

CE 561 Homework 4: (assigned 09/21/09, due 09/29/09)

- (1) Use collision theory to estimate the pre-exponential factor for the reaction $\text{OH} + \text{CH}_3\text{Cl} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{Cl}$ at 298 K. Use a hard-sphere collision diameter of 4.2 Å for CH_4 and 3.2 Å for OH. Report your result in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ and compare your result to the experimental value of $2.4 \times 10^{12} \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$. If we were to assign a 'steric factor' or 'reaction probability' for this reaction, what would it be?
- (2) The Lennard-Jones diameter and well depth for argon (from viscosity data) are 3.418 Å and 124.0 K, respectively (well-depths are usually given in temperature units, the corresponding energy in Joules is given by multiplying by Boltzmann's constant in J/K). At low enough temperatures, two argon atoms could form a weakly-bound diatomic 'molecule' (held together by only dispersion forces).
- (a) If the two argon atoms obey the Lennard-Jones potential, what will be the equilibrium 'bond length' in the argon dimer?
- (b) What will be the fundamental vibrational frequency of the dimer?
- (c) At what temperature is the thermal energy, $k_B T$, equal to one vibrational quantum of energy for this molecule?
- (3) A linear triatomic molecule such as OCS (like CO_2 , but with one oxygen replaced by sulfur) has two bond-stretching internal coordinates r_{OC} and r_{CS} . Assume the potential energy for the linear internal motion is given by

$$V = \frac{f_{\text{OC}}(r_{\text{OC}} - r_{\text{OC}}^o)^2}{2} + \frac{f_{\text{CS}}(r_{\text{CS}} - r_{\text{CS}}^o)^2}{2}$$

with $f_{\text{OC}} = 13.8 \text{ mdyne}/\text{Å}$, $f_{\text{CS}} = 8.1 \text{ mdyne}/\text{Å}$, $r_{\text{OC}}^o = 1.16 \text{ Å}$, and $r_{\text{CS}}^o = 1.56 \text{ Å}$. Perform a normal mode analysis of this molecule, considering only the degrees of freedom for linear motion. There are 3 degrees of freedom (change of position of each of the three atoms in 1-dimension) for the linear motion. One eigenvalue will be zero – corresponding to translation of the whole molecule. Find all three eigenvalues (normal mode frequencies) and eigenvectors (normal mode motions).

Hint: This is exactly like the example in the notes