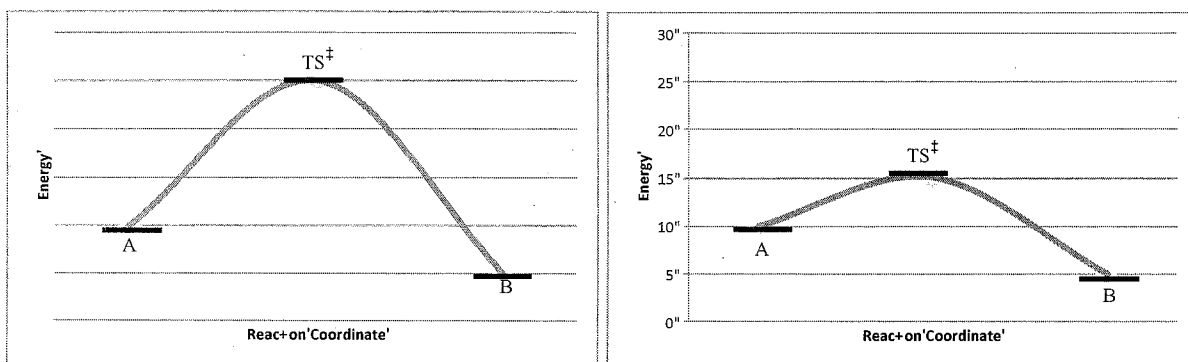


Key

**Chem 51A - SSI 2014**  
**Discussion 7 Worksheet**  
Dr. Renee Link

This worksheet will focus on concepts to be discussed or already discussed, in Chapter 6. Those concepts being 1) Organic Reactions 2) Thermodynamics 3) Kinetics.

**Reaction coordinate diagrams** (RCD) and can be used as a visual way to examine the progress of a reaction. You should be able to identify and/or draw a reaction coordinate diagram with the proper labeling of the starting materials, product, transition state and activation energy ( $E_a$ ). One final thing you can visualize on a RCD is the **change in enthalpy** ( $\Delta H$ ).



The change in enthalpy of a reaction is, essentially, the changes in energy that result in the forming and breaking of bonds. This is a **thermodynamic property**.

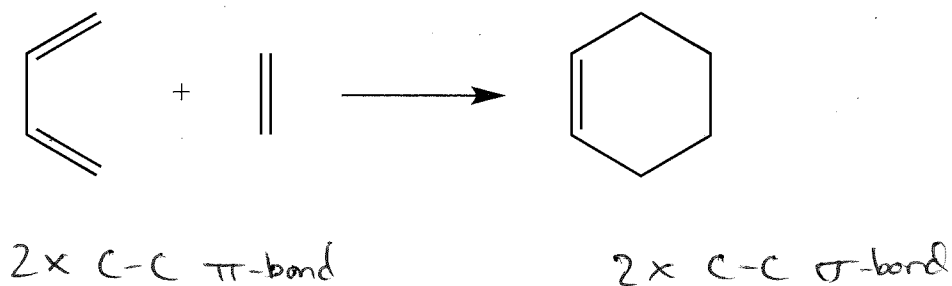
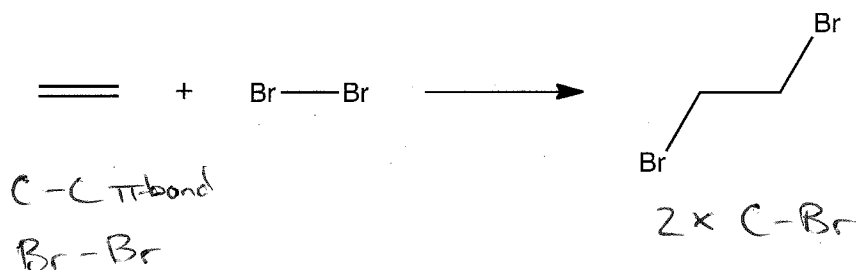
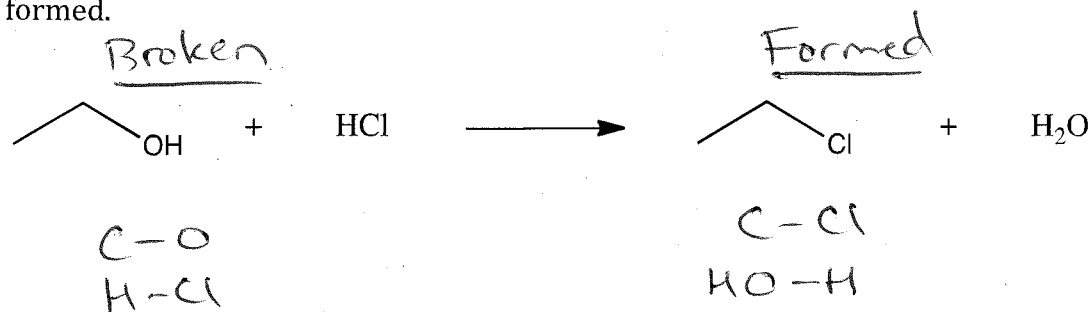
**Thermodynamics** of a reaction have no relation to the **kinetics** of a reaction.

Is bond breaking endothermic or exothermic? What about bond forming?

Bond breaking takes energy (is endothermic) and bond forming releases energy (is exothermic).

To calculate the  $\Delta H$  of a reaction, the **bond dissociation energies (BDE's)** of the bonds in question are used. BDE's are calculated from **homolytic** bond cleavages. However, because enthalpy is a **state function**, we can use these homolytic bond cleavage values for the **heterolytic** bond cleavages we will discuss.

For each of the below reactions, identify what bonds are broken and what bonds are formed.



You are expected to be able to look at a BDE table and calculate the  $\Delta H$  of a reaction. *Do not memorize BDE tables.* If you would like some practice, and you do, use the table in Appendix C of your textbook to calculate the  $\Delta H$  of the above reactions. As a hint, the pi bond of a double bond is not equal to the sigma bond of a double bond. See if you can figure out the value for the pi bond component of a double bond.

As you should remember from General Chemistry,

$$\Delta G = \Delta H - T\Delta S$$

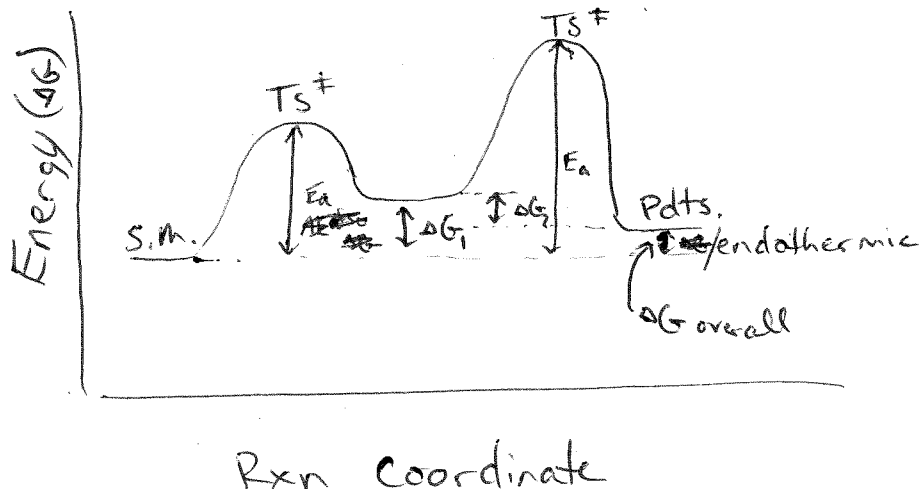
Generally,  $T\Delta S$  is so small that it can be ignored and  $\Delta G \approx \Delta H$ . That being said, you must still be able to plug in values to the above equation and determine whether a reaction is spontaneous or not and why.

Also from General Chemistry, you should remember

$$\Delta G = RT \ln K_{eq}$$

for equilibrium processes. Again, you must still be able to plug values into the above equation and determine what side of an equilibrium process is favored and why. Processes that fall under equilibrium are some you are familiar with, such as acid/base reactions, and others that you have recently learned about, like chair conformations. You should be capable of determining product/reactant ratios of any given equilibrium.

Draw an overall **endothermic** two-step reaction coordinate diagram labeling the transition states, the activation energies, the individual  $\Delta G$  changes and the overall  $\Delta G$  change where the **second** transition state is the one highest in energy.



**Kinetics** is the study of reaction rates. Remember that kinetics and thermodynamics are separate, distinct concepts.

What determines the speed of a single-step reaction?

The  $\Delta G^\ddagger$  (the height of the barrier) from starting materials (S.M.) to the transition state.

What determines the speed of a multi-step reaction?

The  $\Delta G^\ddagger$  (height of the barrier) from starting materials to the highest energy transition state.

Yet another facet of General Chemistry that has returned: **rate law equations**.

Individual reactions can have one or more steps, as you already know from the RCD you drew above. Reactions that occur in one-step are called **concerted**. Reactions that occur in more than one step are called **stepwise**. Whether a reaction is concerted or stepwise has **nothing** to do with how many reagents are being used and is entirely dependent on the mechanism of the reaction. Both of the below reactions could be concerted or stepwise.

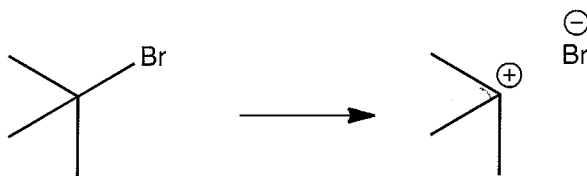


Similarly, whether a reaction is concerted or stepwise has **nothing** to do with the **order** of a reaction. The order of a reaction is dependent on what step of the reaction is the **rate-determining**, or slowest, step (RDS). Obviously, in a concerted reaction there is only one step and that is the rate-determining step.

What was the RDS of the two-step RCD you drew above, again?

The second step.

Once you have decided what the rate-determining step is, you must examine what species are involved with it. An RDS with only one species involved is **unimolecular**. For example, the below process is a unimolecular process.



The rate law of a reaction with a unimolecular RDS is

$$\text{rate} = k[A]$$

What is the rate order with respect to A?

1

What is the overall order of this rate law?

1

If a reaction ( $A + B \rightarrow C$ ) has a rate law first order in A and zeroth order in B, how does quadrupling the concentration of B affect the rate? What if you double A?

Changing B does not affect the rate. Doubling A doubles the rate.

An RDS with two species involved is called a **bimolecular** process.



The rate law of a bimolecular reaction is

$$\text{rate} = k[A][B]$$

What is the rate order with respect to A?

1

What is the rate order with respect to B?

1

What is the overall order of this rate law?

2

If a reaction ( $A + B \rightarrow C$ ) has an <sup>RDS</sup> with a rate law of  $\text{rate} = k[A][B]$ , how does quadrupling the concentration of B affect the rate? What if you double A?

$$\begin{aligned} \text{rate} &= k[A][4B] \text{ means rate } \times 4 \\ \text{rate} &= k[2A][B] \text{ means rate } \times 2 \end{aligned}$$

If the reaction is changed to  $A + B + C \rightarrow D$  and the rate law remains the same, if you double the concentration of C, how does the rate change? What does this mean for the presence of C in the <sup>RDS</sup>?

C must be involved after the RDS, so changing concentration of C has no effect on the rate.

\*Know that catalysts reduce energy of the transition state and, by extension, the activation energy of a reaction, **not** the energy levels of the starting materials or the products.