

Chemistry 4000 Fall 2021 Test 1 Solutions

1. (a)

$$\begin{aligned}k &= Ae^{-E_a/(RT)} \\&= (5.01 \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1}) \exp\left(\frac{-4.18 \times 10^3 \text{ J K}^{-1}\text{mol}^{-1}}{(8.314 \text{ J K}^{-1}\text{mol}^{-1})(233 + 273.15 \text{ K})}\right) \\&= 1.86 \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1}\end{aligned}$$

(b) The collision cross-section is related to the pre-exponential factor by $k = \sigma \bar{u}_{\text{rel}} L$. We start by calculating the relative speed. I'm going to use average molar masses here, partly because we aren't told what the isotopes are, and partly because this is a calculation with a crude theory. It's just not the place for excessive precision.

$$M_{\text{OOH}} = 2(15.999) + 1.008 \text{ g mol}^{-1} = 33.006 \text{ g/mol}$$

$$M_{\text{OH}} = 15.999 + 1.008 \text{ g mol}^{-1} = 17.007 \text{ g mol}^{-1}$$

$$\begin{aligned}\mu_m &= [(33.006)^{-1} + (17.007 \text{ g mol}^{-1})^{-1}]^{-1} \\&= 11.224 \text{ g mol}^{-1} \\&\equiv \frac{11.224 \text{ g mol}^{-1}}{1000 \text{ g kg}^{-1}} = 1.1224 \times 10^{-2} \text{ kg mol}^{-1}\end{aligned}$$

$$\begin{aligned}\bar{u}_{\text{rel}} &= \sqrt{\frac{8RT}{\pi\mu_m}} \\&= \sqrt{\frac{8(8.314 \text{ J K}^{-1}\text{mol}^{-1})(2200 \text{ K})}{\pi(1.1224 \times 10^{-2} \text{ kg mol}^{-1})}} \\&= 2037 \text{ m s}^{-1}\end{aligned}$$

$$A_{\text{ct}} = \sigma \bar{u}_{\text{rel}} L$$

$$\therefore \sigma = A_{\text{ct}} / \bar{u}_{\text{rel}} L$$

$$\begin{aligned}A &= \frac{5.01 \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1}}{1000 \text{ L m}^3} \\&= 5.01 \times 10^7 \text{ m}^3 \text{ mol}^{-1}\text{s}^{-1}\end{aligned}$$

$$\begin{aligned}\therefore \sigma &= \frac{5.01 \times 10^7 \text{ m}^3 \text{ mol}^{-1}\text{s}^{-1}}{(2037 \text{ m s}^{-1})(6.022 \text{ } 140 \text{ } 76 \times 10^{23} \text{ mol}^{-1})} \\&= 4.08 \times 10^{-20} \text{ m}^2\end{aligned}$$

I find it much easier to interpret a radius than an area.

$$\begin{aligned}r_{AB} &= \sqrt{\sigma/\pi} \\&= \sqrt{4.08 \times 10^{-20} \text{ m}^2/\pi} \\&= 1.14 \times 10^{-10} \text{ m} \equiv 1.14 \text{ \AA}\end{aligned}$$

This is small. The Wikipedia page for the $\bullet\text{OOH}$ radical (<https://en.wikipedia.org/wiki/Hydroperoxyl>) gives the O-O bond length in this molecule as 1.46 Å, and that's not even taking the hydrogen atom into account. Strictly speaking then, this reaction is **not** collision limited. On the other hand, r_{AB} is not tiny. Let's think a little harder about this reaction: it requires a transfer of a hydrogen atom from $\bullet\text{OOH}$ to $\bullet\text{OH}$, so it seems likely that a successful reaction will require the hydrogen atom of $\bullet\text{OOH}$ to interact with the oxygen atom of $\bullet\text{OH}$. The van der Waals radii of H and O are, respectively, 1.10 and 1.40 Å. The fact that r_{AB} is much smaller than the sum of the van der Waals radii can have two explanations. The first is that only a fraction of the collisions with the correct orientation result in reaction. The second (which is just a variation on the first) is that the steric requirement is fairly strict: only a narrow range of collision angles results in the transfer of the hydrogen atom.

2.

$$\begin{aligned}
 q_{\text{vib}} &= \frac{\exp\left(-\frac{\hbar\omega_0}{2k_B T}\right)}{1 - \exp\left(-\frac{\hbar\omega_0}{k_B T}\right)} \\
 &= \frac{\exp\left(-\frac{hc\tilde{\nu}_0}{2k_B T}\right)}{1 - \exp\left(-\frac{hc\tilde{\nu}_0}{k_B T}\right)} \\
 &= \frac{\exp\left(\frac{-(6.626\,070\,015 \times 10^{-34} \text{ J Hz}^{-1})(2.997\,924\,58 \times 10^{10} \text{ cm s}^{-1})(559.71 \text{ cm}^{-1})}{2(1.380\,649 \times 10^{-23} \text{ J K}^{-1})(350 + 273.15 \text{ K})}\right)}{1 - \exp\left(\frac{-(6.626\,070\,015 \times 10^{-34} \text{ J Hz}^{-1})(2.997\,924\,58 \times 10^{10} \text{ cm s}^{-1})(559.71 \text{ cm}^{-1})}{(1.380\,649 \times 10^{-23} \text{ J K}^{-1})(350 + 273.15 \text{ K})}\right)} \\
 &= 0.722
 \end{aligned}$$

3.

$$\begin{aligned}
 k &= \frac{L}{k_B T} \sqrt{\frac{8}{\pi\mu k_B T}} \int_0^\infty \epsilon_k \sigma_R(\epsilon_k) e^{-\epsilon_k/k_B T} d\epsilon_k \\
 &= \frac{L}{k_B T} \sqrt{\frac{8}{\pi\mu k_B T}} \int_{\epsilon_a}^\infty \epsilon_k \sigma^* \arctan\left(\frac{\epsilon_k - \epsilon_a}{k_B T}\right) e^{-\epsilon_k/k_B T} d\epsilon_k
 \end{aligned}$$

The integrals we were given involve $\arctan(x)$, so the obvious thing to do is to make

the substitution

$$\begin{aligned}
x &= \frac{\epsilon_k - \epsilon_a}{k_B T} \\
\therefore \epsilon_k &= k_B T x + \epsilon_a \\
\therefore d\epsilon_k &= k_B T dx \\
\therefore k &= \sigma^* \frac{L}{k_B T} \sqrt{\frac{8}{\pi \mu k_B T}} \int_0^\infty (k_B T x + \epsilon_a) \arctan(x) \exp\left[-\left(x + \frac{\epsilon_a}{k_B T}\right)\right] k_B T dx \\
&= \sigma^* L \sqrt{\frac{8}{\pi \mu k_B T}} e^{-\epsilon_a/k_B T} \left\{ k_B T \int_0^\infty x \arctan(x) e^{-x} dx + \epsilon_a \int_0^\infty \arctan(x) e^{-x} dx \right\} \\
&= \sigma^* L \sqrt{\frac{8}{\pi \mu k_B T}} e^{-\epsilon_a/k_B T} (0.9648 k_B T + 0.6214 \epsilon_a) \\
&= \sigma^* L \sqrt{\frac{8 k_B T}{\pi \mu}} e^{-\epsilon_a/k_B T} \left(0.9648 + 0.6214 \frac{\epsilon_a}{k_B T} \right) \\
&= \sigma^* L \bar{u}_{\text{rel}} e^{-\epsilon_a/k_B T} \left(0.9648 + 0.6214 \frac{\epsilon_a}{k_B T} \right)
\end{aligned}$$

The short answer to my question is “not quite”. Just as we did with a pure hard-sphere collision reactive cross-section, we get the simple collision theory result with a correction term.

4. (a) I carried out a redundant coordinate scan with the dihedral angle as the scanned coordinate. I scanned from 0 to 360° in 5° increments. I used the B3LYP functional with the 6-31G++(d,p) basis set and spin-restricted wavefunctions. My graph is shown in figure 1.
- (b) In the following table, M denotes a minimum and TS a transition state.

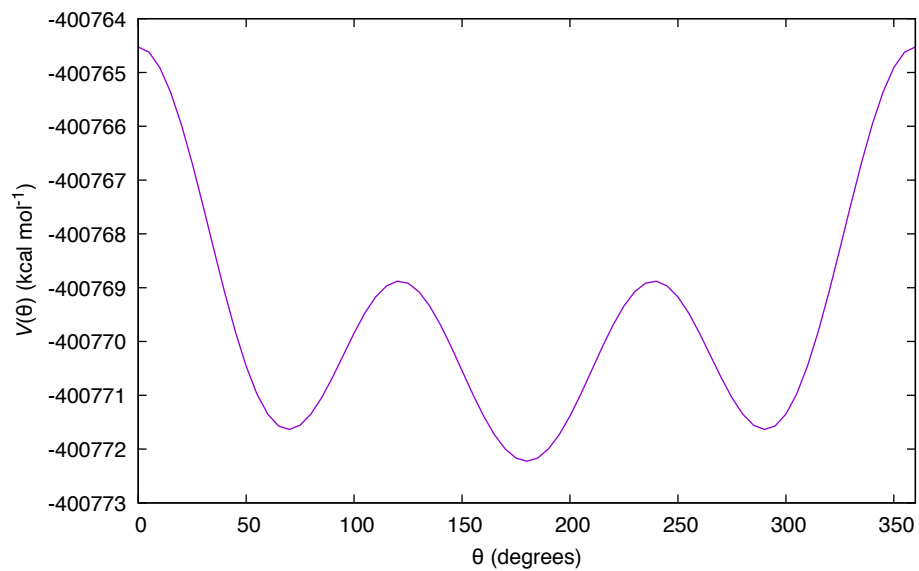
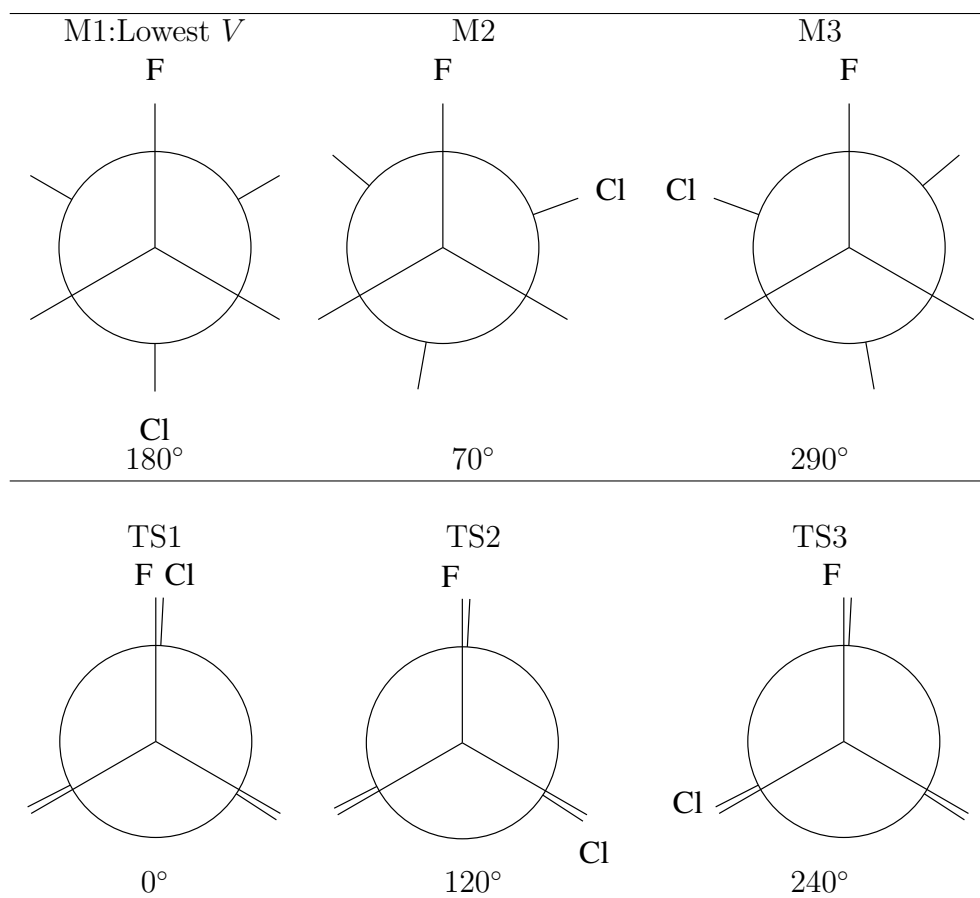


Figure 1: Potential energy vs F-C-C-Cl dihedral angle in CH₂FCH₂Cl. Computational details in text.



M2 and M3 have the same energy, as do TS2 and TS3.

In the following calculations, I used energies from the data file generated by GaussView.

Barrier between M2 and M3 (TS1):

$$\begin{aligned}
 E_a &= E(\text{TS1}) - E(\text{M2}) \\
 &= -400764.53 - (-400771.63) \text{ kcal mol}^{-1} \\
 &= 7.10 \text{ kcal mol}^{-1} \\
 &\equiv (7.10 \text{ kcal mol}^{-1})(4.184 \text{ J cal}^{-1}) \\
 &= 29.7 \text{ kJ mol}^{-1}.
 \end{aligned}$$

Barrier for M2 \rightarrow M1:

$$\begin{aligned}
 E_a &= E(\text{TS2}) - E(\text{M2}) \\
 &= -400768.88 - (-400771.63) \text{ kcal mol}^{-1} \\
 &= 2.75 \text{ kcal mol}^{-1} \\
 &\equiv (2.75 \text{ kcal mol}^{-1})(4.184 \text{ J cal}^{-1}) \\
 &= 11.5 \text{ kJ mol}^{-1}.
 \end{aligned}$$

Barrier for M1 \rightarrow M2:

$$\begin{aligned}
 E_a &= E(\text{TS2}) - E(\text{M1}) \\
 &= -400768.88 - (-400772.22) \text{ kcal mol}^{-1} \\
 &= 3.34 \text{ kcal mol}^{-1} \\
 &\equiv (3.34 \text{ kcal mol}^{-1})(4.184 \text{ J cal}^{-1}) \\
 &= 14.0 \text{ kJ mol}^{-1}.
 \end{aligned}$$

- (c) There are two minimum energy states: M1 and M2/3. I'm going to reoptimize at M1 and at one of the other two points and simultaneously do a frequency calculation to get the partition functions. The results are in the following table:

Conformation	Degeneracy	$\epsilon_0/\text{hartree}$	$\hat{q}(\text{bottom})$
M1	1	-638.671 167	3.002×10^{-15}
M2/3	2	-638.670 227	3.399×10^{-15}

The degeneracy of 2 for M2/3 is to account for the fact that two distinct equilibria¹ have these statistics. \hat{q} does not take this factor into account, so we will need to include it explicitly in our calculations. Note that I didn't adjust the pressure for this calculation, so we will get equilibrium constants at 1 atm. (I hadn't mentioned anything about this in the question, so I'm not going to get picky about it here.) Incidentally, on reoptimizing M2, the dihedral angle changed to 69.68°, so the equilibrium dihedral is not exactly 70°.

¹And if you know anything about prochirality, you might have noticed that the two equilibria are distinct.

The equilibrium we are treating is $M1 \rightleftharpoons M2/3$. We start by calculating the difference in energies:

$$\begin{aligned}
 \Delta\epsilon_0 &= \epsilon_0(M2/3) - \epsilon_0(M1) \\
 &= -638.670\,227 - (-638.671\,167) \text{ hartree} \\
 &= 0.000\,940 \text{ hartree} \\
 &\equiv (0.000\,940 \text{ hartree})(4.359\,745 \times 10^{-18} \text{ J hartree}^{-1}) \\
 &= 4.10 \times 10^{-21} \text{ J}
 \end{aligned}$$

The equilibrium constant is

$$\begin{aligned}
 K &= \frac{q_{M2/3}}{q_{M1}} e^{-\Delta\epsilon_0/k_B T} \\
 &= \frac{2(3.399 \times 10^{-15})}{3.002 \times 10^{-15}} \exp\left(\frac{-4.10 \times 10^{-21} \text{ J}}{(1.380\,649 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})}\right)
 \end{aligned}$$

Note the factor of 2 in the partition function of M2/3, which accounts for the fact that these two conformations together have twice as many accessible states as either one of them.

$$\therefore K = 0.84$$