Chemistry 366
Thermodynamics
FINAL Exam
MAY 15, 2008

Name ___________________________

Full credit will be given to correct answers only when ALL the necessary steps are shown. DO NOT GUESS THE ANSWER.

This is a closed book exam, and you are responsible to be sure that your exam has no missing pages 11 pages).

If you consider that there is not enough information to solve a problem, you have to specify the missing information and describe the problem solving procedure.

GATE RULES

Rule7

Before you were born, your parents weren't as boring as they are now. They got that way from paying your bills, cleaning your clothes, and listening to you talk about how cool you are. So before you save the rain forest from the parasites of your parents generation, try delousing the closet in your own room.

Rule 8

Your school may have done away with winners and losers, but life has not. In some schools they have abolished failing grades and they'll give you as many times as you want to get the right answer. This doesn't bear the slightest resemblance to anything in real life.

Rule 9

Life is not divided into semesters. You don't get the summers off and very few employers are interested in helping you find yourself. Do that in your own time.

Rule 10

Television is NOT real life. In real life people actually have to leave the coffee shop and go to jobs.

Rule11

Be nice to nerds. Chances are you'll end up working for one.

Once you start the exam, you have up to 2.5 hours to solve it.

Honor Statement

I have neither give nor received aid in this examination.

Full signature ______________________________

Problem 1 (50 points)

At 39.9°C, the vapor pressure of water is 55.03 Torr (component A) and that of methanol (component B) is 255.6 Torr. Using data from the following table, calculate the activity coefficients for both components using a Raoult's law standard state.

x_A	y_A	P (Torr)
0.0490	0.0175	257.9
0.3120	0.1090	211.3
0.4750	0.1710	184.4
0.6535	0.2550	156.0
0.7905	0.3565	125.7

Problem 2 (50 points)

Consider the following sets of populations for four equally spaced energy levels:

ε/k (K)	Set A	Set B	Set C
300	5	3	4
200	7	9	8
100	15	17	16
0	33	31	32

a) Demonstrate that the sets have the same energy.

b) Determine which of the sets is the most probable.

c) For the most probable set, is the distribution of energy consistent with a Boltzmann distribution?

Problem 3(50 points)

a) Evaluate the partion function for Si at 298 Kgiven the following energy levels:

Level (n)	Energy (cm^{-1})	Degeneracy
0	0	1
1	77.1	3
2	223.2	5
3	6298	5

b) At what temperature will the n=3 energy level contribute 0.1 to the electronic partition function?

Problem 4 (50 points)

Determine the internal energy of HCl ($B = 10.59\ \text{cm}^{-1}$ and $\tilde{\nu} = 2886\ \text{cm}^{-1}$) under standard thermodynamic conditions.

Problem 5(50 points)

If you are cooking pasta remember that you need about one liter of water for every 100 g of pasta. So for a pound of pasta you need about a gallon of water. Therefore determine the amount of salt required to increase the boiling temperature of 4 liters of water by 2K.

Hint: Assume ideal behavior of the salt, which is a strong electrolyte, and multiply by 2 the formula for boiling point elevation that we discussed in class.

Problem 6(50 points)

Consider the reaction:

$$H_2(g) + D_2(g) \rightleftharpoons 2\ HD(g) \tag{1}$$

a) Using statistical mechanics, what would be an approximate value of the equilibrium constant? Explain your answer.

b) Based on statistics if we have n_H atoms of hydrogen H and n_D atoms of deuterium, D, we may be able to construct n_p diatomic molecules, where

$$n_p \;=\; \frac{n_H + n_D}{2} \tag{2}$$

Now we consider in how many way can we build n_{HD} molecules? From combinatorial analysis we get

$$W(n_{HD}) \;=\; \frac{n_p!\ 2^{n_{HD}}}{n_{H_2}!\ n_{D_2}!\ n_{HD}!}\ , \tag{3}$$

where

$$n_{H_2} \;=\; \frac{n_H - n_{HD}}{2} \tag{4}$$

$$n_{D_2} \;=\; \frac{n_D - n_{HD}}{2} \tag{5}$$

For example if we have 800 H atoms and 200 of D atoms, calculate from Eq.(3) the number of distinguishable ways of building 160 HD molecules, $W(n_{HD} = 160)$.

c) Given n_H, n_D, and Eq.(3), determine the value of n_{HD} as a function of n_H and n_D that gives the maximum number of ways to build HD molecules. In other words find the max of $W(n_{HD})$.

Hint: You do not need to use the method of Lagrange multipliers.

d) For the value of n_{HD} that gives the largest value of $W(n_{HD})$, calculate the equilibrium constant for Eq.(1) assuming an arbitrary volume V.

e) How does the value of K in d) compares with the value of K in a)?

Bounus question 1(20 points)

Calculate the maximum amount of salt that can be dissolved in one liter of water at 100 C.

Hint: Consider the following equilibrium:

$$NaCl(s) \rightleftharpoons Na^{+}(aq) \ + \ Cl^{-}(aq) \tag{6}$$

Assume that the enthalpy and entropy changes do not depend on temperature, and that the activity coefficients for the ionic species are equal to unity.

Bounus question 2 (20 points)

Prove Eq. (3) in Problem 6.