

Chemistry 271 – 23XX

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

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

General Chemistry and Energetics

Final Exam (200 points total)

Your Section # or time: \_\_\_\_\_

May 13, 2016

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.

N=63+3

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:**

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

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

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

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

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

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

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

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

$$\ln K_{eq} = (-\Delta H^\circ/R)(1/T) + \Delta S^\circ/R$$

$$\Delta S = q/T$$

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

$$S = k_B \ln W$$

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

$$\Delta G = \Delta G^\circ + RT \ln Q$$

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

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

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

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

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

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

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

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

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

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

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

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

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

**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. (50 pts) Fundamental thermodynamics**

$\Delta G$  is the change in free energy, but as we have discussed, free energy isn't exactly an energy, and it's also not obvious what is free about it. Other than that, the name is perfectly sensible: G stands for "Gibbs."

(a; 8 pts) There are two meanings for "free": (1) as in liberated, "Born Free," or "Free at last," (2) as in no-cost, "There ain't no such thing as a free lunch." Identify which meaning applies to G and what the "free" means in "free energy." Explain how this relates to the equation  $\Delta G = -nFE_{\text{cell}}$ .

(+2) ① -liberated. It is the energy that is liberated by the reaction to do useful work of some kind - when  $\Delta G = 0$ , the rxn is at equilibrium and cannot do anything further.

In the case of  $\Delta G = -nF E^{\circ}_{\text{cell}}$ , the  $\Delta G$  is available to do electrical work, so  $\ominus \Delta G \leftrightarrow \oplus E^{\circ}_{\text{cell}}$

(b; 2 pts) The idea that free energy is minimized when a system reaches equilibrium is really a statement of the (circle one): 1<sup>st</sup> ②<sup>nd</sup> or 3<sup>rd</sup> Law of Thermodynamics.

(c; 2 pts) The First law of Thermodynamics says that energy ② is conserved.

(d; 8 pts) If you memorized the equation  $G = G^{\circ} + RT \ln P$ , but forgot the sign, how could you figure out whether + or - is logically correct? Also, what does the superscript  $^{\circ}$  in  $G^{\circ}$  stand for?

We know that expansion or dilution ④ is spontaneous whereas compression or concentration is not. Therefore G should decrease as P or [ ] decreases and we see that the ⊕ sign ② gives this dependence. (It doesn't justify the "ln".)

The  $^{\circ}$  stands for standard state ② - 1M / 1 atm. Thus when  $P = 1 \text{ atm}$   $G = G^{\circ} + RT \ln 1 = G^{\circ}$  ✓

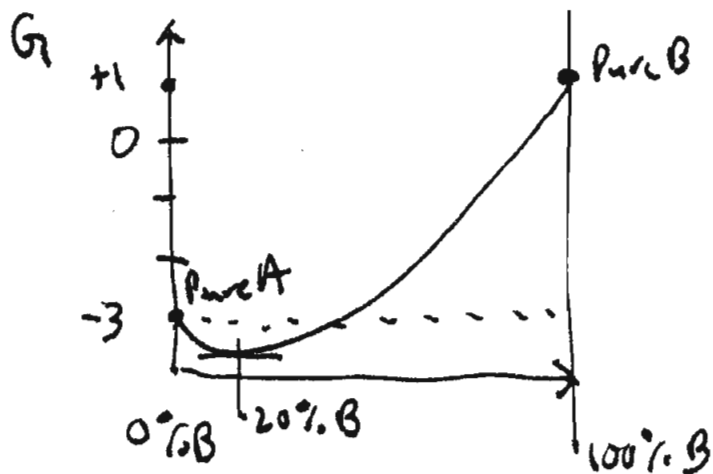
(e; 20 pts; 2 pts each) Consider the reaction  $A(aq) \rightleftharpoons B(aq)$ , with the standard state molar free energy of

$A = G^\circ_A = -3$  kJ/mole at 298 K and the molar free energy of  $B = G^\circ_B = 1$  kJ/mole at 298 K.

Circle or write in correct answers in the table below:

The equilibrium constant expression in terms of [A] and [B] is	$K_c = \frac{[B]}{[A]}$ (+2)		
The standard state free energy change for $A \rightarrow B$ , $\Delta G^\circ_{rxn}$ , is	$\Delta G^\circ_{rxn} = +4$ kJ/mole (+2)		
The observed $\Delta G_{rxn}$ at equal concentrations of A and B is	$\Delta G_{rxn} = +4$ kJ/mole (+2) $\Delta G = \Delta G^\circ + RT \ln Q \rightarrow 1$		
The observed free energy change $\Delta G_{rxn}$ at 2.4 M A and 0.5 M B is	$\Delta G_{rxn} = \frac{0.114}{(or\ 0.1)}$ kJ/mole $= +4 + 8.314 \cdot 298 \ln \frac{0.5}{2.4}$		
The numerical value of $K_c$ at 298 K is	$K_c = 0.199$ (or 0.2) (+2) $K_c = e^{-\Delta G^\circ / RT} = e^{-4000 / (8.314 \cdot 298)}$		
The total free energy of an equilibrium mixture of A and B is (circle one):	Less than -3 kJ/mole (+2)	Between +1 and -3 kJ/mole	Cannot be determined
To answer the question above I would need to know (circle one):	The exact concentrations of A and B	answered it already (+2)	There is no way to answer
$K_{eq}$ at 400 K is (circle one):	Cannot be determined (+2)	Greater than $K_{eq}$ at 298 K	Less than $K_{eq}$ at 298 K
To answer the question above I would need to know (circle one):	Both $\Delta H^\circ$ and $\Delta S^\circ$ values (assuming they are constant) (+1)	Only the sign of $\Delta H^\circ$ (assumed constant) (+2)	Already answered
$\Delta G_{rxn}$ at equilibrium is	$\Delta G_{rxn} = 0$ kJ/mole (+2)		

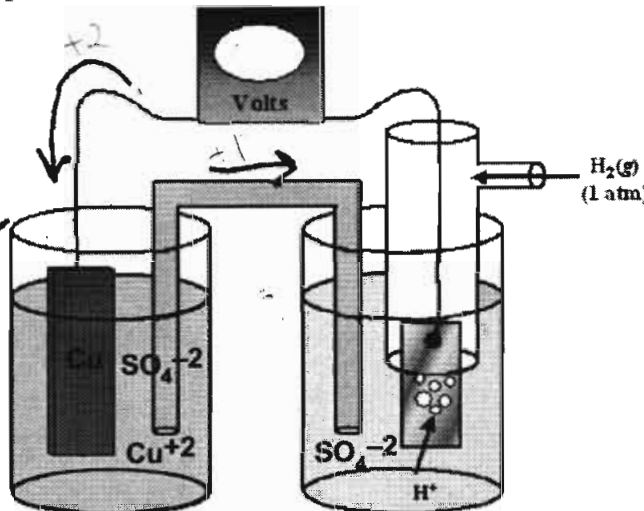
(f; 10 pts) Sketch the graph for total free energy of an A+B mixture as a function of the percent found as B (i.e. the x-axis ranges from 0% to 100% B), given a total concentration [A]+[B] of 1 M, at 298 K.



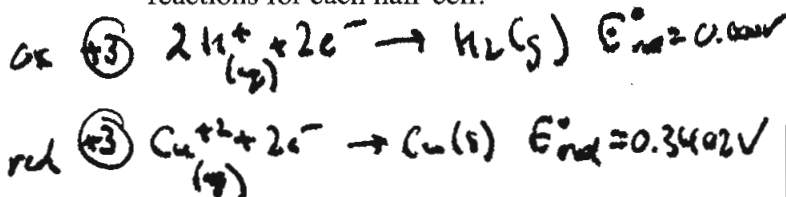
+2 for idea  
 +2 for  $G$  at a minimum w.r.t. B closer to A (should be 22)  
 +2 for min  $G < -3$   
 +2 for end values (-3, +1)  
 +2 for correct shape of curve

**2. Electrochemistry (40 pts)**

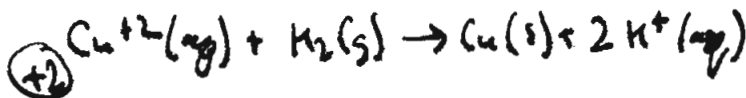
Consider the electrochemical cell below. On the left is a  $\text{Cu}(s)|\text{Cu}^{2+}(aq)$  half-cell, with  $1\text{M Cu}^{2+}(aq)$ ,  $E^\circ_{\text{red}} = 0.3402\text{ V}$ . On the right there is a standard hydrogen ( $\text{H}_2(g)|\text{H}^+$ ) electrode ( $E^\circ_{\text{red}} = 0.000\text{ V}$  by definition), except someone has replaced the solution with  $\text{H}_2\text{SO}_4$  of unknown concentration, making it a "non-standard hydrogen electrode" (NSHE). The  $\text{SO}_4^{2-}$  ion is an inert spectator. **The measured cell voltage is  $0.3175\text{ V}$ , with the Cu electrode acting as the cathode.** (Recall that what happens at the cathode is due to the fact that both words start with a consonant.)



(a; 6 pts) Write down the balanced reduction half-reactions for each half-cell.



(b; 4 pts) Write down the balanced overall redox reaction and calculate  $E^\circ_{\text{cell}}$ .



$\textcircled{+2}$   $E^\circ_{\text{cell}} = 0.3402\text{ V} - 0\text{V} = 0.3402\text{ V}$

(c; 3 pts) On the diagram, draw in the direction of electron flow in the external circuit and the direction of sulfate ion flow through the salt bridge.  $\textcircled{+3}$  for correct

(d; 3 pts) How could you tell just visually, after a while, that the copper electrode is the cathode?

$\textcircled{+3}$  Cu would plate out on the electrode and it would get thicker/heavier or solution would go from blue to colorless

(e; 6 pts) Calculate  $\Delta G^\circ$  and the equilibrium constant for the reaction.

$\textcircled{+1}$   $\Delta G^\circ = -nF E^\circ_{\text{cell}} = -2 (96500 \frac{\text{C}}{\text{mole}}) (0.3402\text{ V})$   $\rightarrow \text{J/C}$

$= -65700\text{ J/mole}$   $\textcircled{+2}$   
(or  $-70$ )

$\textcircled{+1}$   $K = e^{-\Delta G^\circ / RT} = e^{+65700 / (8.314 \cdot 298)}$   $\textcircled{+2}$  if consistent  $= 3.3 \times 10^{11}$



**3. van't Hoff (25 pts)**

We know that  $\Delta G = \Delta H - T\Delta S$  in general, and  $\Delta G^\circ = -RT \ln K_{eq}$  for chemical equilibrium.

(a; 8 pts) Use these two equations to derive the van't Hoff equation.

too much!

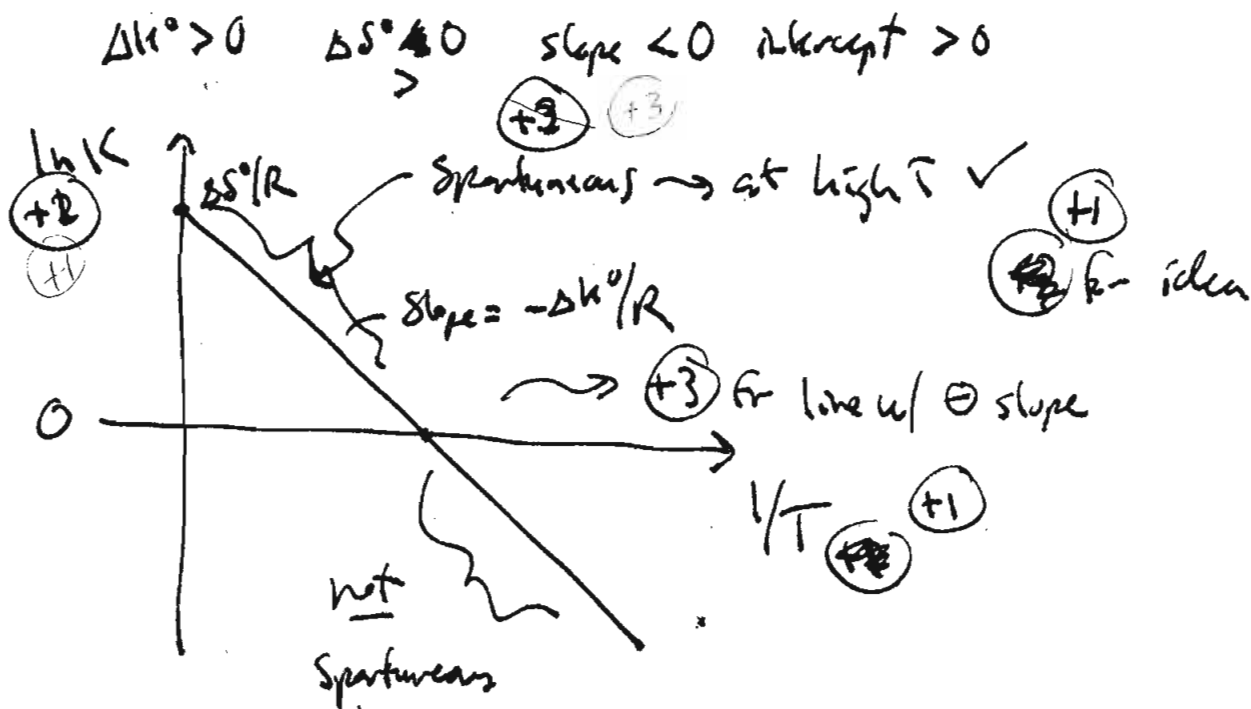
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_{eq} \quad (+3) \text{ for this simple idea}$$

$$\ln K_{eq} = \frac{\Delta H^\circ}{-RT} - \frac{T\Delta S^\circ}{-RT} \quad (+2) \text{ for any calculation}$$

$$\ln K_{eq} = \left(-\frac{\Delta H^\circ}{R}\right) \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (+3) \text{ for final form}$$

$$y = m x + b$$

(b; 9 pts) Sketch a van't Hoff plot for an endothermic disordering reaction. Label the axes. Indicate on your plot the temperature range over which the reaction would be spontaneous.



(c; 2 pts) Give an example of an endothermic disordering reaction.

(+2) melting ice, melting DNA, dissolving urea

(c; 6 pts) What does LeChatelier's principle predict for the effect of heating up an endothermic disordering reaction, and why? What particular aspect of the van't Hoff plot puts this idea on a quantitative basis?



+ heat

- Heat is a reactant <sup>(+2)</sup> LeC says it will go better at higher T <sup>(+2)</sup> where more heat is provided.

- The  $\ominus$  slope of the plot <sup>(+2)</sup> says that  $K$  goes ~~less~~ for a lesser extent as  $T \downarrow$ , greater extent as  $T \uparrow$ .

#### 4. Applications (45 pts)

DNA hybridization, single-stranded W + single-stranded C  $\rightleftharpoons$  W•C duplex, is an exothermic ordering reaction. The exothermicity comes from forming noncovalent hydrogen bonds and base stacking interactions.

(a; 4 pts) What are the signs of  $\Delta H^\circ$  and  $\Delta S^\circ$  for hybridization?

$$\Delta H^\circ < 0, \quad \Delta S^\circ < 0$$

(+2)                      (+2)

(b; 6 pts) Give two different molecular explanations that contribute to the sign of  $\Delta S^\circ$ .

(+3) - Two separate DNA molecules have to travel around together

(+3) - The range of conformations available to dsDNA is much more restricted.

The melting temperature  $T_m$  is defined as the temperature at which half of the DNA strands are in single-stranded form and half of them are in double stranded form. If we start with equal concentrations of W and C, this means that  $[W \cdot C] = [W] = [C]$  at  $T_m$ .

(c; 9 pts) For starting concentrations of  $3 \times 10^{-6}$  M each W and C, what are  $[W]$ ,  $[C]$ , and  $[W \cdot C]$  at equilibrium at  $T_m$  (noting that the concentration of  $W \cdot C$  is given in terms of double-stranded DNA helices)? What is the numerical value of K? What is the numerical value of  $\Delta G^\circ$ ?

$$[W \cdot C] = [W] = [C]$$

$$x = 3 \times 10^{-6} - x = 3 \times 10^{-6} - x$$

$$x = 1.5 \times 10^{-6} \text{ M}$$

$$[W \cdot C] = [W] = [C] = \overset{+3}{1.5 \times 10^{-6} \text{ M}}$$

$$K = \frac{[W \cdot C]}{[W][C]} = \frac{1}{1.5 \times 10^{-6} \text{ M}} = 6.67 \times 10^{+5} \text{ (m}^{-1}\text{)}$$

$\overset{+3}{}$  for consistent

Not  $\overset{+3}{}$   $K=1$  b/c it's not  $A \rightleftharpoons B$ !

$\hookrightarrow$  assumption  $T_m = 325 \text{ K}$   
 - covered during exam -

$$\Delta G^\circ = -RT \ln K$$

$$= -8.314 \times 325 \times \ln 6.67 \times 10^5$$

$$\Delta G^\circ = -36.2 \text{ kJ/mole}$$

at  $T_m \overset{+3}{}$  for consistent

(d; 4 pts) At what concentrations of W, C, and  $W \cdot C$  would  $\Delta G^\circ$  equal zero at  $T_m$ , corresponding to  $K = 1$ ?

DNA has a density of about  $1.7 \text{ g/cm}^3$ , and a 12-mer oligonucleotide has a molecular weight of about 4000 g/mole. What is the molar concentration of DNA in an aqueous "solution" that is 50 % DNA by volume?

Should have been more

would need  $\Delta G^\circ = -RT \ln K = 0$  so  $K=1$

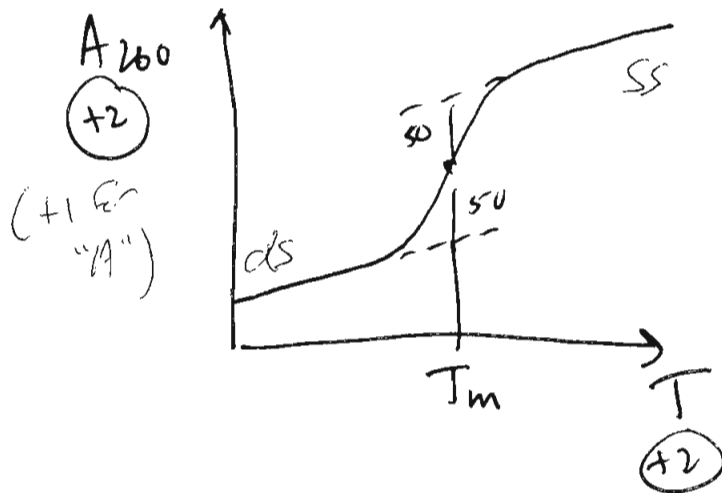
$\overset{+2}{}$  therefore  $[W \cdot C] = [W] = [C] = 1 \text{ M each}$   $[W \cdot C] = [W] = [C]$   
so that we are at  $T_m$

$$\frac{500 \text{ ml DNA}}{1 \text{ liter}} \cdot \frac{1.7 \text{ g}}{\text{ml}} \cdot \frac{1}{4000 \text{ g/mole}} = 0.2125 \text{ M oligonucleotide}$$

$\overset{+2}{}$  for idea



(e; 10 pts) Sketch a UV absorbance melting curve for DNA, labeling the axes and the  $T_m$ .



+2 for a curve that goes up  
 +2 for  $T_m$   
 +2 for cooperative appearance

(f; 3 pts) What is the function of Photosystem I (the one on the right hand side of the Z scheme)?

Use  $h\nu$  to make a strong reducing agent that can donate electrons to  $NADP^+$  to make  $NADPH$  to fix  $CO_2$ .

(g; 3 pts) What is the function of Photosystem II? What is its by-product?

+2 - Provide electrons to replenish those lost by PS I.

+1 -  $O_2$

(h; 6 pts) Assuming that the early Earth was a reducing environment (in other words, there were lots of reducing agents like  $H_2S(aq)$  or  $Fe(s)$  lying around), which photosystem probably evolved first, and why?

- PSI is needed directly for the plant to grow - the  $P700^+$

+3 can be ~~re-~~ re-reduced at environmental reducing agents

- As the supply of reducing agents decreased, PS II would be needed to tap into the infinite source of  $e^-$  in  $H_2O$

cred. for anything reasonable.

**5. More about why thermodynamics works the way it does (40 pts).**

(a; 6 pts) State the Third Law of Thermodynamics.

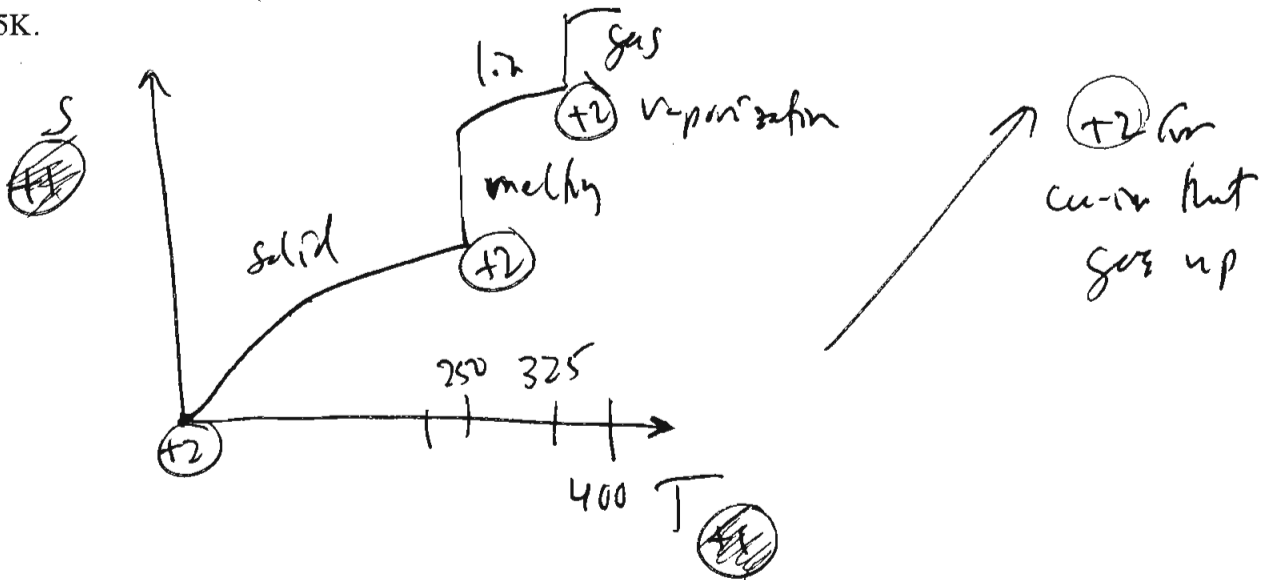
~~(just)~~  
 At absolute zero,  $T$ , the entropy of a pure uniform solid is zero. Otherwise  $S$  is ~~never~~ always  $> 0$ .  
 [Just " $S > 0$  at  $T = 0$ " is okay]

(b; 6 pts) We have noted that there is no absolute energy scale. In contrast, tabulated entropy values

$S^\circ$  (entropy at 1 atm and 298 K) are given as absolute numbers. Explain how it is possible to obtain absolute entropies, by describing qualitatively how the numbers are obtained.

$\Delta S$   $\int \frac{dq}{T}$  so as we add heat to a substance to bring it to  $T$  starting at absolute zero we can calculate  $\Delta S$  relative to  $0$ , therefore an absolute  $S$ . In practice, ~~but~~ we integrate exptl data on heat capacity vs.  $T$ .

(c; 8 pts) Sketch a curve for  $S$  vs.  $T$ , for  $T$  from 0 to 400K, for a substance that melts at 250 K and boils at 325K.





(f; 6 pts) Finally, based on what you know about H-bonding in water, rationalize why Trouton's rule fails for water, and predict whether  $\Delta H^\circ_{\text{vap}}/T_b$  for water is larger or smaller than the value predicted by Trouton's rule.

- Strong H-bonding in water means that the enthalpy of vaporization is much larger than for the other molecules, and the gain in entropy upon going into the gas is much larger breaking up ordered water structure.

$\Delta H^\circ_{\text{vap}}/T$  is larger than  $80 \text{ J/K}$  due to highly ordered H bond network in  $\text{H}_2\text{O}(l)$ .

Page	Score
2	/20
3	/30
4	/22
5	/18
6	/19
7	/16
8	/13
9	/22
10	/20
11	/14
12	/6
<b>Total</b>	<b>/200</b>

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