5.4 Elementary Reactions

Essential knowledge statements from the AP Chemistry CED:

- The rate law of an elementary reaction can be inferred from the stoichiometry of the molecules participating in a collision.
- Elementary reactions involving the simultaneous collision of three or more particles are rare.

5.7 Introduction to Reaction Mechanisms

Essential knowledge statements from the AP Chemistry CED:

- A reaction mechanism consists of a series of elementary reactions, or steps, that occur in sequence. The components may include reactants, intermediates, products, and catalysts.
- The elementary steps when combined should align with the overall balanced equation of a chemical reaction.
- A reaction intermediate is produced by some elementary steps and consumed by others, such that it is present only while a reaction is occurring.
- Experimental detection of a reaction intermediate is a common way to build evidence in support of one reaction mechanism over an alternative mechanism.

In Topic 5.2, you were given the following advice about determining the order of a reactant:

The order must be determined from experimental data. You CANNOT assume that the order of a reactant is simply its coefficient in the overall chemical equation. This is because the overall equation does not tell us exactly how the reactant particles collide with each other in order for bonds to break and/or form.

In Topics 5.4 and 5.7, you should understand that an elementary reaction, also known as an elementary step in a mechanism, is a special type of particle-level reaction.

If you are asked to write the rate law for an elementary step in a mechanism, you CAN say that the order with respect to a certain reactant is equal to its coefficient in the elementary step. This is because an elementary step represents a collision event between reactant particles.

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The chemical equation shown above provides information about the reactants and the products. However, it does not provide details about how this chemical reaction takes place at the particle level.

Step #1: $NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$

Step #2: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$

Overall Equation: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

1. The reaction mechanism shown above has been proposed for the reaction between $NO_2(g)$ and $CO(g)$. This proposed mechanism consists of two elementary steps.

   (a) Write the rate law for elementary step #1: ________________________________

   (b) Write the rate law for elementary step #2: ________________________________

1. (continued)

(c) An intermediate is a substance that is formed as a product in an earlier step of a mechanism and then consumed as a reactant in a later step of the mechanism. An intermediate is not included in the overall balanced chemical equation.

Which substance is classified as an intermediate in this mechanism? ____________________

2. A reaction mechanism is shown below that consists of two elementary steps.

Step #1: $O_3(g) \rightarrow O_2(g) + O(g)$

Step #2: $O_3(g) + O(g) \rightarrow 2\ O_2(g)$

(a) Write the rate law for elementary step #1: ____

(b) Write the rate law for elementary step #2: ____

(c) Which substance is classified as an intermediate in this mechanism? ____________________

(d) Write the balanced equation for the overall chemical reaction. _________________________

3. A reaction mechanism is shown below that consists of two elementary steps.

Step #1: $Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$

Step #2: $ClO(g) + O_3(g) \rightarrow Cl(g) + 2\ O_2(g)$

(a) Write the rate law for elementary step #1: ____

(b) Write the rate law for elementary step #2: ____

(c) Which substance is classified as an intermediate in this mechanism? ____________________

(d) A catalyst is a substance that is consumed as a reactant in the first step of a mechanism and then formed as a product in a later step of the mechanism. A catalyst is not included in the overall balanced chemical equation.

Which substance is classified as a catalyst in this mechanism? _________________________

(e) Write the balanced equation for the overall chemical reaction. _________________________

$$2\ NO_2Cl(g) \rightarrow 2\ NO_2(g) + Cl_2(g)$$

4. The decomposition of $NO_2Cl(g)$ occurs according to the equation shown above. A student has proposed the following two-step mechanism for this reaction.

Step #1: $NO_2Cl(g) \rightarrow NO_2(g) + Cl(g)$

Step #2: $Cl(g) + NO_2Cl(g) \rightarrow NOCl(g) + ClO(g)$

(a) Identify a specific error that causes the student's mechanism to be incorrect.

(b) Without making any changes to step #1, correct the error described in part (a) by writing new chemical formulas for the products of step #2 of this mechanism.

5.5 Collision Model

Essential knowledge statements from the AP Chemistry CED:

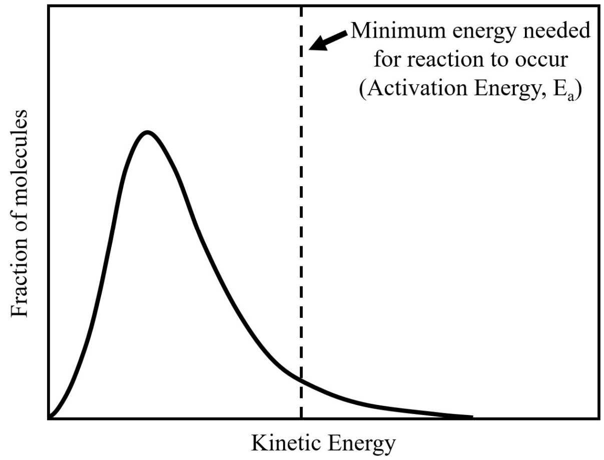
- For an elementary reaction to successfully produce products, reactants must successfully collide to initiate bond-breaking and bond-making events.
- In most reactions, only a small fraction of the collisions leads to a reaction. Successful collisions have both sufficient energy to overcome energy barriers and orientations that allow the bonds to rearrange in the required manner.
- The Maxwell–Boltzmann distribution curve describes the distribution of particle energies; this distribution can be used to gain a qualitative estimate of the fraction of collisions with sufficient energy to lead to a reaction, and also how that fraction depends on temperature.

In Topic 5.1, you learned that the rate of a reaction is influenced by changes in reactant concentrations, temperature, and surface area. Changing these variables affects the frequency of collisions between reactant particles. The reactant particles must undergo successful collisions in order for the products to be formed in a chemical reaction.

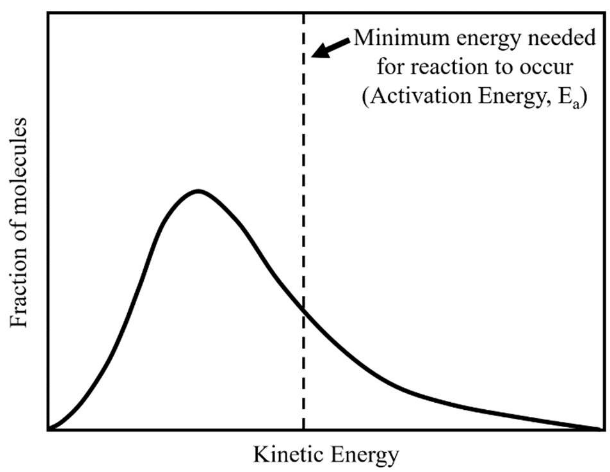
When two reactant particles collide with each other, there are two properties of the collision that will help to determine if the collision is successful, (i.e., result in the formation of the products).

- The collision must occur with a sufficient amount of energy that is required to overcome the activation energy barrier. (More information on the activation energy, E_a, of a reaction will be presented in Topic 5.6.)
- When reactant particles collide, they must have the proper orientation (or alignment) so that certain chemical bonds can be formed and/or broken.

5. The graph below shows a distribution for the collision energies of reactant molecules for a chemical reaction at a certain temperature. The dashed vertical line represents the activation energy (E_a), which is the minimum amount of energy that is required in order for the reactants to be converted into products.



(a) On the diagram above, color or shade in the region/area that represents the fraction of collisions that have enough energy to overcome the activation energy barrier.



(b) Does the diagram above represent a sample of reactant molecules at a lower temperature or a higher temperature than the sample represented by the diagram in part (a)? Justify your answer.

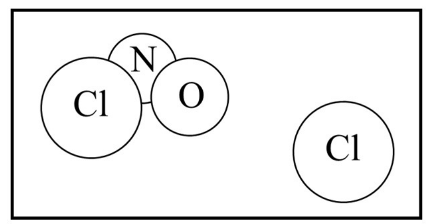
5. (continued)

(c) Explain how a higher temperature affects the collisions between reactant particles so that a chemical reaction occurs at a faster rate at a higher temperature.

You may find the following web sites helpful. Explore how the appearance of the Maxwell Boltzmann distribution curve is affected by changes in temperature.

bit.ly/2_Curves bit.ly/Activation_Energy

$\boxed{NOCl(g) + Cl(g) \rightarrow NO(g) + Cl_2(g)}$

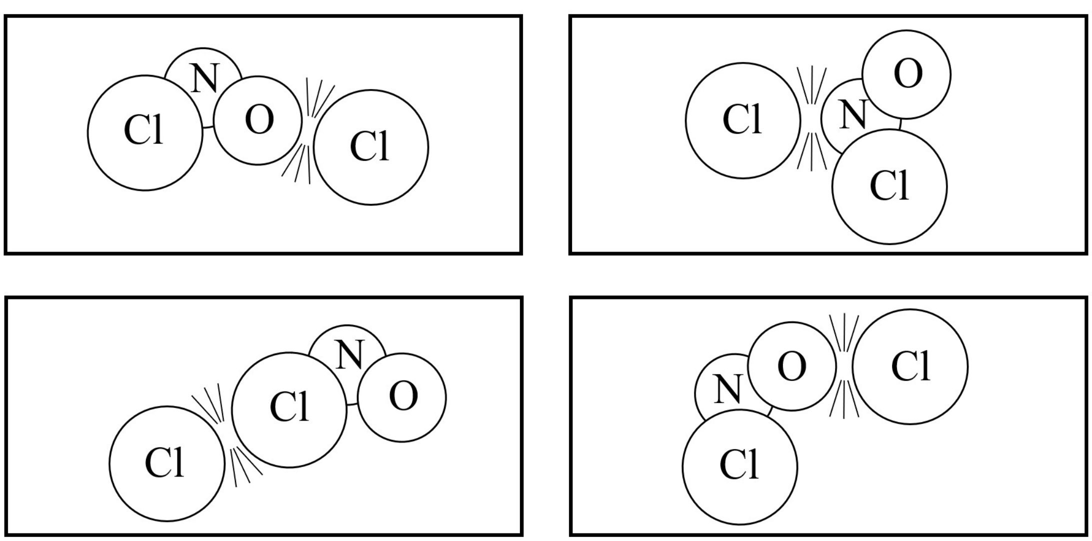


6. A chemical reaction takes place between NOCl(g) and Cl(g) according to the equation shown above on the left. Diagrams that represent the reactant particles are shown above on the right.

(a) During this reaction, a bond is broken between __________ and __________.

(b) During this reaction, a bond is formed between __________ and __________.

(c) The diagrams below represent collisions between the reactant particles. Select the diagram that shows the orientation (or alignment) of particles that is most likely to result in the formation of the products of this reaction.



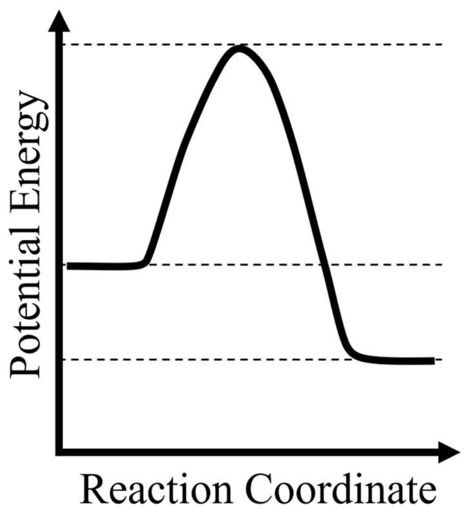
5.6 Reaction Energy Profile

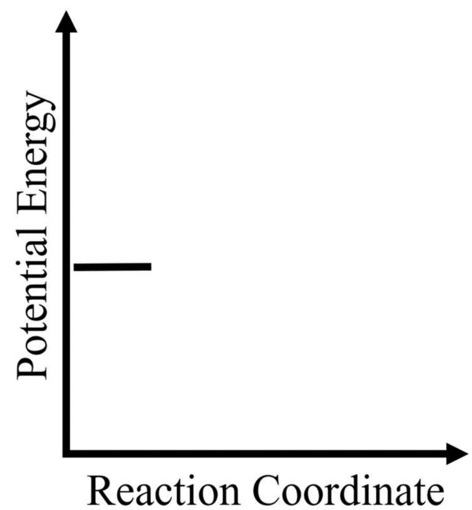
Essential knowledge statements from the AP Chemistry CED:

- Elementary reactions typically involve the breaking of some bonds and the forming of new ones.
- The reaction coordinate is the axis along which the complex set of motions involved in rearranging reactants to form products can be plotted.
- The energy profile gives the energy along the reaction coordinate, which typically proceeds from reactants, through a transition state, to products. The energy difference between the reactants and the transition state is the activation energy (E_a) for the forward reaction.
- The Arrhenius equation relates the temperature dependence of the rate of an elementary reaction to the activation energy needed by molecular collisions to reach the transition state.

Additional information related to Topic 5.6 will be provided in Unit 6.

- Topic 6.1 – Endothermic and Exothermic Processes
- Topic 6.2 – Energy Diagrams





7. The diagram shown above on the left represents a reaction energy profile for a chemical reaction. The diagram shown above on the right represents an incomplete reaction energy profile for a different chemical reaction.

   (a) On the diagram shown above on the left…

      (i) …write an "R" to indicate the potential energy of the reactants and a "P" to indicate the potential energy of the products.

      (ii) …draw a star (★) to indicate the location of the transition state along the reaction coordinate pathway.

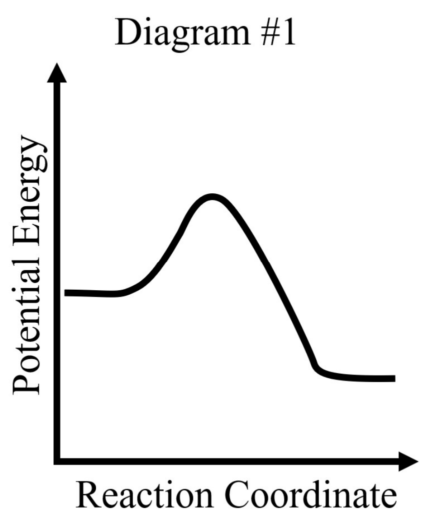
      (iii) …draw a vertical arrow (↕) to indicate the magnitude of the activation energy (E_a) barrier for the reaction.

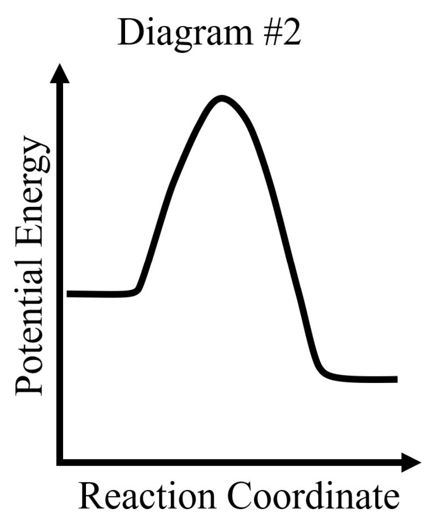
7. (continued)

(b) Does the diagram shown on the previous page on the left represent the energy profile of a chemical reaction that is classified as endothermic or exothermic? Justify your answer.

(c) If you answered "endothermic" in part (b), complete the energy diagram shown on the previous page on the right so that it represents the energy profile of an exothermic chemical reaction.

If you answered "exothermic" in part (b), complete the energy diagram shown on the previous page on the right so that it represents the energy profile of an endothermic chemical reaction.





8. Two energy diagrams are shown above, with the major difference between them being the relative magnitude of the activation energy (E_a). Assuming constant temperature, which diagram, #1 or #2, represents a reaction that should occur at a faster rate? Justify your answer.

$$k = Ae^{(-E_a/RT)}$$

The equation shown above is known as the **Arrhenius equation**.

k = the rate constant, A = the frequency factor

E_a = activation energy (which is normally reported in units of J/mol or kJ/mol)

R = the ideal gas constant (8.314 J mol^{-1} K^{-1})

T = the absolute temperature (in K) at which the reaction is carried out

The Arrhenius equation is NOT included on the AP Chemistry Equations and Constants sheet, and you will NOT be asked to do any calculations with this equation on the AP Exam. However, it can be helpful to examine the Arrhenius equation in order to recognize the relationships between the rate constant (k), the activation energy (E_a), and the reaction rate.

9. Circle the correct words to complete the following sentences.

A relatively <u>small</u> rate constant is associated with a relatively (slow fast) reaction rate.

A relatively <u>large</u> rate constant is associated with a relatively (slow fast) reaction rate.

A relatively <u>small</u> activation energy (E_a) is associated with a relatively (slow fast) reaction rate.

A relatively <u>large</u> activation energy (E_a) is associated with a relatively (slow fast) reaction rate.

<u>Increasing</u> the temperature at which a reaction is carried out should (decrease increase)

the reaction rate and (decrease increase) the magnitude of the rate constant (k).

<u>Decreasing</u> the temperature at which a reaction is carried out should (decrease increase)

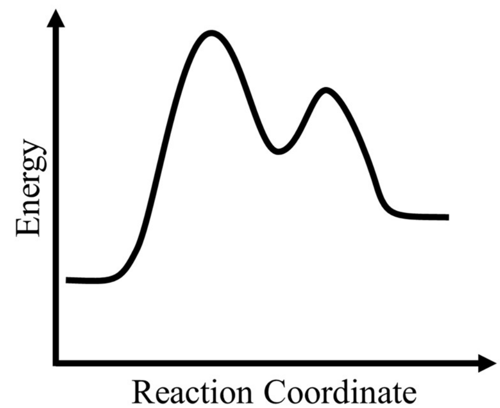
the reaction rate and (decrease increase) the magnitude of the rate constant (k).

It is important to know that if you change the temperature at which a reaction is carried out, this will <u>NOT</u> change the magnitude of the activation energy (E_a) for the reaction.

5.8 Reaction Mechanism and Rate Law

Essential knowledge statement from the AP Chemistry CED:

- For reaction mechanisms in which each elementary step is irreversible, or in which the first step is rate limiting, the rate law of the reaction is set by the molecularity of the slowest elementary step (i.e., the rate-limiting step).



10. The diagram shown above represents a reaction energy profile for a chemical reaction. Answer the following questions based on the information in the diagram.

    (a) Is it more likely that this reaction occurs in a single step or in a two-step process? Justify your answer by referring to specific information from the energy profile.

    (b) If you answered "two-step process" in part (a), draw a circle (●) on the energy profile to indicate the location of an intermediate that is formed along the reaction coordinate pathway.

    (c) If you answered "two-step process" in part (a), select one of the following that is more likely to be true for this reaction.

The first step is a slower step, and the second step is a faster step.	The first step is a faster step, and the second step is a slower step.

    (d) Justify your choice in part (c) by referring to specific information from the energy profile.

On the AP Exam, the steps of a proposed reaction mechanism are usually labeled as either *slow* or *fast*. Only one step of the mechanism is labeled as *slow*. The slow step in a mechanism is known as the **rate-limiting step** or the **rate-determining step.** This elementary step of the mechanism is the one that limits or determines the overall reaction rate.

In order for a proposed reaction mechanism to be considered plausible or valid, the rate law that is derived from the mechanism must be consistent with the rate law that has been determined from the analysis of experimental data for the reaction.

---

11. The following represents a proposed mechanism for a chemical reaction.

Step #1: $NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$ *slow*

Step #2: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ *fast*

(a) Write the balanced chemical equation for the overall reaction.

(b) Write the rate law for this reaction, based on the rate-determining step.

12. The following represents a proposed mechanism for a chemical reaction.

Step #1: $N_2O(g) \rightarrow N_2(g) + O(g)$ *slow*

Step #2: $N_2O(g) + O(g) \rightarrow N_2(g) + O_2(g)$ *fast*

(a) Write the balanced chemical equation for the overall reaction.

(b) Write the rate law for this reaction, based on the rate-determining step.

$$O_3(g) \ + \ 2\ NO_2(g) \ \rightarrow \ N_2O_5(g) \ + \ O_2(g)$$

13. A kinetics experiment is performed to study the reaction represented by the equation shown above. Based on the analysis of the experimental data, it is determined that this reaction is first-order with respect to $O_3(g)$ and first-order with respect to $NO_2(g)$.

    (a) Write the rate law for this reaction. ______________________________

    (b) A two-step mechanism has been proposed for this reaction. The first step of the mechanism is the slow, rate-determining step, and the second step is a fast step. Write the correct chemical equation for step 1 of this proposed mechanism.

Step	Chemical Equation	Relative Speed
1		*slow*
2	$NO_3(g) \ + \ NO_2(g) \ \rightarrow \ N_2O_5(g)$	*fast*

5.9 Steady-State Approximation

Essential knowledge statement from the AP Chemistry CED:

- If the first elementary reaction is not rate limiting, approximations (such as steady state) must be made to determine a rate law expression.

In Questions #11 – #13, the rate law for the overall reaction was based on elementary step #1 of the proposed mechanism because step #1 was identified as the slow, rate-determining step.

In Topic 5.9, you will see how the process of writing a rate law for a proposed mechanism becomes more complicated when step #2 of the mechanism is identified as the slow step.

$$2\ NO(g) \ + \ Br_2(g) \ \rightarrow \ 2\ NOBr(g)$$

14. A kinetics experiment is performed to study the reaction represented by the equation shown above.

    (a) Is it likely that this reaction occurs in a single elementary step? Justify your answer.

    (b) Based on the analysis of experimental data, it is determined that this reaction is second-order with respect to $NO(g)$ and first-order with respect to $Br_2(g)$. Write the rate law for this reaction.

14. (continued)

The following represents a proposed mechanism for this reaction. The steps of this mechanism have not been identified as slow or fast.

Step #1: $NO(g) + Br_2(g) \rightarrow NOBr_2(g)$

Step #2: $NOBr_2(g) + NO(g) \rightarrow 2\ NOBr(g)$

(c) Is it likely that step #1 could be identified as the slow, rate-determining step in this mechanism? Justify your answer in terms of the rate law written in part (b).

Step #1: $NO(g) + Br_2(g) \rightleftarrows NOBr_2(g)$ *fast equilibrium*

Step #2: $NOBr_2(g) + NO(g) \rightarrow 2\ NOBr(g)$ *slow*

In the proposed mechanism shown above, the second step is identified as the slow, rate-determining step. The rate law for elementary step #2 is written as follows.

$$\text{rate} = k_2[NOBr_2][NO]$$

The substance $NOBr_2$ is classified as an intermediate in this mechanism because it is formed in step 1 and then consumed in step 2. The initial concentration of $NOBr_2$ is unknown. Therefore $NOBr_2$ (or any intermediate for that matter) cannot be included in the rate law of an overall reaction.

You will now see how the intermediate $NOBr_2$ can be replaced in this rate law, based on the information for step #1.

Step #1 of this mechanism is identified as a fast, reversible step. The reversibility of a chemical reaction is indicated by the double arrow ($\rightleftarrows$). The term **equilibrium** refers to a situation in which *the rate of the forward reaction is equal to the rate of the reverse reaction*.

$$\text{Rate of the } \underline{\text{forward}} \text{ reaction in step \#1} = k_1[NO][Br_2]$$

$$\text{Rate of the } \underline{\text{reverse}} \text{ reaction in step \#1} = k_{-1}[NOBr_2]$$

Combining these two expressions gives the following.

$$k_1[NO][Br_2] = k_{-1}[NOBr_2]$$

$$[NOBr_2] = \frac{k_1}{k_{-1}}[NO][Br_2]$$

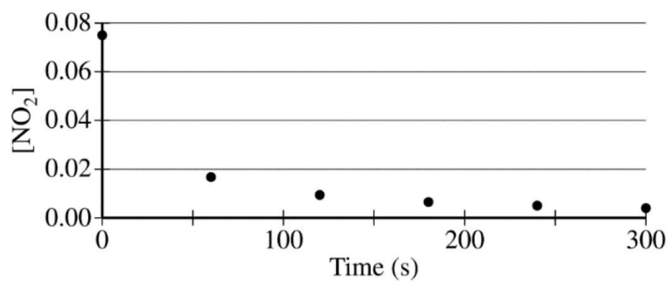
Substituting this relationship for [$NOBr_2$] into the rate law for the rate-determining step (Step #2), we get the following.

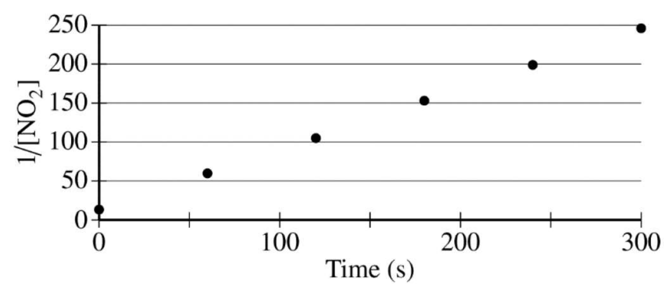
$$\text{rate for step \#2} = k_2[NOBr_2][NO] = k_2\frac{k_1}{k_{-1}}[NO][Br_2][NO] = k[NO]^2[Br_2]$$

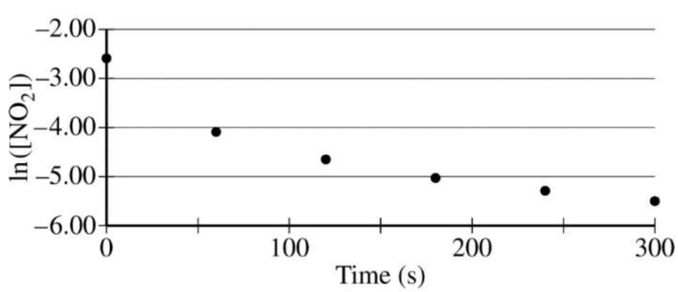
This rate law is consistent with the experimentally determined rate law written in part (b) because it shows that the reaction is second-order with respect to NO and first-order with respect to Br_2.

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

15. At elevated temperatures nitrogen dioxide, $NO_2(g)$, decomposes according to the equation shown above. The concentration of a sample of $NO_2(g)$ is monitored over time as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.







15. (continued)

(a) What is the order of the reaction with respect to $NO_2(g)$? Justify your answer.

(b) Write the rate law for this reaction. ______________________________

(c) Consider two possible mechanisms for the decomposition reaction.

(i) Is the rate law described by mechanism I shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Mechanism I

Step #1:	$NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$	*slow*
Step #2:	$NO_3(g) \rightarrow NO(g) + O_2(g)$	*fast*

(ii) Is the rate law described by mechanism II shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Mechanism II

Step #1:	$NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$	*fast equilibrium*
Step #2:	$N_2O_4(g) \rightarrow 2\ NO(g) + O_2(g)$	*slow*

5.10 Multistep Reaction Energy Profile

Essential knowledge statement from the AP Chemistry CED:

- Knowledge of the energetics of each elementary reaction in a mechanism allows for the construction of an energy profile for a multistep reaction.

---

16. Nitrogen dioxide, $NO_2(g)$ reacts with fluorine, $F_2(g)$, to produce nitryl fluoride, $NO_2F(g)$. A proposed reaction mechanism is shown below that consists of two elementary steps.

Step #1: $NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g)$ *slow*

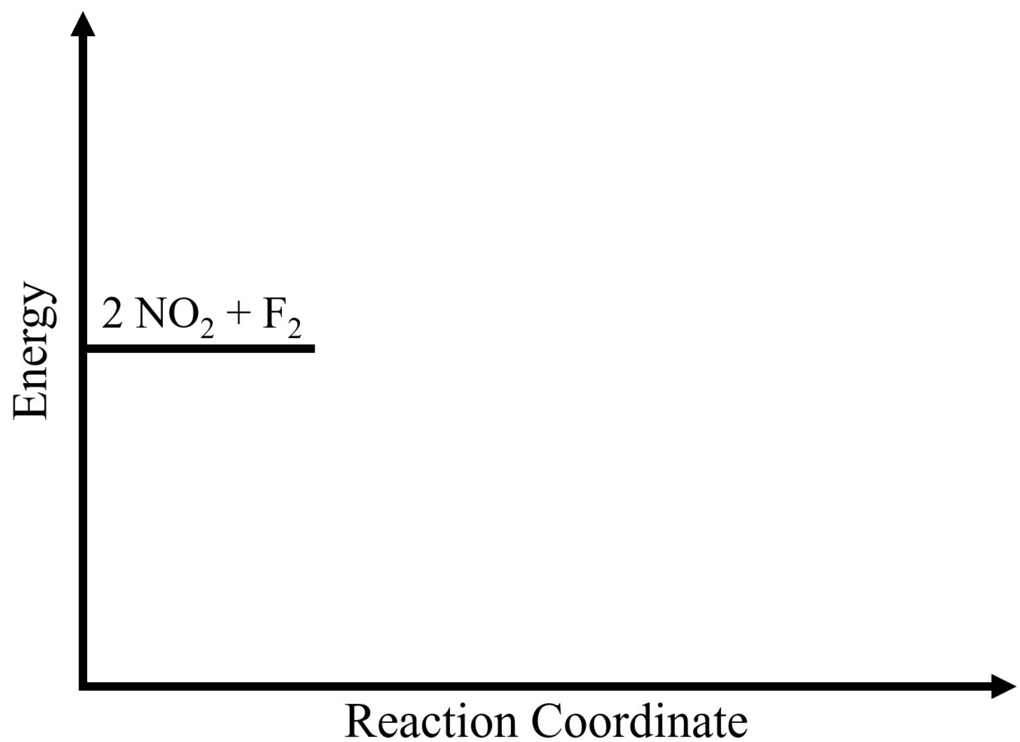
Step #2: $NO_2(g) + F(g) \rightarrow NO_2F(g)$ *fast*

(a) Write the balanced equation for the overall chemical reaction.

(b) Write the rate law for this reaction, based on the rate-determining step of the proposed mechanism.

(c) It is determined that this overall chemical reaction is classified as exothermic. On the incomplete energy diagram below, draw a curve that shows the following two details.

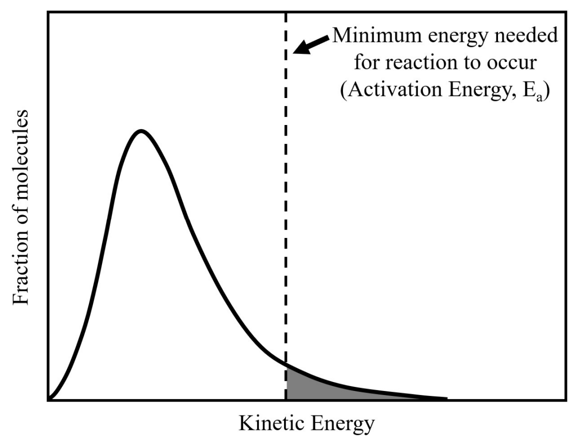
- the relative activation energy values for the two elementary steps of the proposed reaction mechanism
- the change in energy for the overall chemical reaction



5.11 Catalysis

Essential knowledge statements from the AP Chemistry CED:

- In order for a catalyst to increase the rate of a reaction, the addition of the catalyst must increase the number of effective collisions and/or provide a reaction path with a lower activation energy relative to the original reaction coordinate.
- In a reaction mechanism containing a catalyst, the net concentration of the catalyst is constant. However, the catalyst will frequently be consumed in the rate-determining step of the reaction, only to be regenerated in a subsequent step in the mechanism.
- Some catalysts accelerate a reaction by binding to the reactant(s). The reactants are either oriented more favorably or react with lower activation energy. There is often a new reaction intermediate in which the catalyst is bound to the reactant(s). Many enzymes function in this manner.
- Some catalysts involve covalent bonding between the catalyst and the reactant(s). An example is acid-base catalysis, in which a reactant or intermediate either gains or loses a proton. This introduces a new reaction intermediate and new elementary reactions involving that intermediate.
- In surface catalysis, a reactant or intermediate binds to, or forms a covalent bond with, the surface. This introduces elementary reactions involving these new bound reaction intermediate(s).



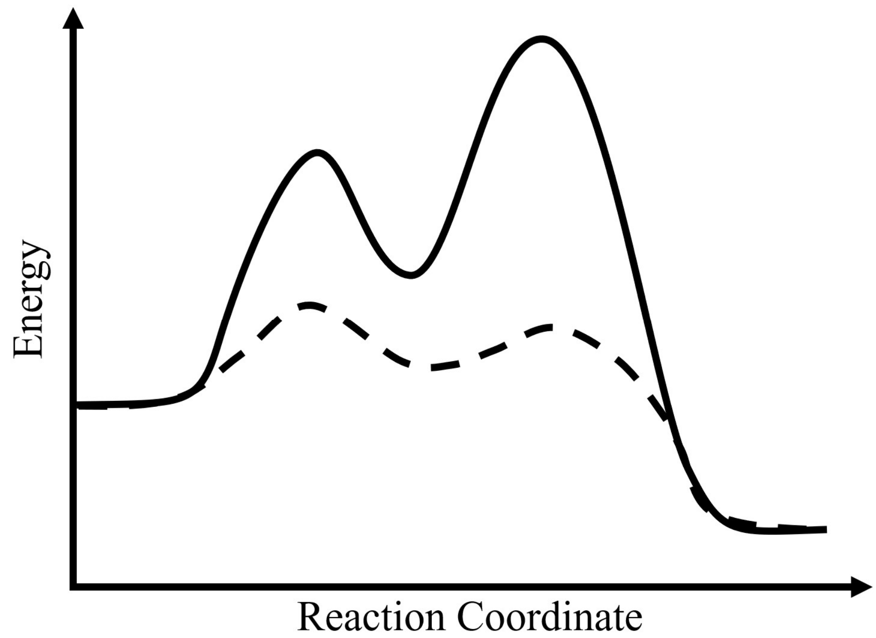
The graph above shows a distribution for the collision energies of reactant molecules for a chemical reaction at a certain temperature. The dashed vertical line represents the activation energy (E_a), which is the minimum amount of energy that is required in order for the reactants to be converted into products. The shaded region represents the fraction of collisions that have enough energy to overcome the activation energy barrier.

Explore how the shaded area is affected when the activation energy for the reaction is decreased.

bit.ly/Activation_Energy

Important information about catalysts

- The presence of a catalyst increases the reaction rate by providing an alternate reaction pathway with a lower activation energy.
- Adding a catalyst to the reaction mixture does NOT change the temperature at which the reaction is carried out.
- A catalyst does NOT change the potential energy values for either the reactants or the products. The difference in energy between the products and the reactants will remain the same.



17. In the energy diagram shown above, which reaction pathway represents a reaction that occurs in the presence of a catalyst? Justify your answer.