Chemistry 4000/5000/7000 Fall 2021
Assignment 3

Due: November 17th

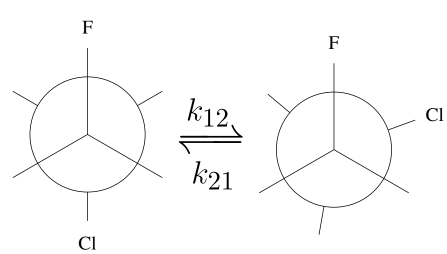
This assignment will be submitted electronically. As usual, I will accept neatly handwritten, scanned answers. However, any figures you generate should be included with your written answers in a single document. In some questions, I will require additional files. The file names should be mentioned in your report so that I can make the correct associations between the written work and files. The report and any additional files should be sent as attachments to a single 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.

Suggestion: Read through the entire assignment before doing any of the work. Try to think ahead about what data you will need in later parts of the assignment. This may save you a bit of time setting up and running calculations.

In the midterm, you studied the equilibrium between the rotamers of CH_2FCH_2Cl. In this assignment, you will study the kinetics of this process using transition-state theory. Specifically, you will study the kinetics of



Note that we will deal with the rate constant for transition from the lowest-energy conformer to *one* of the secondary minima.

1. Carry out a geometry optimization for

    (a) the lowest-energy conformer,

    (b) the secondary minimum, and

    (c) the transition state separating them.

    Report the following parameters for each of these structures in a table:

    - the energy,
    - the dihedral angle,
    - the F-C-C bond angle,
    - the Cl-C-C bond angle, and
    - the carbon-carbon bond length.

    [14 marks]

2. Calculate the rate constant k_{12} at 25 °C using transition-state theory. [7 marks]

3. Calculate the reverse rate constant at 25 °C, k_{21}. [5 marks]

4. Calculate the equilibrium constant at 25 °C for the reaction. (This is a simple calculation if you remember some basic chemical kinetics.) [1 mark]

5. Use the Wigner formula to estimate the importance of tunneling in this process. Submit the `.log` file from this calculation along with your assignment. [13 marks]

    Note: the textbook outlines a more efficient calculation of this correction than was presented in class. The differences are relatively minor, but will save you a significant amount of computing time.

6. As we have seen, the Wigner formula is often significantly in error, although it tends to give the correct order of magnitude for the tunneling correction. Based on your calculation, comment on whether it would be worthwhile to put more effort into calculating the tunneling correction for this process. [2 marks]

Bonus: If you wanted to lump together the two secondary minima, i.e. treat them as one species, what effect would this have on k_{12} and k_{21}? Explain briefly. [2 marks]