ChE 528
Problem Set 5
Due Thursday 10/9/2003

1. Go through the Beta version of the Quantum Web Module on the CRE website. Write a paragraph of what you learned. Include a list of four things that you liked and four things that need to be improved.

2. List four approximations that were made in developing the transition state theory and how seriously will each affect the estimate of the frequency factor A?

3. Approximately how much error would be introduced in the $H \overset{d_1}{\cdots} H \overset{d_2}{\cdots} Br$ transition state example given in Laidler if the distances d_1 and d_2 were off by a factor of 2 or more? How abut if the frequencies were off by 1/2? Which is the most critical measurement for calculating any of the parameters?

4. Calculate the specific reaction rate at 300K for the reaction

$$F + H_2 \rightarrow HF + H$$

using both collision theory and transition state theory. Use Cerius[2] (or literature references) to estimate any parameters you may need. We will use in this Cerius2 to study the S_{N2} reaction:

$$F + H_2 \rightarrow HF + H$$

We will calculate the thermo-physical properties of the reactants and the transition state in order to estimate the partition functions, the rate constant, and the activation energy of this reaction.

After following the procedure to load Cerius2, you can follow these steps. (In the following, "click" implies a left click)

I. The H_2 Molecule:

(i) Draw the H_2 molecule:

1. In the Visualizer window, click on **STICK** and change it to **BALL & STICK**
2. In the Visualizer window, click **Build** and select **3-D Sketcher**
3. In the Sketcher window, choose **Sketch with** and select **H**
4. Click once the model window and you will see a hydrogen atom
5. Click again and you will form the H-H molecule

You have now constructed the H_2 molecule

(ii) Optimize the molecule:

1. In the Sketcher window, click and hold **CLEAN**. You will see that the bond distance changes; this is a preliminary optimization of the structure
2. In the Visualizer window, click on **BUILDERS 1** and change it to **QUANTUM 1**.
3. Click on the **MOPAC** tab and click **Run**

4. Rename your file as "H2" (or anything else you may prefer) in the **File Prefix**, change the **Task** to **Geometry Opt. and Frequency** and the **Method** to **PM3**. You may want to run different methods to compare the results.
5. Click on **RUN** and let the run finish; a graph of the IR spectra of H_2 will pop up. Again, because of a graphic bug, you will need to minimize the window and double click on the icon to restore the window.

You have now optimized the H_2 molecule

(iii) Note the results:

1. In the Visualizer window, click on **Geometry** then **Measurements**. You can measure the distance by clicking on the button in the pop-up window and clicking on the H and H atoms in the model window
   What is the H-H bond length? _____
2. In the Visualizer window under MOPAC, click on **Analyze** and choose **Files**. The last run is usually chosen as the default file. If it is not, select the *H2.out* file (or whatever name you selected for your file).
3. Note these values shown in this window:
   What is the Heat of Formation? _____
   What is the Dipole Moment? _____
4. In the Visualizer window under MOPAC, click on **Analyze** and choose **Vibrations**. With the model window visible select a frequency and left click the **Animate** button in order to animate the vibrations. To stop the animation, just left click on the same or another frequency.
   Note the various frequencies: _____, _____
   What do these frequencies represent? _____, _____
5. Run the **Geometry Opt. and Frequency** task again, this time click on **More**, then check **Thermophysical Properties** and choose a temperature range from 290 K to 310 K. After the run is over, click **Analyze**, **Files** and click on **Examine File**. You will see the various partition functions, enthalpies and entropies at various temperatures.
   Note the various properties at 300 K:
   Heat of formation: _____
   Enthalpy: _____
   Cp: _____
   Entropy: _____
   Zero-point energy: _____
   qtrans = _____
   qrot = _____
   qvib = _____

You have now calculated the necessary properties of the H_2 molecule

II. The Transition state F-H-H:

(i) Draw the F-H-H transition state:

1. Start a new session
2. In the Sketcher window, choose **Sketch with** and select **H**
3. Click on the model window at three points to get the H-H-H structure
4. In the Sketcher window, choose **Edit Element** and select **F**

5. Click on the first H atom in the model window; it will now be replaced by F
   The transition state optimization done by Cerius2 is a local optimization process; hence it is necessary to start from appropriate values of the initial guess of the transition structure. Hence, we will use the following geometry as the initial guess.
6. In the Sketcher window, click on **Stretch** and then click on the two hydrogen atoms in the model window
7. Click and hold at another point in the model window and drag your mouse. You will see that the bond length changes (it will elongate or shrink depending on which way you drag the mouse). Adjust the F-H distance to *1.4* A^o. You may have to change the view to **STICK** in order to see these distances clearly.
8. Similarly, change the H-H distance also to 1.4 A^o.
9. In the Sketcher window, click on **Angle** and then click on the two hydrogen atoms and the H atom (outer H first, middle H next and then H) in the model window
10. Click and hold and drag the mouse to change the H-H-H angle close to *180* degrees.

You have now constructed an appropriate starting point for the FHH transition state.

(ii) Optimize the transition state and note the results:

1. In the Visualizer window, click on **BUILDERS 1** and change it to **QUANTUM 1**.
2. Click on the **MOPAC** tab and click **Run**. Rename your file as "FHH" (or anything else you may prefer) in the **File Prefix**, change the **Task** to **TS Optimization** and the **Method** to **PM3**.
3. Click on **RUN** and let it run. Did anything happen to the molecule in the model window? _____
4. In the Run window, change the **Task** to **Frequency** and the **Method** to **PM3**.
5. Now analyze the vibrations as in the previous case. Are there any negative vibrations? If so, how many? _____
   A true transition state will have once negative frequency corresponding to the stretching of the bond that is being formed.
6. After making sure the configuration found is a true transition state, we can start measuring the bond lengths and the angle. In the Visualizer window, click on **Geometry** then **Measurements**. You can measure the distance by clicking on the Distance button in the pop-up window and clicking on the two atoms at the two ends of the bond. You can also measure the FHH angle by clicking on the Angle button and select the atom F, H, and then H.
   What is the F-H bond length? _____
   What is the H-H bond length? _____
   What is the F-H-H angle? _____
7. Note the various positive frequencies: _____, _____
   What vibrations do these frequencies represent? _____, _____
8. You may calculate the partition functions and other thermo-physical properties of this transition state as follows:

- While running the **Frequency** task, click on **More**, then check **Thermophysical Properties** and choose a temperature range from 290 K to 310 K.
- After the run is over, **Analyze, Files** and click on **Examine File**. You will see the various partition functions, enthalpies and entropies at various temperatures
  Note the various properties at 300 K:
  Heat of formation: _____
  Enthalpy: _____
  Cp: _____
  Entropy: _____
  Zero-point energy: _____
  qtrans = _____
  qrot = _____
  qvib = _____

You can now use Transition State theory to calculate the rate of reaction.

5. Circle the correct answer and explain where requested.

   A. The reason that the values of the rotational quantum number, J, have "little, if any" effect on reaction cross section is that the rotational energy, even for values of J as high as 5, is negligible in comparison with minimum kinetic energy necessary for reaction.

   True False Explain

   B. The maximum value of the impact parameter, b_{max}, at which a reactive collision will occur, increases with increasing relative velocity of the reactants.

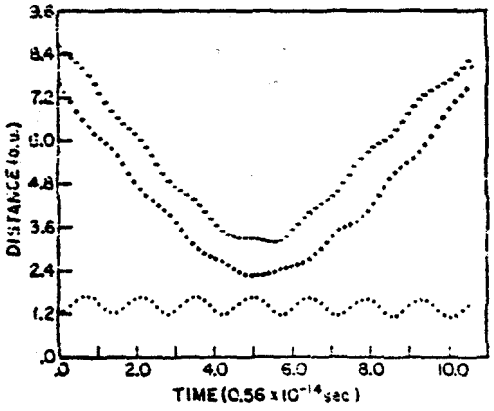
   True False Explain

   C. The minimum kinetic energy necessary for a reactive collision to occur is the difference between the potential energy barrier height relative to the classical ground state and the vibrational energy in the $v = 0$ quantum state.

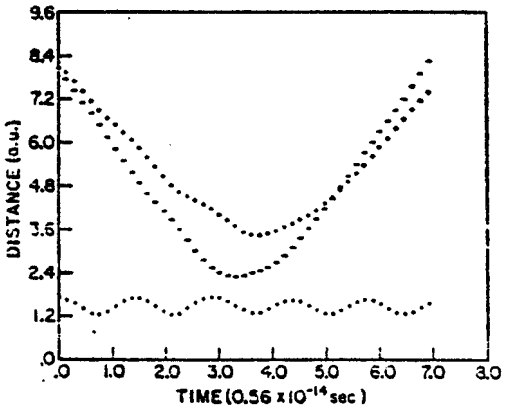
   True False Explain

   D. Each of the Figures below show a non-reactive collision for the same kinetic energy but different quantum states *J*, *v*. If the velocity were increased so that the kinetic energy were very much above the threshold value, which figure (A or B) represents the system which would have the greatest reaction cross section.

   True False Explain



A



B

E. The threshold velocity increases with increasing rotational quantum number but decreases with increasing vibrational quantum number.

True False Explain

F. In the Karplus Theory the impact parameter, b, is chosen randomly in a Monte Carlo procedure in the calculation of the reaction cross section.

True False Explain

G. The minimum kinetic energy (given in terms of the relative velocity) that two molecules (atoms) must have in order to react is equal to the height of the potential energy barrier.

True False Explain

H. The reaction cross section is a function of the frequency of vibration of the reacting molecule.

True False Explain

I. For a "head on collision" in which the impact parameter is zero, the reaction probability for a H_2 molecule in the $v = 0$ vibrational state with no rotation is 1.0.

True False Explain

J. The activation energy is greater than the threshold energy, but less than the barrier height.

True False Explain

K. The sum of the $v = 0$ vibrational energy and threshold kinetic energy is the <u>minimum</u> total energy (relative to the classical ground state) necessary for reaction to occur.

True False Explain

L. The molecular trajectories were calculated by systematically choosing various values of the impact parameter, rotational and vibrational quantum numbers, and the orientation of the H_2 molecule relative to the H molecule and then solving the 12 Hamiltonian Equations numerically.

True False Explain

M. If the reaction probability calculated from the collision trajectories is found to be the following function of the impact parameter

$$P_r = \left[(2 - b)/2\pi\right] \text{ for } b \le 2 \text{ a.u.}$$
$$P_r = 0 \quad \text{for } b > 2 \text{ a.u.}$$

where b and the number 2 are in atomic units (a.u.). The reaction cross section is

(1) 8/3 sq. a.u. $\left(a_o^2\right)$
(2) 4/3 sq. a.u.
(3) 2 sq. au.
(4) 12.56 sq. a.u.
(5) None of the above
(6) Not possible to calculate from the above information

Optional

6. Use Cerius^2 to explore the properties of molecules of your choice. Write a paragraph describing all that you could find out about the molecule using Cerius^2?