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

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

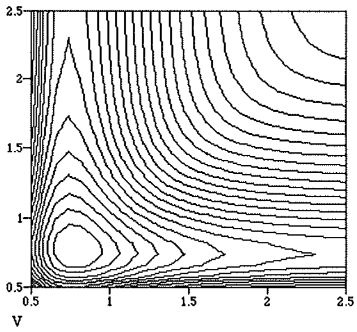
   occurs with a bimolecular reaction rate constant of $k_{bi} = 11.4 \times 10^9\ M^{-1}s^{-1}$.

   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.

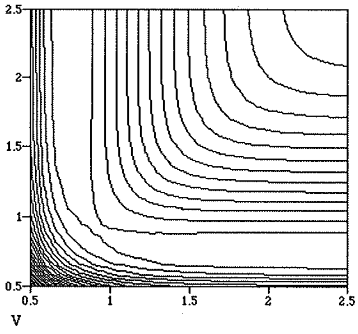
   b.) Calculate the reaction radius R^*. How does this compare with the sum of the physical radii of the reactants? Physically, how could you explain any difference you observe? Give your answers in nm. (Be careful to ensure your units work out.)

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



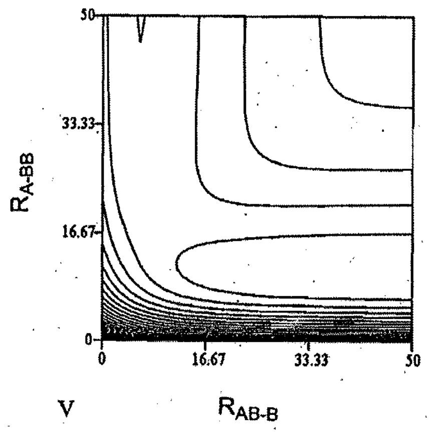
(a) Draw a cut through the potential energy surfaces at the equilibrium bond distance. (In other words, sketch the slice through the potential for one of the A-B bond distances set at R_{eq}.)
(b) What happens when you excite ABA to its first excited state?

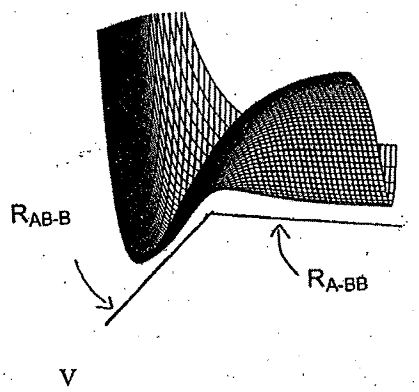
4. Shown below is a potential energy surface for the general reaction AB + B → A + B_2. The reaction is assumed to be collinear.

   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?





1) $$z = \sigma \left(\frac{8kT}{\pi m}\right)^{1/2} N_D$$

$$\sigma = \pi d^2 = \pi\left(2 \cdot 150 \times 10^{-12}\,m\right)^2 = 2.827 \times 10^{-19}\,m^2$$

$$m = \frac{28.02\,g}{mol} \cdot \frac{10^{-3}\,Kg/g}{6.022 \times 10^{23}\,mol^{-1}} = 4.653 \times 10^{-26}\,Kg$$

$$N_D = \frac{N}{V} = \frac{P}{\cancel{k}T} = \frac{101\,325\,Pa \cdot}{1.38 \times 10^{-23}\,J/\cancel{K} \cdot 300\cancel{K}} = \frac{101\,325}{1.38 \times 10^{-23} \cdot 300}\quad \frac{N/m^2}{J}$$

$$\frac{\dfrac{\cancel{Kg\,m/s^2}}{m\cancel{{}^2}}}{\cancel{Kg\,m^2/s^2}} = \frac{1}{m^3} = \frac{1}{V}$$ ✓

$$N_D = 2.447 \times 10^{25}/m^3$$

See continued calc on Mathcad

$\sigma := \pi \cdot \left(2 \cdot 150 \cdot 10^{-12} \mathrm{m}\right)^2$ $\sigma = 2.827 \times 10^{-19} \mathrm{m}^2$ $g := \frac{\mathrm{kg}}{1000}$

$\mathrm{mass} := 28.02 \frac{g}{\mathrm{mol}} \cdot \frac{1}{6.022 \cdot 10^{23} \mathrm{mol}^{-1}}$ $m = 1\,\mathrm{m}$

$N_D := \frac{101325\mathrm{Pa}}{1.38 \cdot 10^{-23} \frac{J}{K} \cdot 300K}$

This is PV=NkT, rearranged to N/V=P/kT

$N_D = 2.447 \times 10^{25} \frac{1}{\mathrm{m}^3}$

$$\frac{1000 \cdot \frac{L}{\mathrm{m}^3}}{22.4 \cdot \frac{L}{\mathrm{mol}}} \cdot \frac{6.022 \cdot 10^{23}}{\mathrm{mol}} \cdot \frac{273K}{300K} = 2.446 \times 10^{25} \frac{1}{\mathrm{m}^3}$$

↑

Scaling ideal gas result gives same answer

$$z := \sigma \cdot \left(\frac{8 \cdot 1.38 \cdot 10^{-23} \frac{J}{K} \cdot 300K}{\pi \cdot \mathrm{mass}} \right)^{\frac{1}{2}} \cdot N_D$$

$z = 3.294 \times 10^{9}\,\mathrm{Hz}$ This is the collision frequency of one N2 molecule

$\tau := \frac{1}{z}$

$\tau = 3.036 \times 10^{-10}\,\mathrm{s}$ This is the duration between collisions

2) a) $$D_{cl} = \frac{kT}{6\pi\eta R_{cl}} = \frac{1.38\times10^{-23}\,J/K \cdot 300K}{6\pi\ 0.413\times10^{-3}\,N/m^2 \cdot s \cdot (0.39\times10^{-9}\,m)}$$

Units: $$\frac{\frac{\cancel{Kg\,m^2/s^2}}{\cancel{K}} \cdot \cancel{K}}{\frac{\cancel{Kg\,m/s^2}}{\cancel{m^2}} \cdot s \cdot \cancel{m}} = m^2/s \quad ✓$$

$$D_{cl} = 1.3636\times10^{-9}\,\frac{m^2}{s}\left(\frac{10^9\,nm}{1m}\right)^2\left(\frac{s}{10^9\,ns}\right) = 1.36\ nm^2/ns$$

$$D_{\text{⬡}} = \frac{1.38\times10^{-23}\,J/K \cdot 300K}{6\pi \cdot 0.413\times10^{-3}(0.35\times10^{-9}\,m)} \cdot 10^9\,\frac{nm^2\,s}{m^2\,ns} = 1.52\ nm^2/ns$$

b) $$11.4\times10^9\,M^{-1}s^{-1} = 4\pi R^* D N_A$$

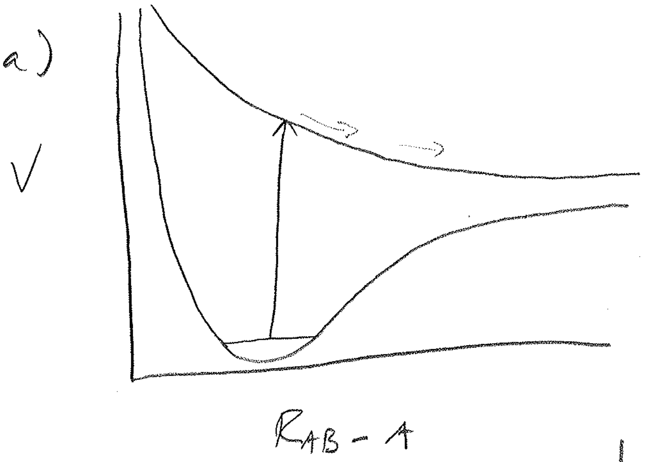
$$R^* = \frac{11.4\times10^9\,L/\cancel{mol}\,\cancel{s^{-1}}}{4\cdot\pi\,(1.3636\times10^{-9}\,m^2/\cancel{s} + 1.5194\times10^{-9}\,m^2/\cancel{s})\cdot 6.022\times10^{23}\,\cancel{mol^{-1}}}$$

$$R^* = 5.225\times10^{-7}\,\frac{\cancel{L}}{\cancel{m^2}}\ \frac{\cancel{m^3}}{1000\,\cancel{L}}\left(\frac{10^9\,nm}{\cancel{m}}\right) = 0.522\ nm$$

$R_{cl}+R_{\text{⬡}} = 0.74$ nm.

R^* is smaller than $R_{cl}+R_{\text{⬡}}$. There is some activation control to this reaction. The nature of the control could be in the form of a barrier to reaction, which would decrease reaction probability from unity, or perhaps some orientational effects, as we're dealing with anisotropic species.

3) a)

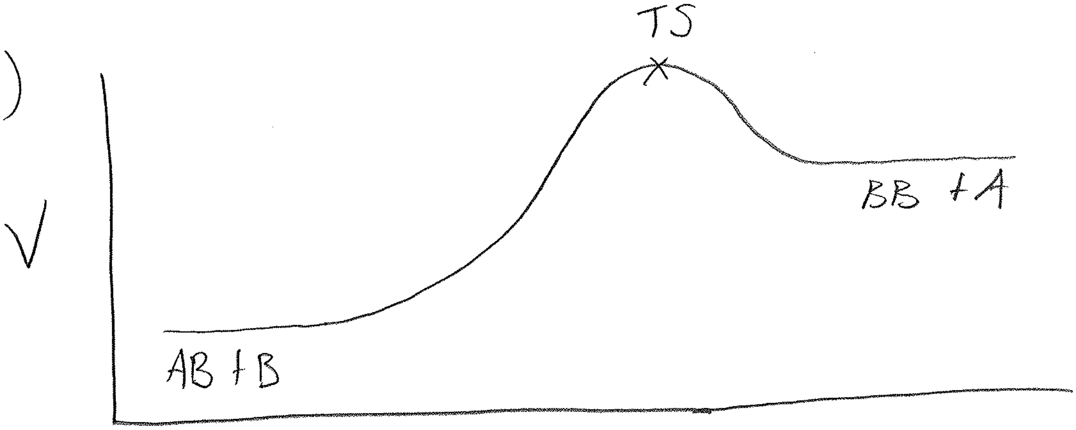


b) The molecule will dissociate

4) The B-B distance is initially large, reaches a constant value, then the A-B distance increases. See arrows on diagram

a) We have climbed uphill, this is an endothermic reaction.

b)

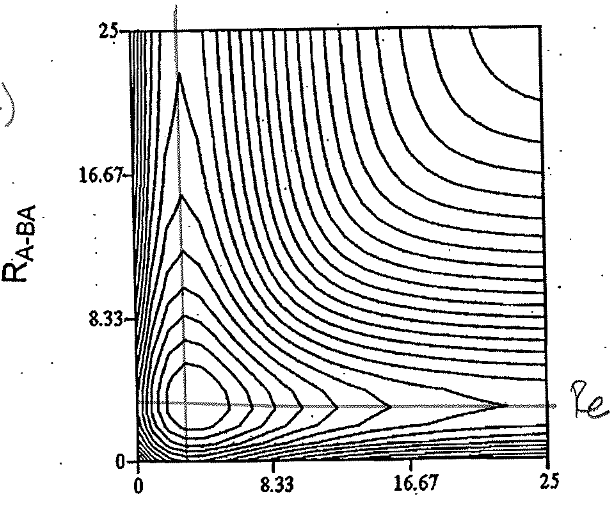


This is a late transition state; it is after the diagonal (where $R_{A-BB} = R_{AB-B}$).

c) It is likely that increased translational energy will be ineffective at facillitating the reaction, and that vibrations <u>might</u> help.

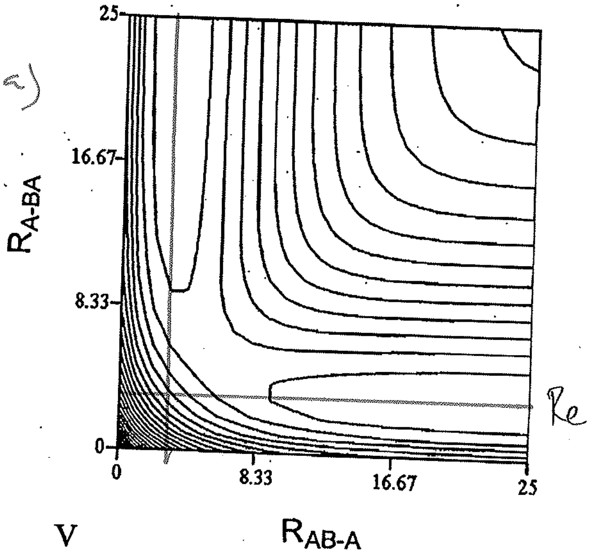
Ground Electronic State

2 a)

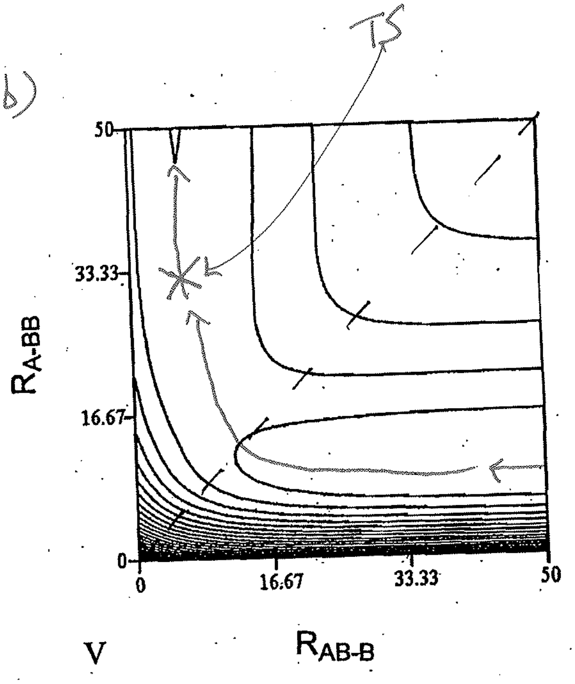


First Excited Electronic State

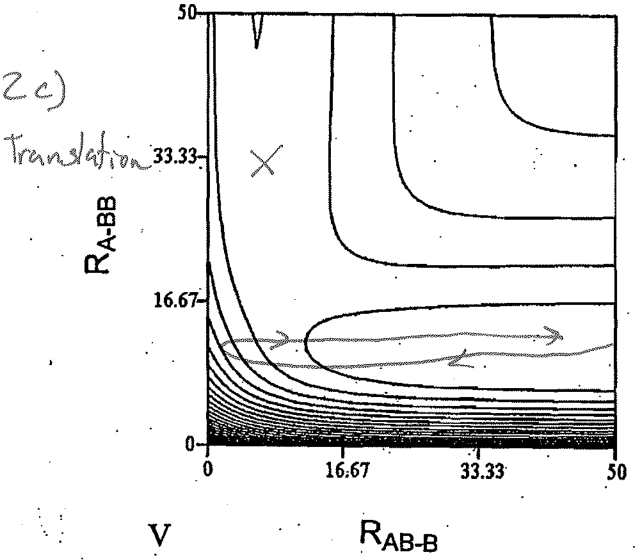
2 a)



2 b)



2 c)



2 c)
Vibration