Chemistry 549
Spring, 2004
Problem Set 4
Due Monday, April 12

Read Chapter 10 and Appendices 1 and 2.

1) Problem 10.6 in the text,

2) Write a *Mathematica* program to calculate the rate constant for a general collinear reaction of the form

$$A + BC \rightarrow products$$

Your program should have the following sections in it:

1. A table of physical constants that you can use later (k_B, h, etc) and relevant conversion factors (wave numbers to joules, etc).
2. A section containing the physical properties of the reactants and transition state (temperature, masses, frequencies, bond lengths, etc.) Do not input the moments of inertia; the program should calculate them from the masses and bond lengths.
3. Calculate and print the deBroglie lengths and the translational partition functions. Print the ratio of translational partition functions of the transition state to those of the reactants.
4. Calculate and print the moments of inertia and the rotational partition functions. Print the ratio of rotational partition functions for the transition state to those of the reactants.
5. Calculate and print all the vibrational partition functions. Print the ratio vibrational partition functions of the transition state to those of the reactants.
6. Calculate and print the rate constant, k(T), for $F+H_2$ at 300K, and express your answer in liter/mol/sec. You may use the values in the textbook to check your work. Note that the text puts the rotational symmetry factor into the quantity L.

3) Generalize the previous program to allow you to calculate and plot k(T) for a range of temperatures. This is easier than it sounds. What you do is set up the program *without defining the value of T*. Then at the end of the program you add the instructions similar to

```
Do[Print["T=  ", T, "   k=  ", rateconstant], {T, Tmin, Tmax, Tinc}]
Plot[rateconstant, {T, Tmin, Tmax}, PlotRange → All]
```

Here *Tmin* is the lower end of the temperature range, *Tmax* is the upper end, and *Tinc* is the step size that you want printed out.
Use this program to evaluate and plot the rate constant for $F+H_2$ between 300 and 500K in steps of 100K.

4) Use your program to calculate the isotope effect for the reaction $Cl+H_2$. The potential parameters are taken from J. Chem. Phys. **90**, 3110 (1989), Table VII. I have copied the necessary information below. The atoms are labeled as A+BC.

Transition state property	$Cl+H_2$	$Cl+D_2$
R_{AB} (Bohr)	2.64	2.64
R_{BC} (Bohr)	1.88	1.88
V_{barr} (kcal/mol)	7.70	7.70
$\hbar w_{str}$ (cm^{-1})	1362	987
$\hbar w_{bend}$ (cm^{-1})	712	505

Note that the listed barrier height, V_{barr}, does not include the zero point energy of the reactants or the transition state. You have to do that yourself.

Calculate $\frac{k_{H_2}}{k_{D_2}}$ for 200 < T < 600 K.

5) Normal mode analysis of linear triatomic molecules:

1. Write a *Mathematica* program to solve for the frequencies and normal modes of a symmetric triatomic molecule, ABA, and compare your results with the values derived in lecture. To do this, you need to read how *Mathematica* handles matrices, determinants, etc. If you are unable to get the program to do everything in one run, it is OK to re-enter the results from the frequency analysis in order to solve for the normal modes.
2. Derive the matrix equation needed to solve the previous problem for an asymmetric triatomic molecule, ABC. You need to specify two force constants and three masses.
3. Write a *Mathematica* program to solve for the frequencies and normal modes of the asymmetric triatomic molecule.