

Theories of Reaction Rates

6.3

In section 6.2, you explored the rate law, which defines the relationship between the concentrations of reactants and reaction rate. Why, however, does the rate of a reaction increase with increased concentrations of reactants? Why do increased temperature and surface area increase reaction rates? To try to explain these and other macroscopic observations, chemists develop theories that describe what happens as reactions proceed on the molecular scale. In this section, you will explore these theories.

Collision Theory

Why do factors such as temperature and concentration increase or decrease the rate of a reaction? To answer this question, chemists must first answer another question: What causes a reaction to occur? One obvious answer is that a reaction occurs when two reactant particles collide with one another. This answer is the basis for **collision theory**: In order for a reaction to occur, reacting particles (atoms, molecules, or ions) must collide with one another.

The Effect of Concentration on Reactant Rates

You can use simple collision theory to begin to understand why factors such as concentration affect reaction rate. If a collision is necessary for a reaction to occur, then it makes sense that the rate of the reaction will increase if there are more collisions per unit time. More reactant particles in a given volume (that is, greater concentration) will increase the number of collisions between the particles per second. Figure 6.7 illustrates this idea.

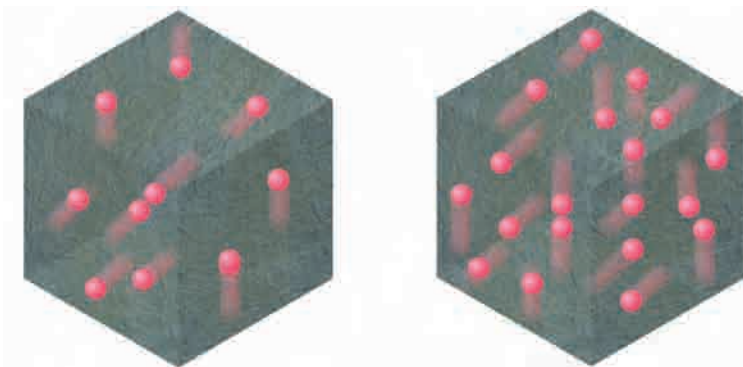


Figure 6.7 At increased reactant concentrations, there is an increased number of collisions per second.

Collision Theory and Surface Area

You can also use simple collision theory to explain why increasing the surface area of a solid-phase reactant speeds up a reaction. With greater surface area, more collisions can occur. This explains why campfires are started with paper and small twigs, rather than logs. Figure 6.8 shows an example of the effect of surface area on collision rate.

Section Preview/ Specific Expectations

In this section, you will

- **explain**, using the collision theory and potential energy diagrams, how different factors, such as temperature and concentration, control the rate of a chemical reaction
- **analyze** simple potential energy diagrams of chemical reactions
- **communicate** your understanding of the following terms: *collision theory*, *activation energy (E_a)*, *transition state theory*, *potential energy diagram*, *transition state*, *activated complex*



Electronic Learning Partner

Go to the Chemistry 12 Electronic Learning Partner for more information about aspects of material covered in this section of the chapter.



Figure 6.8 Mixtures of grain or coal dust and air are potentially explosive, as shown in this grain elevator explosion.

Beyond Collision Theory

Simple collision theory recognizes that a collision between reactants is necessary for a reaction to proceed. Does every collision result in a reaction? Consider a 1 mL sample of gas at room temperature and atmospheric pressure. In the sample, about 10^{28} collisions per second take place between gas molecules. If each collision resulted in a reaction, *all* gas phase reactions would be complete in about a nanosecond (10^{-9} s)—a truly explosive rate! As you know from section 6.2, however, gas phase reactions can occur quite slowly. This suggests that *not every collision between reactants results in a reaction*.

In order for a collision between reactants to result in a reaction, the collision must be *effective*. An effective collision—one that results in the formation of products—must satisfy the following two criteria. You will investigate these criteria over the next few pages.

For a collision to be effective, it must satisfy both of these criteria:

1. correct orientation of reactants
2. sufficient collision energy

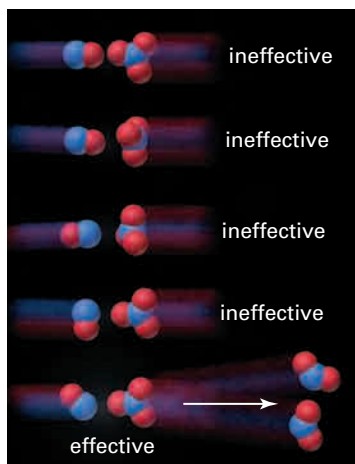


Figure 6.9 Only one of these five possible orientations of NO and NO₃ will lead to the formation of a product.

Orientation of Reactants

Reacting particles must collide with the proper orientation relative to one another. This is also known as having the correct *collision geometry*. The importance of proper collision geometry can be illustrated by the following reaction.

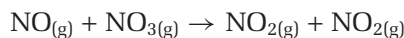


Figure 6.9 shows five of the many possible ways in which NO and NO₃ can collide. Only one of these five possibilities has the correct collision geometry for a reaction to occur. As shown in the figure, only a certain orientation of reactants prior to collision leads to the formation of two molecules of nitrogen dioxide.

Activation Energy

In addition to collision geometry, there is a second factor that determines whether a collision will result in a reaction: the energy of the collision. The reactants must collide with energy that is sufficient to begin to break the bonds in the reactants and to begin to form the bonds in the products. In most reactions, only a small fraction of collisions have sufficient energy for a reaction to occur. The **activation energy**, E_a , of a reaction is the minimum collision energy that is required for a successful reaction.

The collision energy depends on the kinetic energy of the colliding particles. As you know, temperature is a measure of the average kinetic energy of the particles in a substance. If you plot the number of collisions in a substance at a given temperature against the kinetic energy of each collision, you get a curve like the one in Figure 6.10. The type of distribution that is shown by this curve is known as a *Maxwell-Boltzmann distribution*. The dotted line indicates the activation energy. The shaded part of the graph indicates the collisions with energy that is equal to or greater than the activation energy.

How does the distribution of kinetic energy change as the temperature of a substance increases? Figure 6.11 shows the distribution of kinetic

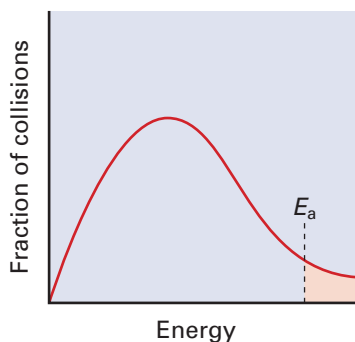
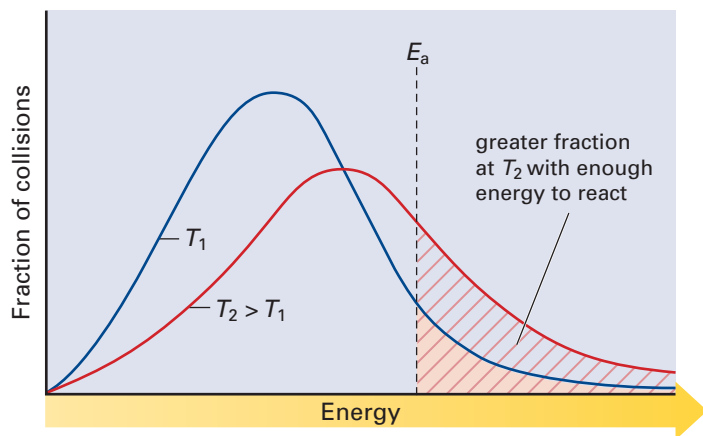


Figure 6.10 The area under a Maxwell-Boltzmann distribution graph represents the distribution of the kinetic energy of collisions at a constant temperature. At a given temperature, only a certain fraction of the molecules in a sample have enough kinetic energy to react.

energy in a sample of reacting gases at two different temperatures, T_1 and T_2 , where $T_2 > T_1$. The activation energy is indicated by the dashed vertical line. Two observations are apparent from the graph:

1. At both temperatures, a relatively small fraction of collisions have sufficient kinetic energy—the activation energy—to result in a reaction.
2. As the temperature of a sample increases, the fraction of collisions with sufficient energy to cause a reaction increases significantly.



For many reactions, the rate roughly doubles for every 10°C rise in temperature.

Transition State Theory

Transition state theory is used to explain what happens when molecules collide in a reaction. It examines the transition, or change, from reactants to products. The kinetic energy of the reactants is transferred to potential energy as the reactants collide, due to the law of conservation of energy. This is analogous to a bouncing basketball. The kinetic energy of the ball is converted to potential energy, which is stored in the deformed ball as it hits the floor. The potential energy is converted to kinetic energy as the ball bounces away.

You can represent the increase in potential energy during a chemical reaction using a **potential energy diagram**: a diagram that charts the potential energy of a reaction against the progress of the reaction. Examples of potential energy diagrams are shown in Figures 6.12 and 6.13 on the next page. The y-axis represents potential energy. The x-axis, labelled “Reaction progress,” represents the progress of the reaction through time.

The “hill” in each diagram illustrates the activation energy barrier of the reaction. A slow reaction has a high activation energy barrier. This indicates that relatively few reactants have sufficient kinetic energy for a successful reaction. A fast reaction, by contrast, has a low activation energy barrier.

A potential energy diagram for an exothermic reaction is shown in Figure 6.12. The reactants at the beginning of the reaction are at a higher energy level than the products. The overall difference in potential energy is the enthalpy change, ΔH . *There is no way to predict the activation energy of a reaction from its enthalpy change.* A highly exothermic reaction may be very slow because it has a high activation energy. Conversely, a reaction that is very fast may release very little heat. The enthalpy change of a reaction is determined by finding the overall energy that is



Go to the Chemistry 12 Electronic Learning Partner to learn more about collision geometry.

Figure 6.11 At increased temperatures, more particles collide with enough energy to react.

transferred. The activation energy of a reaction is determined by analyzing the reaction rate.

A potential energy diagram for an endothermic reaction is shown in Figure 6.13. The reactants at the beginning of the reaction are at a lower energy level than the products. The overall difference in potential energy between reactants and products is the enthalpy change.

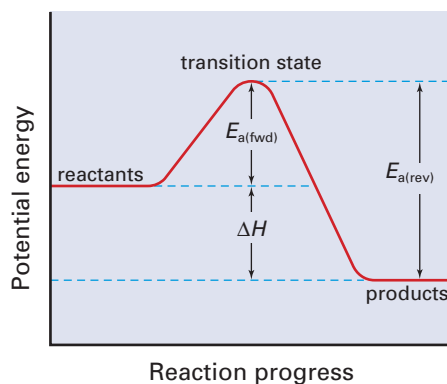


Figure 6.12 A potential energy diagram for an exothermic reaction

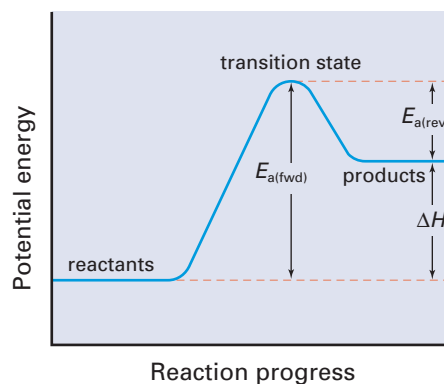
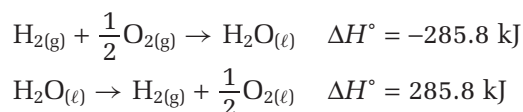


Figure 6.13 A potential energy diagram for an endothermic reaction

You may already know that many reactions can proceed in two directions. For example, hydrogen and oxygen react to form water. Water, however, can also undergo electrolysis, forming hydrogen and oxygen. This is the reverse of the first reaction.



The enthalpy change of the first reaction is the same as the enthalpy change of the second reaction, with the opposite sign. (You can show this using Hess's law.) How are the activation energies of forward and reverse reactions related? For an exothermic reaction, the activation energy of the reverse reaction, $E_{a(\text{rev})}$ equals $E_{a(\text{fwd})} + \Delta H$. For an endothermic reaction, $E_{a(\text{rev})}$ equals $E_{a(\text{fwd})} - \Delta H$. Figures 6.12 and 6.13 show the activation energies of forward and reverse reactions.

The top of the activation energy barrier on a potential energy diagram represents the **transition state**, or change-over point, of the reaction. The chemical species that exists at the transition state is referred to as the **activated complex**. The activated complex is a transitional species that is neither product nor reactant. It has partial bonds and is highly unstable. There is a subtle difference between the transition state and the activated complex. The transition state refers to the top of the “hill” on a potential energy diagram. The *chemical species* that exists at this transition point is called the activated complex.

Tracing a Reaction With a Potential Energy Diagram

Consider the substitution reaction between a hydroxide, OH^- , ion and methyl bromide, BrCH_3 . Methanol, CH_3OH , and a bromide, Br^- , ion are formed.

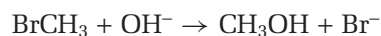


Figure 6.14 is a potential energy diagram for this reaction. It includes several “snapshots” as the reaction proceeds.

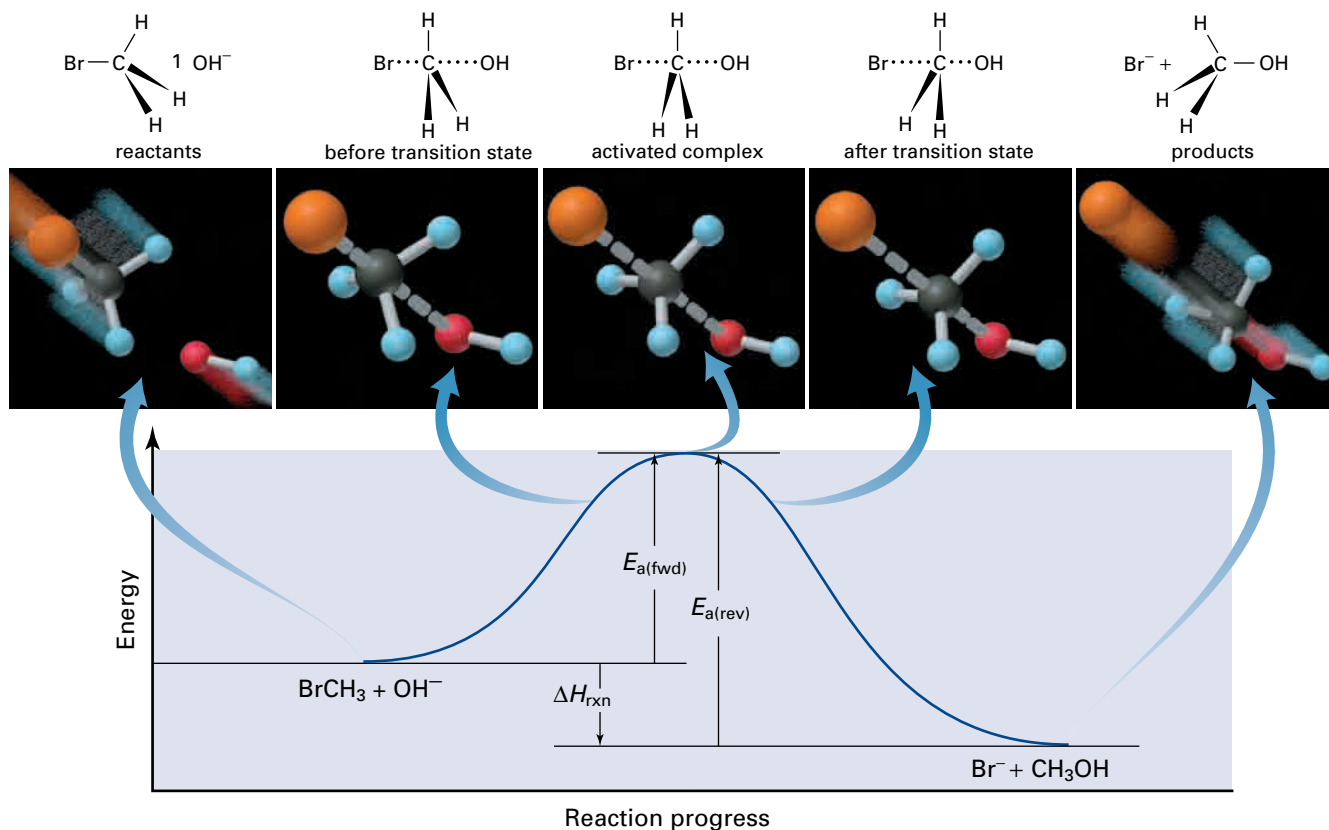


Figure 6.14 As the reactants collide, chemical bonds break and form.

For a successful reaction to take place, BrCH_3 and OH^- must collide in a favourable orientation. The OH^- ion must approach BrCH_3 from the side that is *opposite* to the Br atom. When this occurs, a partial bond is formed between the O of the OH^- ion and the C atom. Simultaneously, the C—Br bond is weakened.

Because the activated complex contains partial bonds, it is highly unstable. It can either break down to form products or it can decompose to re-form the reactants. The activated complex is like a rock teetering on top of a mountain. It could fall either way.

Sample Problem

Drawing a Potential Energy Diagram

Problem

Carbon monoxide, CO , reacts with nitrogen dioxide, NO_2 . Carbon dioxide, CO_2 , and nitric oxide, NO , are formed. Draw a potential energy diagram to illustrate the progress of the reaction. (You do not need to draw your diagram to scale). Label the axes, the transition state, and the activated complex. Indicate the activation energy of the forward reaction, $E_{a(\text{fwd})} = 134 \text{ kJ}$, as well as $\Delta H = -226 \text{ kJ}$. Calculate the activation energy of the reverse reaction, $E_{a(\text{rev})}$, and show it on the graph.

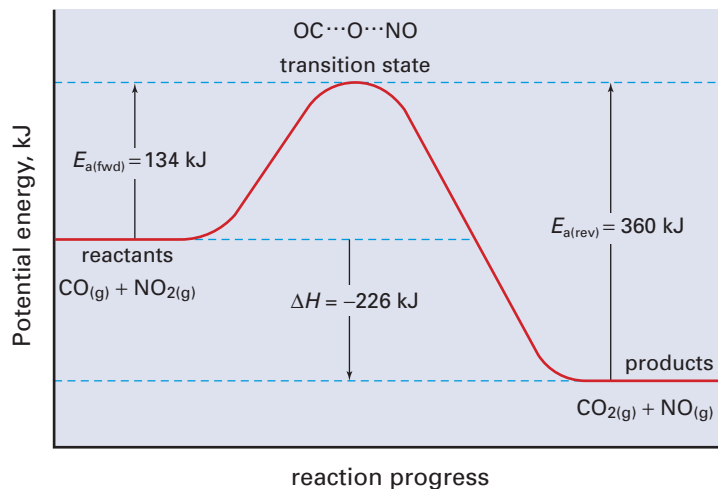
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Solution

Since $E_{a(\text{rev})} = \Delta H + E_{a(\text{fwd})}$

$$\begin{aligned} E_{a(\text{rev})} &= 226 \text{ kJ} + 134 \text{ kJ} \\ &= 360 \text{ kJ} \end{aligned}$$

The activation energy of the reverse reaction is 360 kJ.

**Check Your Solution**

Look carefully at the potential energy diagram. Check that you have labelled it completely. Since the forward reaction is exothermic, the reactants should be at a higher energy level than the products, and they are. The value of $E_{a(\text{rev})}$ is reasonable.

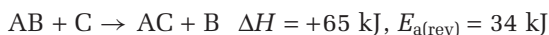
Practice Problems

13. The following reaction is exothermic.



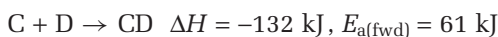
Draw and label a potential energy diagram for the reaction. Propose a reasonable activated complex.

14. Consider the following reaction.



Draw and label a potential energy diagram for this reaction. Calculate and label $E_{a(\text{fwd})}$. Include a possible structure for the activated complex.

15. Consider the reaction below.



Draw and label a potential energy diagram for this reaction. Calculate and label $E_{a(\text{rev})}$. Include a possible structure for the activated complex.

16. In the upper atmosphere, oxygen exists in forms other than $\text{O}_{2(\text{g})}$.

For example, it exists as ozone, $\text{O}_{3(\text{g})}$, and as single oxygen atoms, $\text{O}_{(\text{g})}$. Ozone and atomic oxygen react to form two molecules of oxygen.

For this reaction, the enthalpy change is -392 kJ and the activation energy is 19 kJ . Draw and label a potential energy diagram. Include a value for $E_{a(\text{rev})}$. Propose a structure for the activated complex.

Temperature Dependence of Reaction Rates: Applications

As you saw in Figure 6.11, when reactions occur at higher temperatures, the percent of particles that have sufficient kinetic energy to react (E_a) increases. Since a greater percent of reactant particles have enough energy to react, the rate of the reaction increases.

Chemists exploit the temperature dependence of reaction rates by carrying out chemical reactions at elevated temperatures to speed them up. In organic chemistry, especially, reactions are commonly performed under *reflux*: that is, while boiling the reactants. To prevent reactants and products from escaping as gases, a water-cooled condenser tube is fitted to the reaction vessel. The tube condenses the vapours to liquids and returns them to the reaction vessel. Figure 6.15 shows an experiment performed under reflux.

At home, you take advantage of the temperature dependence of chemical reactions all the time. For example, to keep your food fresh, you store it in a refrigerator. If you have ever left milk or vegetables in the refrigerator for several weeks, however, you have probably observed that refrigeration does not *stop* food from spoiling. Instead, it decreases the *rate* of the reactions that cause spoilage. When you want to cook your food quickly, you increase the temperature of the stove. This increases the rate of the reactions that take place as the food cooks.

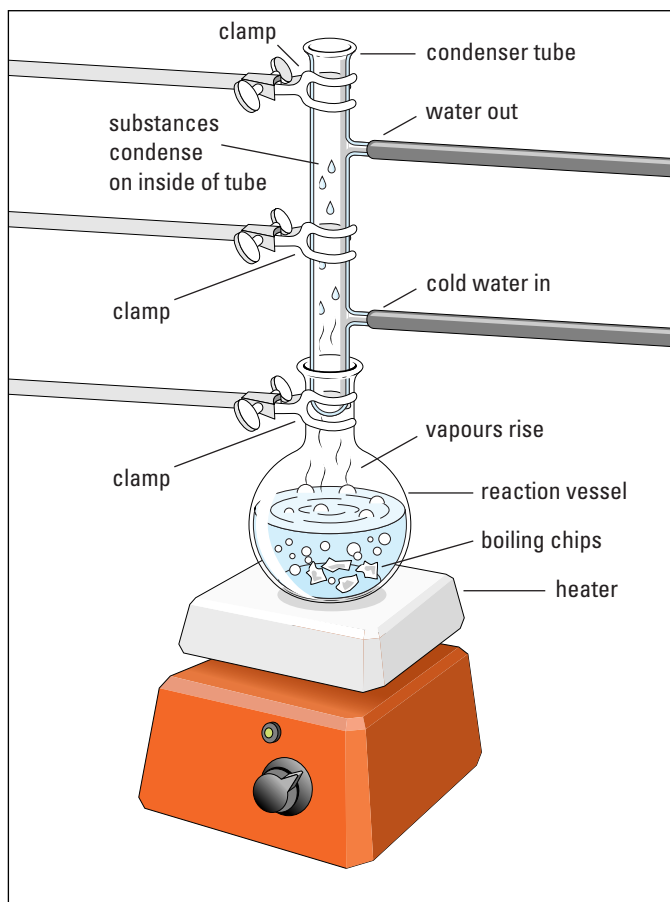


Figure 6.15 As the reactants are boiled under reflux, the vapours condense and are returned to the reaction vessel. In this way, a chemical reaction can be carried out at the boiling point of the reactants at atmospheric pressure, with no loss of reactants, products, or solvent.

Web  LINK

www.mcgrawhill.ca/links/chemistry12

The chirping rate of a cricket is dependent on temperature, much like chemical reaction rates are. Why does this suggest that a cricket is a cold-blooded creature? Search the Internet to determine the mathematical relationship between ambient temperature and the chirping rate of a cricket. Start your search by going to the web site above and clicking on **Web Links**.