Chem. 562
Fall 2009

Name __________________________

Please put your name on all pages.

Exam 3

Calculators are not allowed for this exam.

You will find that for many questions it is useful to know that $e^{-1} \approx 0.4$ and that other powers can be obtained using $e^{-n} = (e^{-1})^n \approx (0.4)^n$.

1. This exam contains 9 pages of questions and instructions, three pages of equations, a page of wavefunctions, a periodic table, and a page of constants and conversion factors.

2. Show your work and make your reasoning clear.

3. You have 2.0 hours to work on the exam.

1.__________/20

2.__________/25

3.__________/15

4.__________/20

4.__________/20

Total_______/100

Answer the following 4 miscellaneous questions about entropy and collision theory.

1a. (5 pts). What is the statistical prediction for the entropy of a perfect crystal at T=0 ? Give a mathematical explanation.

1b. (5 pts.) If there are two ways to orient each molecule in a crystal, how many ways W are there to orient a mole (N_A – Avagardo's number) of such molecules? Use that result to calculate the entropy of the crystal of N_A molecules.

1c (5 pts). Qualitatively explain how the entropy would be different for a gas of indistinguishable and non-interacting <u>polyatomic</u> versus <u>monatomic</u> molecules.

Chem. 562 Name ___________________________
Fall 2009

1d. (5 pts.) Consider an elementary bimolecular reaction. If the masses of the gaseous molecules magically increased their masses by a factor of three (such as by forming non-reactive trimers), what does collision theory predict for the change in the rate constant?

2. To estimate the population of a state, scientists often talk about energy levels in terms of kT. Answer the following questions to learn why.

2a. (5 pts.) Derive the equation for q^v for a harmonic oscillator.

2b. (5 pts) Write an expression that gives the population of the eigenstate ε_i for a harmonic oscillator.

2c. (10 pts) Consider a harmonic oscillator that has an energy level spacing of kT. For each eigenstate drawn below, label its population.

——— 3kT

——— 2kT

——— kT

——— 0

2d. (5 pts) In lecture, we found that I_2, which has a frequency of $\tilde{\upsilon} = 215\ cm^{-1}$, has 23% of its population in the $\upsilon=1$ level and that Cl_2, which has a frequency of $\tilde{\upsilon} = 560\ cm^{-1}$, has 6% of its population in the $\upsilon=1$ level. Using your results above, what is the approximate population of $\upsilon=1$ for BrI, which has a frequency of $\tilde{\upsilon} = 410\ cm^{-1}$? Show your work.

Answer the following 2-part question to learn about the density of the atmosphere.

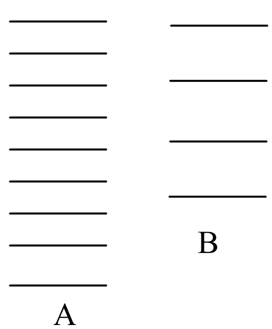
3a. (5 pts.) Write the expression for the ratio of the number of molecules in a state with energy ε_1 to the number in a state with energy ε_0 at a temperature T.

3b. (10 pts.) The energy of a particle in a gravitational field is $\varepsilon = mgh$ where *m* is the mass of the particle, *h* is the height above a reference point, and $g \approx 10$ m/s2 is the acceleration of gravity. Estimate the ratio of the number density of O_2 at 8314 m compared to that at sea level. Assume that the temperature is 320 K.

Name ___________________________

4a. (5 pts.) Derive the equation for the equilibrium constant K for the chemical reaction $A \leftrightarrow B$, where the eigenstates of A and B are spaced by ε_A and ε_B, respectively, and the relative energy of B is offset by $\Delta\varepsilon_{AB}$. Start from the definition of K = [B]/[A].

4b. (5 pts) If the eigenstates have the relative spacings drawn below, explain whether the equilibrium constant will favor A or B and why.



4c. (5 pts) Calculate K for $\varepsilon_A = kT$, $\varepsilon_B = 2kT$ and $\Delta\varepsilon_{AB} = 2\ kT$ for vibrational mode in the high temperature limit. Round your answer to 1 significant digit.

4d. (5 pts) To make K = 1, what value would $\Delta\varepsilon_{AB}$ need to be? Write an expression (do not evaluate).

Name ___________________________

5a. (5 pts) Write out the equation for the canonical partition function Q in terms of the molecular translational, rotational, and vibrational partition functions (e.g. q^T, q^R, q^V) for a homonuclear diatomic gas in the high temperature limit.

5b. (5 pts.) Find the equation for <E^T> for the homonuclear diatomic gas.

Name ___________________________

5d. (10 pts) Shown below is Cp measured as a function of T for Cl_2, Br_2 and I_2. Answer the following questions, assuming that the gases are non-interacting. As a reminder, Cp = Cv + R, and that Cv = $\left(\frac{\partial\langle E\rangle}{\partial T}\right)_V$.

1. What values of Cp should Cl_2, Br_2 and I_2 reach as the temperature is raised?
2. At T = 300 K, why does Cl_2 have a much lower value of Cp than I_2?
3. What value would you expect Cp to reach at high T for a linear triatomic like HCN? Explain.