

**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

Rule 7

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.

Rule 11

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

x_A	y_A	P (Torr)	a_A	a_B	γ_A	γ_B
0.0490	0.0175	257.9	0.082	0.991	1.67	1.04
0.3120	0.1090	211.3	0.419	0.737	1.34	1.07
0.4750	0.1710	184.4	0.573	0.598	1.21	1.14
0.6535	0.2550	156.0	0.723	0.455	1.11	1.31
0.7905	0.3565	125.7	0.814	0.316	1.03	1.55

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

- Demonstrate that the sets have the same energy.
- Determine which of the sets is the most probable.
- For the most probable set, is the distribution of energy consistent with a Boltzmann distribution?

a) The total energy is equal to the sum of energy associated with a given level times the number of particles in that level. We will leave the energy in units of

ϵ/k when performing the sum, then multiply the result by k after summation to convert the answer to joules. For set A:

$$\begin{aligned}
 E &= \sum_n \epsilon_n a_n = \epsilon_0 a_0 + \epsilon_1 a_1 + \epsilon_2 a_2 + \epsilon_3 a_3 \\
 &= (0 \text{ K})(33) + (100 \text{ K})(33) + (200 \text{ K})(33) + (300 \text{ K})(33) \\
 &= (4400 \text{ K})(1.38 \times 10^{-23} \text{ J K}^{-1}) = 6.07 \times 10^{-20} \text{ J}
 \end{aligned}$$

Repeating this calculation for Sets B and C reveals that all three sets contain the same energy.

- b) The most probable distribution of energy will be that distribution with the greatest weight. Calculating the weight associated with the distributions for each set reveals that set C is the most probable:

$$W_A = \frac{N!}{\prod_n a_n!} = \frac{N!}{a_0!a_1!a_2!a_3!} = \frac{60!}{(33!)(15!)(7!)(5!)} = 1.21 \times 10^{27}$$

$$W_B = \frac{N!}{\prod_n a_n!} = \frac{60!}{(31!)(17!)(9!)(3!)} = 1.31 \times 10^{27}$$

$$W_C = \frac{N!}{\prod_n a_n!} = \frac{60!}{(32!)(16!)(8!)(4!)} = 1.56 \times 10^{27}$$

- c) The occupation numbers corresponding to the Boltzmann distribution are given by:

$$a_i = Np_i = \frac{Ne^{-\beta\epsilon_i}}{q}$$

The ratio of any two occupation numbers for a set of non-degenerate energy levels is given by:

$$\frac{a_i}{a_j} = e^{-\beta(\epsilon_i - \epsilon_j)} = e^{-\left(\frac{\epsilon_i - \epsilon_j}{k}\right)\frac{1}{T}}$$

The above expression suggests that the ratio of occupation numbers can be used to determine the temperature. For set C, comparing the occupation numbers for level 2 and level 0 results in:

$$\frac{a_2}{a_0} = e^{-\left(\frac{e_2 - e_0}{k}\right) \frac{1}{T}}$$

$$\frac{8}{32} = e^{-\left(\frac{200 \text{ cm}^{-1} - 0 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}}\right) \frac{1}{T}}$$

$$T = 144 \text{ K}$$

Repeating the same calculation for level 3 and level 0:

$$\frac{a_3}{a_0} = e^{-\left(\frac{e_3 - e_0}{k}\right) \frac{1}{T}}$$

$$\frac{4}{32} = e^{-\left(\frac{300 \text{ cm}^{-1} - 0 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}}\right) \frac{1}{T}}$$

$$T = 144 \text{ K}$$

The distribution of energy in set C is in accord with the Boltzmann distribution.

Problem 3(50 points)

a) Evaluate the partition function for Si at 298 K given 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?

a)

$$\begin{aligned}
 q_E &= \sum_n g_n e^{-\frac{E_n}{kT}} = 1e^{0} + 3e^{-\frac{77.1 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + 5e^{-\frac{223.2 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + 5e^{-\frac{6298 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} \\
 &= 1 + 3e^{-\frac{77.1 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + 5e^{-\frac{223.2 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + 5e^{-\frac{6298 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} \\
 &= 1 + 3(0.689) + 5(0.340) + 5(6.22 \cdot 10^{-14}) \\
 q_E &= 4.77
 \end{aligned}$$

b) Focusing on the contribution to q_E from the $n = 3$ level:

$$\begin{aligned}
 0.1 &= g_3 e^{-\frac{E_3}{kT}} = 5e^{-\frac{6298 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(T)}} \\
 3.91 &= \frac{6298 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(T)} \\
 T &= \frac{6298 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(3.91)} \\
 T &= 2318 \text{ K}
 \end{aligned}$$

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.

The translational and rotational energetic degrees of freedom will be in the high temperature limit; therefore, their contribution to the molar internal energy will be $3/2 RT$ and RT , respectively, with $n = 1 \text{ mol}$. The vibrational contribution still remains, and is calculated as follows:

$$\begin{aligned}
 q_v &= \frac{1}{1 - e^{-\beta h c \tilde{\nu}}} \\
 U_V &= \frac{-N}{q_v} \left(\frac{\partial q_v}{\partial \beta} \right)_V = \frac{-n N_A}{q_v} \left(\frac{\partial}{\partial \beta} (1 - e^{-\beta h c \tilde{\nu}})^{-1} \right)_V \\
 &= \frac{-n N_A}{q_v} \left(- (h c \tilde{\nu} e^{-\beta h c \tilde{\nu}}) (1 - e^{-\beta h c \tilde{\nu}})^{-2} \right) \\
 &= \frac{n N_A h c \tilde{\nu} e^{-\beta h c \tilde{\nu}}}{1 - e^{-\beta h c \tilde{\nu}}} = \frac{N_A h c \tilde{\nu}}{e^{\beta h c \tilde{\nu}} - 1} \\
 &= \frac{n N_A (6.626 \times 10^{-34} \text{ J s}) (3.00 \times 10^{10} \text{ cm s}^{-1}) (2886 \text{ cm}^{-1})}{e^{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(2886 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})}} - 1} \\
 &= n (0.03 \text{ J mol}^{-1}) \\
 U_{V,m} &= 0.03 \text{ J mol}^{-1} \\
 U_{\text{total},m} &= U_{T,m} + U_{R,m} + U_{V,m} = \frac{3}{2} RT + RT + 0.03 \text{ J mol}^{-1} = 6.19 \text{ kJ mol}^{-1}
 \end{aligned}$$

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.

From our analysis in class we have an expression for the change in boiling temperature,

$$\Delta T_b = K_b \gamma m , \quad (1)$$

where m is the molality

In the case of water, $K_b = 0.561 \text{ K kg/mol}$, since we can consider the ideal case, $\gamma = 1$, we get

$$2 \text{ K} = 0.51 \frac{\text{K kg}}{\text{mol}} m \quad (2)$$

In our case we can approximate that 4 L weight 4 kg.

$$m = 3.92 \frac{\text{mol}}{\text{kg}} = \frac{x}{4 \text{ kg}} , \quad (3)$$

or

$$x = 15.7 \text{ mol of NaCl} , \quad (4)$$

So we need a mass of

$$\text{mass}_{\text{NaCl}} = (23.0 + 35.5) \frac{\text{g}}{\text{mol}} 15.7 \text{ mol} = 917.6 \text{ g} , \quad (5)$$

Our answer to two sig figs is:

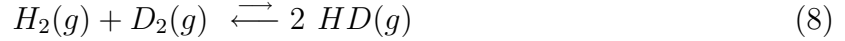
$$\text{mass}_{\text{NaCl}} = 920. \text{ g of NaCl} , \quad (6)$$

or

$$\text{mass}_{\text{NaCl}} = 230. \text{ g of NaCl per liter of water} . \quad (7)$$

Problem 6(50 points)

Consider the reaction:



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

From statistical mechanics we know that the equilibrium constant can be expressed in terms of the molecular partition function as

$$K = \frac{(q_{HD})^2}{q_{H_2} q_{D_2}}. \quad (9)$$

The molecular partition functions q_i s are almost the same except for the symmetry factor in the rotational partition function. For q_{HD} we have a $\sigma_{HD} = 1$, while for molecular hydrogen and deuterium we have a $\sigma_{H_2} = \sigma_{D_2} = 2$. Therefore

$$K \approx \frac{\left(\frac{1}{\sigma_{HD}}\right)^2}{\frac{1}{\sigma_{H_2}} \frac{1}{\sigma_{D_2}}} = 4. \quad (10)$$

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

$$n_p = \frac{n_H + n_D}{2} \quad (11)$$

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

$$W(n_{HD}) = \frac{n_p! 2^{n_{HD}}}{n_{H_2}! n_{D_2}! n_{HD}!}, \quad (12)$$

where

$$n_{H_2} = \frac{n_H - n_{HD}}{2} \quad (13)$$

$$n_{D_2} = \frac{n_D - n_{HD}}{2} \quad (14)$$

For example if we have 800 H atoms and 200 of D atoms, calculate from Eq.(12) the number of distinguishable ways of building 160 HD molecules, $W(n_{HD} = 160)$.

For $n_{HD} = 160$, $n_H = 800$, and $n_{D_2} = 200$, we have $n_p = 500$, $n_{D_2} = 20$, and $n_{H_2} = 320$.
Therefore

$$W(n_{HD}) = \frac{500! 2^{160}}{320! 20! 160!} = 7.35 \times 10^{214}, \quad (15)$$

c) Given n_H , n_D , and Eq.(12), 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.

Since we do not need to use the Lagrange multipliers, we need to express $W(n_{HD})$ as a function of n_D , n_H , and n_{HD} , and take the natural log of W .

$$\ln [W(n_{HD})] = \ln(n_p!) + n_{HD} \ln(2) - \ln(n_{H_2}!) - \ln(n_{D_2}!) - \ln(n_{HD}!) \quad (16)$$

Since we taking the log of a factorial we can use the Stirling's approximation

$$\ln(N!) \approx N \ln(N) - N \quad (17)$$

and get

$$\begin{aligned} \ln [W(n_{HD})] &= \ln(n_p!) + n_{HD} \ln(2) - n_{H_2} \ln(n_{H_2}) + n_{H_2} \\ &\quad - n_{D_2} \ln(n_{D_2}) + n_{D_2} - n_{HD} \ln(n_{HD}) + n_{HD} \end{aligned} \quad (18)$$

Now, for a fixed value of n_H and n_D , we can take the derivative with respect to n_{HD} recalling that n_p is independent of n_{HD} , and that n_{H_2} and n_{D_2} depend on n_{HD} ,

$$\begin{aligned} \frac{d \ln [W(n_{HD})]}{d n_{HD}} &= \ln(2) + \frac{1}{2} \ln(n_{H_2}) + \frac{1}{2} - \frac{1}{2} \\ &\quad \frac{1}{2} \ln(n_{D_2}) + \frac{1}{2} - \frac{1}{2} - \ln(n_{HD}) - 1 + 1 \end{aligned} \quad (19)$$

Next we set the left hand side equal to zero

$$0 = \ln \left(\sqrt{4 \frac{n_{H_2} n_{D_2}}{n_{HD}^2}} \right) \quad (20)$$

or

$$\begin{aligned} 1 &= 4 \frac{n_{H_2} n_{D_2}}{n_{HD}^2} = \frac{(n_D - n_{HD})(n_H - n_{HD})}{n_{HD}^2} \\ &= \frac{n_D n_H - (n_H + n_D)n_{HD} + n_{HD}^2}{n_{HD}^2} \end{aligned} \quad (21)$$

Finally we get that the value of n_{HD} that maximizes W is given by the following relation:

$$n_{HD} = \frac{n_H n_D}{n_H + n_D} \quad (22)$$

d) For the value of n_{HD} that gives the largest value of $W(n_{HD})$, calculate the equilibrium constant for Eq.(8) assuming an arbitrary volume V .

From e) we have the value of n_{HD} , now we calculate the values of n_{H_2} and n_{D_2} ,

$$n_{H_2} = \frac{1}{2} [n_H - n_{HD}] = \frac{1}{2} \left[n_H - \frac{n_H n_D}{n_H + n_D} = \frac{1}{2} \frac{n_H^2}{n_H + n_D} \right] \quad (23)$$

and

$$n_{D_2} = \frac{1}{2} \frac{n_D^2}{n_H + n_D} \quad (24)$$

Finally we can express the equilibrium constant as a function of the concentrations:

$$K = \frac{(n_{HD}/V)^2}{(n_{H_2}/V) (n_{D_2}/V)} = \frac{n_{HD}^2}{n_{H_2} n_{D_2}} = 4 \quad (25)$$

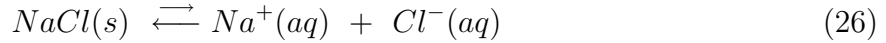
e) How does the value of K in d) compares with the value of K in a)?

They are exactly the same

Bonus 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:



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.

In this problem we are looking at the equilibrium between the solid $NaCl(s)$ and its ions in water. Thus the equilibrium constant, assuming ideal behavior $\gamma'_s = 1$, is given by:

$$K = [Na^+(aq)] [Cl^-(aq)] = x^2, \quad (27)$$

but we also know that the equilibrium constant as a function of temperature is related to the change in Gibbs energy,

$$K = \exp\left(-\frac{\Delta G_{rxn}^o}{R T}\right) = \exp\left(\frac{\Delta S_{rxn}^o}{R}\right) \exp\left(-\frac{\Delta H_{rxn}^o}{R T}\right). \quad (28)$$

where R is actually $R \text{ mol}$

In our case the changes in entropy and enthalpy at $T = 298.0K$ are

$$\Delta S_{rxn}^o = S_f^o[Na^+(aq)] + S_f^o[Cl^-(aq)] - S_f^o[NaCl(s)] \quad (29)$$

$$\Delta H_{rxn}^o = \Delta H_f^o[Na^+(aq)] + \Delta H_f^o[Cl^-(aq)] - \Delta H_f^o[NaCl(s)] \quad (30)$$

From the tables we get

$$\Delta S_{rxn}^o = \text{mol}\left(59.0 \frac{J}{K \text{ mol}}\right) + \text{mol}\left(56.5 \frac{J}{K \text{ mol}}\right) - \text{mol}\left(72.13 \frac{J}{K \text{ mol}}\right) = 43.4 \text{ J/K} \quad (31)$$

$$\Delta H_{rxn}^o = \text{mol}\left(-240.12 \frac{kJ}{\text{mol}}\right) + \text{mol}\left(-167.16 \frac{kJ}{\text{mol}}\right) - \text{mol}\left(-411.15 \frac{kJ}{\text{mol}}\right) = -3.87 \text{ kJ} \quad (32)$$

With these values we find that our equilibrium constant is given by:

$$K(T) = \exp(72.13/(molR)) \exp(-3.87 \text{ kJ}/(molR)) = \exp(5.22) \exp(-465 \text{ K}/T) \quad (33)$$

Therefore for $T = 373.0 \text{ K}$, we get

$$K(373 \text{ K}) = 53.2 = x^2. \quad (34)$$

This result implies that the molar concentration of the ionic species with the solid phase is equal to 7.29 M or 7.29 moles of salt per liter of solution, if we neglect the change in volume due to the ions. Finally, the maximum amount of salt is 424 g of $\text{NaCl}(s)$ per liter of water.

Bonus question 2 (20 points)

Prove Eq. (12) in Problem 6. We start by considering n_p molecules, and consider the number of way can select n_{H_2} molecules out of n_p ,

$$C_{n_p}^{n_{H_2}} = \frac{n_p!}{n_{D_2}! (n_p - n_{H_2})!} \quad (35)$$

Now we are left with $n_p - n_{H_2}$ molecules, and we want to consider the number of ways that we can select n_{D_2} molecules out of $n_p - n_{H_2}$,

$$C_{n_p - n_{H_2}}^{n_{D_2}} = \frac{(n_p - n_{H_2})!}{n_{H_2}! (n_p - n_{H_2} - n_{D_2})!} \quad (36)$$

Notice that $n_{HD} = n_p - n_{H_2} - n_{D_2}$ therefore the number of ways that we can select n_{HD} molecules out of n_{HD} is one, but for each molecule we have two choices between HD or DH , therefore we have $2^{n_{HD}}$ possible ways of selecting n_{HD} molecules

Finally the number of way that we can select n_{H_2} , n_{D_2} , and n_{HD} molecules out of n_p molecules is

$$W(n_{HD}) = \frac{n_p!}{n_{D_2}! (n_p - n_{H_2})!} \frac{(n_p - n_{H_2})!}{n_{H_2}! (n_p - n_{H_2} - n_{D_2})!} 2^{n_{HD}} = \frac{n_p! 2^{n_{HD}}}{n_{H_2}! n_{D_2}! n_{HD}!} \quad (37)$$