Chemistry 562 **Spring 2012**

Due beginning of class on Friday, May 11th

(Make your reasoning clear. We need to understand your reasoning, not just see the final result.)

1. What is the collision frequency and the time between collisions of a N_2 molecule in an N_2 gas at 1 atm and 300 K? Use a radius of 150 pm for N_2. You may assume that N_2 is an ideal gas.

2. In a dichloromethane solvent, the bimolecular reaction of chlorine radical with cyclohexane

$$Cl + C_6H_{12} \rightarrow HCl + C_6H_{11}$$

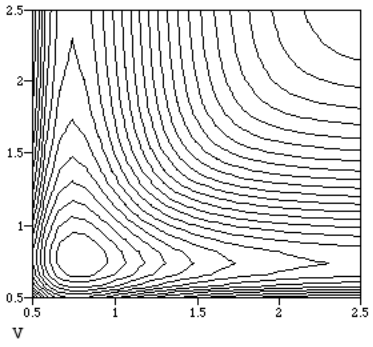
occurs with a bimolecular reaction rate constant of $k_{bi} = 11.4 \times 10^9\ M^{-1}s^{-1}$.

a.) Calculate the diffusion constants of Cl and C_6H_{12} in dichloromethane at 300 K using the Stokes-Einstein equation (equation 24.34). The viscosity of dichloromethane is 0.413 mPa-s and the radius of C_6H_{12} is 0.35 nm. For Cl, use a radius of 0.39 nm (This is the radius of a weak, Cl-dichloromethane complex.). Give your answers in units of nm^2/ns.

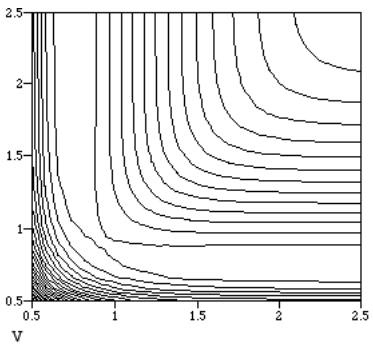
b.) Calculate the reaction radius R^*. How does this compare with the sum of the physical radii of the reactants? Physically, how could you explain any difference you observe? Give your answers in nm. (Be careful to ensure your units work out.)

3. Shown below are the contour plots and surface plots of the potential energy surfaces for the ground and first excited state of a triatomic molecule ABA. (The angle is set to 180 deg.)

Ground State



Excited State



(a) Draw a cut through the potential energy surfaces at the equilibrium bond distance. (In other words, sketch the slice through the potential for one of the A-B bond distances set at R_{eq}.)
(b) What happens when you excite ABS to its first excited state?

4. Shown below is a potential energy surface for the general reaction $AB + B \rightarrow A + B_2$. The reaction is assumed to be collinear.

   a.) Is the reaction exothermic or endothermic?

   b.) Draw the reaction coordinate on the contour plot and then sketch the reaction coordinate, showing products, reactants, and the transition state with the correct relative energies. (This should just be a 2-D sketch.) Is the reaction barrier a late barrier or an early barrier?

   c.) Do you expect the reaction to be faster if B approaches AB with greater translational energy? Do you expect the reaction to be faster if AB is vibrationally excited?