

Factors That Affect Reaction Rates

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CHAPTER 1

Factors That Affect Reaction Rates

Lesson Objectives

The student will:

- describe how temperature, concentration, surface area, and the addition of a catalyst affect the rate of a chemical reaction.
- define a catalyst and describe how it affects the potential energy diagram of a reaction.
- identify a catalyst in chemical equations.

Vocabulary

- catalyst
- effective collision

Introduction

Chemists use reactions to generate a desired product. For the most part, a reaction is only useful if it occurs at a reasonable rate. For example, a reaction that took 8,000 years to complete would not be a desirable way to produce brake fluid. However, a reaction that proceeded so quickly that it caused an explosion would also not be useful (unless the explosion was the desired result). For these reasons, chemists wish to be able to control reaction rates. In order to gain this control, we must first know what factors affect the rate of a reaction. We will discuss some of these factors in this section.

Effect of Temperature on Rate of Reaction

Increased Temperature

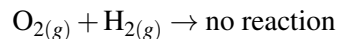
The rate of reaction was discussed in terms of three factors: collision frequency, the collision energy, and the geometric orientation. Remember that the collision frequency is the number of collisions per second. The collision frequency is dependent, among other factors, on the temperature of the reaction.

When the temperature is increased, the average velocity of the particles is increased. As a result, the average kinetic energy of these particles is also increased. The result is that the particles will collide more frequently because the particles move around faster and will encounter more reactant particles, but this is only a minor part of the reason why the rate is increased. Just because the particles are colliding more frequently does not mean that the reaction will definitely occur.

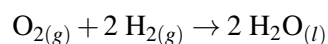
The major effect of increasing the temperature is that more of the particles that collide will have the amount of energy needed to have an **effective collision**, or a collision that results in a reaction. In other words, more particles

will have the activation energy needed to overcome the activation energy barrier and form the activated complex. The effect of raising the temperature, therefore, is to produce more activated complexes. With the greater number of activated complexes that are formed, the faster the rate of reaction.

At room temperature, the hydrogen and oxygen in the atmosphere do not have sufficient energy to attain the activation energy needed to produce water.



At any one moment in the atmosphere, there are many collisions occurring between these two reactants. When this reaction does occur, it is exothermic, which tends to mean that the reaction should occur. We find, however, that water does not form from the oxygen and hydrogen molecules colliding in the atmosphere because the activation energy barrier is just too high, causing all the collisions to rebound. When the necessary energy is supplied to the molecules, the molecules overcome the activation energy barrier, the activated complex is formed, and water is produced:



Decreased Temperature

There are times when the rate of a reaction needs to be slowed down. Using the factors as specified previously, one of ways to accomplish this would be to keep the reactants in separate containers so that there can be no collisions between the particles. At times that might not be practical, so lowering the temperature could also be used to decrease the number of collisions that would occur and to reduce the kinetic energy available for activation energy. If the particles have insufficient activation energy, the collisions will result in rebounds rather than reaction. Using this idea, when the rate of a reaction needs to be lower, keeping the particles from having sufficient activation energy will keep the reaction at a lower rate.

A Generalization for Increased Temperature

The rate of most reactions can be dramatically increased with increased temperature. For reactions that normally occur at room temperature, a general rule of thumb is that for every increase of 10°C , the rate will be doubled. If the temperature for these reactions is increased by 20°C , the rate will be increased by a factor of 4; increasing the temperature by 40°C , the rate will be increased by a factor to 16. For any specific reaction, however, the actual rate increase will have to be determined by experimentation.

Examples of Temperature on Reaction Rate

Society uses the effect of temperature on reaction rate every day. Food storage is a prime example of how the temperature effect on reaction rate is utilized by society. Consumers store food in freezers and refrigerators to slow down the processes that cause it to spoil. The decrease in temperature decreases the rate at which the food will break down or be broken down by bacteria.

When milk, for instance, is stored in the refrigerator, the molecules in bacteria have less energy. This means that while molecules will still collide with other molecules, few of them will react because the molecules do not have sufficient energy to overcome the activation energy barrier. Bacterial growth in milk is slowed down because the cellular molecules do not have enough energy to undergo chemical reactions crucial to cell reproduction. If that same carton of milk was at room temperature, the milk would react (in other words, spoil) much more quickly. Now most of the molecules will have sufficient energy to overcome the energy barrier, and at room temperature, many more collisions will be occurring. This allows for the milk to spoil in a fairly short amount of time.

For a classroom demonstration of the effect of temperature on reaction rate (**8b**), see <http://www.youtube.com/watch?v=t0x10CXjB04> (4:41).



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Effect of Concentration

Increasing Concentration

If you had one red ball and one green ball flying around randomly in an enclosed space and undergoing perfectly elastic collisions with the walls and with each other, in a given amount of time, the balls would collide with each other a certain number of times as determined by probability. If you now put two red balls and one green ball in the room under the same conditions, the probability of a collision between a red ball and the green ball would exactly double. The green ball would have twice the chance of encountering a red ball in the same amount of time.

In terms of chemical reactions, a similar situation exists. Particles of two gaseous reactants or two reactants in solution have a certain probability of undergoing collisions with each other in a reaction vessel. If you double the concentration of either reactant, the probability of a collision doubles. The rate of reaction is proportional to the number of collisions per unit time. Assuming that the percent of successful collision does not change, then having twice as many collisions will result in twice as many successful collisions. The rate of reaction is proportional to the number of collisions per unit time, so increasing the concentration of either reactant increases the number of collisions, the number of successful collisions, and the reaction rate.

Some reactions occur by a single collision between two reactant molecules, while other reactions occur by a series of collisions between multiple reactant particles. We will consider the case of the single step now and the case of the multiple step reactions later in the chapter.

The rate of a single collision chemical reaction at a given temperature can be expressed as a product of the concentrations of the reactants. For the reaction $A_{(g)} + B_{(g)} \rightarrow AB_{(g)}$, the reaction rate can be expressed as:

$$\text{Rate} = k[A][B]$$

where k is a constant for the reaction called the reaction constant and $[A]$ and $[B]$ are the molarities of the reactants.

If only the concentration of A is doubled, the equation would become $\text{Rate} = k[2A][B]$, and the rate would double the previous rate.

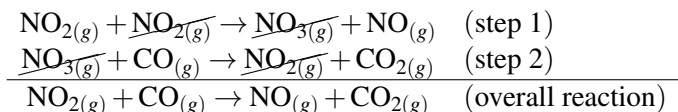
If only the concentration of B is doubled, the equation would become $\text{Rate} = k[A][2B]$, and once again the rate would double the previous rate.

If the concentrations of both A and B are doubled, the equation becomes $\text{Rate} = k[2A][2B]$, and the rate would now be four times the original rate.

Experimental Determination of Reaction Rate

When the reaction involves a series of collisions, the relationship between the reaction rate and the concentration of any single reaction can only be determined by a laboratory procedure. Consider the reaction below between NO_2

and CO. This reaction does not occur by a single collision but rather in a two step process.



The effect of the concentration of a reactant on the rate of this multiple step reaction can only be known through experimentation. Let's look at one experiment in order to determine how the concentration of the reactants affects the rate of the reaction.

Example:

For the hypothetical reaction $A + B \rightarrow C + D$, the following data (**Table 1.1**) was collected in an experiment to attempt to determine the effect of increasing the concentration of the reactants on the rate.

TABLE 1.1: Sample Data

Trial	[A] (mol/L)	[B] (mol/L)	Rate (mol/L · s)
1	1.0	1.0	5.0×10^{-3}
2	2.0	1.0	5.0×10^{-3}
3	1.0	2.0	$10. \times 10^{-3}$

Determine the effect of increasing the [A] and increasing [B] on the rate of the reaction.

Solution:

Step 1: Try to find two trials where the concentration of A is changing while the concentration of B remains the same.

In this case, in trials 1 and 2, [A] changes while [B] remains constant. Since [A] is changing and [B] is staying the same, any change in the reaction rate would be due to the change in [A].

Step 2: Determine the effect of changing the concentration of A on the reaction rate.

From trial 1 to trial 2, the concentration of A has doubled. The reaction rate in these two trials, however, did not change.

Therefore, the concentration of A has no effect on the rate for this reaction.

Step 3: Try to find two trials in which [B] changes while [A] stays the same.

In trials 1 and 3, the concentration of B changes while A stays the same. From trial 1 to trial 3, the concentration of B doubles. The reaction rate also doubled between these two trials. When the concentration of B doubled, the reaction rate also doubled. Therefore, we can conclude that the reaction rate is directly proportional to the concentration of B.

Therefore, when the concentration of A is increased, there is no effect on the rate of the reaction. When the concentration of B is doubled, the rate is doubled. In other words, increasing the concentration of B increases the rate.

Example of the Effect of Concentration on Reaction Rate

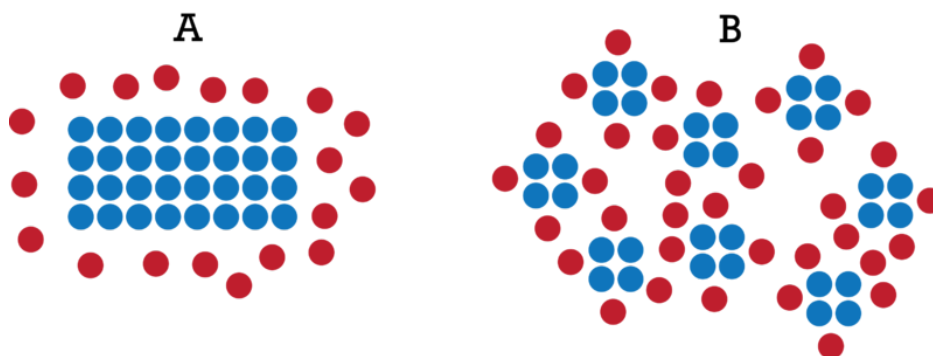
The chemical test used to identify a gas as oxygen relies on the fact that increasing the concentration of a reactant increases reaction rate. The reaction we call combustion refers to a reaction in which a flammable substance reacts with oxygen. If we light a wooden splint (a thin splinter of wood) on fire and then blow the fire out, the splint will continue to glow in air for a period of time. If we insert that glowing splint into any gas that does not contain oxygen, the splint will immediately cease to glow - that is the reaction stops. Oxygen is the only gas that will support

combustion. Air is approximately 20% oxygen gas. If we take that glowing splint and insert it into pure oxygen gas, the reaction will increase its rate by a factor of five since pure oxygen has 5 times the concentration of oxygen that is in air. When the reaction occurring on the glowing splint increases its rate by a factor of five, the glowing splint will suddenly burst back into full flame. This test of thrusting a glowing splint into a gas is used to identify the gas as oxygen. Only a greater concentration of oxygen than that found in air will cause the glowing splint to burst into flame.

Effect of Surface Area

The Relationship Between Surface and Reaction Rate

Consider a reaction between reactant red and reactant blue, where reactant blue is in the form of a single lump (**Figure A** below). Then compare this to the same reaction where reactant blue has been broken up into many smaller pieces (**Figure B** below).



In **Figure A**, only the blue particles on the outside surface of the lump are available for collision with reactant red. The blue particles on the interior of the lump are protected by the blue particles on the surface. If you count the number of blue particles available for collision, you will find that only 20 blue particles could be struck by a particle of reactant red. In **Figure B**, however, the lump has been broken up into smaller pieces, and all the interior blue particles are now on a surface and available for collision. As a result, more collisions between blue and red will occur. The reaction in **Figure B** will occur at faster rate than the same reaction in **Figure A**. Increasing the surface area of a reactant increases the frequency of collisions and increases the reaction rate.

You can see an example of this in everyday life if you have ever tried to start a fire in the fireplace. If you hold a match up against a large log in an attempt to start the log burning, you will find it to be an unsuccessful effort. Flammable materials like wood require a significant input of activation energy for the reaction to occur. The reaction between wood and oxygen is an exothermic reaction, so once the fire has been started, the heat released by the first reactions will provide the activation energy for the succeeding reactions. However, holding a match against a large log will not cause enough reactions to occur to keep the fire going. Instead, the log needs to be broken up into many small, thin sticks called kindling. These thinner sticks of wood provide many times the surface area of a single log. Now a match will be able to cause enough reactions in the kindling to successfully start a fire.

There have been, unfortunately, cases where serious accidents were caused by the failure to understand the relationship between surface area and reaction rate. One such example occurred in flour mills. A grain of wheat is not very flammable, but if the grain of wheat is pulverized and scattered through the air, only a spark is needed to cause an explosion. A small spark then is sufficient to start a very rapid reaction that can destroy the entire flour mill. In a 10-year period from 1988 to 1998, there were 129 grain dust explosions in mills in the United States. Flour mills now have huge fans to help circulate the air in the mill through filters in order to remove the majority of the flour dust particles. Coal mines suffer a similar problem. In coal mines, huge blocks of coal must be broken up by drilling

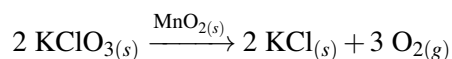
before the coal can be brought out of the mine. This drilling produces fine coal dust that mixes into the air, and a spark from a tool can cause a massive explosion in the mine. In modern coal mines, lawn sprinklers are used to spray water through the air in the mine in order to reduce the coal dust in the air.

Examples

You can observe the effect of surface area in the following manner: take two solids, put them together, and observe the reaction, then as a comparison, put one of these solids into solution, add the other solid, and observe the reaction. For example, if you were to take a few grams of copper(II) chloride and place them into a beaker along with a piece of aluminum foil, it would take a numbers days, if not weeks, before you would observe any significant changes. However if you were to make a solution of the copper(II) chloride before adding the aluminum foil, you would observe an almost immediate reaction. In this case, the surface area of only one of the reactants was changed, but that change would dramatically affect the rate of reaction because the copper(II) chloride ions could individually interact with the atoms present in the aluminum foil.

Effect of a Catalyst

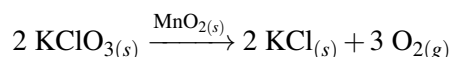
The final factor that affects the rate of the reaction is the presence of a catalyst. A **catalyst** is a substance that speeds up the rate of the reaction without itself being consumed by the reaction. There are a number of different catalysts, such as surface catalysts, which merely provide a surface for intermediate products to adhere to, and catalysts that are used at the beginning of a reaction but are completely reproduced at the end. The substances called enzymes in biology are catalysts that help carry out numerous chemical reactions in the body. Many commercial preparations of chemicals for industry rely on catalysts to prepare their products in a more cost effective manner. For example, iron oxide or vanadium oxide is used in combination with platinum as surface catalysts in the production of sulfuric acid (H₂SO₄).



The catalyst manganese dioxide makes the above reaction occur much faster than it would occur by itself under standard conditions. When the reaction has reached completion, the MnO₂ can then be removed from the reaction vessel in the same condition as it was before the reaction.

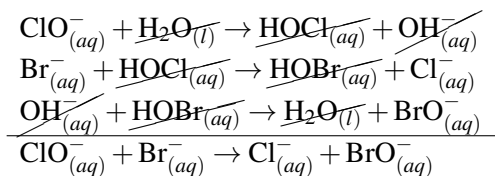
A Catalyst is Not a Reactant

It is important to emphasize that a catalyst is a substance that speeds up the rate of the reaction but is itself not consumed by the reaction. In other words, the catalyst is not seen in the reaction as either a reactant or a product. Consider the reaction to produce sulfuric acid again:



The reaction above is very slow unless you add manganese dioxide as a catalyst. Manganese dioxide is a black powder, while potassium chlorate is a white powder. After heating the potassium chlorate and obtaining the oxygen gas at the end of the reaction, all of the black MnO₂ can be recovered. You should note that the catalyst is not written into the equation as a reactant or product but is noted above the yields arrow. This is standard notation for a catalyst.

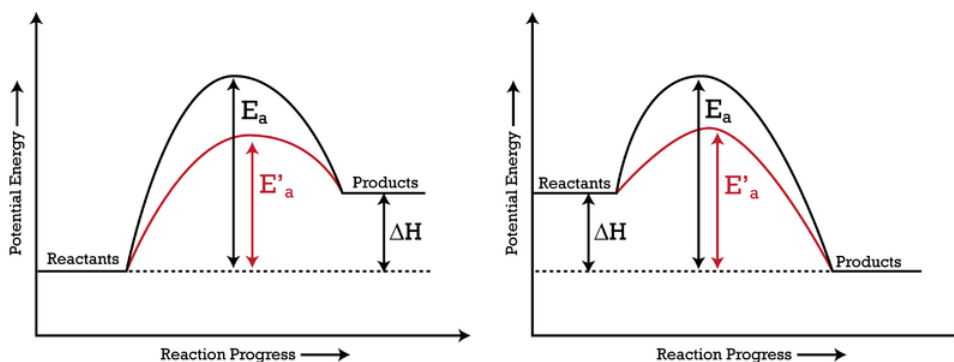
Look at the following three-step process below:



In this three-step process, all of the reactions are added together, and substances that appear on both sides of the equation are eliminated before writing the final overall equation. Notice how $\text{H}_2\text{O}_{(l)}$ is consumed in the first equation of the sequence and then produced in the final equation of the sequence. Since $\text{H}_2\text{O}_{(l)}$ is consumed and then produced, it is a catalyst. The presence of the water molecule causes this reaction to occur at a higher rate than it will occur without the presence of water. Therefore, although water is used in the reaction, it is reproduced so that the total amount of water is available at the end. This is also the behavior of a catalyst.

Catalysts Provide a Different Path with Lower Activation Energy

Some reactions occur very slowly without the presence of a catalyst. In other words, the activation energy for these reactions is very high. When the catalyst is added, the activation energy is lowered because the catalyst provides a new reaction pathway with lower activation energy.



Remember that the catalyst does not get consumed in the reaction, so the reactants and products positions are not affected by the addition of the catalyst. In the left figure above, the endothermic reaction shows the catalyzed reaction in red with lowered activation energy, designated E'_a . The new reaction pathway has lower activation energy, but it has no effect on the energy of the reactants, the products, or the value of ΔH .

The same is true for the exothermic reaction in the figure on the right. The activation energy of the catalyzed reaction (again designated by E'_a) is lower than that of the reaction without a catalyst. The new reaction pathway provided by the catalyst for the exothermic reaction shown in the right figure affects the energy required for reactant bonds to break and product bonds to form.

These two videos discuss the factors affecting reaction rate (**8b**, **8c**, **8d**). The first video discusses factors affecting reaction rate and the second one is a humorous example of a catalyzed reaction: http://www.youtube.com/watch?v=1iFMRsU_Nlo (9:45), <http://www.youtube.com/watch?v=eZsur0L0L1c> (0:35).



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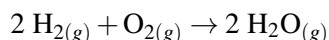
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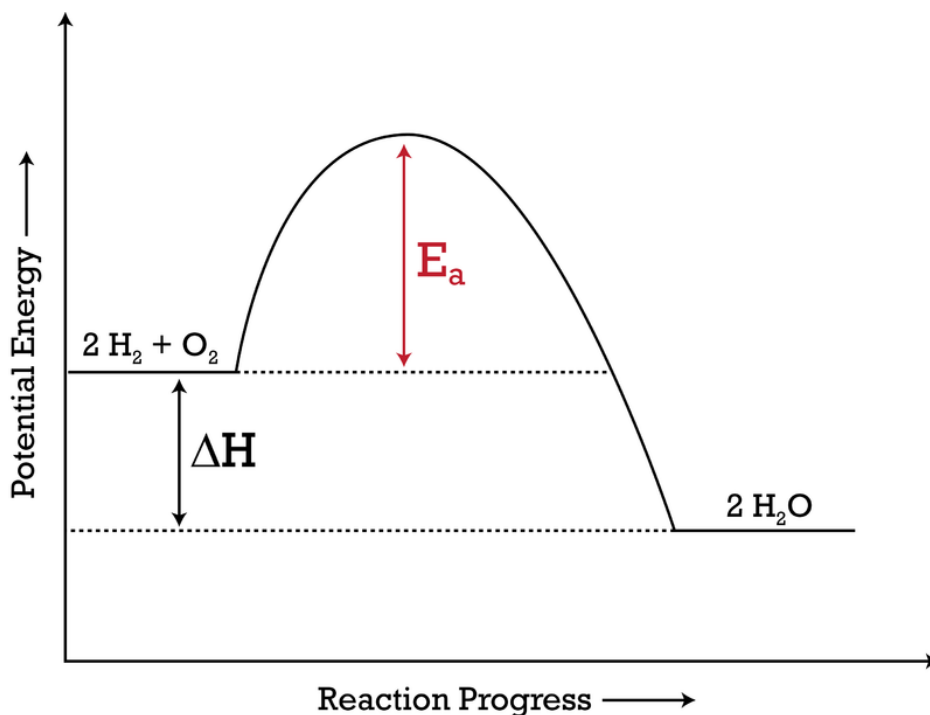
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Surface Catalysts and Enzymes

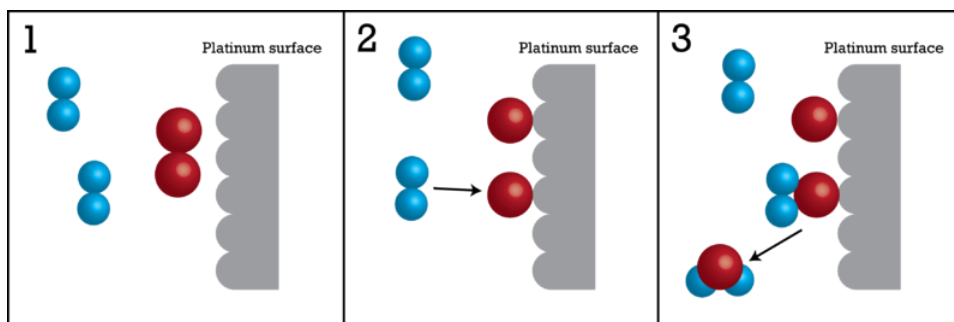
An example of a surface catalyst is platinum, which acts as a surface catalyst in the reaction where hydrogen and oxygen form water.



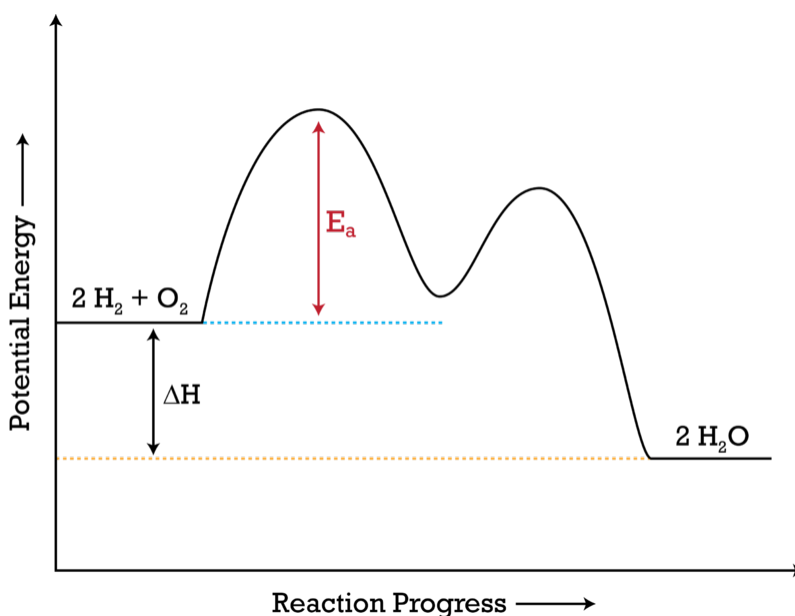
This reaction is so slow that under standard conditions, it essentially doesn't occur. This is why the hydrogen and oxygen gases in our atmosphere do not react with each other. Even if hydrogen and oxygen gases are mixed in a reaction vessel, no reaction occurs. This reaction has a very high activation energy requirement, and standard conditions simply do not provide sufficient energy for the reaction to occur. In comparison, if a piece of platinum is dropped into a small container of hydrogen and oxygen gas at room conditions, a small explosion occurs as this reaction goes to completion almost immediately.



In order for hydrogen gas and oxygen gas to react without a catalysis, all the reactant particles need to collide in a single collision with enough activation energy to break the bond in both the hydrogen molecules *and* break the double bond in the oxygen molecule. Under standard conditions, these particles are not nearly energetic enough for a collision to provide that much activation energy, so no reaction occurs.



If a platinum surface is available, the oxygen molecules can strike the platinum surface, thus breaking the bond holding the oxygen atoms together. The oxygen atoms then adhere to the surface of the platinum. This collision requires less energy than the collision necessary when platinum is not present. Later, a hydrogen molecule can collide with one of the oxygen atoms adhering to the platinum surface. This collision breaks the bond in the hydrogen molecule so that the hydrogen and oxygen can combine and leave the surface of the platinum. Eventually, another hydrogen molecule repeats this process with the final oxygen atom. When all the oxygen atoms have left the surface of the platinum, the platinum is exactly the same as it was before the reaction. In this way, the reaction has occurred with several smaller collisions rather than one large one. Therefore, in the presence of a platinum catalyst, this reaction will occur at room temperature. The reaction rate has been significantly increased. The fact that the platinum increases the reaction rate but is not permanently consumed qualifies it as a catalyst in this reaction.



In the potential energy diagram, the reactants and products are exactly the same as before because it is the same reaction. Since the products and reactants are the same, they have the same enthalpy stored in their bonds, so ΔH will be exactly the same for both reactions. What has changed is the energy barrier. The reaction mechanism for the catalyzed reaction is different, as the reaction does not occur by the same process. The catalyst provides a different reaction path for the same reaction, and the new path has a lower activation energy requirement. The lower activation energy allows for a much faster reaction rate.

Lesson Summary

- An increase in temperature results in an increase in reaction rate because there is an increase in the number of collisions (minor factor) and the number of particles that have sufficient energy to overcome the activation barrier. A decrease in temperature has the opposite effect.
- A rule of thumb used for the effect of temperature on the rate is that if the temperature is increased by 10°C, the rate is doubled.
- Increasing the concentration of a reactant increases the frequency of collisions between reactants and will increase the reaction rate.
- Increasing the surface area of a reactant increases the number of particles available for collision and will increase the number of collisions between reactants per unit time.
- Increasing the frequency of collisions increases the reaction rate.
- The catalyst is a substance that speeds up the rate of the reaction without itself being consumed by the reaction. The catalyst provides a new reaction pathway with lower activation energy.
- The new reaction pathway has lower activation energy, but this has no effect on the energy of the reactants, the products, or the value of ΔH .

Further Reading / Supplemental Links

The *learner.org* website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos, but there is no charge. The website has two videos that relate to this lesson called “Molecules in Action” and “On the Surface.”

- <http://learner.org/resources/series61.html>

This video is a ChemStudy film called “Teacher Training for Catalysis.” The film is somewhat dated, but the information is accurate.

- <http://www.youtube.com/watch?v=9SigDuaQOpo>

Review Questions

1. Why does an increase in temperature increase the rate of the reaction?
2. Why does higher temperature increase the reaction rate?
 - a. more of the reacting molecules will have higher kinetic energy
 - b. increasing the temperature causes the reactant molecules to heat up
 - c. the activation energy will decrease
 - d. increasing the temperature causes the potential energy to decrease
3. When the temperature is increased, what does not change?
 - a. number of collisions
 - b. activation energy requirement
 - c. number of successful collisions
 - d. all of the above change
4. What is the rule of thumb used for the temperature dependence on the rate?

- The rule of thumb for the temperature effect on reaction rates is that a reaction rate will double for each 10°C rise in temperature. The rate of reaction for a hypothetical reaction was found to be 0.62 mol/L · s at 6°C. What would be the rate at 46°C?
- Explain how concentration affects reaction rate using the collision theory. You may want to include a diagram to help illustrate your explanation.
- Why is the increase in concentration directly proportional to the rate of the reaction?
 - The kinetic energy increases.
 - The activation energy increases.
 - The number of successful collisions increases.
 - All of the above.
- For the reaction $\text{H}_{2(g)} + \text{Cl}_{2(g)} \rightarrow 2 \text{HCl}_{(g)}$, an experiment shows that if the concentration of $\text{H}_{2(g)}$ is doubled, the rate of reaction stays the same. If the concentration of $\text{Cl}_{2(g)}$ doubles, the rate of the reaction quadruples. What is the explanation for this observation?
 - The reaction is nearing completion and all $\text{H}_{2(g)}$ is used up.
 - The reaction occurs in more than one step.
 - Excess $\text{Cl}_{2(g)}$ has been added.
 - Not enough information is given.
- The mechanism for a reaction is as follows:



Which of the following would have the greatest effect on the rate of reaction?

- Increase [NO]
 - Increase [Br₂]
 - Increase [NOBr₂]
 - Increase [NO] and [Br₂]
- Consider the following reaction mechanism. For which substance would a change in concentration have the greatest effect on the rate of the overall reaction?



- A, B, C
 - A
 - B
 - C
- The following data (**Table 1.2**) were obtained for the decomposition of N_2O_5 in $\text{CCl}_4(aq)$ at 45°C. Determine the effect of decreasing the $[\text{N}_2\text{O}_5]$ on the rate of the reaction.

$$\begin{aligned} \frac{[\text{N}_2\text{O}_5]_{\text{trial 2}}}{[\text{N}_2\text{O}_5]_{\text{trial 1}}} &= \frac{0.274}{0.316} = 0.867 \\ \frac{\text{rate}_{\text{trial 2}}}{\text{rate}_{\text{trial 1}}} &= \frac{0.34}{0.39} = 0.87 \end{aligned}$$

TABLE 1.2: Trial

Trial	N ₂ O ₅ mol/L	Rate(mol/L · s)
1	0.316	0.39
2	0.274	0.34
3	0.238	0.29
4	0.206	0.25
5	0.179	0.22

12. Why, using the collision theory, do reactions with higher surface area have faster reaction rates?
13. Choose the substance with the greatest surface in the following groupings:
- a block of ice or crushed ice
 - sugar cubes or sugar crystals
 - a piece of wood or wood shavings
 - O_{2(s)} or O_{2(g)}
 - AgNO_{3(s)} or AgNO_{3(aq)}
14. Lighter fluid is sometimes used to get a barbecue coals to begin to burn. Give a complete explanation for
- the purpose of the lighter fluid; and,
 - the purpose of the coals.
15. Draw a potential energy diagram for an exothermic reaction labeling the following:
- the activation energy of 125 kJ
 - the enthalpy of -85 kJ/mol
 - the reactants and product
 - the axes
 - the activation energy for the catalyzed reaction
16. The main function of a catalyst is to
- provide an alternate reaction pathway
 - change the kinetic energy of the reacting particles
 - eliminate the slow step
 - add another reactant
17. What happens when a catalyst is added?
- the activation energy of the forward reaction is lowered
 - the activation energy of the reverse reaction is lowered
 - the activation energy in general is lowered
 - the enthalpy of the reaction is lowered
18. Given the reaction mechanism shown below, which species is the catalyst?



- CO_(g)
- COCl_{2(g)}
- COCl_(g)
- Cl_(g)

19. Catalysts are used in all parts of society from inside our bodies to the largest industries in the world. Give an example of a catalyst and explain its usefulness.