Chemistry 163C Problem Set #9
Due Thursday, 6/5 at the beginning of class

1) Determine the diffusion controlled rate constant for two reacting molecules in aqueous solution at 25°C where each has a 5.0 Å radius. Note that the viscosity of water at 25°C is approximately 0.9 cP, where 1 cP = 10^{-3} kg m^{-1} s^{-1}. Next, determine the diffusion controlled rate constant for two molecules where one has a radius of 1.0 Å and the other has a radius of 9.0 Å. By what percentage does the rate change for the molecules of unequal size? How do your results compare to that from the theoretical limit of $8RT/3\eta$?

2) For the ozone decomposition scheme

$$O_3 \xrightarrow{k_1} O_2 + O$$
$$O_2 + O \xrightarrow{k_2} O_3$$
$$O_3 + O \xrightarrow{k_3} 2O_2$$

use the steady state approximation for [O] to show

$$\frac{d[O_3]}{dt} = \frac{-2k_1 k_3 [O_3]^2}{k_2[O_2] + k_3[O_3]}$$

What conditions will make this reaction appear to be first order in $[O_3]$?

3) The following gas phase reaction at 300K is first order at high concentration of CH_3NC but second order at low concentration.

$$CH_3NC \xrightarrow{k} CH_3CN$$

a) Propose a reaction scheme that accounts for these observations. (Hint: look at the Lindemann mechanism in our book, section 19.3.) b) Apply steady state theory to your reaction scheme to develop a differential rate law that accounts for your observations. c) The pre-exponential factor for this reaction is 3.92 x 10^{13} s^{-1}. Determine $\Delta S^{\ddagger}$ and explain whether your result is consistent with your proposed mechanism.

4) The molecule I_3^- is linear and undergoes unimolecular dissociation according to the following reaction.

$$I_3^- \xrightarrow{k} I_2 + I^-$$

There are two possible transition states: linear I_3^- (with elongated bonds) or bent I_3^-. a) Use transition state theory to determine the temperature dependence of A (the pre-exponential factor) for each case. Treat vibrational modes as being in the ground state. b) Would you be able to distinguish these cases experimentally? c) Develop an expression for $\Delta S^{\ddagger}$ for each case.

From Engel & Reid 3rd Edition, Chapter 18, Problems: 1, 2, 17, 23, 26, 27