Chemistry 549
Spring, 2004
Problem Set 5
Due Friday, April 30

These problems are based on the material in Chapters 8, 9, and 11 plus the supplementary material handed out in class.

1. Problem 11.1

2. Problem 11.2

3. Use the RRKM program to calculate the rate constants for HCl elimination from chloroethylene in problem 11.12 over the temperature range 1200 to 2200 K. Ignore the effects of rotation. Note that $k_\infty$ is found in both files fort90 and fort20. File fort22 contains the bimolecular rate constant $k_p$. The unimolecular rate constant that you need is given by $k_{uni} = k_p[M]$, and [M] is printed in fort90. $k_{uni}$ also is printed as $k_{wc}$ (weak collision) in fort90.
   A. Calculate the rate constants for HCl and DCl elimination in the high pressure limit, and plot their ratio as a function of temperature. Calculate $E_\infty$ and $A_\infty$ for both reactions.
   B. Calculate the pressure falloff curve for HCl elimination, using Ar as the buffer gas. You may assume that the potential parameters in the sample input file that I sent you apply to this molecule as well. To get the $k_{uni}$ to converge to the high pressure limit, you should set the IVR parameter to zero in input 22F.

4. Write a *Mathematica* program to calculate the deflection function for a repulsive exponential and also for a Lennard-Jones potential. If you have trouble setting up the do loop, it is OK to calculate the angles point by point and then plot the results later. Here are some useful suggestions:

   (a) Have the program plot the potential function.
   (b) Find the turning point, $r_c$, by using the FindRoot command, taking r = b as an initial guess.
   (c) To prevent instability in the numerical integral, the lower limit of integration must be a little larger than $r_c$. In other words, start the integral from a point $r_c(1+e)$. You should make $e$ as small as possible, adjusting it by trial and error.

   Now here are the details of the problem.

   A. Use the potential energy function $V = Ae^{-r/a}$, with $A$ = 100 eV and $a$ = 1 Angstrom. It helps to express the energies and distances in reduced units.

Calculate and plot the function $c(b)$ for E = 2 eV, and show the values for small and large values of b. Repeat this calculation for the potential

$$V = 4e\left|\left(\frac{r}{s}\right)^{12} - \left(\frac{r}{s}\right)^{6}\right|$$

for $e$ = 1 eV, $s$ = 1 Angstrom. Calculate and plot the function $c(b)$ for E = 2 eV and find the rainbow angle.

5. Construct the Newton Diagram for collisions of *Rb* with $CH_3Cl$.

The temperature of the Rb and $CH_3Cl$ beams are $T_1$ = 600K and $T_2$ = 300K. Assume that Rb and $CH_3Cl$ each have the most probable thermal velocities.
It will be very helpful to use *Mathematica* for this problem.

A. Calculate the initial laboratory velocities $v_1$ (for *Rb*), $v_2$ (for $CH_3I$), and the velocity of the center-of mass, $V_{CM}$.
B. Consider next the case of elastic scattering. Let $q_{CM}$ be the CM scattering angle of Rb. Calculate the laboratory velocities and laboratory scattering angles of Rb for $q_{CM}$ varying from 0 to 360 degrees.
C. We will leave reactive scattering for another day.