

Chemistry 271, Section 22xx

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Your Name: Key

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

General Chemistry and Energetics

Exam II (100 points total)

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

April 7, 2010

You have 52 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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$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$$

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

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

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

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

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

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

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

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

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

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

$$S = k \ln W$$

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

$$L' = L(1 - v^2/c^2)^{1/2}$$

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

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

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

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

$$n_i/n_o = \exp[-(E_i - E_o)/kT]$$

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

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

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

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.”

**1. (12 pts) Multiple choice: Circle the single best answer for each question**

(A; 4 pts) The "predominant configuration" is

- +4  c. A set of microstates that is more likely to be observed than any other possible configuration, at equilibrium.
- a. The microstate that has the most uniform distribution of energy.  
 b. The microstate that corresponds to a Boltzmann distribution of particles.  
 d. Only observed when systems are small enough so molecules can be enumerated.  
 e. None of the above.

(B; 4 pts) The Joule experiment on the expansion of an ideal gas into a vacuum showed that

- +4  b. The enthalpy change for the isothermal expansion of an ideal gas is zero.
- a. The entropy change for the isothermal expansion of an ideal gas is negative.  
 c. The free energy change for any expansion of an ideal gas is negative.  
 d. The heat transfer  $q$  for expansion of an ideal gas into vacuum is positive.  
 e. None of the above.

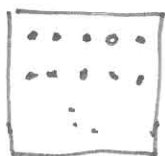
(C; 4 pts) State functions are useful in thermodynamics because

- +4  b. The value of a state function for a system is independent of the path taken to arrive there.
- a. Crashing them gets us into the news.  
 c. The use of state functions allows us to avoid doing any work.  
 d. They are independent of temperature.  
 e. They are independent of concentration.

**2. (28 pts) Short-answer questions**

(a; 6 pts) Briefly describe what a DNA microarray is and how it is used.

- A microarray is a slide or surface on which distinct DNA molecules have been synthesized or deposited, such that we know which DNA occupies every spot



no picture needed

- A sample of DNA or RNA is applied to the array and the extent of hybridization to each spot is measured. This tells us the composition of the sample mixture, i.e. what mRNA's are being expressed.

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(b; 5 pts) What is the difference between a voltaic cell and an electrolytic cell? What metal is obtained from its oxide using an industrially important electrolytic cell?

- A ~~voltaic~~ voltaic cell uses a spontaneous electrochemical reaction to provide useful electric ~~power~~ current, whereas an electrolytic cell uses an external voltage source to drive a non-spontaneous reaction
- (+3)
- (+2) - Aluminium (Hall-Heroult) ... or Zn, Na, Ca, Mg, Cu, Ni, Pb, Ag, Au

(c; 8 pts) Give an example of an exothermic ordering reaction. Briefly explain why exothermicity *per se* makes a reaction thermodynamically favorable, but on the other hand explain why at high enough temperature an exothermic ordering reaction will become nonspontaneous.

- (+2) - protein folding - fetal development - water freezing
- (+3) - Exothermicity means the reaction transfers heat to the environment - this increases the entropy of the surroundings.

(+2 for each answer) - At high enough  $T$ ,  $\Delta G = \Delta H - T\Delta S$  must go from  $\ominus$  to  $\oplus$  if  $\Delta S$  is negative. This is because the entropy increase in the surroundings gets smaller as  $T \uparrow$ , so eventually it cannot compensate for ordering in the system. (+1)

(d; 4 pts) What is required to describe a microstate of a sample of a gas?

- (+2 for any three) [ - The position, velocity, rotational, vibrational, and electronic state of every molecule must be specified. (The PC can be described by any three of  $n, V, P, T$ )

(e; 5 pts) Define a "high energy bond" or "high energy molecule" and give an example.

- (+3) A high energy bond or molecule liberates free energy upon conversion to products. The bond itself still requires energy to break, but it converts to something more stable.

- (+2) ATP, phosphoanhydride, thermite,  $\text{Al} + \text{Fe}_2\text{O}_3$ , TNT
- for any one

**3. (22 pts) Applied thermodynamics**

DNA hybridization is described by the equilibrium  $W + C \rightleftharpoons W \cdot C$ , with equilibrium constant  $K_{hyb}$ . We assume that  $\Delta H^\circ = -70000$  cal/mole and  $\Delta S^\circ = -185$  cal/mole K.

Recall that the  $T_m$  for DNA melting is defined as the temperature at which  $\alpha = 1/2$ , i.e. half of the total concentration  $C_T$  of strands are in double-stranded form. Thus  $[WC] = (C_T \times 1/2)/2 = C_T/4$  (we divide by 2 because y Molar  $W \cdot C$  has a strand concentration of 2y M),  $[W] = (C_T \times 1/2)/2 = C_T/4$ , and  $[C] = C_T/4$ .

Therefore, the equilibrium constant  $K_{hyb} = [W \cdot C]/[W][C] = 4/C_T$  at  $T = T_m$ . For  $C_T = 2.5 \mu\text{M}$ , the thermodynamic values above give  $T_m = 55^\circ\text{C}$ .

We want to measure the temperature  $T_{0.05}$  at which  $\alpha = 0.05$ .

(a; 4 pts) What is  $K_{hyb}$  in terms of  $C_T$  when  $\alpha = 0.05$ , so  $[WC] = C_T \times 0.05/2$ ?

$$K_{hyb} = \frac{[WC]}{[W][C]} = \frac{C_T \times 0.05/2}{(C_T \times 0.95/2)^2} = \frac{0.1}{C_T \cdot 0.95^2} = \frac{0.111}{C_T}$$

Common mistakes  
 $[W]=[C]=\frac{C_T}{4}$ , or  $0.05C_T$

(b; 12 pts) The van't Hoff equation we used in class is  $\ln(K_{eq}) = (-\Delta H^\circ/R)(1/T) + (\Delta S^\circ/R)$ . First, plug in the expression for  $K_{hyb}$  at  $T_m$  for  $K_{eq}$  and " $T_m$ " for T. Second, write a similar equation by plugging in the expression for  $K_{hyb}$  at  $T_{0.05}$  for  $K_{eq}$  and " $T_{0.05}$ " for T. Subtract one equation from the other and solve to obtain an expression for  $T_{0.05}$  in terms of  $T_m$  and  $\Delta H^\circ$ . Give a numerical answer for  $T_{0.05}$ .

$$\begin{aligned} \textcircled{+1} \quad \ln K_{hyb} &= -\frac{\Delta H^\circ}{R} \left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R} \\ \textcircled{+2} \quad \ln \left(\frac{4}{C_T}\right) &= -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_m}\right) + \frac{\Delta S^\circ}{R} \\ \textcircled{+2} \quad \ln \left(\frac{0.111}{C_T}\right) &= -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_{0.05}}\right) + \frac{\Delta S^\circ}{R} \\ \textcircled{+3} \quad \ln \left(\frac{4}{C_T} \cdot \frac{C_T}{0.111}\right) &= -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_m} - \frac{1}{T_{0.05}}\right) \end{aligned}$$

$$\begin{aligned} &= \left(\frac{1}{55+273} + \frac{1.987}{-70000} \ln 36.1\right) \\ &= \frac{1}{328\text{K}} - 1.018 \times 10^{-4} \\ &= 0.00295^{-1} \\ &= \underline{339\text{K}} = \underline{66^\circ\text{C}} \end{aligned}$$

$\textcircled{+2}$  for K or C

$$\frac{1}{T_m} - \frac{1}{T_{0.05}} = -\frac{R}{\Delta H^\circ} \ln \left(\frac{4}{0.111}\right)$$

$$\frac{1}{T_{0.05}} = \frac{1}{T_m} + \frac{R}{\Delta H^\circ} \ln \left(\frac{4}{0.111}\right)$$

$$\textcircled{+2} \quad T_{0.05} = \left( \frac{1}{T_m} + \frac{R}{\Delta H^\circ} \ln \left(\frac{4}{0.111}\right) \right)^{-1}$$

(c; 6 pts) As you know, oligonucleotide  $T_m$  tends to increase with length. In detecting SNPs (single-nucleotide polymorphisms or single-base pair differences between people's genome sequences), we use hybridization to oligonucleotides that are as short as possible but no shorter. Based on optimizing hybridization signal and specificity, explain this statement.

as oligo gets shorter, specificity signal

The shorter the oligo, the lower the  $T_m$ , and the greater the difference between correct and incorrect hybridization. Most students thought about the stability. They said longer oligos melt at high T, so longer ones have no signal. But if the probe is too long there will be no difference in stability. But if the probe is too short it won't hybridize well to either target and signal is too weak. And high  $T_{emp}$  causes problem with hybridization (they thought hybridization happens when they are melting).

4. (22 pts) Thermodynamics

The Second Law of Thermodynamics states that the entropy of the universe increases for any spontaneous process:  $\Delta S_{system} + \Delta S_{surroundings} \geq 0$ . We derived the "master relation"  $\Delta S_{system} - q_{system}/T \geq 0$  to convert the 2<sup>nd</sup> Law to a form that refers only to the system.

(a; 6 pts) What restriction does the master relation require for the nature of the interaction between the system and the surroundings? Briefly and qualitatively explain the origin of the second term's dependence on "1/T".

Problems

Some answers are like "it has to be at constant T" "it can't absorb energy from outside the system" etc. They (+3) - The system cannot exchange matter with the surroundings. don't understand only heat and work.

As  $T \uparrow$ , the increase in entropy for a given amount of heat decreases. The addition of more disorder to an already disordered system does not give a large ratio of  $w$ 's. ( $w = \#$  of microstates) (71) they have no idea.

(b; 3 pts) For a reversible process carried out at constant T and P we were able to replace the master relation with the equation  $\Delta S - \Delta H/T \geq 0$ , which motivated us to define the Gibbs free energy  $G = H - TS$ . How does this give us a simple condition for spontaneity?

$\Delta S - \Delta H/T \geq 0$   
 $T\Delta S - \Delta H \geq 0$   
 $\Delta H - T\Delta S \leq 0$

Many students explained why this  $\Delta G$  is better, but didn't derive it. Some knew  $\Delta G \leq 0$  for a spontaneous reaction, but don't know how to get it for from this.

(+3)  $\Delta G = \Delta H - T\Delta S \leq 0$  for any spontaneous process. Score for the page 1/15

We showed that  $G_A = G_A^\circ + RT \ln P_A$  describes the molar free energy of substance A.

(c; 9 pts) For the reaction  $A \leftrightarrow 2B$ , use this equation to calculate the free energy change  $\Delta G$  for converting a mole of A to 2 moles of B. At equilibrium we know that  $\Delta G = 0$  for any infinitesimal change. Use this to demonstrate that a ratio of partial pressures must be a constant,  $K_p$ .

$$\Delta G = G(2B) - G(A)$$

$$\begin{aligned} (+3) \quad \Delta G &= 2(G_B^\circ + RT \ln P_B) - (G_A^\circ + RT \ln P_A) \\ &= \underbrace{2G_B^\circ - G_A^\circ} + 2RT \ln P_B - RT \ln P_A \\ &= \Delta G^\circ + RT(2 \ln P_B - \ln P_A) \end{aligned}$$

$$(+3) \quad \Delta G = \Delta G^\circ + RT \ln \left( \frac{P_B^2}{P_A} \right) = \Delta G^\circ + RT \ln Q$$

$$0 = \Delta G^\circ + RT \ln \left( \frac{P_B^2}{P_A} \right)$$

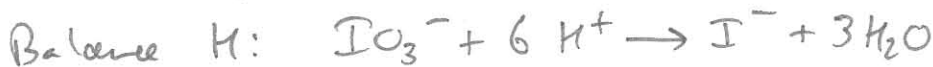
$$\Delta G^\circ = -RT \ln \left( \frac{P_B^2}{P_A} \right)$$

Both sides ~~are~~ must be independent of  $P_A$  and  $P_B$ , so  $K_p = \frac{P_B^2}{P_A}$

(d; 4 pts) We see that even if the standard state molar free energy of substance B is more positive than that of substance A, there will still be some B present at equilibrium. Give a qualitative argument based on microstates that rationalizes this conclusion.

Consider a large collection of  $N$  molecules of A. If we convert some of them to B, there are many ways to do it  $\left( \frac{N!}{B!(N-B)!} \right)$ , where  $B = \#$  of molecules of B produced)

Thus making a small amount of B causes a large increase in  $\#$  of microstate (entropy).

**5. (16 pts) Electrochemistry**Consider the reduction of the iodate anion  $\text{IO}_3^-$  to iodide,  $\text{I}^-$ .(a; 8 pts) Balance the half-reaction in acidic solution. Its standard reduction potential  $E^\circ_{\text{red}} = 1.085 \text{ V}$ . Why is the iodate anion a relatively good oxidizing agent?

Many students used the  $E^\circ_{\text{red}}$  value as an explanation of why iodate is a good oxidizing agent

+1  
+1 each step if final half-rea is wrong  
(+4)

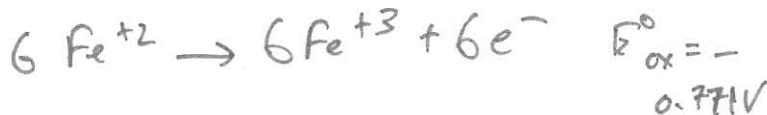
- (+2) The oxidation # of I in  $\text{IO}_3^-$  is +5 - it is an electron-deficient & electronegative atom  $\rightarrow$  therefore has a strong tendency to be reduced and  $\therefore$  oxidize someone else.
- (+2) many don't get to this point

The reduction of ferric iron to ferrous iron is described by  $\text{Fe}^{+3} + \text{e}^- \rightarrow \text{Fe}^{+2}$ ,  $E^\circ_{\text{red}} = 0.771 \text{ V}$ .(b; 8 pts) What is the net reaction if  $\text{IO}_3^-/\text{I}^-$  are in one half cell and  $\text{Fe}^{+3}/\text{Fe}^{+2}$  in the other, all at standard conditions? What is  $E^\circ_{\text{cell}}$ ?

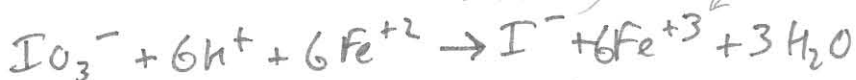
- (+2) Reverse the  $\text{Fe}^{+3}$  reduction



- (+2) Balance electrons



- (+2) Add reactions



(charge is +17 on each side)

$$E^\circ_{\text{cell}} = 1.085 \text{ V} - 0.771 \text{ V} = 0.314 \text{ V} \quad (+2)$$

Some calculate it in this way:

$$E^\circ_{\text{cell}} = 1.085 \text{ V} - 6 \times 0.771 \text{ V}$$

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3	/22
4	/16
5	/15
6	/13
7	/16
<b>Total</b>	

Score for the page 1/16