

Chemistry 271, Section 23xx  
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University of Maryland, College Park

Your Name: Key  
Your SID #: \_\_\_\_\_

General Chemistry and Energetics  
Exam I (100 points total)

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

November 6, 2013

You have 50 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.

Useful Equations:

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

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

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

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

$$S = k_B \ln W$$

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

$$R = N_A k_B$$

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

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

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

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

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

$$n_i/n_0 = \omega_i \exp[-(\varepsilon_i - \varepsilon_0)/kT]$$

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

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

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

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

$$E = \sum n_i \varepsilon_i$$

$$N = \sum n_i$$

$$H = E + PV$$

Chemical standard state: 1 M solutes, pure liquids, 1 atm gases

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. (30 pts) Fundamental thermodynamics

(a; 6 pts) Define what it means to be a "state function." Explain why it does not make sense to say that a mole of gas has a definite "work content" or "heat content."

- (+3) - A state function has a value that is independent of the path taken to reach the state referred to.
- (+3) - Work and heat are path dependent - we end up different depending on how a system is prepared.

(b; 8 pts) Define what it means for a thermodynamic variable to be "intensive" or "extensive" and give an example of each.

- (+2) Intensive = characteristic of each part of a system, like
- (+2)  $T, P, \mu_x$  - independent of size.
- (+2) Extensive = a property depending on the size or extent of the system - like  $E, V, N, S, H, G$ .

(c; 16 pts) Fill in the table below for the signs of  $\Delta G$  and an example of each reaction.

Type of Reaction	Temp. Range	Sign of $\Delta G$	Example
Exothermic Ordering $\Delta H < 0$ $\Delta S < 0$	Low T	(-)	protein folding, ice freezing
	High T	(+)	
Exothermic Disordering	Low T	(-)	combustion and heating
	High T	(-)	
Endothermic Ordering	Low T	(+)	Compressing a mixture of C, H, N, O in a box, opening it & finding a statue of Elvis.
	High T	(+)	
Endothermic Disordering	Low T	(+)	Ice or protein or DNA melting.
	High T	(-)	

(+1) each

(+2) each

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

**2. (18 pts) Hemoglobin Equilibria**

Polycythemia, the overproduction of red blood cells, can be caused by defective regulation of RBC production (primary polycythemia), or it can be a physiological response to inadequate tissue oxygenation (secondary polycythemia). Polycythemia can cause problems if blood viscosity increases.

Primary

(a; 3 pts) Polycythemia may also increase athletic performance in endurance events. Explain why.

(+3) More RBC's  $\rightarrow$  carry more  $O_2 \rightarrow$  ~~generate~~ more aerobic capacity.  $\uparrow VO_{2max}$

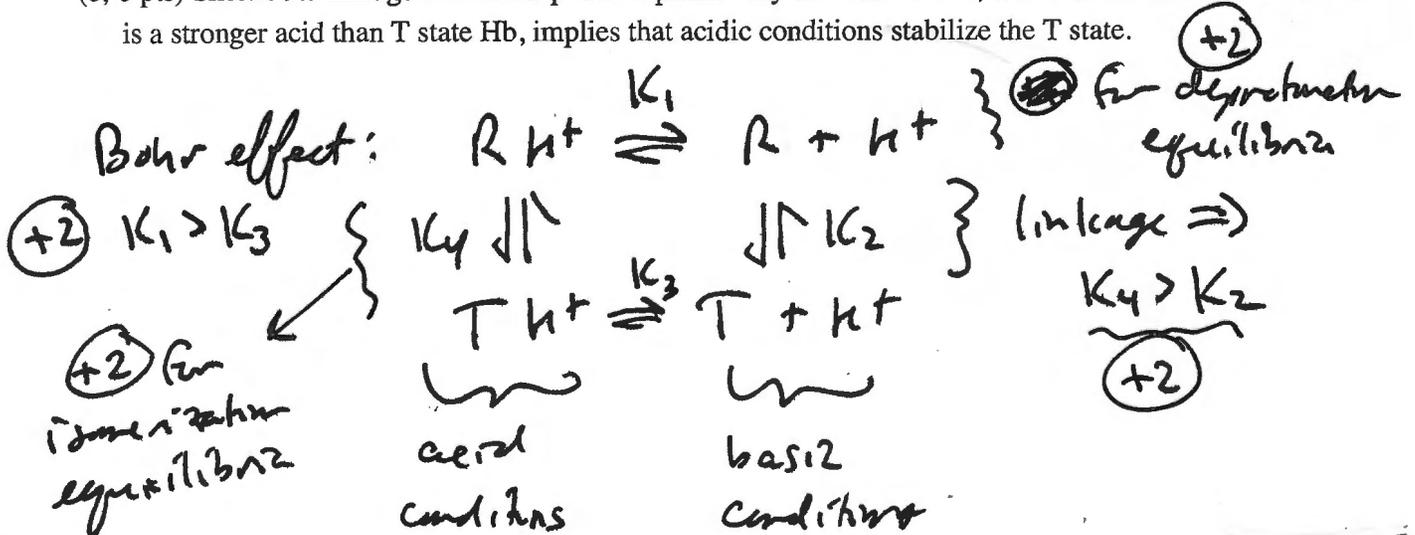
(b; 7 pts) There are many human hemoglobin variants, discovered either by random screening or by analysis of patients who present with health issues. "Hemoglobin Chesapeake" is a mutant with very high oxygen affinity (strong binding). Explain why the patient with Hb Chesapeake suffered from secondary polycythemia. Would you expect him to exhibit extreme athletic performance? Why or why not?

(+3) Very strong  $O_2$  binding  $\rightarrow$  cannot deliver  $O_2$  in tissues.

(+2) Body responds by to low oxygenation by making more RBC's.

(+1) Should not have extreme performance because the polycythemia is an attempt to compensate for the decreased  $VO_2$ .  
(+1) for any explanation

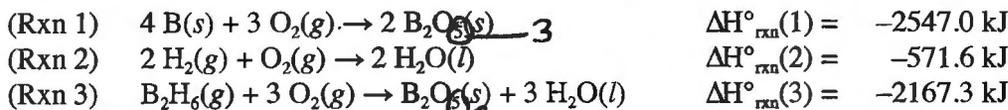
(c; 8 pts) Sketch the linkage relationship that explains why the Bohr effect, which is the fact that R state Hb is a stronger acid than T state Hb, implies that acidic conditions stabilize the T state.



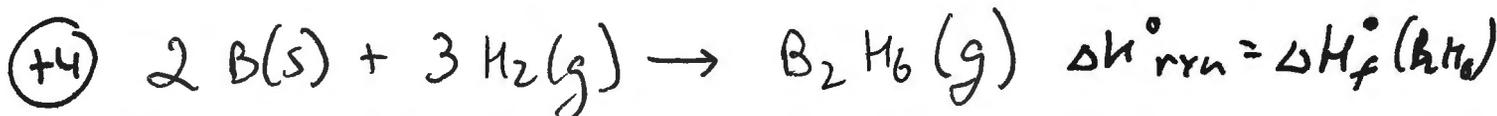
partial credit +1 for any linkage equilibrium Score for the page \_\_\_\_\_  
+2 for drawing a box with linkage

3. (20 pts) Hess's Law

(Adapted from MacQuarrie et al., *General Chemistry*). Diborane, B<sub>2</sub>H<sub>6</sub>, cannot be made directly from boron and hydrogen, but its standard molar enthalpy of formation (ΔH<sub>f</sub><sup>o</sup>) can be determined using the heats of reaction ΔH<sub>rxn</sub><sup>o</sup> for the three combustion reactions below. The standard states of elemental boron, hydrogen, and oxygen, for which ΔH<sub>f</sub><sup>o</sup> = 0, are B(s), H<sub>2</sub>(g), and O<sub>2</sub>(g).

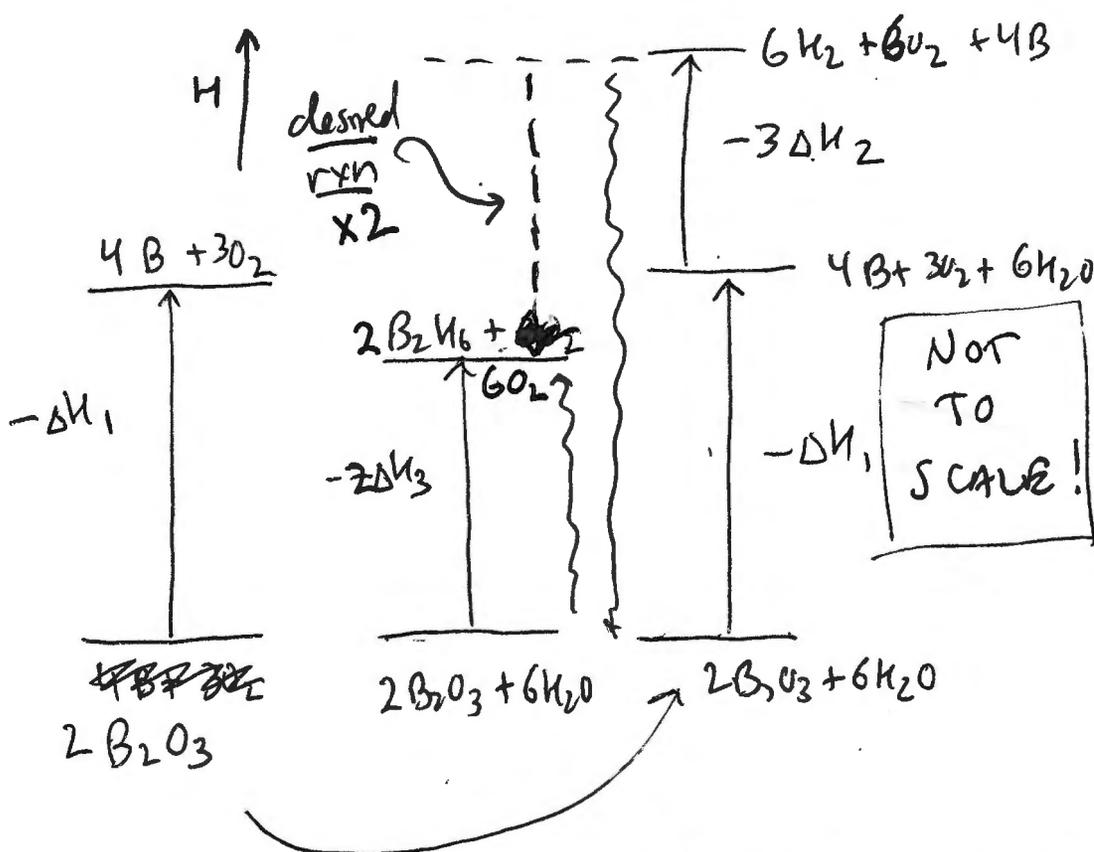


(a; 4 pts) What is the chemical reaction that defines the formation of diborane from its elements, i.e. the reaction that defines ΔH<sub>f</sub><sup>o</sup> of diborane? *represents*



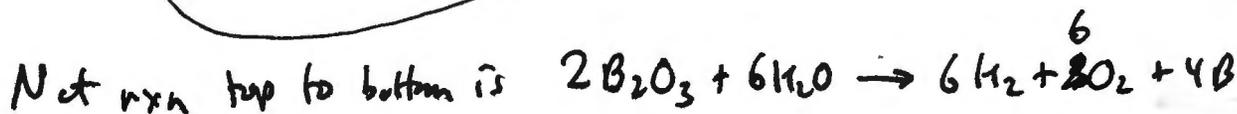
(+2) for incorrect stoichiometry, +1 for anything w/ an element

(b; 8 pts) Sketch a graphical picture of how the three reactions above allow you to use Hess's law to determine the standard molar enthalpy of formation (ΔH<sub>f</sub><sup>o</sup>) of diborane.



] elements

- (+2) for anything that looks like Hess's law
- (+2) for idea of getting to elemental reference state
- (+2) for correct rxns
- (+2) for stoichiometry



Can go either via  $4 B + 3 O_2 + 6 H_2O$  or via  $2 B_2H_6 + 6 O_2$

(c; 8 pts) Calculate the standard molar enthalpy of formation ( $\Delta H_f^\circ$ ) of diborane.

From bottom to top on the diagram:  $(+3)$

+2 for any calculation  
+3 for  $\pm 951.3 \text{ kJ/mol}$  -  
or just adding all of them

$$-2 \Delta H^\circ(\text{rxn 3}) - 2 \Delta H_f^\circ(\text{B}_2\text{H}_6) = -\Delta H^\circ(\text{rxn 1}) - 3 \Delta H^\circ(\text{rxn 2})$$

So 
$$\Delta H_f^\circ(\text{B}_2\text{H}_6) = \frac{1}{2} (\Delta H^\circ(\text{rxn 1}) + 3 \Delta H^\circ(\text{rxn 2}) - 2 \Delta H^\circ(\text{rxn 3}))$$

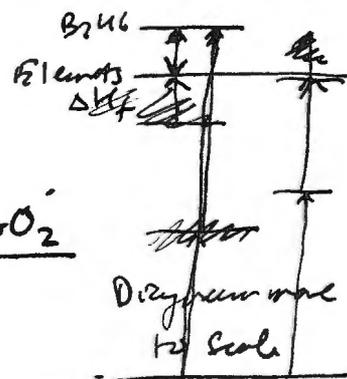
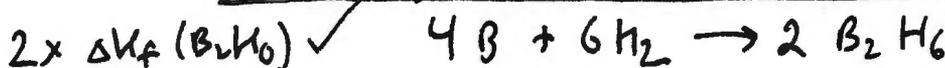
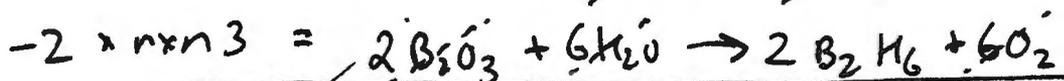
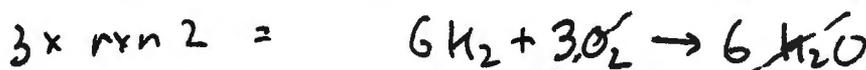
$$= \frac{1}{2} (-2547 + 3(-571.6) - 2(-2167.3)) \text{ kJ}$$

$$= \frac{1}{2} (72.8) = +36.4 \text{ kJ/mol}$$

[which is why you can't make diborane from B + H<sub>2</sub>]

72.8 is +8 if it is consistent w/ part (a)

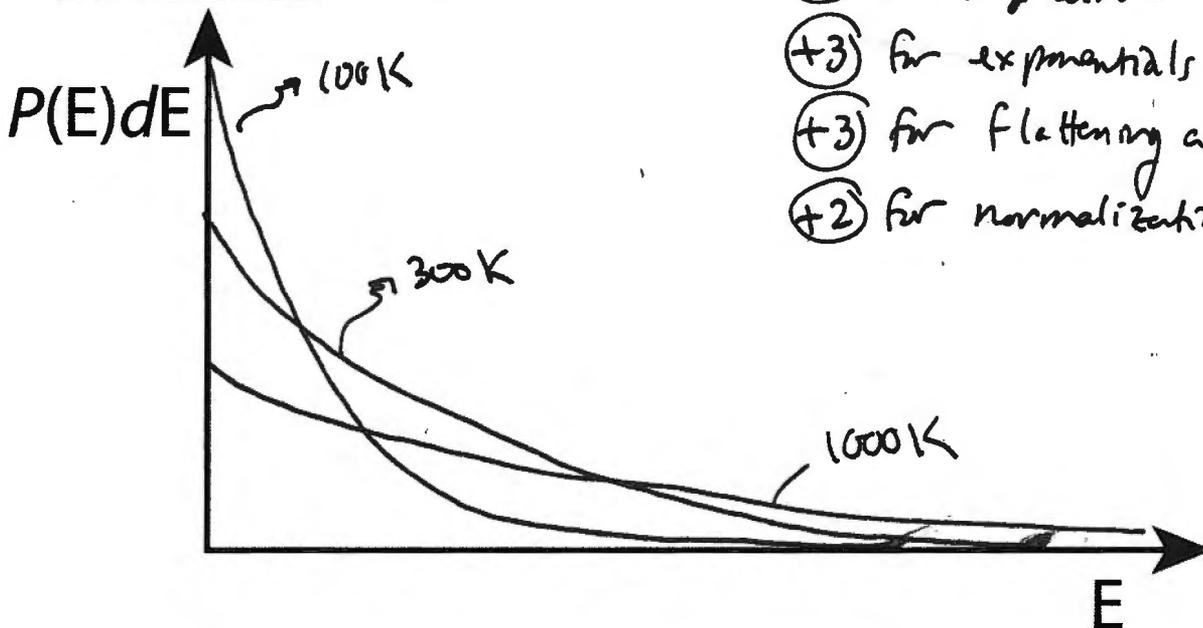
not needed



4. (12 pts) Boltzmann

(a; 9 pts) Sketch the distribution of energy among particles at 100 K, 300 K, and 1000 K on the axes below, where  $P(E)dE$  is the probability of finding a particle of energy between E and E+dE (this is just what we graphed in class). Ignore the degeneracy factor in the Boltzmann distribution. Remember that the curves must be normalized.

- $(+1)$  for any curve
- $(+3)$  for exponentials
- $(+3)$  for flattening at higher T
- $(+2)$  for normalization



(b; 3 pts) Qualitatively explain why adding a little bit of heat to the 100 K sample gives a larger  $\Delta S$  than adding the same amount of heat to the 1000 K sample.

Adding heat at 100K promotes ~~states~~ low-energy molecules into states where there were previously very few occupants  $\rightarrow$  large increase in  $W$ .

At high  $T$ , many states are occupied and the incremental difference is small.

$+1$  for anything  
 $+1$  for sensible difference is small.  
 $+1$  for correct ~~ans~~ +2 for "Marine barracks"

5. (20 pts) Statistical Mechanics

(a; 8 pts) Consider a box containing 8 red balls and 4 green balls that are otherwise identical. If you reach in blindly and pull out 6 balls, how many ways (= microstates) are there to pull out the combinations below? Hint: for each case, calculate  $W$  for pulling  $n$  red and  $W$  for  $m$  green and multiply them.

- (1)  $W_1$ : 3 red and 3 green?
  - (2)  $W_2$ : 4 red and 2 green?
- What is the ratio  $W_2/W_1$ ?

(1) 8 ways to pull first red, 7 ways for 2nd, 6 for third

~~4!~~ 3! indistinguishable permutations  
 so  $W(3 \text{ red}) = \frac{8!}{3! 5!}$   $+1$

$W(3 \text{ green}) = \frac{4!}{1! 3!}$   $+1$

$W_1 = \frac{8 \cdot 7 \cdot 6}{6} \cdot 4 = 224$   $+1$

(2)  $W_2 = \frac{8!}{4! 4!} \cdot \frac{4!}{2! 2!} = \frac{8 \cdot 7 \cdot 6 \cdot 5}{2 \cdot 2 \cdot 4} = 420$   $+1$

$\frac{W_2}{W_1} = \frac{420}{224} = \frac{60}{32} = \frac{15}{8} = 1.875$

Factorials	
0!	1
1!	1
2!	2
3!	6
4!	24
5!	120
6!	720
7!	5,040
8!	40,320
9!	362,880
10!	3,628,800
12!	$4.79 \times 10^8$
15!	$1.31 \times 10^{12}$
20!	$2.43 \times 10^{18}$
25!	$1.55 \times 10^{25}$
30!	$2.65 \times 10^{32}$
40!	$8.16 \times 10^{47}$
60!	$8.32 \times 10^{81}$

$+2$  Score for the page \_\_\_\_\_

(b; 8 pts) If the box instead contains 40 red balls and 20 green balls, how many ways are there to pull out:

(3)  $W_3$ : 15 red and 15 green?

3 (4)  $W_4$ : 20 red and 10 green?

4 What is the ratio  $W_4/W_3$ ?

$$W_3 = \frac{40!}{15!25!} \cdot \frac{20!}{15!5!} = 6.24 \times 10^{14}$$

$$W_4 = \frac{40!}{20!20!} \cdot \frac{20!}{10!10!} = 2.58 \times 10^{16}$$

$$W_4/W_3 = 40.84$$

(c; 4 pts) What do the different ratios you obtained have to do with the themes we discussed in this class? If you were unable to do the problem, predict the relationship between the ratios and discuss it.

(+2)  $W_2$  and  $W_4$  correspond to the predominant configuration -

(+2) As the # of particles goes up the PC becomes more dominant, and we see  $\frac{W_4}{W_3} > \frac{W_2}{W_1}$   $41 > 2 \checkmark$ .

Page	Score
2	/30
3	/18
4	/12
5	/17
6	/11
7	/12
<b>Total</b>	<b>/100</b>

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