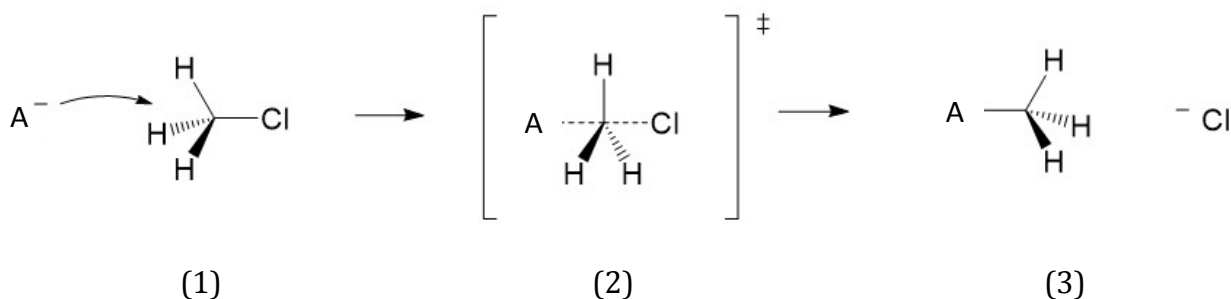<u>**KINETICS – Spartan Activity**</u>

Goals:
- o Determine the activation energy for an SN2 reaction.
- o Use the activation energy of the reaction to determine the rate constant as a function of temperature.
- o Become more comfortable using Spartan.

The reaction below illustrates an S_N2 reaction mechanism.

(1)   (2)   (3)

In the mechanism the A^- species is a generic anion and is classified as a Lewis base. It attacks the central carbon and replaces the chloride on the molecule. Notice the inversion of the hydrogen atoms. The molecule in the [ ] represents the transition state, where the C-Cl bond is elongated as the bond begins to break and the A-C distance is decreasing as the bond forms. The dotted lines indicate partial bonds.

1. Consider chloromethane, CH_3Cl. Describe which atoms have a partial charge on them and explain why.

2. Why do you think the A^- species attacks the carbon?

3. Which species do you expect will have the highest energy; (1), (2), or (3)? Explain your answer.

**Modeling the System in Spartan**

A: Build the Reactants in Spartan

- From the Organic palette choose the sp^3-hybridized carbon, then add a –Cl to one of the bonds.

- Orient the molecule the way you see it in (1) in the reaction mechanism above. Your build should look like the picture to the right.
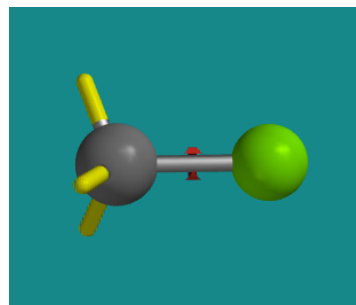
- Add another –Cl behind the CH$_3$- group and not bonded to it. Click on the eraser and remove the bond from this second chlorine atom.
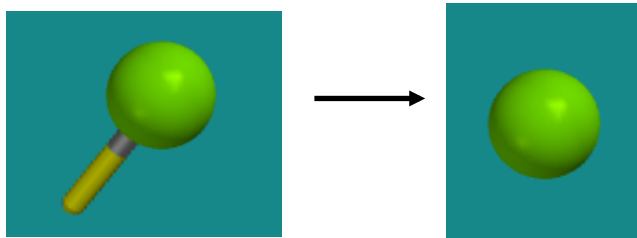

- Minimize the energy with the [icon] button. Your build should now look like the figure below.
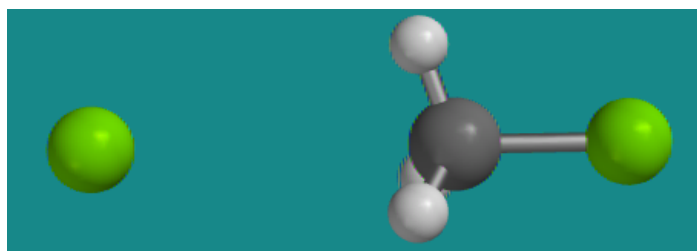
B: Identify the Transition State

- Now specify the mechanism of the reaction and identify the transition state. Go to Build/Transition State. Click on the BOND between the carbon atom and the bound chlorine atom, then click on the chlorine atom, then click on the chlorine atom again. Another blue arrow should appear point from the bond to the chlorine atom. This indicates that the chlorine will take the electrons in the bond with it when it leaves.

- Next click on the unbound Cl, then click on the C, then click again on the unbound chloride ion. A dotted line should appear between the two with a blue arrow pointing from the chloride ion to the dotted line. This indicates that the chloride ion is going to donate electrons to the bond it will form with the carbon.
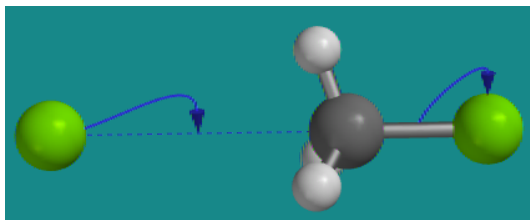

- Finally, go back to Build/Transition State and hit the ⟲ button that is in the bottom right corner. The arrows should disappear and your transition state will look like the figure below.
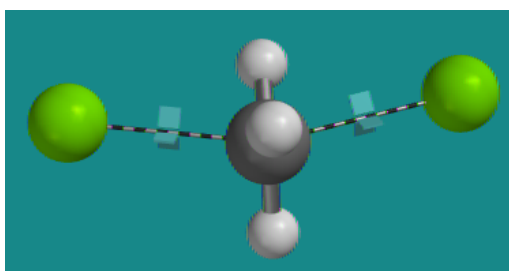

C: Constrain the Bond Lengths

- The equilibrium bond distance of the C-Cl bond in chloromethane is 1.767 Å. So we are going to set the range of Cl⁻ to C bond length to 5 – 1.767 Å. (5 Å is far enough to say that the two aren't bonded.) Go to Geometry/Constrain Distance and then click on the unbound Cl, then click on the C. In the bottom bar of the Spartan screen you will see the options pop up:
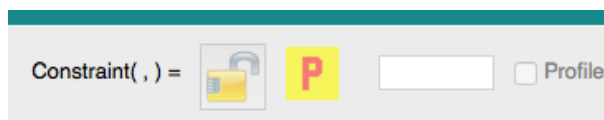
- Click on the lock symbol, then check the Profile box. Input 5 Å to 1.767 Å in 11 steps. Make sure you hit ENTER after typing in the number so they will actually be entered in the box.
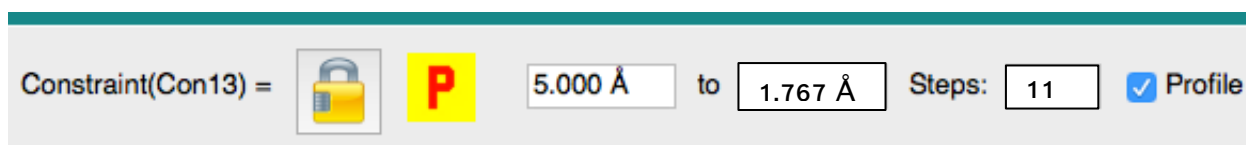
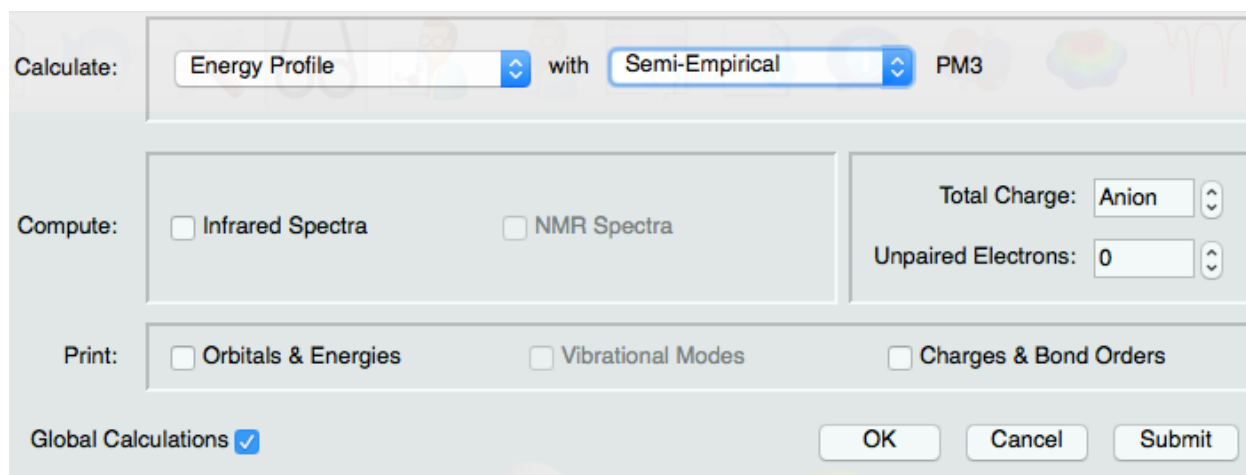- Now repeat the process for the carbon and the bound chlorine. This time go from 1.767 Å to 5 Å in 11 steps. When this is complete we are ready to perform the energy calculations.

Constraint(Con14) = 🔓 **P** | 1.767 Å | to | 5.000 Å | Steps: | 11 | ✓ Profile
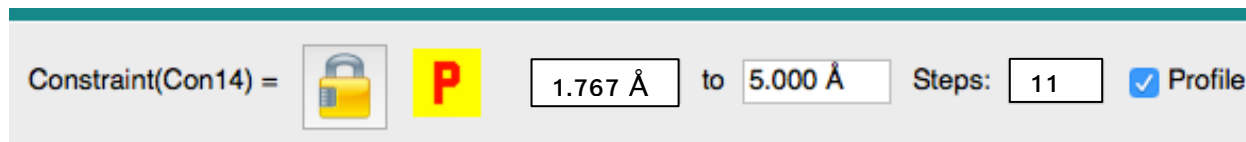
D: Perform the Energy Calculations

- Go to Setup/Calculations. Under Calculate select Energy Profile with Semi-Empirical. Change the Total Charge to Anion (because the unbound Cl is an anion), then hit Submit. Name the file "Energy Profile SN2".

Calculate: | Energy Profile | with | Semi-Empirical | PM3

Compute:
- ☐ Infrared Spectra
- ☐ NMR Spectra

Total Charge: Anion
Unpaired Electrons: 0

Print:
- ☐ Orbitals & Energies
- ☐ Vibrational Modes
- ☐ Charges & Bond Orders

Global Calculations ✓   OK   Cancel   Submit

- When the calculation is complete it will ask you if you'd like to open the new document. Select Yes.

E: Create the Energy Diagram

- Click on the spreadsheet icon in the tool bar. Add the energies to the spreadsheet by clicking on Add... and selecting "E" from the menu.

- Add the bond lengths to the spreadsheet by going back to Geometry/Constrain Distance, select the originally bound Cl atom and the C atom. When the bottom bar appears hit the "P" button. The bond lengths for each step should appear in the spreadsheet.

Constraint(Con1) = 🔓 **P** | 5.000 Å | ☐ Profile

- Now select the Plots icon on the tool bar. Click on the plus sign. Select "Constrain (Con1)" for the x-axis (this will be our reaction coordinate) and "E" for the y-axis. The plot will appear in the plot window, but if you hit the left-facing arrow it will put the plot in the build window.
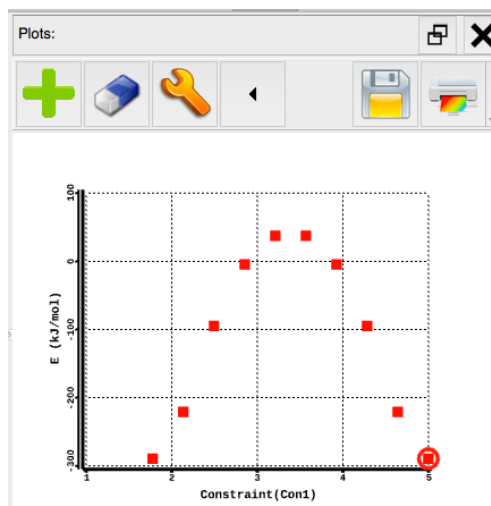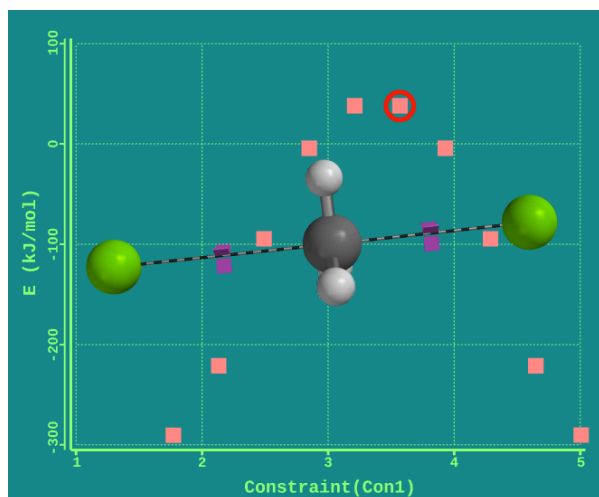
- Whether the plot is in the build window or not, you can use the animation controls in the lower right corner to see each of the steps individually or play them all in order.
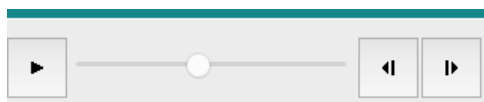

F: Explore S$_N$2 Reactions

1. Repeat the procedure above for the following reactions:

   - F$^-$ + CH$_3$Cl → CH$_3$F + Cl$^-$
   - I$^-$ + CH$_3$Cl → CH$_3$I + Cl$^-$
   - OH$^-$ + CH$_3$Cl → CH$_3$OH + Cl$^-$

   To determine the equilibrium bond length (the shortest length for the constrained F-C, I-C, or O-C bonds), build just methyl fluoride, just methyl iodide, and just methanol separately. Minimize the energy of the build and then Measure Distance of the F-C, I-C, or O-C bond. The constrained bonds will be 5 – X Å, where X is the equilibrium distance you measured independently. Use the same values as above for the C-Cl bond constraints (1.767 – 5 Å).

2. Copy the data from the Spartan spreadsheets for each reaction into MS Excel and plot the three data sets in the same figure. Compare the reactions. What characteristics do you notice?

3. Based on your data, which Lewis base (F, Cl, I, or OH) is bound more tightly to the methyl group? Explain your answer.

4. Based on your data which Lewis base do you think is the best "leaving group"? Explain your answer.

5. Determine the activation energy and use MS Excel to calculate the rate constant for each reaction at 20 °C. Refer to an independent cell that has the temperature in it so that you can change the temp and see how the rate constant changes.

6. Some students executed a lab where they investigated the rate of the S_N2 reaction, the hydrolysis of chloromethane:
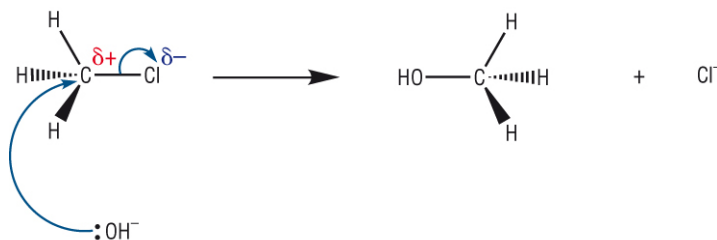
Their experimental data is provided in the table below.

Experiment	$[CH_3Cl]_0$, M	$[OH^-]_0$, M	Initial reaction rate, M/s
1	0.001	1	4.90E-07
2	0.002	1	9.80E-07
3	0.001	2	9.80E-07
4	0.002	2	1.99E-06

Determine the rate law, the rate constant, and the activation energy of this reaction.

7. How well do your simulations match the experimental data? Explain your answer.

8. Given your simulated activation energy and rate constant for the hydrolysis of chloromethane, at what temperature would you need to run the reaction to match the experimental rate of the reaction above? Is this reasonable? Explain your answers.

9. If you were to change the level of theory in your calculations would get different values for the activation energies of these reactions, but they would still be ~two orders of magnitude greater than the true values. Since Spartan is not good at predicting the absolute value of these energies, what is Spartan good for?