

CE 561 Homework 4: (instructor's solutions in red)

- (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_3Cl 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?

An upper limit for the pre-exponential factor is given by the gas-kinetic collision rate divided by the concentration of A and the concentration of B. We saw in class that, for the simple hard-sphere collision, the total collision rate is given by

$$Z_{AB} = \sigma_{AB} \left(\frac{8kT}{\pi\mu} \right)^{1/2} N_A N_B, \text{ or } k_{AB} = \sigma_{AB} \left(\frac{8kT}{\pi\mu} \right)^{1/2}$$

Putting in the numbers for this problem, with species $A = \text{CH}_3\text{Cl}$ and species $B = \text{OH}$.

$$\sigma_{AB} = \pi d_{AB}^2$$

$$d_{AB} = (d_A + d_B)/2 = (4.2 + 3.2)/2 \text{ \AA} = 3.7 \text{ \AA} = 3.7 \times 10^{-10} \text{ m}$$

$$\sigma_{AB} = \pi (3.70 \times 10^{-10} \text{ m})^2 = 4.30 \times 10^{-19} \text{ m}^2$$

$$k = 1.38 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$$

$$T = 298 \text{ K}$$

$$m_A = 50.5 \text{ g mol}^{-1} = 8.38 \times 10^{-26} \text{ kg molecule}^{-1}$$

$$m_B = 17 \text{ g mol}^{-1} = 2.82 \times 10^{-26} \text{ kg molecule}^{-1}$$

and

$$\mu = 12.72 \text{ g mol}^{-1} = 2.11 \times 10^{-26} \text{ kg molecule}^{-1}$$

so

$$k_{AB} = 3.03 \times 10^{-16} \text{ m}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

or

$$k_{AB} = 1.8 \times 10^{14} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$$

This collision rate constant is an upper limit for the pre-exponential factor for the reaction – we expect that

$$A < 1.8 \times 10^{14} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$$

This is almost two orders of magnitude larger than the experimental value. If we were to assign a reaction probability, it would be $P = (2.4 \times 10^{12} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1} / 1.8 \times 10^{14} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}) = 0.013$. The observed pre-exponential factor is just 1.3% of the gas-kinetic collision rate constant.

- (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?

(a) The Lennard-Jones potential is given by

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

The equilibrium bond length is at the minimum in this potential, or where the derivative of the potential with respect to bond length is zero. Taking the derivative with respect to r gives

$$\frac{dV}{dr} = \frac{-24\epsilon}{r} \left[2 \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

Setting this equal to zero and solving for r gives

$$r = 2^{1/6} \sigma = 1.122\sigma = 3.84 \text{ angstroms}$$

(b) The fundamental vibrational frequency of a diatomic molecule is given by

$$\nu_e = \frac{1}{2\pi} \sqrt{\frac{f_r}{\mu}}$$

where

$$f_r = \left(\frac{d^2V}{dr^2} \right)_{r=r_e}$$

Taking the second derivative of the potential gives

$$\frac{d^2V}{dr^2} = \frac{24\epsilon}{r^2} \left[26 \left(\frac{\sigma}{r} \right)^{12} - 7 \left(\frac{\sigma}{r} \right)^6 \right]$$

Substituting into this the equilibrium r ($r = 2^{1/6} \sigma$) gives

$$\left. \frac{d^2V}{dr^2} \right|_{r=r_{eq}} = 36 \frac{2^{2/3} \epsilon}{\sigma^2} = 0.8374 \text{ J m}^{-2}$$

The reduced mass of the pair of argon atoms is $39.95/2 = 19.98 \text{ g/mol} = 3.32 \times 10^{-26} \text{ kg}$.

So, the vibrational frequency is

$$\nu_e = \frac{1}{2\pi} \sqrt{\frac{0.8374}{3.32 \times 10^{-26}}} = 8.0 \times 10^{11} \text{ s}^{-1}$$

This is a very low vibrational frequency compared to a real molecule. Converting it to wavenumbers by dividing by the speed of sound gives 27 cm^{-1} .

(c) One vibrational quantum of energy is given by $h\nu = 6.626 \times 10^{-34} \text{ (J s)} * 8.0 \times 10^{11} \text{ s} = 5.3 \times 10^{-22} \text{ J} = 319 \text{ J/mol}$. The thermal energy, $k_B T$, is equal to this when T is $5.3 \times 10^{-22} \text{ J} / 1.38 \times 10^{-23} \text{ (J/K)} = 38.4 \text{ K}$. Notice that the well-depth is only 124 K (from the problem statement), which is about 3 vibrational quanta.

- (3) A linear triatomic molecule such as OCS (like CO₂, 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

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

with $f_{OC} = 13.8$ mdyne/Å, $f_{CS} = 8.1$ mdyne/Å, $r_{OC}^o = 1.16$ Å, and $r_{CS}^o = 1.56$ 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

Let the 3 degrees of freedom be the x position of the S, C, and O atoms (x_S, x_C, x_O). Then, we can re-write V in terms of (x_O, x_C, x_S) as

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

This can then be re-written in terms of the mass-weighted cartesian coordinates

$$q_O = \sqrt{m_O}x_O, \quad q_C = \sqrt{m_C}x_C, \quad q_S = \sqrt{m_S}x_S$$

$$V = \frac{f_{OC}\left(\frac{q_C}{\sqrt{m_C}} - \frac{q_O}{\sqrt{m_O}} - r_{OC}^o\right)^2}{2} + \frac{f_{CS}\left(\frac{q_S}{\sqrt{m_S}} - \frac{q_C}{\sqrt{m_C}} - r_{CS}^o\right)^2}{2}$$

Then the mass-weighted Cartesian force constant matrix is

$$\underline{\underline{F}} = \begin{bmatrix} \frac{d^2V}{dq_O^2} & \frac{d^2V}{dq_Odq_C} & \frac{d^2V}{dq_Odq_S} \\ \frac{d^2V}{dq_Odq_C} & \frac{d^2V}{dq_C^2} & \frac{d^2V}{dq_Cdq_S} \\ \frac{d^2V}{dq_Odq_S} & \frac{d^2V}{dq_Cdq_S} & \frac{d^2V}{dq_S^2} \end{bmatrix}$$

$$\underline{\underline{F}} = \begin{bmatrix} \frac{f_{OC}}{m_O} & \frac{-f_{OC}}{\sqrt{m_O}\sqrt{m_C}} & 0 \\ \frac{-f_{OC}}{\sqrt{m_O}\sqrt{m_C}} & \frac{f_{OC} + f_{CS}}{m_C} & \frac{-f_{CS}}{\sqrt{m_C}\sqrt{m_S}} \\ 0 & \frac{-f_{CS}}{\sqrt{m_C}\sqrt{m_S}} & \frac{f_{CS}}{m_S} \end{bmatrix}$$

At this point, we could use Maple or something to find analytical expressions for the eigenvalues and eigenvectors of this matrix, but the result would be too large and messy to be useful, so we might as well substitute in the numbers first.

$$\underline{\underline{F}} = \begin{bmatrix} 0.8625 & -0.9959 & 0 \\ -0.9959 & 1.8250 & -0.4130 \\ 0 & -0.4130 & 0.2527 \end{bmatrix} \frac{\text{mdynes} \cdot \text{mole}}{\text{\AA} \cdot \text{g}}$$

The eigenvalues of this matrix are

$$\lambda_1 = 0, \lambda_2 = 0.4354, \lambda_3 = 2.505 \frac{\text{mdynes} \cdot \text{mole}}{\text{\AA} \cdot \text{g}}$$

To convert to more familiar units, we can multiply by

$$10^{-8} \text{ J/mdyne}, 10^{10} \text{ \AA/m}, 1000 \text{ g/kg}, \text{ and } 6.022 \times 10^{23} \text{ molecules/mole}$$

$$\lambda_1 = 0, \lambda_2 = 2.62 \times 10^{28}, \lambda_3 = 1.51 \times 10^{29} \text{ s}^{-2}$$

(check the cancellation of the units)

These eigenvalues are related to the normal mode vibrational frequencies by

$$\lambda_i = 4\pi^2 \nu_i^2$$

so the two non-zero vibrational frequencies are

$$\nu_2 = 2.58 \times 10^{13} \text{ s}^{-1}, \nu_3 = 6.18 \times 10^{13} \text{ s}^{-1}.$$

To convert these to the more familiar units of wavenumbers (cm^{-1}) we divide by the speed of light ($3 \times 10^{10} \text{ cm/s}$) to get frequencies of 859 cm^{-1} and 2060 cm^{-1} .

The corresponding eigenvectors are

$$\underline{x}_1 = [0.5161, 0.4470, 0.7306]$$

$$\underline{x}_2 = [0.6864, 0.2943, -0.6650]$$

$$\underline{x}_3 = [0.5123, -0.8447, 0.1549]$$

These eigenvectors represent displacements in the mass-weighted coordinates. To get displacements in the Cartesian coordinates, we divide these by the square-roots of the molecular weights. This gives the normal mode displacements as

$\underline{y}_1 = [0.1290, 0.1290, 0.1290]$ – the zero eigenvalue corresponds to the same motion of all three atoms – this is translation of the whole molecule.

$\underline{y}_2 = [0.1716, 0.0850, -0.1174]$ – this mode (with frequency 859 cm^{-1}) corresponds to stretching of both bonds, but primarily the C-S bond, which changes in length about 2.3 times as much as the C-O bond. The stretching is symmetric, meaning that both bonds get shorter at the same time, and both bonds get longer at the same time.

$\underline{y}_3 = [0.1281, -0.2438, 0.0274]$ – this mode (with frequency 2060 cm^{-1}) corresponds to stretching of both bonds, slightly concentrated in the C-O bond, which changes in length

about 1.4 times as much as the C-S bond. This stretching mode is asymmetric, meaning that when the C-O bond is getting longer, the C-S bond is getting shorter.