

ACTIVITY 30

Activation Energy and Catalysis

WHY?

Not all collisions between molecules result in a reaction. The molecules must have enough energy for the reaction to occur. The minimum energy that is needed is called the *activation energy*. Catalysts are substances that lower the activation energy and thereby increase the rate of reactions. Catalysts are essential in the production of industrial chemicals. Biological catalysts, which are called *enzymes*, are essential for life and for the development of new pharmaceutical products.

LEARNING OBJECTIVES

- Understand the factors that limit the rate of a chemical reaction
- Be able to determine the activation energy of a chemical reaction from reaction rate data
- Recognize how catalysts can increase reaction rates

SUCCESS CRITERIA

- Ability to produce a complete list of factors that affect the rate of a chemical reaction
- Ability to identify three or more ways that the rate of a chemical reaction can be increased
- Correct determination of activation energies from reaction rate data
- Correct quantitative prediction of how large a rate increase will be produced by a given change in activation energy

PREREQUISITES

- **Activity 5:** *Balanced Chemical Reaction Equations*
- **Activity 27:** *Entropy of the Universe and Free Energy*
- **Activity 28:** *Rates of Chemical Reactions*
- **Activity 29:** *Reaction Mechanisms*

INFORMATION

For a reaction to occur, molecules must collide. The frequency of the collisions affects the rate of the reaction. The frequency can be changed by increasing or decreasing the concentrations of the reactants, and by changing the temperature to change the velocities of the molecules.

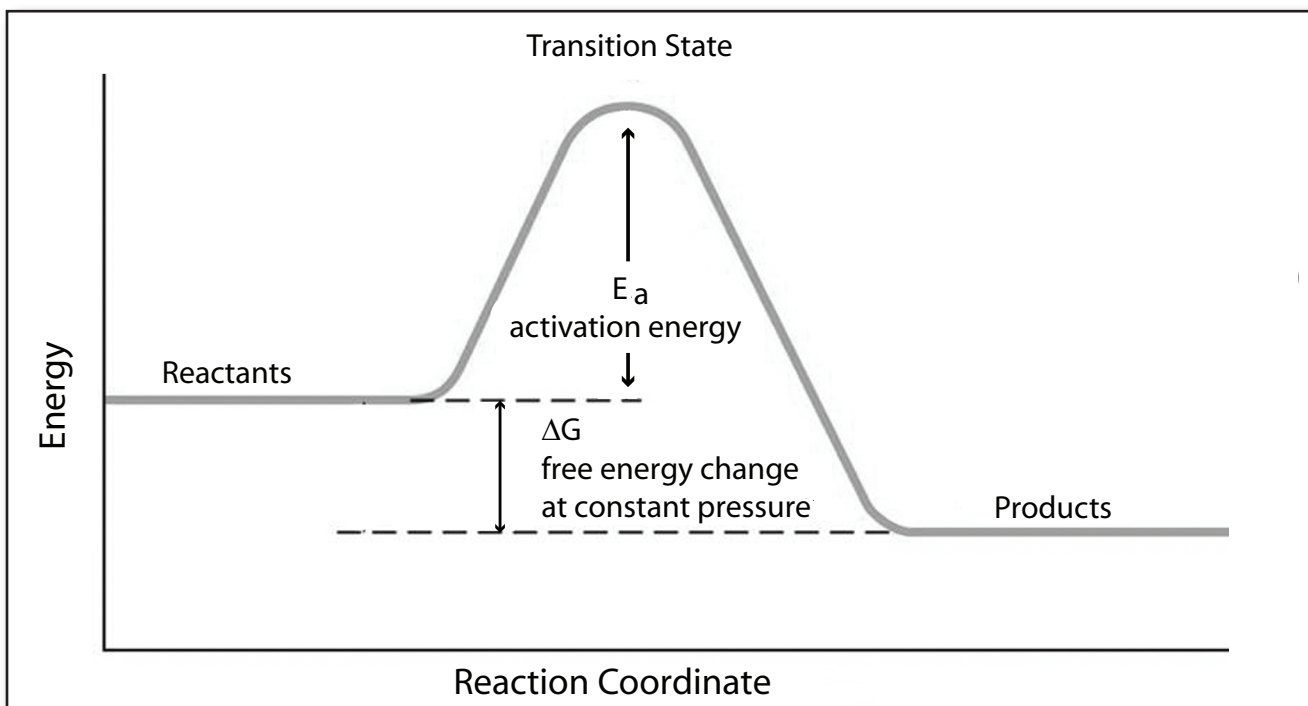
But even when molecules collide, they do not all react. In order to react, the two molecules must be oriented in just the right way. Unfortunately, there is nothing that can be done to control molecular orientations, except in very sophisticated experiments.

Molecules must also have enough energy for the reaction to occur. Some minimum energy is needed because existing bonds must be broken and new bonds must be formed. The point in the reaction at which this reconstruction is occurring is called the *transition state* or *activated complex*, and the energy needed to reach the transition state is called the *activation energy*, E_a . Only those molecules that have this amount of energy or more will react and produce products. The energy of the molecules can be changed by raising or lowering the temperature.

MODEL 1: Energy vs Reaction Coordinate Diagram

An energy vs reaction coordinate graph is used to show how the potential energy of the reactants changes as the reactants turn into products. The reaction coordinate is a measure of the progress of the reaction along the reaction pathway.

Figure 30.1



KEY QUESTIONS

1. Is the change in free energy for the reaction in **Model 1** positive or negative?
2. According to **Model 1**, which has the higher energy, the reactants or the transition state?
3. Which molecules are more likely to reach the transition state and pass over to products when they collide, those with high velocities and kinetic energies or those with low velocities and kinetic energies?

4. As the temperature increases, does the fraction of molecules with high kinetic energies increase or decrease?
5. In view of **Model 1** and your answers to Key Questions 1-4, why do you think the rate of a chemical reaction increases with increasing temperature?
6. Draw an arrow on the diagram in **Model 1** to indicate the magnitude of the activation energy for the reverse reaction (products going back to reactants). Do you think the rate constant of the reverse reaction will be larger or smaller than that of the forward reaction? Explain your answer in terms of the fraction of molecules that have enough kinetic energy to reach the transition state.

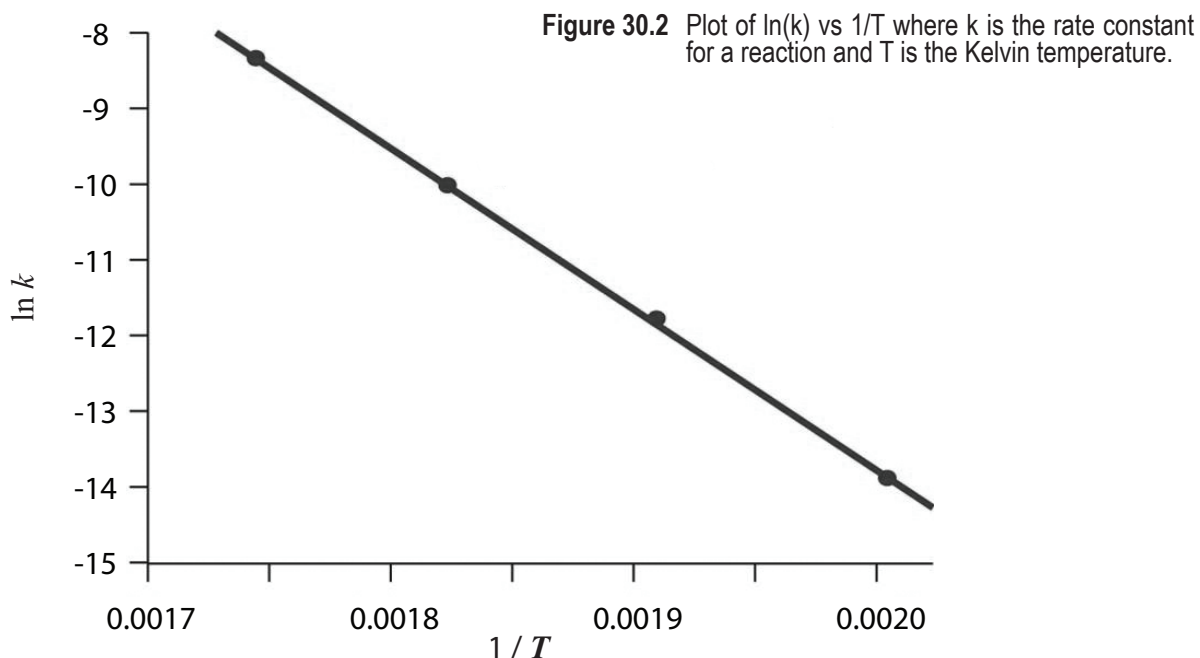
EXERCISES

1. Hydrogen and chlorine react to produce hydrochloric acid, but the reverse reaction also occurs at a slower rate. Consider the reaction $2\text{HCl} \rightarrow \text{H}_2 + \text{Cl}_2$. Draw two diagrams, one showing an orientation of the two HCl molecules that is unfavorable for this reaction, and one showing an orientation that is favorable for this reaction.
2. Give two or more reasons why some collisions between molecules might not result in a chemical reaction.

3. Draw an energy vs reaction coordinate diagram to illustrate a reaction in which the free energy of the products is greater than the free energy of the reactants. Label all quantities as in **Model 1**.
4. Using your diagram from Exercise 3, identify which reaction (forward or reverse) has the larger activation energy and which has the larger reaction rate constant.

INFORMATION

Because a reaction is faster at higher temperatures, the rate constant for the reaction must be larger. The activation energy for a reaction therefore can be determined from experimental measurements of the rate constant at several temperatures. When such data is plotted in the form $\ln(k)$ vs $1/T$ as shown in Figure 30.2, a straight line is produced. This result means that the rate constant varies exponentially with $1/T$ as given by the Arrhenius equation.



MODEL 2: The Arrhenius Equation

$$k = Ae^{-\frac{E_a}{RT}}$$

A is the frequency factor. The frequency factor depends on how often molecules collide when the concentrations are 1M, and on whether the molecules are properly oriented when they collide. A is the value that the rate constant k would have if all the molecules had enough energy to react, e.g., when the activation energy $E_a = 0$ or the Kelvin temperature T is very large.

KEY QUESTIONS

7. Since the gas constant R has units of J/mol K, what are the units of E_a in the Arrhenius equation?
8. Does the Arrhenius equation predict that the rate constant will increase or decrease if the activation energy gets larger?
9. Does the Arrhenius equation predict that the rate constant will increase or decrease as the temperature increases?

EXERCISES

5. Show that the Arrhenius equation produces the following equation by taking the natural logarithm of both sides and using the property $\ln(ab) = \ln(a) + \ln(b)$.

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T}$$

6. The equation in Exercise 5 corresponds to that of a straight line when $\ln(k)$ is plotted versus $1/T$. Identify the quantities in the equation that determine the slope of the line and the quantity that determines the intercept at $1/T = 0$.
7. The line in Figure 30.2 is described by $\ln(k) = 28.5 - (2.1 \times 10^4 \text{ K})/T$. Determine the frequency factor and the activation energy for that reaction.

PROBLEMS

1. Fireflies flash at a rate that is temperature dependent. At 29 °C the average firefly flashes at a rate of 3.3 flashes every 10 seconds. At 23 °C the average rate is 2.7 flashes every 10 seconds. Use the Arrhenius equation to determine the activation energy for the flashing process.

INFORMATION

A catalyst, as shown in Model 3, changes the mechanism of a chemical reaction and lowers its activation energy. The catalyst participates in intermediate steps of the reaction, but it is neither produced nor consumed in the reaction so the balanced reaction equation remains the same.

MODEL 3: Catalysts

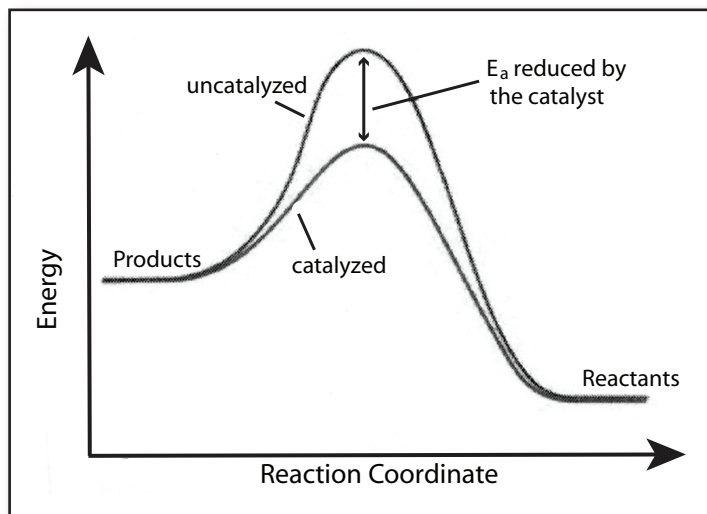


Figure 30.3

KEY QUESTIONS

10. What effect does a catalyst have on the activation energy of a reaction?
11. What effect does a catalyst have on the change in free energy of a reaction?
12. What effect does a catalyst have on the mechanism of a reaction?
13. What effect does a catalyst have on the stoichiometry of a reaction?
14. How does the rate of the rate limiting step in a reaction with a catalyst compare with the rate of the rate limiting step without the catalyst?

15. What are at least three ways that the rate of a chemical reaction can be increased?

PROBLEMS

2. A catalyst reduces the activation energy for a reaction from 17 kJ/mol to 2 kJ/mol. By what factor is the rate accelerated? Assume that the frequency factor A does not change, and that the temperature is 200 K.