6.3 Explaining Reaction Rates

After an icy winter storm, you might sprinkle crystals of a chemical such as calcium chloride around to melt the ice (**Figure 1**). The calcium chloride dissolves in any liquid water. This chemical reaction releases thermal energy that melts the ice, which then allows more calcium chloride to go into solution and melt more ice. You may have found that the ice will melt faster if you break it up before you sprinkle the calcium chloride. You probably do not think about it, but what you are doing is increasing the surface area of the ice to increase the reaction rate! So what is happening at the level of the ions and molecules? In this section, you will explore theories that explain how surface area and other factors, including the chemical nature of the reactants, concentration of reactants, surface area, temperature, and the presence of a catalyst affect reaction rate.

Figure 1 Calcium chloride or other salts will melt ice more quickly if the ice is broken up first, exposing more surface area.

collision theory the theory that chemical reactions can occur only if reactants collide with proper orientation and with enough kinetic energy to break reactant bonds and form product bonds

Collision Theory

Collision theory states that chemical reactions can occur only if reactant atoms, molecules, or ions collide. Furthermore, the reactant entities must collide at an orientation and with enough kinetic energy that any bonds in the reactants will break and new bonds will form, making the products. The rate of a reaction depends on the frequency and the proportion of collisions that convert reactants into products. An increase in the frequency of effective collisions leads to a higher reaction rate.

Orientation

Some orientations for collisions between molecules or ions can lead to reactions while others cannot. This is sometimes called the collision geometry. As an example, think about the decomposition reaction of nitrosyl bromide gas, BrNO(g), represented by the following equation:

$$2\,\mathrm{BrNO(g)} \rightarrow 2\,\mathrm{NO(g)} + \mathrm{Br_2(g)}$$

According to collision theory, only some collisions between reactants are oriented so that a chemical reaction is possible, such as the collisions illustrated in **Figure 2(a)** and **(b)**. If the bromine atoms in the nitrosyl bromide molecules do not make direct contact, the reactants cannot form products and there will be no reaction, such as in the case shown in **Figure 2(c)**.

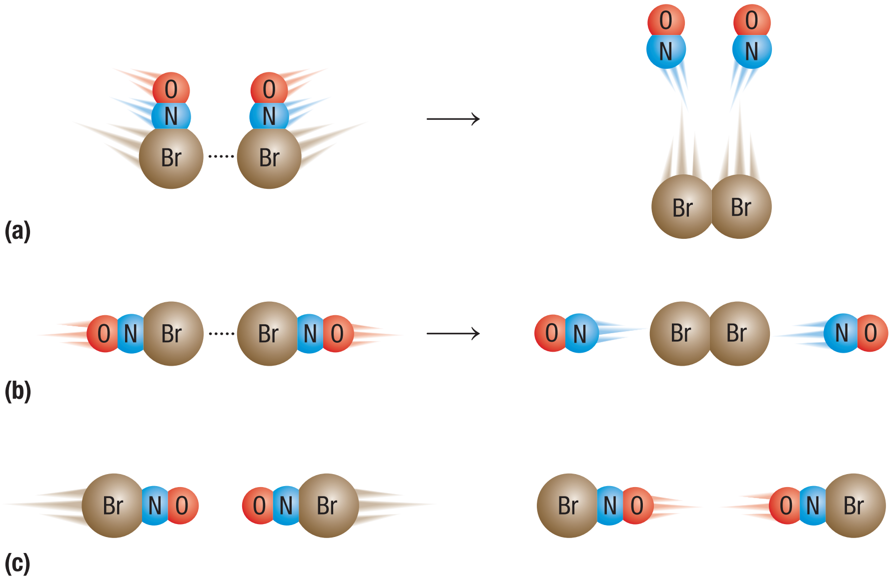

Figure 2 Several possible orientations for a collision between 2 nitrosyl bromide molecules. In (a) and (b), the orientations of the bromine atoms allow them to contact one another, so the chemical reaction can occur. In (c), the orientation of the bromine atoms prevents the bromine atoms from interacting, so the molecules move apart without reacting.

Activation Energy

The orientation of the reactant entities is only one factor in an effective collision. For a reaction to occur, the reactants must also have sufficient kinetic energy. The minimum amount of energy a reactant entity must have for a collision to be effective is called the **activation energy (E_a)**. Activation energy serves two purposes: it is used to overcome the electrostatic repulsive forces between colliding entities, and it is used to weaken the bonds of the reactants.

activation energy (E_a) the minimum energy that reactant molecules must possess for a reaction to be successful

You can think of activation energy as a potential energy hill or barrier. This concept of activation energy may be easier to understand if you think of a ball rolling (without obstacles or friction) on a smooth surface, such as the one shown in **Figure 3**. At point A, the ball has a certain quantity of potential energy. If you add kinetic energy, perhaps by pushing the ball, the ball will roll up the hill. As it rolls up the hill, the ball slows down as some of the kinetic energy is transformed into potential energy. If there is sufficient kinetic energy to reach the top of the hill (the same or more than the activation energy), the ball will roll down to the other side. In Figure 3, the ball has a higher potential energy at point B than it had at point A. If the ball had less kinetic energy at the start of its roll than the activation energy, it would have climbed only partway up the hill and then returned to point A.

A Model for Activation Energy

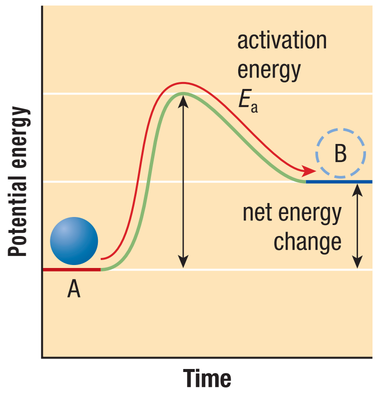

Figure 3 From point A to point B, there is a net increase in overall energy (kinetic plus potential). The ball must have a lot of energy (activation energy) to get up the hill.

In a chemical reaction, the potential energy is the energy stored in the bonds within and among the entities of the reactants, and the kinetic energy is their movement. When entities collide in an appropriate orientation, a chemical reaction can only proceed if the kinetic energy is enough to break these bonds. This quantity of energy is the activation energy (analogous to the hill in Figure 3). If the kinetic energy is sufficient, the bonds will rearrange to form the products. If the reactants do not have enough kinetic energy, the bonds of the reactants will not break and the reaction will not proceed.

For example, in the reaction represented in Figure 2, two Br–N bonds must be broken and one Br–Br bond must be formed. It takes considerable energy (243 kJ/mol) to break a Br–N bond. If 2 nitrosyl bromide molecules do not have enough kinetic energy to get over this potential energy hill, or barrier, the reaction will not take place.

The change in potential energy over the progress of this reaction between nitrosyl bromide molecules is illustrated in **Figure 4**. The unstable arrangement of atoms found at the top of the potential energy hill is called the **activated complex**, or transition state. The activation energy, E_a, represents the energy difference between reactants and the activated complex.

activated complex an unstable arrangement of atoms containing partially formed and unformed bonds that represents the maximum potential energy point in the change; also called the transition state

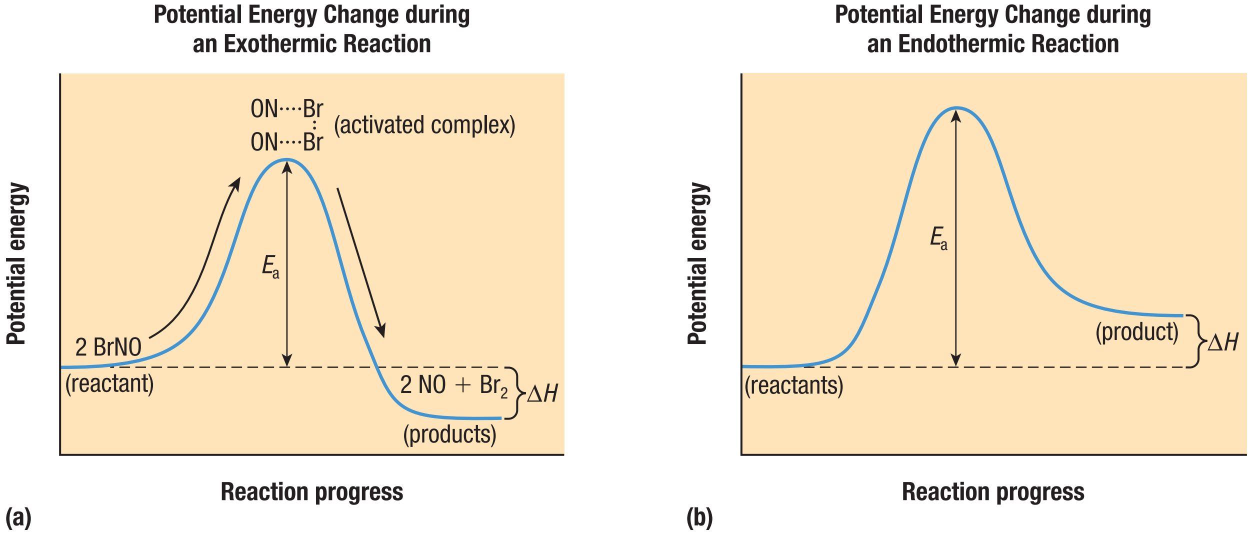

Figure 4 The change in potential energy as a function of reaction progress for (a) the reaction $2\ BrNO(g) \rightarrow 2\ NO(g) + Br_2(g)$ and (b) an endothermic reaction

Notice how, as with the ball in Figure 3, the potential energy of the products of this reaction is not the same as the potential energy of the reactants. In Section 5.3, you saw that the net change in energy between reactants and products is called the enthalpy change, ΔH. Exothermic reactions release energy and have a negative ΔH, and the reaction depicted in Figure 4(a) is an exothermic reaction. Figure 4(b) illustrates the change in potential energy during a hypothetical endothermic reaction. The potential energy gain comes from the conversion of kinetic energy. Endothermic reactions absorb energy and have a positive ΔH.

Temperature of the Reaction System

Experimental evidence shows that a relatively small increase in temperature seems to have a very large effect on reaction rate. An increase of about 10 °C will often double or triple the rate of a reaction. Temperature is considered to be a measure of the average kinetic energy of a substance. Therefore, in any sample of a substance at a given temperature, the individual entities in the sample will have different kinetic energies. Some of the entities will therefore be moving more quickly than others, so only a proportion will have a quantity of kinetic energy that equals or exceeds the activation energy. If you increase the temperature, the average kinetic energy of the entities increases. As a result, more entities in the sample will have enough kinetic energy to break the bonds of the reactants and form an activation complex. In addition, the increase in kinetic energy will also increase the rate and force of collisions between reactants, which will increase the probability that the collisions will be effective.

For a given activation energy, E_a, a much larger fraction of entities of a reactant will have the required kinetic energy at a higher temperature than at a lower temperature. A temperature rise that is a small increase in overall energy might cause a very large increase in the number of entities that have energy exceeding the activation energy. For reactants in the gas state, this relationship between the numbers of entities of a reactant and their kinetic energy is represented by a graph called the Maxwell–Boltzmann distribution (**Figure 5**).

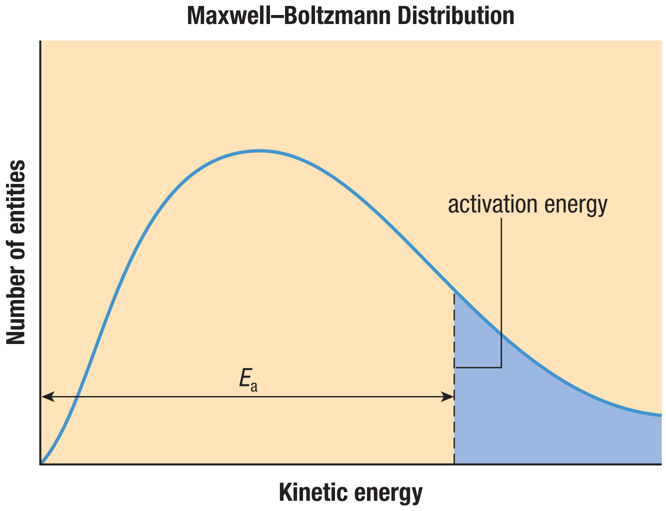

Figure 5 Only entities with kinetic energy equal to or greater than the activation energy can be involved in an effective collision. These entities are represented by the shaded area to the right of the dotted line.

At a given temperature, only a certain fraction of the reactant entities will possess enough kinetic energy to equal or exceed the activation energy, E_a. **Figure 6** on the next page shows how the Maxwell–Boltzmann distribution changes when temperature is changed. At the lower temperature, T_1, the fraction of entities that have kinetic energy equal to or greater than the activation energy is quite small. In Figure 6, this is represented by the shaded area to the right of the line that represents the activation energy and under the line for T_1. When the temperature is raised to T_2, the fraction of reactant entities with kinetic energy equal to or greater than the activation energy increases dramatically. Therefore, there are many more entities that are capable of making effective collisions at the higher temperature (provided they collide in a productive orientation). Experimental evidence shows that, for most chemical reactions, reaction rates increase exponentially with temperature. This is consistent with the theory that increases in temperature exponentially increase the probability of effective collisions.

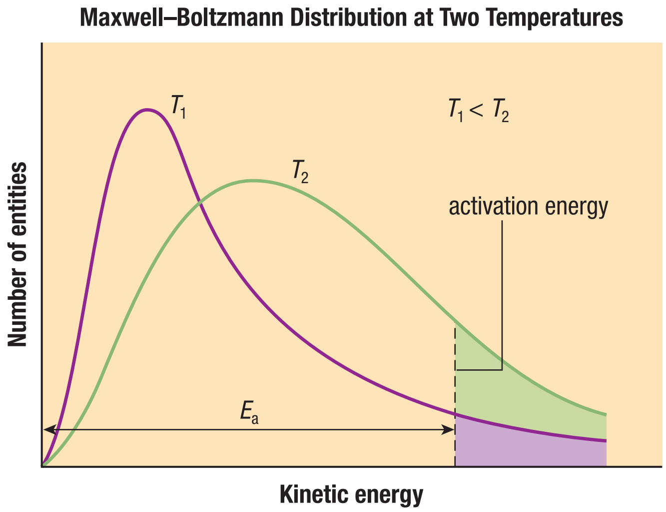

Figure 6 When the temperature of a reaction mixture is increased from T_1 to T_2, the number of entities capable of having effective collisions increases significantly.

Mini **Investigation**

Modelling Energy Distribution of Molecules

Skills: Performing, Observing, Analyzing

SKILLS HANDBOOK **A2.4**

In this activity, you will work with a group to model how temperature changes the distribution of energy among entities in a substance.

Equipment and Materials: 5 tokens per student (such as paper clips or pieces of paper)

1. Obtain 1 token, then pair up with a fellow student. Both of you should have 1 token. Each token represents an effective collision between reactants.
2. As a class, form 2 rings so that 1 ring is inside the other and each person is facing his or her partner in the other ring.
3. Play rock, paper, scissors with your partner in the other ring. Whenever one of you wins, the losing partner must pass 1 token to the winner. If there is no winner, then you both keep your tokens.
4. As a class, shift positions so that all students in the inner circle move 1 person to the right, giving everyone a new partner.
5. Repeat Steps 3 and 4 twice, then record the number of tokens held by each person in the class.
6. Repeat Steps 3 to 5 an additional three times.
7. Take note of who your current partner is. Obtain another token and return to the circle. Everyone in the class should now be in the same position but have 1 more token than at the end of Step 6. This additional token represents an increase in temperature.
8. Repeat Steps 3 to 6.

A. Do you think you could have predicted how many tokens each person would have at the end of the activity? Why or why not? T/I

B. How is obtaining an additional token in Step 7 similar to an increase in temperature? T/I

C. After each round, were the tokens distributed equally or were there many students who had many more tokens than others? How does this model the kinetic energy of entities of a substance at a given temperature? T/I

D. Relate the results of this activity to the effects of temperature on the probability of effective collisions in a reaction mixture. T/I

Chemical Nature of Reactants

For any reactant, the bond type, strength, and number determine the activation energy required for a successful collision. Reactions involving the breaking of fewer bonds per reactant proceed faster than those involving the breaking of a larger number of bonds per reactant. Weaker bonds are broken at a faster rate than stronger bonds. For example, it takes less energy to break a single C−C bond than a double C=C bond. Reactions between molecules are usually slower than reactions between ions. This is because, in molecules, covalent bonds have to be broken and new bonds re-formed. This slows down reaction rates.

The size and shape of a molecule or ion can also affect reaction rate. Some reactions involve complicated molecular substances or complex ions. These are often less reactive than smaller, less complex entities. This is in part because more bonds must be broken. However, it is also less likely that complex molecules or ions will collide in an orientation relative to each other that will be effective in allowing a reaction to occur.

Concentration and Surface Area

You are more likely to bump into another passenger while travelling on a public bus during rush hour than on a less crowded bus in the middle of the day. Similarly, if you increase the concentration of a reactant, the probability of collisions between reactant molecules increases and, hence, a greater number of effective collisions is likely to occur. Therefore, the reaction rate will be expected to increase. **Figure 7** represents two reactions occurring in aqueous solution, with two different concentrations of reactants A and B. Which reaction rate do you predict will be higher?

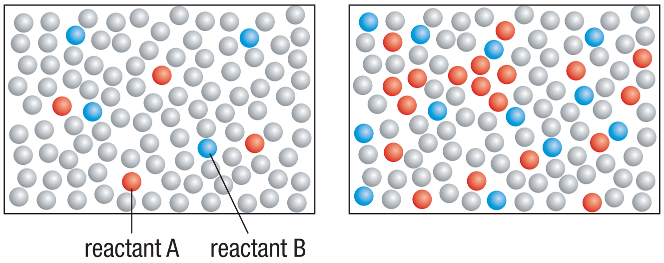

Figure 7 Two reactions occurring in aqueous solution, one with lower concentrations of the reactants and the other with higher concentrations. Identify the number of reactant A–reactant B collisions in each sample.

In a reaction involving reactants in more than one state, such as a solid reactant and a liquid reactant, increasing the surface area of the solid reactant increases the reaction rate. Imagine that you are holding a cube of some substance. Its surface area is the area of the 6 faces of the cube. If you were to cut the cube into many smaller cubes, the total surface area would increase. If you ground the cube into a powder, the surface area would be maximized. This is why many solids are powdered using a mortar and pestle before being used in a reaction.

Chemical entities that are not bound within a crystalline structure are available to react with other entities. Only the atoms, ions, or molecules at the surface of the solid reactant can collide with entities of the other reactant(s). Therefore, increasing the surface area of a solid reactant increases the probability of effective collisions in a similar manner to increases in concentration. In a reaction between a solid and a reactant in the liquid or gas phase, or in aqueous solution, increasing the surface area of the reactant in the solid phase increases the number of collisions per unit time and therefore increases the reaction rate (**Figure 8**).

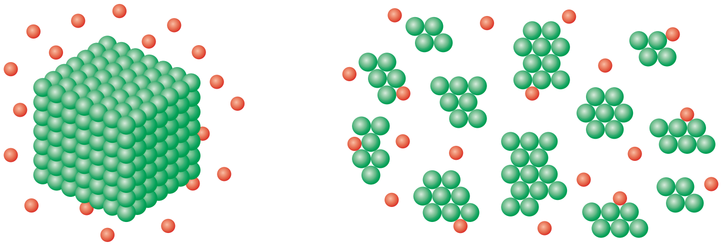

Figure 8 The entities in a solid structure have fewer potential collision sites than the same number of entities split into smaller bits, increasing the total surface area.

Catalyst Theory

For any reaction to occur, the kinetic energy of colliding reactant entities must be equal to or greater than the activation energy. However, catalysts do not increase the number of collisions between reactant entities, nor do they increase the kinetic energy of the entities of reactant(s). Instead, a catalyst provides an alternative pathway for the reaction, which has a lower activation energy. Thus, at any given temperature, a larger fraction of the entities of the reactant(s) will have kinetic energy equal to or greater than this lower activation energy. There is a greater number of effective collisions, and so the reaction rate is increased (**Figure 9**).

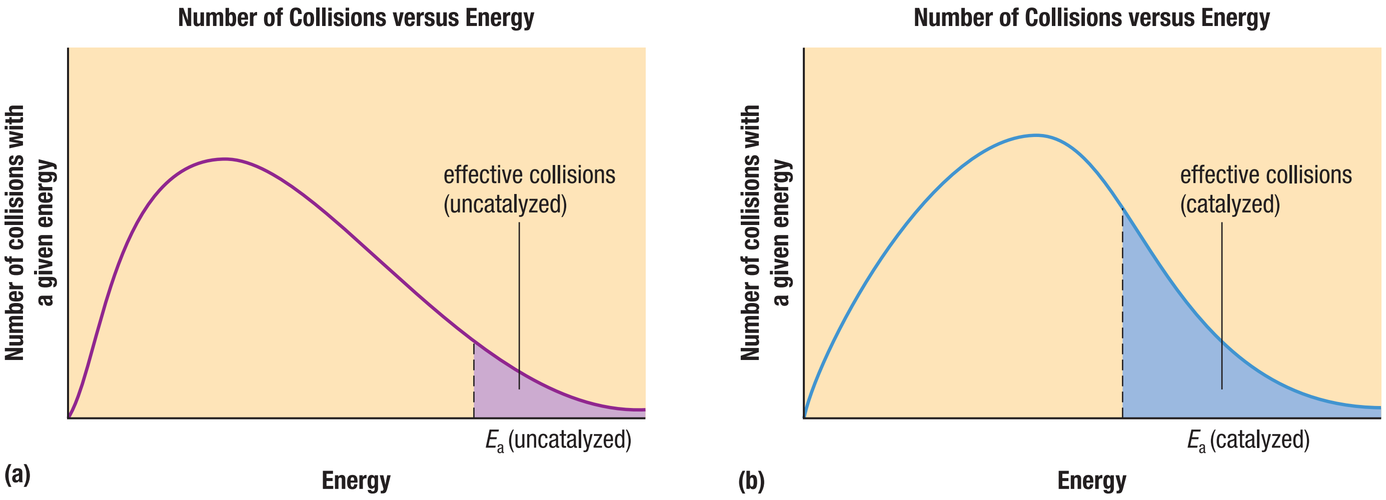

Figure 9 The effect of a catalyst on the number of reaction-producing collisions. Since a catalyst provides a reaction pathway with a lower activation energy, a much greater fraction of the collisions are successful for the catalyzed pathway (b) than for the uncatalyzed pathway (a) (at a given temperature). This allows reactants to become products at a much higher rate, even if the temperature is not increased.

A catalyst is thought to allow a reaction to occur along a different pathway of steps that results in the same overall products. However, as shown in **Figure 10**, although a catalyst lowers the activation energy, E_a, for a reaction, it does not affect the energy difference between products and reactants.

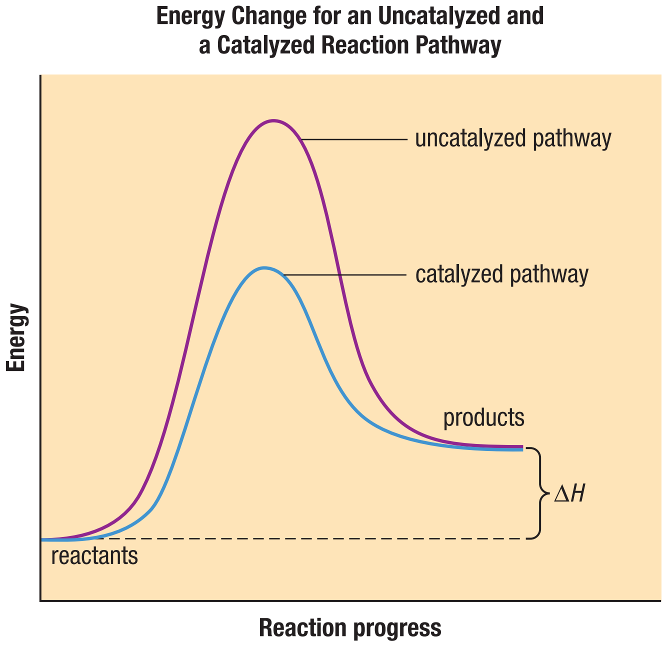

Figure 10 Energy plots for a catalyzed and an uncatalyzed pathway for a given reaction

UNIT TASK BOOKMARK

How can you apply catalyst theory to the Unit Task on page 402?

6.3 Review

Summary

- Collision theory states that, for a chemical reaction to occur: a collision must occur between 2 or more reactant entities; the entities must collide with the correct orientation; and the entities must have a certain minimum energy.
- An effective collision is one in which reactant(s) is converted to product.
- Activation energy, E_a, is the minimum energy required for an effective collision.
- Chemical properties of the reactants determine the activation energy required for an effective collision.
- An activated complex (transition state) is an unstable arrangement of atoms at the maximum potential energy point in the change from reactant(s) to product(s).
- Increasing the surface area and the concentration of a reactant(s) increases the total number of collisions and so the number of effective collisions.
- Increasing the temperature will increase the average kinetic energy of the entities of reactant(s). This will result in more entities having a quantity of kinetic energy the same as or greater than the activation energy and will increase the number of collisions.
- A catalyst provides a reaction pathway with a lower activation energy.

Questions

1. A reaction will occur between zinc and hydrochloric acid. Describe what will happen to the reaction rate under the conditions described below. K/U
   (a) The acid is cooled to 1 °C.
   (b) The reaction mixture is stirred.
   (c) A concentration of 5.0 mol/L hydrochloric acid is used instead of 1.0 mol/L.
   (d) Powdered zinc is used instead of chunks of zinc.
   (e) The reaction is carried out in a darkened room.
2. (a) State the collision theory in your own words.
   (b) Explain why not every collision that occurs results in the formation of a product.
   (c) Explain why increasing the temperature can affect the number of collisions as well as the percentage of effective collisions. K/U
3. Think of an everyday activity, such as a handshake, that requires you to come in contact with something, to be lined up correctly, and to have a certain minimum amount of energy. Describe the activity and explain what would happen if any one of these criteria were not met. A
4. Draw and label two potential energy diagrams, one for an endothermic reaction and one for an exothermic reaction. Show ΔH and E_a. T/I C
5. A common catalyst that is used to speed up the rate of the decomposition of hydrogen peroxide is powdered manganese dioxide. K/U T/I
   (a) Describe what a catalyst is.
   (b) Explain how it affects the rate of a reaction.
   (c) Is manganese dioxide a heterogeneous or homogeneous catalyst?
   (d) Design an experiment to prove that manganese dioxide is a catalyst for this reaction. Include a list of all materials that are required.
6. (a) Write the balanced equation for the reaction between ethylene, C_2H_4 and hydrogen chloride, HCl.
   (b) Represent the reaction using Lewis structures.
   (c) Based on your Lewis structures, suggest an orientation that would result in an effective collision.
   (d) Suggest an orientation that would result in an ineffective collision. K/U T/I C