Kinetics
5.5 Collision Model
5.6 Reaction Energy Profile
5.10 Multistep Reaction Energy Profile
Worksheet Key

1) The table below outlines the results from three experiments, which were conducted at the same temperature, involving the following reaction.

$$O_2(g) + 2\ NO(g) \rightleftharpoons 2\ NO_2(g)$$

Experiment	$[O_2]_{initial}$	$[NO]_{initial}$	Initial Reaction Rate
1	0.022	0.026	0.0256 M/s
2	0.022	0.013	0.0064 M/s
3	0.044	0.013	0.0128 M/s

a. The results show that the initial rate increased when the initial concentration of either reactant increased. Explain why increasing the concentration or partial pressure of a reactant can increase the rate at which the reaction proceeds.

When the concentration of a reactant increases there is more of that reactant circulating within the same volume. As a result there will be more collisions between reactants per second. The reaction rate increases when the collision rate increases.

b. What environmental factor could be altered in order to increase the initial reaction rate in experiment one if the initial concentrations of the reactants remained the same? Justify your answer.

Increasing the temperature would increase the initial reaction rate. By increasing the temperature, you are increasing the average kinetic energy of the molecules in that system. In doing so, you are increasing the average velocity of these particles. The collision rate increases as molecular speed increases. This rule is amplified when the reactants are gases, but it is also true for other states.

c. What is the order of the reaction with respect to NO? Show your work.

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{k[O_2]_1^m[NO]_1^n}{k[O_2]_2^m[NO]_2^n}$$

$$\frac{0.0256 M/\text{s}}{0.0064 M/\text{s}} = \frac{k[0.022]^m[0.026]^n}{k[0.022]^m[0.013]^n}$$

$$4 = \frac{k[0.026]^m}{k[0.013]^m} = 2^m$$

$$m = 2 \text{ (second order for NO)}$$

d. What is the order of the reaction with respect to O_2? Show your work.

$$\frac{\text{Rate 3}}{\text{Rate 2}} = \frac{k[O_2]_3^m[NO]_3^n}{k[O_2]_2^m[NO]_2^n}$$

$$\frac{0.0128M/\text{s}}{0.0064M/\text{s}} = \frac{k[0.044]^m[0.013]^n}{k[0.022]^m[0.013]^n}$$

$$2 = \frac{[0.044]^n}{[0.022]^n} = 2^n$$

$$n = 1 \text{ (first order for } O_2)$$

e. Find the rate law for this reaction.

Rate = $k[NO]^2[O_2]$

f. What is the overall order of this reaction?

The overall order for the reaction is three, as: order = $n + m = 2 + 1 = 3$

g. Find the rate constant, k, for the reaction. (Include the units)

$$\text{Rate} = k[NO]^2[O_2]$$

$$k = \frac{\text{Rate}}{[NO]^2[O_2]} = \frac{0.0256}{(0.026)^2(0.022)} = 1700\ M^{-2}\text{s}^{-1}$$

h. If the same three experiments were conducted at a lower temperature, would the magnitude of the rate constant be greater than, less than, or equal to the value calculated above? Justify your answer.

The magnitude of the rate constant would be less than the value calculated above. At lower temperatures, the frequency of collisions between reactants is reduced. Also, the average *KE* of the reactants is less at lower temperatures, so fewer collisions would produce enough energy (activation energy) to cause a reaction. Thus, the rate at which the reaction proceeds is reduced. As the initial concentrations would be the same, the rate constant must have a smaller magnitude, as Rate = $k[NO]^2[O_2]$.

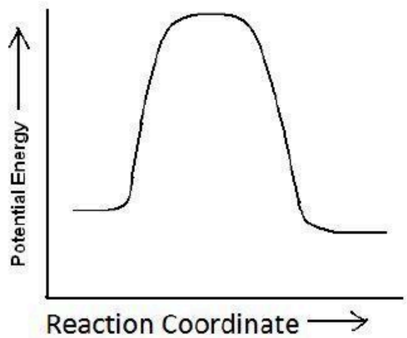
2) Not all collisions between reactants result in the formation of products for any elementary reaction. Explain why this is.

For most reactions, most collisions <u>do not</u> cause a chemical reaction. The orientation of each collision is completely random. Reactants must collide with an orientation that is conducive to the formation of a bond. Also, the collisions must possess sufficient energy (activation energy) to produce a reaction.

3) What is the difference between E_a and ΔE?

The activation energy, E_a, is the minimum amount of energy that is required for a reaction to occur.
The change in energy, ΔE, is the energy that is lost or gained in the chemical reaction. It is the difference between the potential energy locked up in the bonds of the reactants and the potential energy locked up in the bonds of the of the products. Most of the energy is lost or gained in the form of heat, ΔH. The remaining portion of this energy change comes from the work done on or by the system, which is related to changes in pressure and volume that occur during the chemical reaction.

4) The energy profile diagram below was plotted for the following second order elementary reaction: $A + BC \rightleftharpoons AB + C$.



a. At low temperatures a relatively small fraction of collisions between reactants result in the formation of products. Describe the interactions between reactants that collided with an orientation that would produce products, but failed to do so.

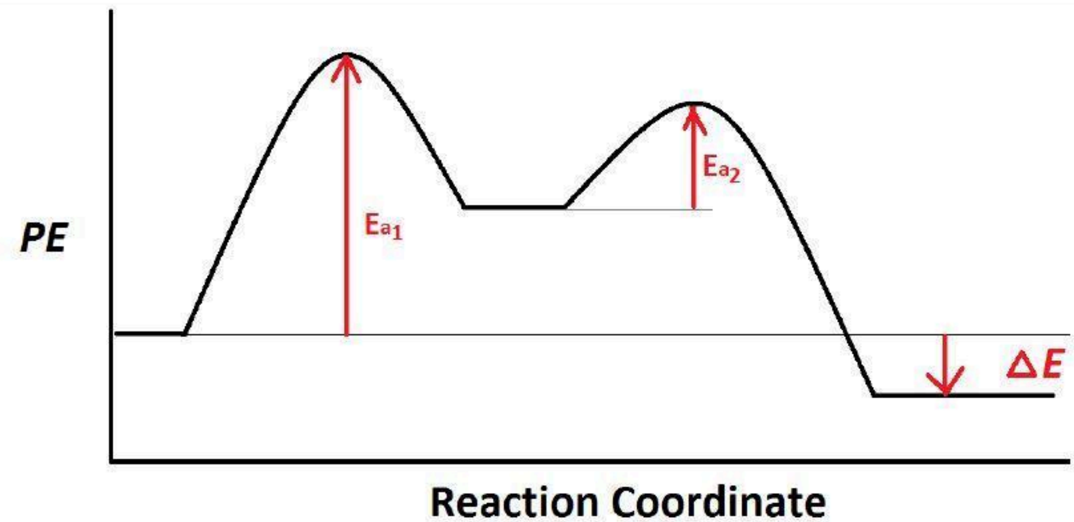
If the two species collide with the correct orientation, but with insufficient energy, the two molecules will bond together temporarily ($A + BC \rightarrow A\text{-}B\text{-}C$); however, they will not produce products. Instead, the temporary bonds will lose *PE*, and they will once again form separate reactants ($A\text{-}B\text{-}C \rightarrow A + BC$).

b. At high temperatures a relatively large fraction of collisions between reactants resulted in the formation of products. Describe the interactions between the reactants from the moment of a collision through to the formation of separate products.

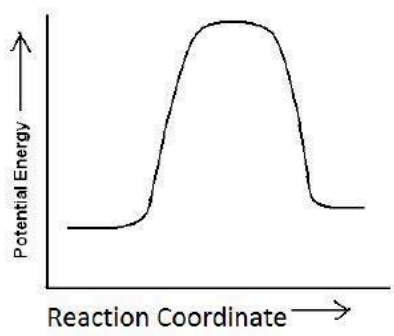
When two molecules collide, the *KE* from their motion is converted into *PE*. This *PE* cultivates itself in the bonds between all of the reacting atoms ($A + BC \rightarrow A\text{-}B\text{-}C$). In this case, A forms a new bond with B, and the bond between B and C lengthens. At the top of the curve, the *PE* contained within the bonds of A-B-C has reached a maximum. At this point we do not have reactants and we do not have products. What we have is an extremely unstable aggregation of all of the atoms contained by the reacting molecules. During the downward section of the graph, the *PE* begins to drop. The electron density

increases between A and B, causing that bond to shorten. The electron density between B and C decreases, causing that bond to continue stretching. When the graph plateaus again, there are two separate species: AB and C.

5) Draw a two step reaction energy profile that satisfies the following conditions. Show the activation energy for each step and the overall energy change.
   a. The first is the rate determining step.
   b. The first step is endothermic.
   c. The second step is exothermic.
   d. The overall process is exothermic.



6) A chemical reaction takes place in a beaker that you are holding. While the reaction is taking place, your hand feels cold.
   a. Sketch a reaction energy diagram for the reaction.

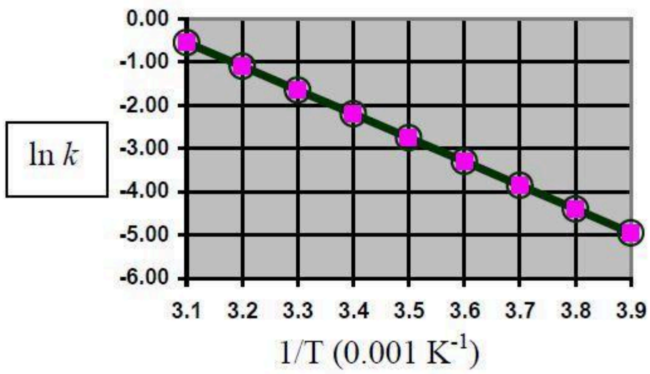


Products contain more *PE*. You need to be able to label the *x* and *y*-axis correctly. Potential energy is on the y-axis. Reaction Coordinate is on the *x*-axis.

   b. Is the reaction endothermic or exothermic?

Endothermic

7) The graph below can be used to find the activation energy, E_a, for a chemical reaction.



a. Label the *y*-axis on the graph. 4.B.3.c.

b. Calculate the activation energy for the reaction in question.

using points (3.2, -1.00) and (3.9, -5.00)

$$slope = \frac{rise}{run} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{-5.00 - (-1.00)}{(3.9\times10^{-3}) - (3.2\times10^{-3})} = -5700K$$

4.B.3.c.

$$slope = -\frac{E_a}{R}$$

$$E_a = -slope \times R = -(-5700\text{ K})(8.314\text{ J/Kmol})$$

$$E_a = 47000\text{ J/mol} = 47\text{ kJ/mol}$$