7.4: Exercise Questions

1. Please estimate the change in Enthalpy (ΔH°), Entropy (ΔS°), and Gibbs free energy (ΔG°) for the substitution reaction shown below using the BDE values provided in Figure 2. For full credit please show your work.

$$\mathrm{Br^-} + \mathrm{H_3C-Cl} \longrightarrow \mathrm{Br-CH_3} + \mathrm{Cl^-}$$
$$\mathrm{C-Cl}\ \ \mathrm{BDE} = 84\ \mathrm{kcal/mol}$$
$$\mathrm{C-Br}\ \ \mathrm{BDE} = 68\ \mathrm{kcal/mol}$$

2. Given your answer above, what side of the reaction (reactants or products) will be favored?
3. Please use the thermodynamic values found at the end of the output files for the starting materials and products to complete the following table. Please provide all energy in Hartree (E_H). The temperature that the thermochemical calculations were performed at was 298.15 K.

	Gibbs Free Energy, $G(E_H)$	Enthalpy, $H(E_H)$	Product of Entropy and Temperature, $T \times S, (E_H)$	Entropy, $S(E_H/K)$
Products				
Starting Materials				

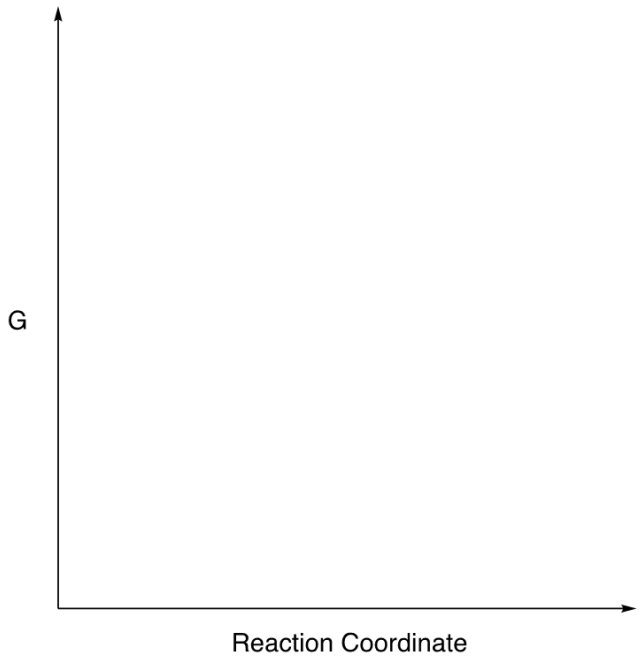
4. Using the values from the table in question 3, please complete the following table calculating the change in Enthalpy (ΔH°), Entropy (ΔS°), and Gibbs free energy (ΔG°) in Hartree and in kcal/mol. For conversion there are 627.5 kcal/mol in 1 Hartree.

ΔG°	ΔH°	ΔS°
Eh	Eh	Eh/K
kcal/mol	kcal/mol	cal/mol*K

5. Please discuss the difference between the estimated thermochemical values from question 1 and the calculated thermochemical values from question 4. Are the calculated values of ΔG°, ΔH°, and ΔS° close to what you expected? Please explain.
6. To help determine the activation free energy of the reaction ($\Delta G^\ddagger$) please complete the following table. We will normalize all the energies so that the energy of the starting materials will be zero. Do this by adding the energy value of the starting materials (in kcal/mol) to the energy values of the transition state and that of the products. (Note: a correct answer will have a TS that is higher in energy than the starting materials which should have a normalized value of 0)

	$G(E_H)$	G (kcal/mol)	Normalized G (kcal/mol)
Starting Materials			
Transition State			
Products			

7. Please draw a reaction coordinate diagram of the substitution reaction between bromide and chloromethane using the data from question 6. For full credit your reaction coordinate diagram should label the starting material, transition state, ΔG°, and $\Delta G^\ddagger$.



8. A. According to the Hammond postulate the transition state should resemble the species it is closest to in energy. Using your data from question 6, should the transition state look more like the reactants or the products?
   B. Using the measuring tool in Avogadro (looks like a ruler) determine the distances between the carbon and bromine atoms and the carbon and chlorine atoms in the transition state to complete the table below.

	$C-Br$ Bond Distance	$C-Cl$ Bond Distance
Distance, Angstroms		

   C. For this question you know that $C-Br$ distance is 2.075 Angstroms in the products and the $C-Cl$ bond distance in the starting materials is 1.846 Angstroms. Does the computer structure of the transition state fit your expectation of what it should look like given the Hammond postulate? In other words, does it look like either the product or starting material as expected? Please explain.

$C-Br$

$$\%\ \text{Difference} = \frac{C-Br_{Ts} - C-Br_{Product}}{C-Br_{Product}} \times 100\% =$$

$C-Cl$

$$\%\ \text{Difference} = \frac{C-Cl_{Ts} - C-Cl_{Product}}{C-Cl_{Product}} \times 100\% =$$
