

Chemistry 271, Section 22xx

Your Name: \_\_\_\_\_

Prof. Jason Kahn

University of Maryland, College Park

Your SID #: \_\_\_\_\_

General Chemistry and Energetics

Exam II (100 points total)

Your Section #: \_\_\_\_\_

November 4, 2009

You have 53 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.

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

**Useful Equations:**

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

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

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

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

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

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

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

$$0 \text{ }^\circ\text{C} = 273.15 \text{ K}$$

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

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

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

$$PV = nRT$$

$$S = k \ln W$$

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

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

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

$$1 \text{ V} = 1 \text{ J}/\text{C}$$

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

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

$$n_i/n_0 = \exp[-(E_i - E_0)/kT]$$

$$T_M = \Delta H^\circ / [\Delta S^\circ + R \ln(C_T/4)]$$

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

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

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

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**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.”

(3 pts extra credit for filling out this page accurately and completely)

**1. (20 pts) Multiple choice: Circle the single best answer for each question**

(a; 4 pts) The Boltzmann distribution refers to the distribution of

- (a) microstates over configurations.
- (b) particles within boxes.
- (c) energy among particles.
- (d) entropy among reactants.
- (e) None of the above.

(b; 4 pts) Free energy is useful because it

- (a) tells us the amount of heat released by a reaction.
- (b) is maximized when reactions come to equilibrium.
- (c) is constant during isothermal expansion of a gas.
- (d) reduces the fundamental spontaneity condition  $\Delta S_{\text{universe}} > 0$  to state functions solely of the system.
- (e) All of the above.

(c; 4 pts) Entropy is given as a logarithm of the number of microstates because

- (a) it must be an increasing and extensive function of  $W$ .
- (b) the number of microstates cannot be calculated.
- (c) the  $K_a$  and  $K_b$  equilibria add to give the water self-dissociation equilibrium.
- (d) Boltzmann chose the functional form arbitrarily.
- (e) None of the above.

(d; 4 pts) Reduced carbon (like humans) and molecular oxygen can coexist because

- (a) our skin protects our contents.
- (b) the kinetics of human oxidation are slow at room temperature.
- (c) redox reactions require electrodes.
- (d) we breathe out oxygen.
- (e) (b) and (d).

(e; 4 pts) The expansion of an ideal gas into a vacuum occurs with

- (a) no work being done.
- (b) no change in internal energy.
- (c) no heat exchange with the surroundings.
- (d) a positive entropy change.
- (e) All of the above.

**2. (40 pts) Redox chemistry**

Ammonium,  $\text{NH}_4^+$  (*aq*), can be converted to nitrate,  $\text{NO}_3^-$  (*aq*), by molecular oxygen,  $\text{O}_2$ (*g*), in acidic solution.

(a; 3 pts) What are the oxidation numbers of nitrogen in ammonium, nitrogen gas, and nitrate?

(b; 10 pts) The balanced reduction half-reaction for the conversion above is good old

$\text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}$ . What is the balanced oxidation half-reaction? What is the balanced overall reaction? (Hint:  $n = 8$ ).

(c; 5 pts) The  $E^\circ_{\text{red}}$  values for the reduction and oxidation half-reactions are +1.23 V and +0.88 V respectively. Calculate  $\Delta E^\circ$  and  $\Delta G^\circ = 270$  (units here:-> ).

(d; 3 pts) The above is all at the chemical standard state. In general, what does this mean in terms of concentrations and partial pressures of reactants and products?

(e; 12 pts) Calculate  $\Delta E$  at pH 7,  $pO_2 = 0.21$  atm, 1 M each  $[NH_4^+]$  and  $[NO_3^-]$ , and 25 °C. Use the fact that  $\Delta E = 0$  at equilibrium or the  $\Delta G^\circ$  from (c) above to calculate the ratio of  $[NH_4^+]/[NO_3^-]$  at equilibrium at pH 7,  $pO_2 = 0.21$  atm, 25 °C. There is no need to worry about  $K_p$  vs.  $K_c$ .

(f; 3 pts) What industrial process is used to make ammonia?

(g; 4 pts) Thinking about the oxidation states of N, and recognizing that  $NO_3^-$  is nearly as good an oxidant as  $O_2$ , why do you think  $NH_4NO_3$  is extremely dangerous? Extra credit: name a city that had a very bad experience with it.

**3. (40 pts) Thermodynamics, DNA, and van't Hoff.**

(a; 4 pts) What does  $\Delta S = q/T$  mean in terms of the effect of adding energy to hot and cold systems?

(b; 8 pts) Sketch a van't Hoff plot for an exothermic ordering reaction like DNA hybridization.

(c; 6 pts) Rationalize the signs of  $\Delta H^\circ$  and  $\Delta S^\circ$  for the hybridization process.

(d; 6 pts) In terms of LeChatelier's principle, why does the reaction become less favorable as temperature increases? In terms of the statistical nature of the universe, why does the reaction become less favorable as temperature increases?

(e; 8 pts) Given  $\Delta H^\circ = -20 \text{ kJ/mol}$  and  $\Delta S^\circ = -53 \text{ J/mol K}$  for a hybridization reaction, calculate  $\Delta G^\circ$  and  $K_{eq}$  at  $20^\circ\text{C}$  and  $60^\circ\text{C}$ .

(f; 8 pts)  $K_{eq} = 2\alpha/(1-\alpha)^2C_t$ , where  $\alpha$  is the fraction of double-stranded DNA and  $C_t$  is the total strand concentration. Given that  $\alpha = 0.5$  at the melting temperature  $T_m$ , use the two main expressions for  $\Delta G^\circ$  to show that  $T_m = \Delta H^\circ/[\Delta S^\circ + R \ln (C_t/4)]$ .

Page	Score
1	/3
2	/20
3	/21
4	/19
5	/12
6	/20
7	/8
<b>Total</b>	

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