Big Idea 4: Kinetics

Rates of chemical reactions are determined by the details of the molecular collisions.

*When all else fails*, remember that chemical reactions are caused by successful collisions of molecules. In order for this to happen, only certain things can affect the rate of a chemical reaction. Concentration of reactants, temperature, surface area, and the presence of a catalyst are the only factors that affect reaction rate.

**LO 4.1** The student is able to design and/or interpret the results of an experiment regarding the factors (i.e., temperature, concentration, surface area) that may influence the rate of a reaction.

Example:

Describe why, on the particle level, temperature affects the rate of a reaction, in terms of the collision model for reactions.

\[
\text{Temp} \quad \rightarrow \quad \text{speed of the particles} \quad \downarrow \quad \text{ener} \quad \downarrow \quad \text{rate} \quad \uparrow
\]

**LO 4.2** The student is able to analyze concentration vs. time data to determine the rate law for a zeroth-, first-, or second-order reaction.

Example:

The graph above is a plot of the natural log of the pressure of a reactant versus time. What is the reaction order of this reaction?

\[\ln P \text{ vs. } t \text{ is linear, then } \text{1st order}\]

- a) 0th order
- b) 1st order
- c) 2nd order
- d) More information is required
LO 4.3 The student is able to connect the half-life of a reaction to the rate constant of a first-order reaction and justify the use of this relation in terms of the reaction being a first-order reaction.

Example:

The gas-phase decomposition of $\text{SO}_2\text{Cl}_2$, $\text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$, is first order in $\text{SO}_2\text{Cl}_2$. At 600 K the half-life for this process is $2.3 \times 10^5$ s. What is the rate constant for this temperature? 

$$t_{1/2} = \frac{0.693}{k} \quad 2.3 \times 10^5 = \frac{0.693}{k} \quad k = 3.01 \times 10^{-6}\text{ s}^{-1}$$

LO 4.4 The student is able to connect the rate law for an elementary reaction to the frequency and success of molecular collisions, including connecting the frequency and success to the order and rate constant, respectively.

Example:

| Slow step | $\text{O}_3 + \text{NO} \xrightleftharpoons[k_1]{k_2} \text{NO}_3 + \text{O}$ |
| Fast step | $\text{O} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{O}_2$ |
| Overall reaction | $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$ |
| Rate | $k_1[\text{O}_3][\text{NO}]$ |

The mechanism for a reaction is shown in the box to the left, with one slow step and one fast step. Which step of the reaction is the rate-determining step?

- a) Slow step
- b) Fast step
- c) Both
- d) Neither

LO 4.5 The student is able to explain the difference between collisions that convert reactants to products and those that do not in terms of energy distributions and molecular orientation.

As molecules collide, if they have enough energy to overcome the activation energy of the reaction. Also, in order for a collision to be successful, the molecules need the proper orientation to yield the expected product.

Example:

Using words and pictures, describe the collision model and how energy and orientation can affect the rate of a reaction.
LO 4.6 The student is able to use representations of the energy profile for an elementary reaction (from the reactants, through the transition state, to the products) to make qualitative predictions regarding the relative temperature dependence of the reaction rate.

Example:

Given the reaction profile on the right, circle the words to correctly complete the statements. The 
reaction is [endothemic/exothermic] and the 
activation energy for the forward reaction is (less than/more than) the activation energy for the 
reverse reaction.

LO 4.7 The student is able to evaluate alternative explanations, as expressed by reaction mechanisms, to determine which are consistent with data regarding the overall rate of a reaction, and data that can be used to infer the presence of a reaction intermediate.

Example:

I. $\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{OI}^-$  
   $\text{OI}^- + \text{H}^+ \rightarrow \text{HOI}$  
   $\text{HOI} + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2 + \text{H}_2\text{O}$  
   $\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$

II. $\underline{\text{H}_2\text{O}_2 + \text{I}^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{HOI}}$  
   $\underline{\text{HOI} + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2 + \text{H}_2\text{O}}$  
   $\underline{\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-}$

Consider, $\text{H}_2\text{O}_2 + 3\text{I}^- + 2\text{H}^+ \rightarrow \text{I}_3^- + 2\text{H}_2\text{O}$

Two proposed mechanisms for the reaction above are listed to the left. If the reaction is found to be first order with respect to $\text{H}_2\text{O}_2$ and first order with respect to $\text{I}^-$, then which mechanism is correct and which step is rate-determining?

a) Mechanism I, with the first step the rate determining step.

b) Mechanism I, with the second step the rate determining step.

c) Mechanism II, with the first step rate determining.

d) Mechanism II, with the second step rate determining.
LO 4.8 The student can translate among reaction energy profile representations, particulate representations, and symbolic representations (chemical equations) of a chemical reaction occurring in the presence and absence of a catalyst.

Label the following on the reaction profile on the right:
- a) Reactants
- b) Products
- c) Intermediate
- d) Activation Energy for first step
- e) Activation energy for 2nd step
Which is faster, the 1st step or 2nd step of the reaction?
Which is rate-determining, the 1st step or the 2nd step of the reaction?

LO 4.9 The student is able to explain changes in reaction rates arising from the use of acid-base catalysts, surface catalysts, or enzyme catalysts, including selecting appropriate mechanisms with or without the catalyst present.

Example:

In a dehydrogenation reaction, a hydrocarbon chain reacts on the surface of a metal catalyst to remove hydrogen and replace it with a double bond between carbon atoms. What type of catalysis is this?

- a) Acid-base catalyst
- b) Surface catalyst
- c) Enzyme catalyst
- d) None