University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Homework Assignment 7; Due at midnight on 3/04/15

1) The energetics of the delocalized electrons (i.e. π electrons) in cyclic conjugated molecules like benzene can be treated as particles on rings. Assume the π electrons in benzene move on a ring of radius 1.39 Angstroms.

a) How many π electrons are there in benzene? Using a particle on a ring model, calculate the energy of the highest occupied molecular orbital (i.e. the HOMO) in benzene. Calculate the energy of the lowest unoccupied molecular orbital (i.e. the LUMO)in benzene.

b) Calculate the energy change when an electron absorbs radiation and passes from the HOMO to the LUMO in benzene.

c) Calculate the wavelength of light that is absorbed when an electron in benzene makes a transition from the HOMO to the LUMO. Note: The experimentally observed wavelength is 268 nm. How good is the particle on a ring approximation for the energetics of delocalized electrons in benzene?

2) Nitric oxide $^{14}N^{16}O$ has a bond length of 121.0 pm. In this problem we will first assume the rotation of NO in the gas phase can be treated classically and then we will compare the classical energy of rotation to the quantum mechanical rigid rotor model. In this problem, neglect the vibration of the N-O bond.

a) Assuming the rotation of $^{14}N^{16}O$ can be treated classically, use the equipartition principle to calculate the average rotational energy per molecule at T=300K.

b) Assume that the rotation of $^{14}N^{16}O$ in the gas phase can be treated using the quantum mechanical rigid rotor model. Determine the quantum state ℓ that corresponds to the average energy calculated in part a. What is the degeneracy of this state?

c) Suppose a $^{14}N^{16}O$ molecule adsorbs from the gas phase onto a flat surface where its subsequent motion can be treated using the quantum mechanical planar rigid rotor model. Assuming the temperature on the surface is still T=300K, determine the average classical rotational energy per molecule and also determine the quantum state that corresponds to this energy.

d) Using your result from part b, calculate the energy level spacing between the J and J+1 rotational states. Similarly, using your result from part c calculate the energy level spacing for the plane rigid rotator. From these energy level spacings, compare the importance of quantum effects in the rotation of $^{14}N^{16}O$ in the gas phase versus on the surface. Calculate the rotational partition functions for each case in b and c. Assume T=300K.

3) Here are some partition function problems for translational, rotational, and vibrational motions.

a) Calculate the translational partition function for the H_2 molecule in a cubic box with each side equal to 10 μm. Assume T=300K. Repeat the calculation for I_2.

b) The bond force constant for H_2 is $\kappa_{H_2} = 550 Nm^{-1}$ whereas the bond force constant for I_2 is $\kappa_{I_2} = 170 Nm^{-1}$. Calculate the bond vibration frequencies ν for H_2 and I_2. For H_2 and I_2 calculate the vibrational partition functions at T=300K and the probabilities of finding each molecule in its ground and first excited vibrational states. Based on your results, are quantum effects more important for the bond vibrations of H_2 or I_2? Explain.

c) The bond length of H_2 is 74 pm and for I_2 the bond length is 267 pm. Calculate the moment of inertia for H_2 and also for I_2. Calculate the rotational partition functions for H_2 and I_2 at T=300K, assuming a rigid rotor model. Calculate also the probabilities of being in the ground rotational state and first excited rotational state for H_2 and I_2. Based on your results, are quantum effects more important for the rotational motion of H_2 or I_2? Explain.

d) Based on your answers for parts a-c, arrange translational, vibrational , and rotational motions in the order of the importance of quantum effects.

4) For hydrogen atoms, the orbital electronic energy is given by $E_n = -\frac{\Re}{n^2}$ where the Rydberg constant $\Re = 2.18 \times 10^{-18} J$ and n=1,2,3... The degeneracy of each orbital goes like $g_n = 2n^2$. Therefore the electronic partition function for hydrogen is:

$$q_{elec} = \sum_{n=1}^{\infty} g_n e^{-E_n/k_BT} = \sum_{n=1}^{\infty} 2n^2 e^{-E_n/k_BT} = e^{-E_1/k_BT} \sum_{n=1}^{\infty} 2n^2 e^{-\Delta E_n/k_BT} = q' e^{-E_1/k_BT}$$

where $q' = \sum_{n=1}^{\infty} 2n^2 e^{-\Delta E_n/k_BT}$ and $\Delta E_n = E_n - E_1$. The probability of being in the nth electronic level is $P_n = \frac{g_n e^{-E_n/k_BT}}{q_{elec}}$ where $g_n=2n^2$.

a) Calculate the population ratios: $\frac{P_2}{P_1}, \frac{P_3}{P_1}$. Assume T=300K.

b) Based on your answer in part a, estimate the reduced electronic partition function q' for hydrogen at T=300K.

c) Repeat the calculations in parts a and b for T=2000K. is there much of a tendency to populate more excited electronic states at this temperature? Explain.

5) Multi-electron atoms have energies and degeneracies quite different from single electron atoms like hydrogen. It is conventional to report such energies in units of wave numbers (i.e. cm^{-1}). You convert energies in wave numbers to Joules by multiplying the wave number energy by a factor of hc where h is Planck’s constant and c is the speed of light: c=3x10^{10} cm s^{-1}. For fluorine (F) atoms the lowest electron energies used in the calculation of q' are:

Level	1	2	3	4	5	6	7
Degenercy g_n	4	2	6	4	2	4	2
Energy (cm^{-1})	0	404	102407	102681	102841	104732	105057

a) Using the data in this table calculate the electronic partition function q' of fluorine at 300Kand 2000K.

b) Calculate the fraction of fluorine atoms in the ground state and first excited states at T=300K and 2000K.

c) Calculate the partition function for fluorine $q = q_{trans} q'_{elec}$ at T=2000K assuming fluorine behaves ideally at this temperature. Assume V=1m^3.