(c) The evidence is that the reaction does not continue, so the energy released during ozone production must be insufficient to break more oxygen molecules into individual atoms.

12.3 CATALYSIS AND REACTION RATES

Practice

(Page 535)
1. Technologists generally use empirical knowledge when doing work with catalysts because they usually use the results of many systematic trial-and-error experiments to find the best catalysts. [In industrial circumstances, a faster reaction that requires the smallest input of energy is the most economical. Knowledge of why is not as important. Most catalysts used by early chemists were found by purely empirical methods, which involved trying many chemicals (even thousands) to see what would work.]
2. Some examples of technological uses of catalysts are:
   - contact lens cleaning apparatus
   - catalytic converters in car exhaust systems
   - catalytic cracking towers in the petrochemical industry.
3. Some examples of natural processes that involve the use of catalysts include:
   - chlorophyll within photosynthesis in plants to speed the combination of carbon dioxide and water into glucose,
   - control of our metabolism by enzymes, which are proteins and catalysts, enzymes within the digestive tract to speed the breakdown of food [Such enzyme–substrate combinations could include: amylase–starch, maltase–maltose, sucrase–sucrose, lipase–lipids, and pepsin–proteins.]
4. Your physical health is dependent on precisely controlled reaction rates. Very small changes in enzyme (catalyst) amounts can cause very large changes in the reactions they control. Consequently, some necessary reactions in your body would probably occur much too slowly if the relevant enzyme were to be damaged—affecting your health and, perhaps, endangering your life.

Investigation 12.1: Iodine Clock Reaction

(Pages 536, 543)
[Two possible designs and experiments are provided. The first tests the relative effectiveness of several potential catalysts; the second tests the effects of various quantities of a single catalyst.]

Purpose
The purpose of this investigation is to create a generalization about the relative effect that potential catalysts have on the rate of a chemical reaction.

Problem
What is the relative effect of the chemicals tested as potential catalysts for increasing the rate of the iodine clock reaction?

Design 1
Different potential catalysts (manipulated variable) are added to solutions A and B. The time of reaction (responding variable) is measured for each catalyst. The control is the reaction of solutions A and B without a possible catalyst added. Controlled variables include the chemical amounts of catalysts added, volumes of reacting solutions A and B, and temperature.
Materials 1
- eye protection
- lab apron
- solution A
- solution B
- three 100 mL beakers
- one 250 mL (waste) beaker
- two medicine droppers
- two 10 mL graduated cylinders
- stopwatch
- dropper bottles of 1.0 mol/L
  - $\text{H}_2\text{SO}_4(\text{aq})$
  - $\text{NaHSO}_4(\text{aq})$
  - $\text{CaCl}_2(\text{aq})$
  - $\text{CuSO}_4(\text{aq})$
  - other potential catalytic solutions

CAUTION: The substances used are corrosive, irritant, and/or toxic. Handle with care, and wear eye protection and a lab apron.

Procedure 1
[Be consistent with whatever technological procedure you use. Every action (other than manipulating the catalyst) should be controlled.]
1. Use two 100 mL beakers to obtain 30–50 mL of solution A and of solution B.
2. Use 10 mL graduated cylinders to measure 5.0 mL of solution A and 5.0 mL of solution B. Use a dropper for getting the bottom of the meniscus on the 5.0 mL line.
3. Pour the 5.0 mL of solution A into the third 100 mL beaker, allowing for a count of five for draining with or without shaking (be consistent).
4. Set the stopwatch to zero, then start it when solution B makes contact with solution A. Again use a consistent count.
5. Swirl the beaker mixture a consistent number of times (e.g., three times).
6. Stop the stopwatch on the first appearance of blue colour and record the reaction time.
7. Rinse and dry the reaction beaker.
8. Repeat steps 2–7 with 2 drops of each catalyst being tested to the solution A before reacting with solution B.

Evidence 1
Potential Catalysts for the Iodine Clock Reaction

<table>
<thead>
<tr>
<th>Potential catalyst*</th>
<th>Volume of A (mL)</th>
<th>Volume of B (mL)</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>5.0</td>
<td>5.0</td>
<td>20.62</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4(\text{aq})$</td>
<td>5.0</td>
<td>5.0</td>
<td>6.03</td>
</tr>
<tr>
<td>$\text{NaHSO}_4(\text{aq})$</td>
<td>5.0</td>
<td>5.0</td>
<td>10.10</td>
</tr>
<tr>
<td>$\text{CaCl}_2(\text{aq})$</td>
<td>5.0</td>
<td>5.0</td>
<td>22.16</td>
</tr>
<tr>
<td>$\text{CuSO}_4(\text{aq})$</td>
<td>5.0</td>
<td>5.0</td>
<td>20.75</td>
</tr>
</tbody>
</table>

* Using two drops of catalyst solution

Analysis 1
On the basis of the evidence gathered in this single experiment with a single trial, the reaction mixture with sulfuric acid as the catalyst reacts the fastest.

Evaluation 1
The design, materials, procedure, and skills were all adequate to obtain trusted evidence. There were many variables to control but with care and thought, the experiment went well. If the reaction mixture did not change to all blue in one instance, then the procedures or skills need to
be modified. Time for more trials would provide more confidence in the evidence gathered and the analysis performed.

The purpose of the investigation was achieved; a reaction mixture with the fastest reaction time was identified.

[Alternatively, the quantity of one catalyst could have been investigated as the manipulated (independent) variable.]

Design 2
Different volumes (manipulated variable) of the same catalyst, sulfuric acid, are added to solutions A and B. The time of reaction (responding variable) is measured. The control is the reaction of solutions A and B without any catalyst added. Controlled variables include the identity and concentration of the catalyst used, volumes of reacting solutions A and B, and temperature.

Materials 2

- eye protection
- lab apron
- solution A
- solution B
- three 100 mL beakers
- one 250 mL (waste) beaker
- two medicine droppers
- two 10 mL graduated cylinders
- dropper bottle of 1.0 mol/L H\textsubscript{2}SO\textsubscript{4}(aq)
- stopwatch

CAUTION: The substances used are corrosive, irritant, and/or toxic. Handle with care, and wear eye protection and a lab apron.

Procedure 2

[Be consistent with whatever technological procedure you use. Every action (other than manipulating the chemical amount of catalyst) should be controlled.]

1. Use two 100 mL beakers to obtain 30-50 mL of solution A and of solution B.
2. Use 10 mL graduate cylinders to measure 5.0 mL of solution A and 5.0 mL of solution B. Use a dropper for getting the bottom of the meniscus on the 5.0 mL line.
3. Pour the 5.0 mL of solution A into the third 100 mL beaker, allowing for a count of, say, five for draining with or without shaking (be consistent).
4. Set the stopwatch to zero, then start it when solution B makes contact with solution A. Again use a consistent count.
5. Swirl the beaker mixture a consistent number of times; e.g., three times.
6. Stop the stopwatch on the first appearance of blue colour and record the reaction time.
7. Rinse and dry the reaction beaker.
8. Repeat steps 2–7 with a different number of drops of the catalyst being tested added to the solution A before reacting with solution B.

Evidence 2

<table>
<thead>
<tr>
<th>Trial</th>
<th>Catalyst</th>
<th>Volume of A (mL)</th>
<th>Volume of B (mL)</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>5.0</td>
<td>5.0</td>
<td>20.62</td>
</tr>
<tr>
<td>2</td>
<td>1 drop H\textsubscript{2}SO\textsubscript{4}(aq)</td>
<td>5.0</td>
<td>5.0</td>
<td>7.62</td>
</tr>
<tr>
<td>3</td>
<td>2 drop H\textsubscript{2}SO\textsubscript{4}(aq)</td>
<td>5.0</td>
<td>5.0</td>
<td>6.03</td>
</tr>
<tr>
<td>4</td>
<td>3 drop H\textsubscript{2}SO\textsubscript{4}(aq)</td>
<td>5.0</td>
<td>5.0</td>
<td>3.90</td>
</tr>
</tbody>
</table>
Analysis 2
On the basis of the evidence gathered in this single experiment with a single trial for each chemical amount, the reaction mixture with three drops of sulfuric acid as the catalyst reacts the fastest.

Evaluation 2
The design, materials, procedure, and skills were all adequate to obtain trustworthy evidence. There were many variables to control, but with care and thought the experiment went well. Time for more trials would provide more confidence in the evidence gathered and the analysis performed.

The purpose of the investigation was achieved; a reaction mixture with the fastest reaction time was identified.

Web Activity: Simulation—a Catalyzed Reaction
(Page 539)
1. The catalytic hydrogenation of ethene involves the following reaction:
   \[ \text{Pt} \quad \text{C}_2\text{H}_4(g) + \text{H}_2(g) \xrightarrow{\text{R}} \text{C}_2\text{H}_6(g) \]
2. The ethene and the hydrogen molecules first diffuse to the catalyst. The molecules then form bonds with the catalyst surface, and the hydrogen breaks into individual hydrogen atoms. The hydrogen atoms then migrate to the ethene molecules where they react to form ethane. The ethane then diffuses away from the surface of the catalyst.

Investigation 12.2: Evidence for an Activated Complex
(Pages 541, 543)
Purpose
The purpose of this investigation is to test the theoretical concept that a catalyzed reaction involves a different activated complex than an uncatalyzed reaction.

Problem
What evidence is there for the existence of a different activated complex for a catalyzed reaction?

Hypothesis
A catalyzed reaction involves an activated complex that is different from that in an uncatalyzed reaction.

Evidence
Before the Reaction
- 0.30 mol/L sodium potassium tartrate is a clear, colourless solution.
- 3% hydrogen peroxide solution is a clear, colourless solution.
- 0.30 mol/L cobalt (II) chloride is a clear, light pink solution.

During the Reaction
- Without the cobalt(II) chloride catalyst, the mixture of sodium potassium tartrate remains clear and colourless while a clear, colourless, odourless gas is produced.
- With the cobalt(II) chloride catalyst, the originally faintly pink solution turns green while a clear, colourless gas is produced. The bubbling appears to happen at a much faster rate and the total reaction finishes sooner than is the case in an uncatalyzed reaction. After the reaction appeared to be complete, the colour of the solution changed back to the original pink.

Analysis
According to the evidence, it appears that the uncatalyzed and catalyzed reactions have different activated complexes because different colour changes occurred during each reaction. There is no
activated complex seen during the uncatalyzed reaction, as was evident from no observable colour changes during the reaction. The catalyzed reaction was initially pink but turned green during the reaction. The green chemical was likely the activated complex. Further evidence to support this interpretation is that the green colour faded, to be replaced with the original pink as the catalyst was regenerated—a characteristic of a catalyst.

**Evaluation**

The design, which includes testing the same reaction with and without a catalyst, is judged to be adequate because the observations noted during the lab were sufficient to answer the problem. The procedure and materials are adequate as the problem could be answered from them. The technological skills of the experimenter are judged to be adequate as the measurement and mixing of chemicals are easy and well done. An improvement to the design could include the collection of the time of reaction so that there is confirmation that the catalyzed reaction did indeed take less time to complete. To further confirm the results, multiple trials at various temperatures could be done with both the catalyzed and uncatalyzed reactions. On the basis of my evaluation of the experiment, I am confident in my experimental evidence.

The hypothesis is judged to be verified because the experimental answer is consistent with the hypothesis. Therefore, the theory of catalysis is judged to be acceptable. I am reasonably confident in this judgment for this experiment.

The purpose was accomplished, but only to a limited extent. Many more investigations of different reactions and catalysts are required to better achieve the purpose.

**Section 12.3 Questions**

*(Page 542)*

1. (a) The reactants, products, and enthalpy change of reaction are the same for both catalyzed and uncatalyzed reactions. The initial and final levels on a chemical potential energy diagram would be the same for both reactions.
   (b) The rate of the reaction, the activation energy, the activated complex(es), and the reaction pathway are different in catalyzed compared to uncatalyzed reactions.

2. (a) The reaction intermediates are C and D as they are produced during one step and consumed in another. They are not included in the net reaction equation.
   (b) The reactants are A, B, and E. They are on the left side of the net reaction.
   (c) The only product of the reaction is F. It is written on the right side of the net reaction.
   (d) \(2 \text{ A} + \text{ B} + \text{ E} \rightarrow \text{ F}\)

3. (a) The activation energy of the net forward reaction is \(E_a = (60 - 0) \text{ kJ} = +60 \text{ kJ}\).
   (b) The activation energy of the net reverse reaction is \(E_a = (60 - (-35)) \text{ kJ} = +95 \text{ kJ}\).
   (c) The net energy change for the net forward reaction is \(\Delta H = (-35 - 0) \text{ kJ} = -35 \text{ kJ}\).
   (d) The net energy change for the net reverse reaction is \(\Delta H = (0 - (-35)) \text{ kJ} = +35 \text{ kJ}\).
   (e) The forward reaction is exothermic because C + D is at a lower chemical potential energy than A + B.

4. The forward reaction, as written, has an activation energy of 60 kJ so, if 55 kJ is available, this reaction will not occur.
5. Similarly, the reverse reaction requires a potential energy increase of 95 kJ so, if only 55 kJ is available, this reaction will not occur.
6. There are many ways in which catalysts provide solutions to technological problems. Catalysts allow chemical reactions to proceed at a faster rate, and allow for reactions to occur appreciably at lower temperatures. For both of those reasons, catalyzed reactions can save money for industries and consumers. Examples of catalysts providing solutions to technological problems include:
• detergents with enzymes to remove various stains (amylases, cellulases, lipases, and proteases)
• brewing or fermentation to produce alcoholic beverages (zymase or yeast catalyst)
• ammonia production to meet the needs for fertilizers (Fe(s) with KOH(s) additive as catalyst)
• automobile catalytic converters to reduce pollution (Pt(s), Rh(s), and Pd(s) catalysts)

7. Purpose
The purpose of this investigation is to test the hypothesis that the molar enthalpy of reaction does not change when a catalyst is added.

Problem
What is the molar enthalpy of decomposition of 20 mL of 2 mol/L aqueous hydrogen peroxide without and with an iron(III) catalyst being added?

Design
20.0 mL of 2 mol/L aqueous hydrogen peroxide is reacted with 5.0 mL of 0.1 mol/L aqueous sodium hydroxide in a polystyrene cup calorimeter. Both solutions are at the same initial temperature. The initial and final temperatures of the reaction mixture are measured, as well as the time it takes for the reacting mixture to reach maximum temperature. A second trial is run with the addition of 0.3 mL of iron(III) nitrate catalyst.

• manipulated variable: presence of iron(III) nitrate catalyst
• responding variable: final temperature of the mixture
• controlled variables: the same reactants; the concentrations of aqueous hydrogen peroxide and sodium hydroxide; the volumes of each solution; the initial temperatures of the solutions

Materials
• eye protection
• 2 x 20.0 mL of 2 mol/L aqueous hydrogen peroxide
• lab apron
• 2 x 5.0 mL of 0.1 mol/L sodium hydroxide
• thermometer (0.1 °C)
• 0.3 mL of 0.1 mol/L iron(III) nitrate
• watch or clock
• 10.0 mL graduated cylinder
• 250 mL beaker
• 25.0 mL graduated cylinder
• polystyrene calorimeter

Analysis
Trial 1: Reaction of hydrogen peroxide and sodium hydroxide.
\[ Q = mc\Delta t \]
\[ = 25.0 \text{ g} \times 4.19 \frac{\text{J}}{\text{g} \cdot ^\circ \text{C}} \times (23.6 - 21.4) ^\circ \text{C} \]
\[ = 230 \text{ J} \]
\[ \Delta_H^\circ = \frac{230 \text{ J}}{0.0200 \text{ L} \times 2 \text{ mol/L}} = 6 \text{ kJ/mol} \]

Trial 2: Reaction of hydrogen peroxide and sodium hydroxide with an iron(III) nitrate catalyst.
\[ Q = mc\Delta t \]
\[ = 25.3 \text{ g} \times 4.19 \frac{\text{J}}{\text{g} \cdot ^\circ \text{C}} \times (23.6 - 21.4) ^\circ \text{C} \]
\[ = 233 \text{ J} \]
\[
\Delta H_m = \frac{233 \text{ J}}{0.0200 \text{ L} \times \frac{2 \text{ mol}}{\text{ L}}} = 6 \text{ kJ/mol}
\]

According to the evidence and the law of conservation of energy, the molar enthalpy of decomposition of hydrogen hydroxide without the catalyst is reported as \(-6 \text{ kJ/mol}\), while the molar enthalpy of decomposition of hydrogen peroxide with the catalyst is reported as \(-6 \text{ kJ/mol}\).

8. **Evaluation**

The percent difference between the catalyzed and uncatalyzed reactions is:

\[
\% \text{ difference} = \left(\frac{6 \text{ kJ/mol} - 6 \text{ kJ/mol}}{6 \text{ kJ/mol}}\right) \times 100 = 1\% \text{ (using unrounded values)}
\]

On the basis of the small percent difference in the values of the molar enthalpy of decomposition of hydrogen peroxide with and without the catalyst, the hypothesis that the molar enthalpy of reaction does not change when a catalyst is added is judged to be acceptable. The evidence gathered supports the hypothesis, although further testing would increase confidence in the judgment made on the hypothesis in this single investigation.

9. **Enzyme: Alcohol Dehydrogenase**

The history of how individual catalysts were discovered and isolated is somewhat complex and difficult to find. As early as the late 1700s and 1800s, scientists observed the digestion of meat by stomach secretions (proteases), and the conversion of starch to sugars by saliva (amylase). In 1897, Hans and Eduard Buchner discovered that yeast extracts (not the living cells themselves) would ferment sugar. The term “enzyme” was used to describe the substances in the extract that caused the fermentation of sucrose. Alcohol dehydrogenase catalyzes the reaction that takes place when sucrose ferments.

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{NAD}^+ \xrightarrow{\text{alcohol dehydrogenase}} \text{CH}_3\text{CHO} + \text{NADH} + \text{H}^+ 
\]

The alcohol dehydrogenase catalyst is contained in the lining of the stomach and in the liver. It may have been discovered by Bateilli and Stern in 1909.

The presence of the alcohol dehydrogenase catalyst allows for the first stage of metabolism for ethanol and other alcohols in the body. The absence of this enzyme would slow down the removal of alcohol from the blood stream. Certain groups of people have less of this catalyst in their bodies, and the result is that alcohol accumulates in their blood stream for greater amounts of time. Currently there are no proven treatments of supplements for this enzyme.

**Industrial Catalyst: Iron and Potassium Hydroxide**

Iron and potassium hydroxide are used industrially to catalyze the reaction:

\[
3 \text{H}_2(g) + \text{N}_2(g) \xrightarrow{\text{Fe-KOH}} 2 \text{NH}_3(g)
\]

The Haber process was patented in 1910 and used expensive platinum and osmium catalysts that have since been replaced with the iron and potassium hydroxide catalysts.

The catalyst acts within a reaction chamber as a surface for the reactants and products to bind to. As these catalysts catalyze both the forward and reverse reactions, the ammonia must be removed to help reduce the significance of the reverse reaction.

The economic implications of this process are substantial. The production of ammonia would not be as inexpensive as it is today without the use of the catalysts, and ammonia is used in a wide variety of manufacturing processes as well as for use as a commercial fertilizer. Currently the Haber process including its iron with potassium hydroxide catalyst is responsible for about half of the fertilizer production for agriculture. Without it, food would be much more expensive as there would be less of it to go around.
(b) Industrial catalysts involved with petroleum refining are particularly important because we use so many products, such as gasoline and plastics, from the refining and upgrading of petroleum.

9. **Risks**
   - Fossil fuels will become more and more scarce.
   - Machinery requiring fossil fuels as an energy source will have to be modified at great expense to run on alternative fuels.
   - Creating petrochemicals from other sources such as vegetable oils to run on existing equipment may be very costly.
   - The amount of carbon dioxide released from fossil fuels is increasing the greenhouse (climate change) gases in the atmosphere.

**Benefits**
- In the short term, fossil fuels are plentiful.
- The cost of finding and developing oil deposits remains less expensive than changing to a new energy source.
- Oil is inexpensive to extract, relative to the cost of producing alternative fuels.
- Petroleum has a high energy density.
- Oil products work in existing equipment.
- Plastics and other items such as detergents that are currently made from oil are easier to make from oil than from other fuels.

**Extension**
10. The health benefits claimed by the manufacturer’s advertisement should have been determined by a clinical study (double blind with a placebo) conducted by an independent group of scientists with the results submitted for publishing in a refereed scientific journal. (See Appendix B.4.)

**Chapter 12 SUMMARY**

**Make a Summary**

(Page 544)

1. **Energy Pathway Diagram of the Reaction of Hydrogen and Fluorine**

During an uncatalyzed reaction, the energy of collision of the reactant entities (assuming correct orientation of the collision) must be sufficient to overcome the activation energy (energy barrier). If a catalyst is added, the reaction increases in rate without changing the enthalpy of reaction. The observed rate increase is explained theoretically by the reduction in the activation energy by providing an alternative pathway involving an activated complex created with/by the catalyst. The alternate pathway may involve more than one reaction step and, therefore, more than one activated complex.