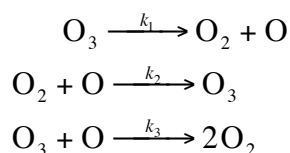


Chemistry 163C Problem Set #9  
Due Thursday, 6/5 at the beginning of class

- 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<sup>-3</sup> kg m<sup>-1</sup> s<sup>-1</sup>. 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/3η?

- 2) For the ozone decomposition scheme

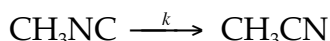


use the steady state approximation for [O] to show

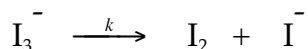
$$\frac{d[\text{O}_3]}{dt} = \frac{-2k_1k_3[\text{O}_3]^2}{k_2[\text{O}_2] + k_3[\text{O}_3]}$$

What conditions will make this reaction appear to be first order in [O<sub>3</sub>]?

- 3) The following gas phase reaction at 300K is first order at high concentration of CH<sub>3</sub>NC but second order at low concentration.



- 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 × 10<sup>13</sup> s<sup>-1</sup>. Determine ΔS<sup>‡</sup> and explain whether your result is consistent with your proposed mechanism.
- 4) The molecule I<sub>3</sub><sup>-</sup> is linear and undergoes unimolecular dissociation according to the following reaction.



There are two possible transition states: linear I<sub>3</sub><sup>-</sup> (with elongated bonds) or bent I<sub>3</sub><sup>-</sup>.

- 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 ΔS<sup>‡</sup> for each case.

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