

Chemistry 271, Section 23xx

Your Name: _____

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Your SID #: _____

General Chemistry and Energetics

Your Section #: (+1 point) _____

Exam II (100 points total)

November 5, 2012

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.

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

Useful Equations:

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

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

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

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

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

$$\Delta H = q_p$$

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

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

$$w = -\int P dV$$

$$\Delta E = q + w$$

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

$$S = k_B \ln W$$

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

$$E = \sum n_i \varepsilon_i$$

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

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

$$N = \sum n_i$$

$$R = N_A k_B$$

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

$$H = E + PV$$

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. (20 pts) Short Answer/True-False

(a; 10 pts) Fill in the blanks: a(n) _____ (1) is an instantaneous description of all the positions, velocities, and electronic/vibrational/rotational states of all the particles in a system. A collection of (1)'s that all have the same observables like P, V, and T is called a(n) _____ (2). The set of all possible (1)'s at a given total energy is called the _____ (3). For a macroscopic system, almost all of the (1)'s in a(n) (3) will belong to the _____ member of the set of (2)'s.

(b; 10 pts) Identify whether each of the following statements about the Boltzmann Distribution is true or false:

(i) Energy is distributed among particles such that all particles have the same energy.

Circle one: True False

(ii) The number of particles with a given energy is an exponentially decreasing function of the energy (ignoring degeneracy). Circle one: True False

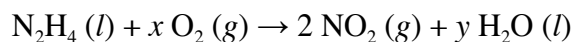
(iii) The B.D. is observed in the maximum possible number of different possible microstates that have a given total energy. Circle one: True False

(iv) The B.D. allows us to determine whether one particular microstate with a given total energy is more likely to be observed than a second particular microstate. Circle one: True False

(v) The B.D. predicts a Gaussian distribution of energy among particles. Circle one: True False

2. (20 pts) Thermochemistry (adapted from Oxtoby)

The combustion of hydrazine (rocket fuel) at 25 °C is described by the equation below:



Balance the equation and calculate the standard enthalpy of reaction $\Delta H_{\text{rxn}}^\circ$ using data in the table at the right. You will need the value for ΔH_f° of $\text{O}_2(g)$. What is it and how do you know? [Note that rocket fuel doesn't burn at 25 °C, but the magic of thermodynamics is that we can calculate the ΔH that would be observed if we could actually do the reaction.]

Heats of Formation (25 °C, 1 atm)	
Substance	ΔH_f° (kJ/mol)
$\text{N}_2\text{H}_4(l)$	50.63
$\text{NO}_2(g)$	33.18
$\text{N}_2(g)$	0
$\text{H}_2\text{O}(l)$	-285.83
$\text{NH}_3(g)$	-46.11
$\text{ZnS}(s)$	-205.98
$\text{ZnO}(s)$	-348.28
$\text{Zn}(s)$	0
$\text{SO}_2(g)$	-296.83
$\text{S}(g)$	278.80
$\text{S}(s, \text{rhombic})$	0
$\text{O}_2(g)$???

3. (15 pts) Solubility Equilibria

What is the pH of a saturated solution of milk of magnesia = magnesium hydroxide $\text{Mg(OH)}_2 (s)$? What would the $[\text{Mg}^{2+}] (aq)$ ion concentration be if the pH were adjusted to 14 with NaOH?

Aqueous Solubility Products (25 °C)

Heterogeneous Equilibrium	K_{sp}
$\text{Mg(OH)}_2 (s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2 \text{OH}^- (aq)$	5.6×10^{-12}
$\text{Ag(OH)} (s) \rightleftharpoons \text{Ag}^+(aq) + \text{OH}^- (aq)$	1.52×10^{-8}
$\text{Al(OH)}_3 (s) \rightleftharpoons \text{Al}^{3+}(aq) + 3 \text{OH}^- (aq)$	1.9×10^{-33}

4. (10 pts) Fundamental Thermodynamics

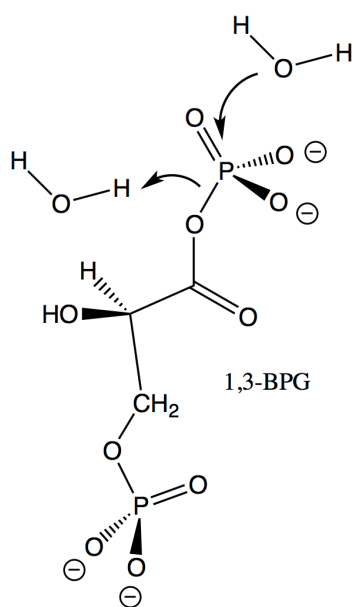
The enthalpy H is defined as $E + PV$. Explain why this definition is convenient in terms of being able to relate calorimetry experiments to state functions.

5. (20 pts) High Energy Bonds

“High energy bonds” are not somehow spring-loaded to release energy upon bond breakage. Rather, they are “high energy” because there is an available reaction pathway that leads to much more stable products, meaning that at equilibrium we see a large excess of products over reactants.

(a; 6 pts) Consider the reaction $A \rightleftharpoons B$, with $K_1 = 10$. We can calculate the fraction of the A+B mixture found as “A”: $[B]$ must be $10 \times [A]$, so the fraction is $[A]/([A]+[B]) = 1/(1+10) = 0.099$. If we couple the $A \rightleftharpoons B$ reaction to $B \rightleftharpoons C$, with $K_2 = 1000$, similarly calculate the fraction of the A+B+C mixture that is found in the form of “A”:

(b; 5 pts) We used ATP as an example of a high-energy molecule. One molecule involved in glycolysis that actually has a higher-energy P–O bond than ATP itself is 1,3-bisphosphoglycerate (1,3-BPG) below. Draw the products of the hydrolysis reaction that breaks the P–O bond as indicated, assuming that the RO^- leaving group picks up a proton from a water molecule so that there is no net consumption or production of protons as written (the other product is HPO_4^{2-} , a form of inorganic phosphate “ P_i ” that is present at pH 7, whereas H_2PO_4^- is not).

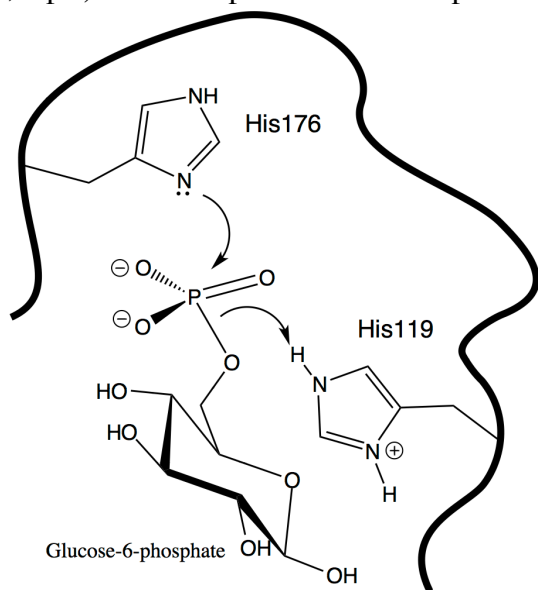


(c; 9 pts) Now, consider the equilibrium between the protonate and deprotonated forms of the product phosphoglyceric acid assuming that K_a is about 10^{-4} as for a typical carboxylic acid. Explain why BPG is a “high energy molecule.” Explain why the bottom P–O bond in BPG is not a high-energy bond.

6. (15 pts) Importance of pH for Enzymes

The importance of active site residue pK_a s is not limited to residues whose only job is to provide or abstract protons. For example, the enzyme glucose-6-phosphatase is responsible for hydrolyzing a phosphate group from glucose-6-phosphate to give glucose and inorganic phosphate P_i . [Irrelevant fun fact: The glucose is then shipped out to the bloodstream to maintain blood glucose homeostasis. Deficiency of this enzyme is the cause of glycogen storage disease I or von Gierke’s disease.]

(a; 5 pts) Draw the product of the step shown in the mechanism below.



(b; 10 pts) G6Pase exhibits a bell-shaped curve for enzymatic activity vs. pH that is very similar to the one we saw for ribonuclease. Explain why the mechanism does not work if the pH is too high, and separately explain why it does not work if the pH is too low. Which histidine residue will have a lower pKa?

Page	Score
1	/1
2	/20
3	/20
4	/15
5	/10
6	/11
7	/14
8	/10
Total	/101

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