12.4: Exercise Questions

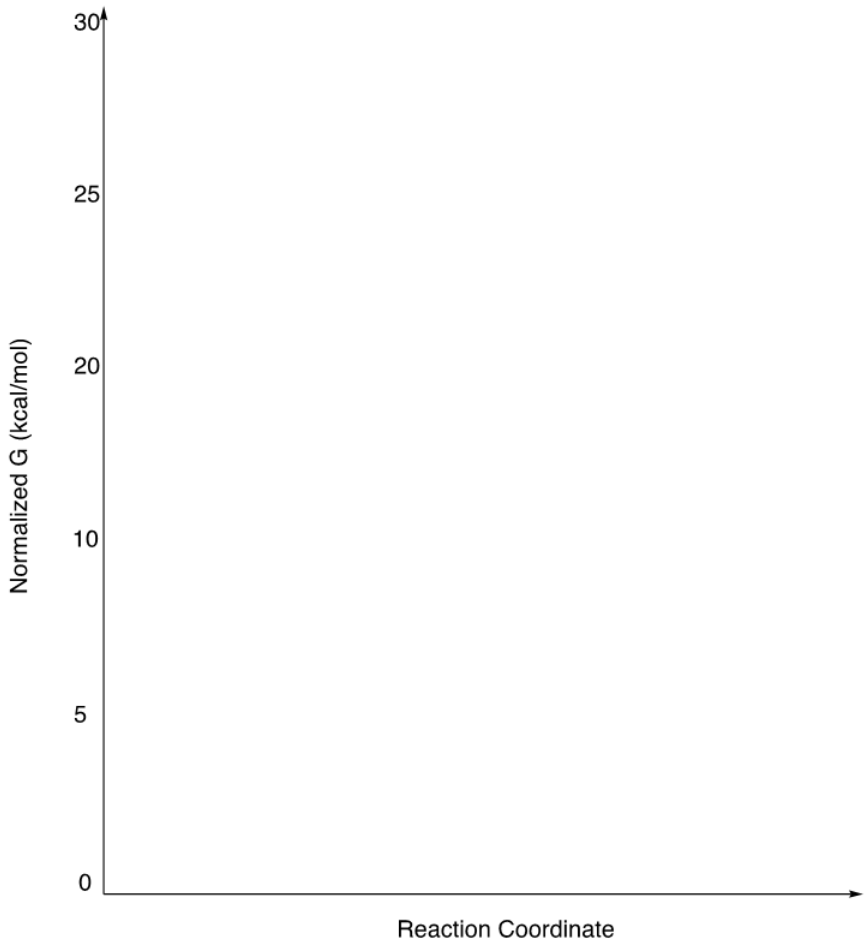
1. Please use the energy values that you calculated in addition to the transition state calculations (provided) to complete the following table. The values provided by Orca are in Hartree. You can then convert these values to kcal/mol by multiplying the values in Hartree by 627.5 kcal/mol. You should then normalize all the values to the oxetane opening starting material by subtracting all energy values by the Gibbs Free Energy that the Oxetane Opening starting material. If done correctly your normalized Oxetane Opening Starting Material should be 0 kcal/mol.

Species	Gibbs Free Energy (Eh)	Gibbs Free Energy (kcal/mol)	Gibbs Free Energy (kcal/mol), normalized to Oxetane Starting Material
Oxetane Opening Starting Material			
Oxetane Opening Transition State	-34.57930416		
Oxetane Opening Products			
Epoxide Opening Starting Material			
Epoxide Opening Transition State	-34.57906255		
Epoxide Opening Products			

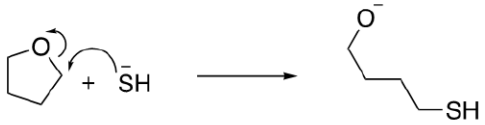
2. Using the values from the table in question one, please calculate the ΔG° and $\Delta G^\ddagger$ for the epoxide and oxetane opening reactions.

Reaction	ΔG° (kcal/mol)	$\Delta G^\ddagger$ (kcal/mol)
Epoxide Opening		
Oxetane Opening		

3. Using the data from question 1 and question 2, please compose a reaction coordinate diagram showing the energetics of both reactions (on the same diagram). For full credit you should draw depictions of the starting materials, transition state, and products of both reactions. Moreover, you should label the ΔG° and $\Delta G^\ddagger$ (with specific values) for both reactions.



4. Are the epoxide and oxetane opening reactions spontaneous? Which reaction do you think will be faster? Please explain.
5. Which cyclic ether is more reactive, the oxetane or epoxide? How does ring strain influence this reactivity? Please explain briefly (~1 paragraph).
6. Tetrahydrofuran (C_4H_8O) is a five-membered cyclic ether analogous to epoxide and oxetane. Predict whether tetrahydrofuran would be more or less reactive to substitution from hydrosulfide than oxetane. Please predict how the $\Delta G^{\ddagger}$ for the opening of THF with the hydrosulfide anion would compare to the $\Delta G^{\ddagger}$ for the opening of an epoxide or an oxetane. Please explain.



7. Which of the measured transition states, epoxide-opening or oxetane-opening, do you expect to be more product like? Please explain your answer using the Hammond Postulate.
8. By pulling up the output files in Avogadro please measure the distances of the carbon-oxygen bonds broken in the reaction and complete the table below. Which transition state has a C-O bond length closer to that of their corresponding starting material? Do these data fit with your answer in question 7?

Reaction	Starting Material C-O Bond Distance, Å	Transition State C-O Bond Distance, Å	Difference, Å
Epoxide Opening			
Oxetane Opening			