp(-mv^2/2kT))$ 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 v^2 comes from the _____ of a sphere of radius v .

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

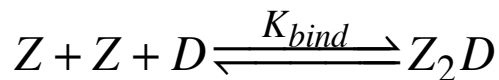
The "2" in S_N2 comes from the fact that _____.

(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?

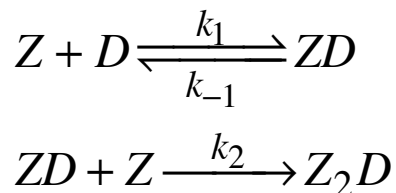
(d; 6 pts) In discussing gas-phase reactions we frequently discussed the need for a collision gas M to catalyze either dissociation or recombination reactions. It is easy to understand that the collision gas can deliver energy to break apart molecules (think of any parking lot). Why is the collision 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 binds to DNA to form an unstable intermediate that either rapidly falls apart or else binds another monomer to form the dimer. 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 $[ZD]$.

(b; 12 pts) Apply the Steady State Approximation to the unstable ZD 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; 9 pts) Show that if the ZD intermediate is so unstable that it almost always falls apart rather than binding another molecule of Z, then the differential rate equation you obtained in (c) reduces to the expression below, which is what we expect for (enter a type of kinetic mechanism)_____ . If you do not trust your answer to (c), receive partial credit for rationalizing the rate law below based on the idea that the ZD intermediate becomes kinetically irrelevant if it never goes on to product: what form would you expect for a reaction with no intermediates?

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

(e; 5 pts) Assume you can measure the initial rate of formation of Z_2D . Qualitatively, how would you determine the order of reaction with respect to Z by doing two rate measurements ?

6. 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 acetaldehyde (the metabolite that we make from ethanol) as a model for reduced organic carbon food, although presumably after being buried in the dark for two million years these microbes no longer feel hung over.

Some E° 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_3CHO (acetaldehyde) to acetate CH_3COO^- and the reduction of Fe^{+3} to Fe^{+2} and determine “ n .” Calculate E° for this reaction.

(b; 5 pts) When we are balancing electrochemical reactions, if we double a reaction we do not double the voltage. Explain why not.

(c; 8 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 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; 11 pts) Fill in the blanks. The terminal electron acceptor for our metabolism is _____.

Strong oxidants are found at the _____ of the typical table of _____,

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	/31
5	/16
6	/38
7	/17
8	/18
9	/17
10	/19
Total	/200

Score for the page _____