P Pearson

14.6: The Effect of Temperature on Reaction Rate

Key Concept Video   The Effect of Temperature on Reaction Rate

As we saw in Sections 14.1 and 14.2, the rates of chemical reactions are, in general, highly sensitive to temperature. Around room temperature, for example, a 10 °C increase in temperature increases the rate of a typical biological reaction by two or three times. Recall that the rate law for a reaction is $\text{Rate} = k[\text{A}]^n$. *The temperature dependence of the reaction rate is contained in the rate constant, k* (which is actually a constant only when the temperature remains constant). An increase in temperature generally results in an increase in k, which results in a faster rate.

The Arrhenius Equation

In 1889, Swedish chemist Svante Arrhenius (1859–1927) wrote a paper quantifying the temperature dependence of the rate constant. The modern form of the **Arrhenius equation** shows the relationship between the rate constant (k) and the temperature in kelvin (T):

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

Activation energy ← $-\frac{E_a}{RT}$

Frequency factor → Ae Exponential factor

[14.24]

In this equation, R is the gas constant (8.314 J/mol · K), A is a constant called the *frequency factor* (or the *pre-exponential factor)*, and E_a is the *activation energy* (or *activation barrier*), which we briefly examined in Section 14.2.

The **activation energy** E_a is an energy barrier or hump that must be surmounted for the reactants to be transformed into products (Figure 14.12). We examine the frequency factor more closely in the next section of the chapter; for now, we can think of the **frequency factor (A)** as the number of times that the reactants approach the activation barrier per unit time.
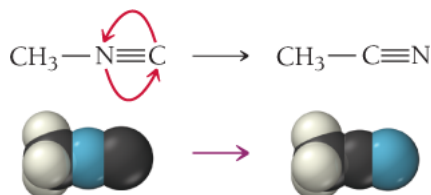

Figure 14.12   The Activation Energy Barrier

Even though the reaction is energetically favorable (the energy of the products is lower than that of the reactants), the reactants must overcome the energy barrier in order to react.

Activation Energy

$$2\,\text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2\,\text{H}_2\text{O}(g)$$
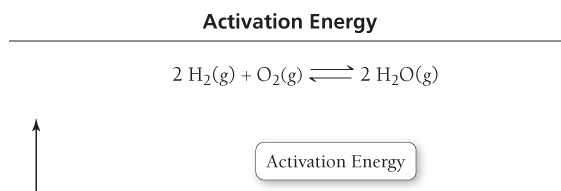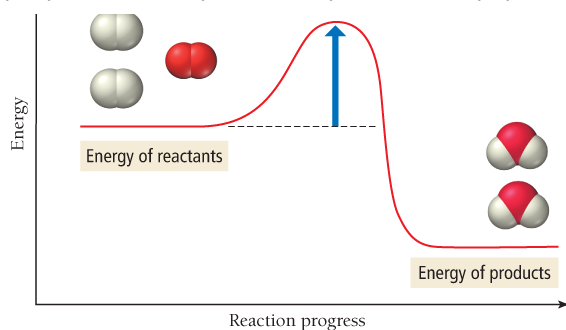
Activation Energy

To understand each of these quantities better, we can look more closely at the simple reaction in which CH_3NC(methyl isonitrile) rearranges to form CH_3NC(acetonitrile):

Let's examine the physical meaning of the activation energy, frequency factor, and exponential factor for this reaction.

The Activation Energy

Figure 14.13 illustrates the energy of a molecule as the reaction proceeds. The x-axis represents the progress of the reaction from left (reactant) to right (product). To get from the reactant to the product, the molecule must go through a high-energy intermediate state called the **activated complex** or **transition state**. Even though the overall reaction is energetically downhill (exothermic), it must first go uphill to reach the activated complex because energy is required to initially weaken the H_3C—Nbond and allow the NC group to begin to rotate:
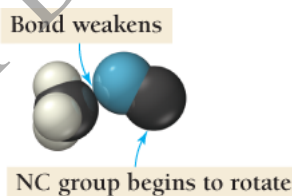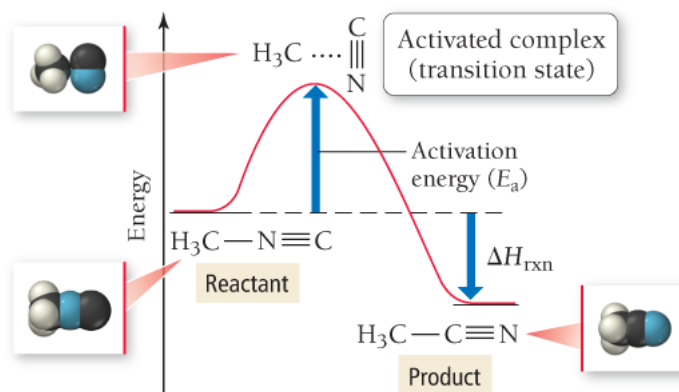

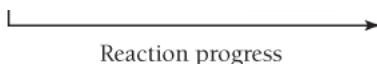Bond weakens

NC group begins to rotate

Figure 14.13 **The Activated Complex**

The reaction pathway includes a transition state—the activated complex—that has a higher energy than either the reactant or the product.

Reaction progress

The energy required to reach the activated complex is the *activation energy. In general, the higher the activation energy, the slower the reaction rate (at a given temperature).*
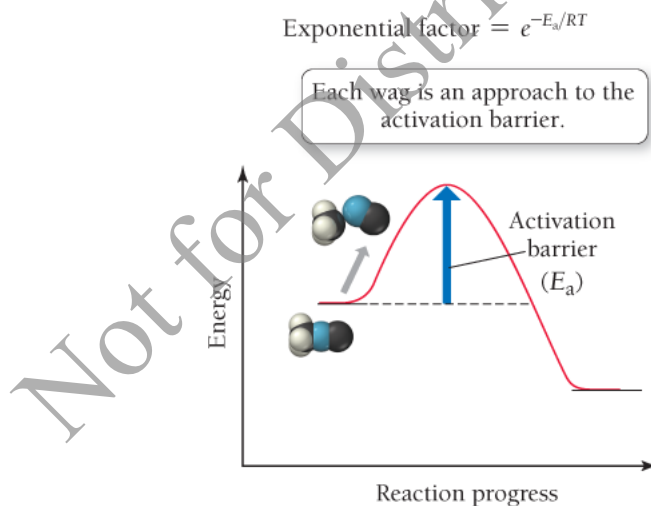
The Frequency Factor

Recall that the frequency factor represents the number of approaches to the activation barrier per unit time. Any time that the NC group begins to rotate, it approaches the activation barrier. For this reaction, the frequency factor represents the rate at which the NC part of the molecule wags (vibrates side to side). With each wag, the reactant approaches the activation barrier. However, approaching the activation barrier is not equivalent to surmounting the barrier. Most of the approaches do not have enough total energy to make it over the activation barrier.

The Exponential Factor

The **exponential factor** ℗ is a number between 0 and 1 that represents the fraction of molecules that have enough energy to make it over the activation barrier on a given approach. The exponential factor is the fraction of approaches that are actually successful and result in the product. For example, if the frequency factor is 10^9/s and the exponential factor is 10^{-7} at a certain temperature, then the overall rate constant at that temperature is 10^9/s $\times 10^{-7} = 10^2$/s. In this case, the CN group is wagging at a rate of 10^9/s. With each wag, the activation barrier is approached. However, for a given wag only 1 in 10^7 molecules has sufficient energy to actually make it over the activation barrier.

The exponential factor depends on both the temperature (T) and the activation energy (E_a) of the reaction.

$$\text{Exponential factor} = e^{-E_a/RT}$$

Each wag is an approach to the activation barrier.

Activation barrier (E_a)

Energy

Reaction progress

A low activation energy and a high temperature make the negative exponent small, so the exponential factor approaches one. For example, if the activation energy is zero, the exponent is zero, and the exponential factor is exactly one $\left(e^{-0} = 1\right)$: every approach to the activation barrier is successful. By contrast, a large activation energy and a low temperature make the exponent a very large negative number, so the exponential factor becomes very small. For example, as the temperature approaches 0 K, the exponent approaches an infinitely large number, and the exponential factor approaches zero $\left(e^{-\infty} = 0\right)$.

As the temperature increases, the number of molecules having enough thermal energy to surmount the activation barrier increases. At any given temperature, a sample of molecules has a distribution of

energies, as shown in Figure 14.14☐. Under common circumstances, only a small fraction of the molecules has enough energy to make it over the activation barrier. Because of the shape of the energy distribution curve, however, a small change in temperature results in a large difference in the number of molecules having enough energy to surmount the activation barrier. This explains the sensitivity of reaction rates to temperature. This sensitivity depends on the magnitude of the activation barrier—*the higher the barrier, the greater the temperature sensitivity of the rate*.

Figure 14.14   Thermal Energy Distribution

At any given temperature, the atoms or molecules in a gas sample have a range of energies. The higher the temperature, the wider the energy distribution and the greater the average energy. The fraction of molecules with enough energy to surmount the activation energy barrier and react (shaded regions) increases sharply as the temperature rises.

Thermal Energy Distribution

As temperature increases, the fraction of molecules with enough energy to surmount the activation energy barrier also increases.

E_a

Activation energy

T_1 T_2

$T_2 > T_1$

Fraction of molecules

Energy
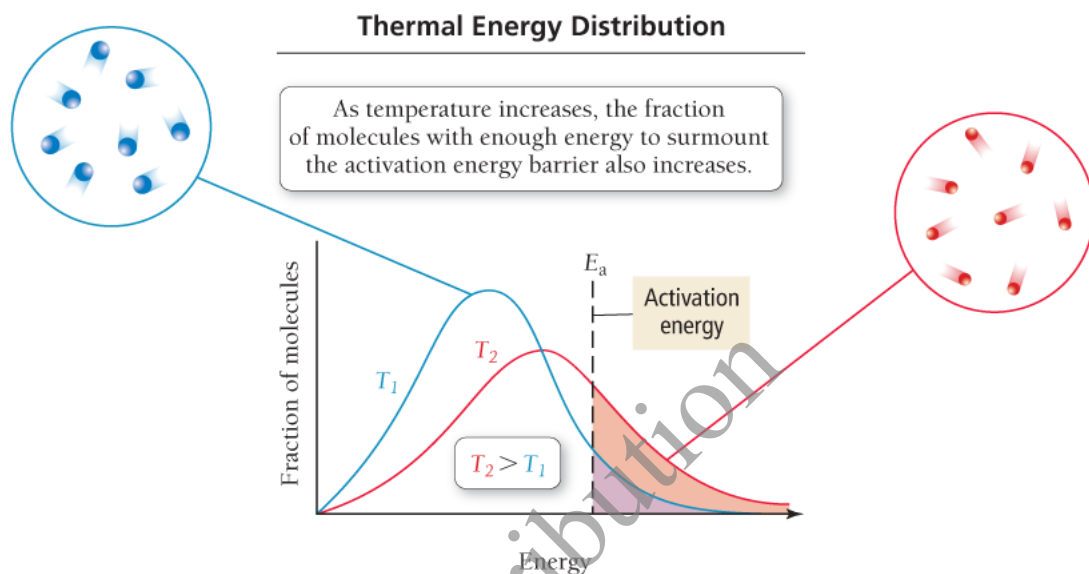
Summarizing Temperature and Reaction Rate:

- The frequency factor is the number of times that the reactants approach the activation barrier per unit time.
- The exponential factor is the fraction of the approaches that are successful in surmounting the activation barrier and forming products.
- The exponential factor increases with increasing temperature but decreases with increasing activation energy.

Arrhenius Plots: Experimental Measurements of the Frequency Factor and the Activation Energy

The frequency factor and activation energy are important quantities in understanding the kinetics of any reaction. To see how we measure these factors in the laboratory, consider again Equation 14.24☐:

$k = Ae^{-E_a/RT}$. Taking the natural log of both sides of this equation, we get the following result:

[14.25]

$$\begin{aligned}
\ln k &= \ln\left(Ae^{-E_a/RT}\right) \\
\ln k &= \ln A + \ln e^{-E_a/RT} \\
\ln k &= \ln A - \frac{E_a}{RT}
\end{aligned}$$

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

$$y = mx + b$$

[14.26]

> Remember that $\ln(AB) = \ln A + \ln B$.

> Remember that $\ln e^x = x$

> Notice that the slope of the line depends on E_a. The higher the activation energy, the steeper the slope and the greater the temperature dependence of the rate constant.

Equation 14.26 ⬚ is in the form of a straight line. *A plot of the natural log of the rate constant (ln k) versus the inverse of the temperature in kelvins (1/T) yields a straight line with a slope of $-E_a/R$ and a y-intercept of ln A.* This type of plot is an **Arrhenius plot** ⓘ and we commonly use it in the analysis of kinetic data, as shown in Example 14.7 ⬚.

> In an Arrhenius analysis, the pre-exponential factor (*A*) is assumed to be independent of temperature. Although the pre-exponential factor does depend on temperature to some degree, its temperature dependence is much less than that of the exponential factor and is often ignored.

Example 14.7 Using an Arrhenius Plot to Determine Kinetic Parameters

The decomposition of ozone shown here is important to many atmospheric reactions:

$$O_3(g) \rightarrow O_2(g) + O(g)$$
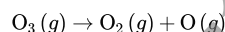
A study of the kinetics of the reaction results in the following data:

Temperature (K)	Rate Constant $(M^{-1} \cdot s^{-1})$	Temperature (K)	Rate Constant $(M^{-1} \cdot s^{-1})$
600	3.37×10^3	1300	7.83×10^7
700	4.85×10^4	1400	1.45×10^8
800	3.58×10^5	1500	2.46×10^8
900	1.70×10^6	1600	3.93×10^8
1000	5.90×10^6	1700	5.93×10^8
1100	1.63×10^7	1800	8.55×10^8
1200	3.81×10^7	1900	1.19×10^9

Determine the value of the frequency factor and activation energy for the reaction.

SOLUTION

To determine the frequency factor and activation energy, prepare a graph of the natural log of the rate constant (ln k) versus the inverse of the temperature (1/T).

$$y = -1.12 \times 10^4 x + 26.8$$
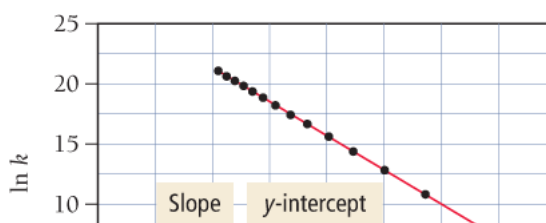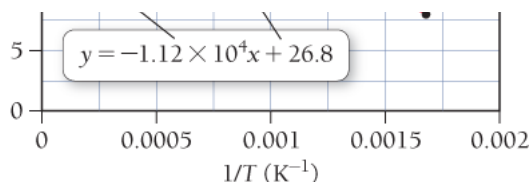
The plot is linear, as expected for Arrhenius behavior. The line that fits best has a slope of -1.12×10^4 K and a y-intercept of 26.8. Calculate the activation energy from the slope by setting the slope equal to $-E_a/R$ and solving for E_a:

$$-1.12 \times 10^4 \text{ K} = \frac{-E_a}{R}$$

$$
\begin{aligned}
E_a &= 1.12 \times 10^4 \ \cancel{K} \left(8.314 \frac{J}{\text{mol} \cdot \cancel{K}} \right) \\
&= 9.31 \times 10^4 \text{ J/mol} \\
&= 93.1 \text{ kJ/mol}
\end{aligned}
$$

Calculate the frequency factor (A) by setting the intercept equal to $\ln A$:

$$
\begin{aligned}
26.8 &= \ln A \\
A &= e^{26.8} \\
&= 4.36 \times 10^{11}
\end{aligned}
$$

Because the rate constants are measured in units of $M^{-1} \cdot s^{-1}$, the frequency factor is in the same units. Consequently, we can conclude that the reaction has an activation energy of 93.1 kJ/mol and a frequency factor of $4.36 \times 10^{11} \ M^{-1} \cdot s^{-1}$.

FOR PRACTICE 14.7   For the decomposition of ozone reaction in Example 14.7⬚, use the results of the Arrhenius analysis to predict the rate constant at 298 K.

In some cases, when either data are limited or plotting capabilities are absent, we can calculate the activation energy if we know the rate constant at just two different temperatures. We can apply the Arrhenius expression in Equation 14.26⬚ to the two different temperatures as follows:

$$\ln k_2 = -\frac{E_a}{R}\left(\frac{1}{T_2}\right) + \ln A \qquad \ln k_1 = -\frac{E_a}{R}\left(\frac{1}{T_1}\right) + \ln A$$

We can then subtract $\ln k_1$ from $\ln k_2$:

$$\ln k_2 - \ln k_1 = \left[-\frac{E_a}{R}\left(\frac{1}{T_2}\right) + \ln A \right] - \left[-\frac{E_a}{R}\left(\frac{1}{T_1}\right) + \ln A \right]$$

Rearranging, we get the two-point form of the Arrhenius equation:

[14.27]

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Example 14.8⬚ demonstrates how to use this equation to calculate the activation energy from experimental measurements of the rate constant at two different temperatures.

Example 14.8 Using the Two-Point Form of the Arrhenius Equation

Consider the reaction between nitrogen dioxide and carbon monoxide:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$
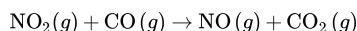
The rate constant at 701 K is measured as $2.57 \text{ M}^{-1} \cdot \text{s}^{-1}$, and that at 895 K is measured as $567 \text{ M}^{-1} \cdot \text{s}^{-1}$. Find the activation energy for the reaction in kJ/mol.

SORT   You are given the rate constant of a reaction at two different temperatures and asked to find the activation energy.

GIVEN:
$T_1 = 701 \text{ K}, k_1 = 2.57 \text{ M}^{-1} \cdot \text{s}^{-1}$
$T_2 = 895 \text{ K}, k_2 = 567 \text{ M}^{-1} \cdot \text{s}^{-1}$

FIND: E_a

STRATEGIZE   Use the two-point form of the Arrhenius equation, which relates the activation energy to the given information and R (a constant).

EQUATION: $\ln \dfrac{k_2}{k_1} = \dfrac{E_a}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

SOLVE   Substitute the two rate constants and the two temperatures into the equation.

Solve the equation for E_a, the activation energy, and convert to kJ/mol.

SOLUTION

$$\ln \frac{567 \ \cancel{M^{-1} \cdot s^{-1}}}{2.57 \ \cancel{M^{-1} \cdot s^{-1}}} = \frac{E_a}{R}\left(\frac{1}{701 \text{ K}} - \frac{1}{895 \text{ K}}\right)$$

$$5.40 = \frac{E_a}{R}\left(\frac{3.09 \times 10^{-4}}{\text{K}}\right)$$

$$E_a = 5.40\left(\frac{\text{K}}{3.09 \times 10^{-4}}\right)R$$

$$= 5.40\left(\frac{\cancel{K}}{3.09 \times 10^{-4}}\right)8.314 \ \frac{\text{J}}{\text{mol} \cdot \cancel{K}}$$

$$= 1.45 \times 10^5 \text{ J/mol}$$

$$= 145 \text{ kJ/mol}$$

CHECK   The magnitude of the answer is reasonable. Activation energies for most reactions range from tens to hundreds of kilojoules per mole.

FOR PRACTICE 14.8   Use the results from Example 14.8⬚ and the given rate constant of the reaction at either of the two temperatures to predict the rate constant for this reaction at 525 K.

Interactive Worked Example 14.8   **Using the Two-Point Form of the Arrhenius Equation**

Conceptual Connection 14.6   **Temperature Dependence of Reaction Rate**

The Collision Model: A Closer Look at the Frequency Factor
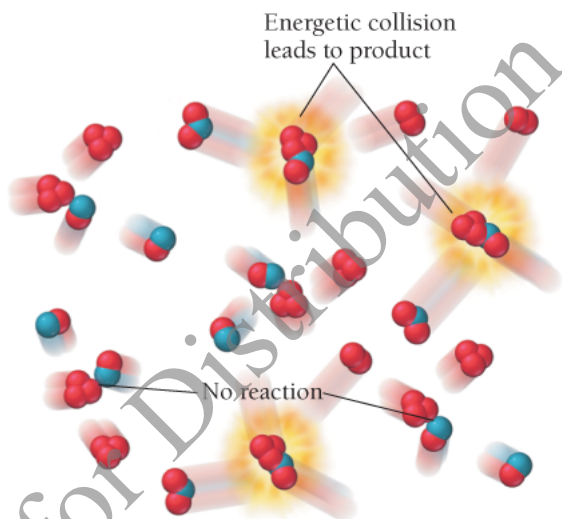
Frequency Factor

We saw previously that the frequency factor in the Arrhenius equation represents the number of approaches to the activation barrier per unit time. Let's refine that idea for a reaction involving two gas-phase reactants:

$$A\,(g) + B\,(g) \rightarrow \text{products}$$
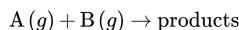
Recall from Section 14.2 that in the **collision model** a chemical reaction occurs after a sufficiently energetic collision between two reactant molecules (Figure 14.15). In collision theory, therefore, each approach to the activation barrier is a collision between the reactant molecules. Consequently, the value of the frequency factor should simply be the number of collisions that occur per second. However, the frequency factors of most (though not all) gas-phase chemical reactions tend to be smaller than the number of collisions that occur per second. As we saw in Section 14.2, not all sufficiently energetic collisions lead to products because the *orientations* of some of the collisions may not be adequate for the reaction to occur.

Figure 14.15   The Collision Model

In the collision model, molecules react after a sufficiently energetic collision with the correct orientation brings the reacting groups together.

In the collision model, we can separate the frequency factor into two distinct parts, as shown in the following equations:

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

Orientation factor   Collision frequency

where p is the **orientation factor** and z is the **collision frequency**. The collision frequency is the number of collisions that occur per unit time, which we can calculate for a gas-phase reaction from the pressure of the gases and the temperature of the reaction mixture. Under typical gaseous conditions, a single molecule undergoes on the order of 10^9 collisions every second. The orientation factor is a number, usually between 0 and 1, which represents the fraction of collisions with an orientation that allows the reaction to occur.

The orientation factor is a measure of how specific the orientation of the colliding molecules must be. A large orientation factor (near 1) indicates that the colliding molecules can have virtually any orientation and the reaction will still occur. A small orientation factor indicates that the colliding molecules must have a highly specific orientation for the reaction to occur.

As an example, consider the reaction represented by the following equation:

$$NOCl(g) + NOCl(g) \longrightarrow 2\, NO(g) + Cl_2(g)$$
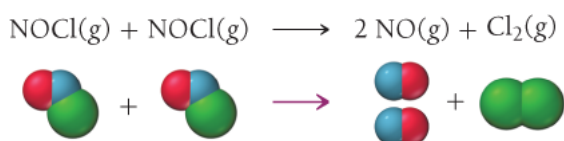
In order for the reaction to occur, two NOCl molecules must collide with sufficient energy. However, not all collisions with sufficient energy lead to products, because the reactant molecules must also be properly oriented. Consider the three possible collision orientations of the reactant molecules shown below. The first two collisions, even if they occur with sufficient energy, do not result in a reaction, because the reactant molecules are not oriented in a way that allows the chlorine atoms to bond. In other words, if two molecules are to react with each other, they must collide in such a way that allows the necessary bonds to break and form. For the reaction of NOCl(g), the orientation factor is $p = 0.16$ This means that only 16 out of 100 sufficiently energetic collisions are actually successful in forming the products.
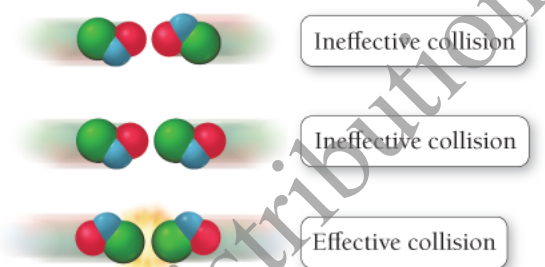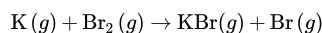

Some reactions have orientation factors that are much smaller than 1. Consider the reaction between hydrogen and ethene:

$$H_2\,(g) + CH_2{=}CH_2\,(g) \rightarrow CH_3{-}CH_3\,(g)$$
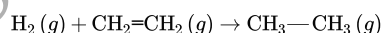
The orientation factor for this reaction is 1.7×10^{-6}, which means that fewer than two out of each million sufficiently energetic collisions actually form products. The small orientation factor indicates that the orientation requirements for this reaction are very stringent—the molecules must be aligned in a *very specific way* for the reaction to occur. Notice that, as we have seen many times, *structure affects properties*. In this case, the structure of the reactants affects how fast the reaction occurs.

Reactions between *individual atoms* usually have orientation factors of approximately 1 because atoms are spherically symmetric and thus any orientation can lead to the formation of products. A few reactions have orientation factors greater than 1. Consider the reaction between potassium and bromine:

$$K\,(g) + Br_2\,(g) \rightarrow KBr(g) + Br\,(g)$$

This reaction has an orientation factor of $p = 4.8$ In other words, there are more reactions than collisions —the reactants do not even have to collide to react! Apparently, through a process dubbed *the harpoon mechanism*, a potassium atom can actually transfer an electron to a bromine molecule without a collision. The resulting positive charge on the potassium and the negative charge on the bromine cause the two species to attract each other and form a bond. The potassium atom essentially *harpoons* a passing

bromine molecule with an electron and *reels it in* through the coulombic attraction between unlike charges.

We can picture a sample of reactive gases as a frenzy of collisions between the reacting atoms or molecules. At normal temperatures, the vast majority of these collisions do not have sufficient energy to overcome the activation barrier, and the atoms or molecules simply bounce off one another. Of the collisions having sufficient energy to overcome the activation barrier, most do not have the proper orientation for the reaction to occur (for the majority of common reactions). When two molecules with sufficient energy *and* the correct orientation collide, something extraordinary happens. The electrons on one of the atoms or molecules are attracted to the nuclei of the other; some bonds begin to weaken while other bonds begin to form and, if all goes well, the reactants go through the transition state and are transformed into the products. This is how a chemical reaction occurs.

Conceptual Connection 14.7   Collision Theory

Interactive