Chemistry 4000/5000/7000 Fall 2021
Test 1

Due: No later than 10:30 a.m. on October 27th

This test can be submitted on paper or electronically. Neatly hand-written work is acceptable.

Total marks: 49

No collaboration is permitted between students for this test. You are not to discuss the questions or their solutions with classmates or with anyone else before the deadline for returning papers. Attempting to get help via an online forum is expressly forbidden.

I may answer questions at my discretion if you require clarifications. Don't hesitate to ask. I will generally propagate any answers offered to one student to the entire class via email.

Detailed solutions or answers are required. Little to no credit will be given for answers presented without your detailed reasoning. However, do look at the number of marks assigned to a question. As a rough rule of thumb, a 10-mark question might require about a page of math, or two to three substantial paragraphs.
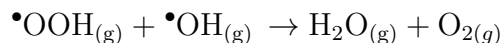
For computational problems, you must provide sufficient detail of the calculation to enable replication. Typically, this would mean the method used and basis set, but other details may be important. Assume that I know my way around GaussView and Gaussian, and ask yourself what I would need to know to reproduce your work.

Note: Some computations may be time-consuming. Don't wait until the last minute to do the computational questions!

Fundamental constants: Please use these values.

$$c = 2.997\,924\,58 \times 10^8 \,\mathrm{m\,s^{-1}}$$
$$h = 6.626\,070\,015 \times 10^{-34} \,\mathrm{J\,Hz^{-1}}$$
$$k_B = 1.380\,649 \times 10^{-23} \,\mathrm{J\,K^{-1}}$$
$$L = 6.022\,140\,76 \times 10^{23} \,\mathrm{mol^{-1}}$$
$$R = 8.314\,462\,618 \,\mathrm{J\,K^{-1}mol^{-1}}$$

1. The following elementary reaction is important in combustion pro- **12 marks** cesses:
$$\bullet OOH_{(g)} + \bullet OH_{(g)} \rightarrow H_2O_{(g)} + O_{2(g)}$$
The pre-exponential factor of this reaction is $5.01 \times 10^{10} \, \text{L} \, \text{mol}^{-1}\text{s}^{-1}$ and the activation energy is $E_a = 4.18 \, \text{kJ} \, \text{mol}^{-1}$.

   (a) Calculate the rate constant at 'Fahrenheit 451'[1] ($233 \, °C$). [2 marks]

   (b) Calculate the collision cross-section for this reaction assuming a typical combustion temperature of $2200 \, \text{K}$ (a typical combustion temperature in internal combustion engines.) Using a quantitative argument, which may require additional data, calculations or estimates, determine whether your calculated cross-section suggests a collision-limited reaction or not. Make sure you indicate the source of any data, unless it is entirely routine chemical data like molar masses. [10 marks]

2. $^{35}Cl_2$ has a vibrational wavenumber of $559.71 \, \text{cm}^{-1}$. Calculate the vi- **3 marks** brational partition function of $^{35}Cl_2$ with respect to the bottom of its potential energy well at $350 \, °C$.

3. In class, we saw that reactive scattering theory "magically" gives the **10 marks** simple collision theory rate constant if

$$\sigma_R(\epsilon_k) = \begin{cases} 0 & \text{for} \quad \epsilon_k < \epsilon_a \\ \sigma^*(1 - \epsilon_a/\epsilon_k) & \text{for} \quad \epsilon_k \geq \epsilon_a \end{cases}$$

You might have wondered if this result is particular to this form of the total reactive cross-section. (It's the kind of thing that theoreticians stare up at the ceiling thinking about late at night.) Let's try a different form for σ_R, namely

$$\sigma_R(\epsilon_k) = \begin{cases} 0 & \text{for} \quad \epsilon_k < \epsilon_a \\ \sigma^* \arctan\left(\frac{\epsilon_k - \epsilon_a}{k_B T}\right) & \text{for} \quad \epsilon_k \geq \epsilon_a \end{cases}$$

Like the case studied in class, this reactive cross-section is a continuous function of ϵ_k, going to zero as $\epsilon_k \rightarrow \epsilon_a^+$.

---

[1]For the Ray Bradbury fans in the class

Calculate the rate constant using reactive scattering theory for this 'arctan' reactive cross-section. Do you get a rate constant similar in form to that from simple collision theory?

The integrals you need cannot be evaluated analytically, but they can be numerically integrated.[2] Here are some useful integrals:

$$\int_0^\infty \arctan(x)e^{-x}dx = 0.6214$$

$$\int_0^\infty x\arctan(x)e^{-x}dx = 0.9648$$

The key to this problem is making a substitution such that you end up with an $\arctan(x)$ term in the integrand.

4. (a) Obtain a potential energy curve vs the F-C-C-Cl dihedral angle **24 marks** for CH_2FCH_2Cl. [5 marks]

   Note: This will take a while. If your job gets interrupted, or if you have to stop it manually, you can restart it from where you left off. (The Gaussian window has a stop button that looks like this: ■.) To continue an interrupted scan, open up the `log` file, dismiss the error message that pops up, look at the scan, and save the data. Note the angle corresponding to the last point. Start a new scan from this angle (adjusting the number of points as needed). Make sure to rename your file before you run it in order to avoid overwriting your existing results! Once you have finished, you can use a text editor to copy the points from your data files into a single file for plotting. You can then use any program you like for plotting (a spreadsheet, Matlab, . . .).

---

[2]There are actually 'analytic' solutions, but they involve strange functions like the so-called cosine integral, $Ci(x) = -\int_x^\infty \cos t\, dt/t$.

(b) Based on your potential energy curve, determine

    i. The most stable conformation

    ii. Any other distinguishable conformations that are local minima on the potential energy surface

    iii. The transition state conformation(s) (There may be more than one distinguishable transition state.)

    iv. The size(s) of the energy barrier(s) separating the conformations in $kJ\,mol^{-1}$ (Again, there may be more than one distinct energy barrier.)

Each conformation requested above should be shown as a Newman projection, and the dihedral angle should be clearly indicated. [9 marks]

(c) Grouping conformations by energy, calculate the equilibrium constant at $25\,°C$ for the conversion from the lowest energy conformation to the next-lowest energy conformation or group of conformations. [10 marks]

Note: If there is more than one conformation of the same energy, you will have to take this degeneracy into account in computing the relevant partition function.