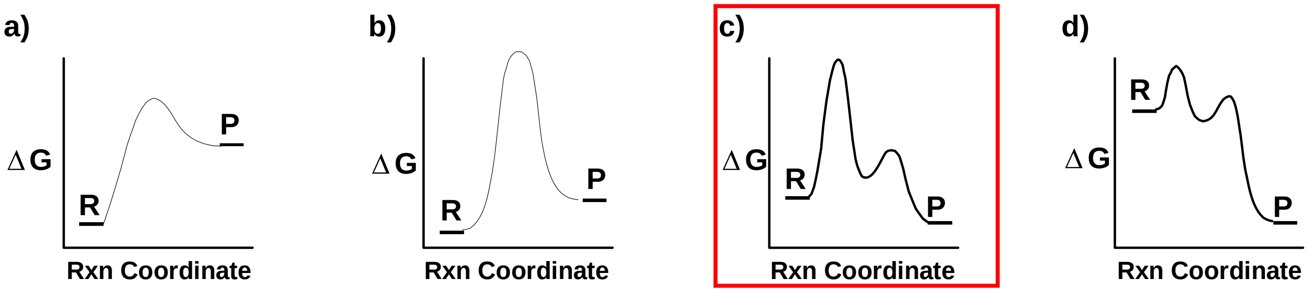
CHEM 1422 - Homework # 3 *ANSWER KEY*

Chemical Kinetics

Due Feb 12, 2009 (2 PM)

Check the box to the right if you want your graded homework to be placed out in the public rack outside Prof. Stanley's office. Otherwise you will have to pick up your homework from Prof. Stanley in person: ☐

1. (3 pts) Which of the following energy diagrams best represents the *slowest* spontaneous reaction? Circle your choice. Give a brief, but clear, explanation for your answer below the diagrams.

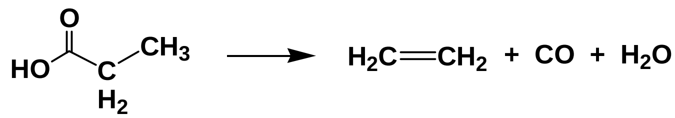


A spontaneous rxn is one that is thermodynamically "downhill" (products are lower in energy than reactants, negative ΔG value). Only c) and d) are spontaneous rxns. The slowest spontaneous rxn will have the largest activation energy, which narrows the choice to c).

2. (5 pts) a) Describe in your own words and terms where the origin of the activation barrier comes from and what it represents in a chemical reaction. **b)** Given the same thermodynamic factors, consider the reaction of two ***small*** molecules or two ***large*** molecules with one another. Which pair should have the ***higher activation energy***? Why?

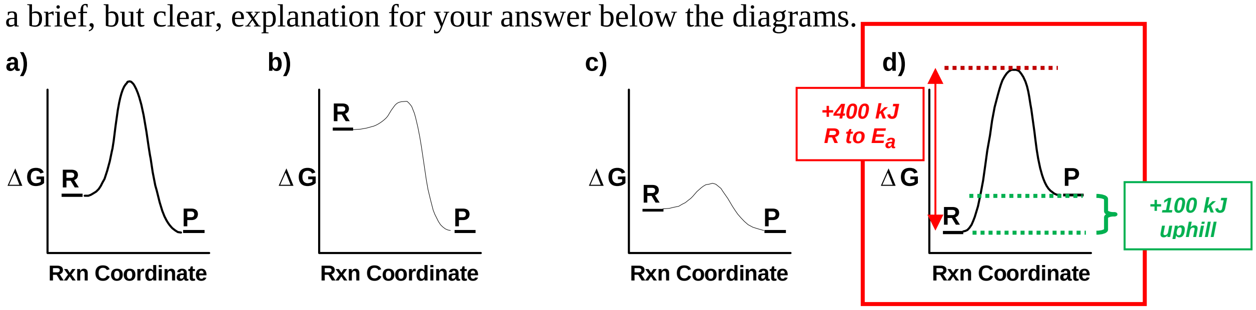
The activation energy represents the probability that two molecules (for a bimolecular rxn) will react when they have a collision. The more reactive the two molecules the more likely they will react when they collide (smaller activation energy, higher probability of reaction). Since most rxns involve the breaking and making of chemical bonds between two parts of two different molecules, the smaller the molecule the fewer "non-reactive" bonds present and the higher the probability that when the two molecules collide the reactive portions of the molecules will come into contact and actually react. For two large molecules, there are many more bonds present that will not react, thus reducing the odds that the two reactive portions of the molecule will come together in the right way to react. Thus two larger molecules will have a lower probability of getting the right portions together to react and thus will have a higher activation energy relative to two small molecules. In biological systems that are composed of large complicated molecules, Mother Nature counters this effect to some extent by designing channels that guide small molecules to the reactive portion of the large enzyme. The use of opposite charges on two large proteins can also help guide the reactive portions of these molecules together, thus increasing the odds of proper rxn occurring.

3. (3 pts) Consider the following reaction and information:



ΔG = +100 kJ/mol   Activation Energy = +400 kJ/mol

Circle the energy curve shown below (**R** = reactants, **P** = products) that best represents the reaction described above? Give a brief, but clear, explanation for your answer below the diagrams.



ΔG = +100 kJ/mol indicates an endoergic or uphill rxn. Only (d) has the product energies higher than the reactants. The activation energy barrier of 400 kJ should be about 4 times larger than ΔG as measured from the reactant energy to the top of the activation energy barrier, which is the case for (d).

4. (5 pts) Consider the following reaction and kinetic data. Circle the correct kinetic rate expression for this reaction. <u>Show all your work and/or discuss your reasoning.</u>

$$2A + B \longrightarrow C + D$$

a) rate = k[A][B] **b)** rate = $k[A]^2$ **c)** rate = k[B] **d)** rate = $k[B]^2$ **e)** rate = $k[A][B]^2$

Exp #	[A]	[B]	Initial Rate (Msec^{-1})
1	0.2 M	0.1 M	0.02
2	0.4 M	0.1 M	0.04
3	0.2 M	0.3 M	0.18
4	0.4 M	0.3 M	0.36

For experiments #1 & #2, the concentration of [A] doubles, while [B] stays the same. Doubling the conc. of [A], then, causes the initial rate to double. Thus there is an exponent of 1 on [A].

For experiments #1 and #3, the conc. of [B] is tripling (factor of 3), while [A] stays the same. When the conc. of [B] triples, the initial rate increases by a factor of 9. Thus, the exponent on [B] is 2 (i.e., $[3]^x = 9$, therefore x = 2). So the kinetic rate expression is: rate = $k[A][B]^2$ Overall, this is a third order rxn.

5. (5 pts) Consider the following reaction and kinetic data. Circle the correct rate constant for this reaction. Clearly show all your work including the rate law that you determine.

$$\mathbf{A + 2B \longrightarrow C + D}$$

a) 2.2 x 10^{-6} M^{-1}sec^{-1} **b)** 22 M^{-1}sec^{-1} **c)** 220 M^{-1}sec^{-1} **d)** 0.05 M^{-1}sec^{-1} **e)** not enough data

Exp #	[A]	[B]	Initial Rate (Msec^{-1})
1	0.2 M	0.1 M	0.002
2	0.2 M	0.2 M	0.002
3	0.4 M	0.2 M	0.008
4	0.8 M	0.4 M	0.032

For experiments #1 & #2, the concentration of [A] stays the same, while [B] doubles. But doubling the conc. of [B] does not cause any change in the initial rate of the reaction. Thus there is an exponent of 0 on [B], which means that it is not in the kinetic rate expression.

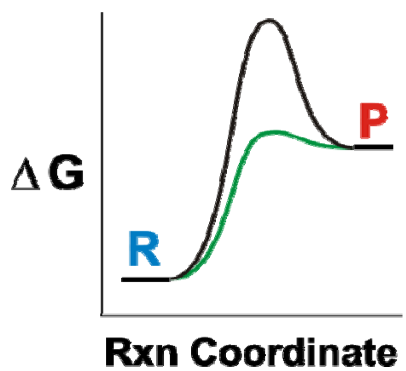
For experiments #2 and #3, the conc. of [A] doubles (factor of 2), while [B] stays the same. When the conc. of [A] doubles, the initial rate increases by a factor of 4. Thus, the exponent on [A] is 2 (i.e., $[2]^x = 4$, therefore x = 2). So the kinetic rate expression is: rate = k$[A]^2$ Overall, this is a second order rxn.

Now that we have figured out the kinetic rate expression, we can calculate *k* the rate constant. You can take any of the four experimental runs and substitute in the various values into the kinetic rate expression and solve for the rate constant. I'll use experiment # 1:

rate = k$[A]^2$ or 0.002 Msec^{-1} = k $[0.2\text{ M}]^2$ or k = (0.002 Msec^{-1})/(0.04 M^2) = 0.05 M^{-1}sec^{-1}

6. (4 pts) Catalysts can be used on non-spontaneous reactions to lower the activation barrier. If a catalyst lowers the activation barrier too much, however, a serious problem can arise. Consider the diagrams shown below. What is the problem for the catalyzed rxn with the lower activation energy? Why can a "substantial" activation barrier actually help an "uphill" chemical reaction if one wants to make as much product as possible?

If you lower the activation energy too much for a non-spontaneous rxn the products will react backwards quickly to make reactants. The presence of an activation barrier can help to slow the back-reaction to the more stable reactants. This is NOT a problem for a spontaneous rxn where the products are significantly more stable than the reactants and will not want to back-react.



7. (5 pts) A reaction has a initial rate of reaction of 0.001 Msec^{-1} at 70°C. This increases to 0.100 Msec^{-1} at 90°C. Calculate the activation energy for this reaction?

First you need to convert the temperatures into kelvin: 70° + 273 = 343 K; 90°C + 273 = 363 K
The Arrhenius equation uses rate constants, what are given in this problem are initial reaction rate. BUT, reaction rates are directly proportional to rate constants, so the ratio of either will be the same!

$$E_a = \frac{R \ln \frac{k_2}{k_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = \frac{8.314\text{ J/molK} \times \ln\left(\frac{0.1}{0.001}\right)}{\left(\frac{1}{343} - \frac{1}{363}\right)} = \frac{(8.314)\ln(100)}{1.61\times10^{-4}} = \frac{(8.314)(4.605)}{1.61\times10^{-4}} = \frac{38.29}{1.61\times10^{-4}}$$

$$E_a = 2.38\times10^5\text{ J/mol} = \boxed{238\text{ kJ/mol}}$$