GETTING OFF TO A SAFE START

Using safer starting materials for chemical reactions

Many industrial chemical processes and laboratories make use of starting materials (reactants) that can be harmful to human health and the environment unless properly handled and stored. If a chemical process uses hazardous substances—for example, those that are highly toxic, harm lung tissue if inhaled, damage skin on contact, or are explosive—there is always the danger that accidents can occur, exposing workers and others to these chemicals or releasing them into the environment. Therefore, green chemistry principles dictate that chemists investigate whether it is possible to reduce the hazards by using safer reactants to produce the same products. A number of chemical companies have made progress in doing this, and others are beginning to look more closely at their processes to reduce hazards. This is particularly important in industrial processes for which very large quantities of chemicals are used. However, even on a smaller scale, safer substitutes might be found for chemicals used in research and student laboratories.

In this module, we will see an example of how to substitute safer chemicals in a process that is typically used in student laboratory courses. A common type of experiment that appears in many laboratory manuals is called a "clock reaction". In such a reaction, a sudden, sharp color change occurs in the solution that contains the reactants when the reaction is complete. Because the sudden appearance of the color makes a striking demonstration, clock reactions are often used in chemical magic shows. In student laboratories, the color appearance also makes it easy to measure reaction time by determining how many seconds pass from the time the reactants are mixed to the time the color change occurs. The effect of changing reactant concentrations or temperature can be studied by measuring how changes in these variables affect the reaction time.

Chemicals such as formaldehyde, mercuric ion, thiosulfates, or bisulfites are typically used in clock reactions. These substances can be carefully handled in the laboratory with special precautions and with safe disposal procedures for chemical waste. However, suppose that ordinary household materials could be used to produce a clock reaction, so that it would pose a lesser risk in the laboratory and would present little risk even in a nonlaboratory situation such as a chemistry magic demonstration for the public or for elementary school students. Although no procedure is totally free of risk, even using consumer-available materials that are generally recognized as safe, the new approach would represent a greener way to demonstrate the same ideas on reaction rates. We will use such a clock reaction in this module.

Green chemistry principle

Get off to a safe start. Identify reactions that use nontoxic/nonhazardous starting materials to make a desired product. This minimizes danger to workers in manufacturing plants when they handle the chemicals and also prevents accidental release of harmful chemicals to the environment if leaks or explosions occur.

Curriculum links

- laboratory safety
- chemical reactions
- rate of reactions

Review the safety guidelines on page iv and the rules of laboratory conduct before beginning these activities.

Activity 1. The vitamin C clock reaction

This experiment, adapted from the January 2002 issue of the *Journal of Chemical Education*,[1, 2] is a clock reaction that uses all household materials.

Materials

distilled water
1000 mg vitamin C tablets
tincture of iodine (2%)
hydrogen peroxide (3%)
liquid laundry starch
250-mL beakers or plastic cups
alcohol thermometer
ice cubes
bucket or tub for ice bath
warm water bath

Procedure

1. Make a vitamin C solution by crushing a 1000 mg vitamin C tablet and dissolving it in 60 mL of distilled water. Label as "vitamin C stock solution".
2. Combine 5 mL of the vitamin C stock solution with 5 mL of iodine and 60 mL of water. Label this "solution A".
3. Prepare "solution B" by adding 60 mL of water to 15 mL of hydrogen peroxide and 2 mL of liquid starch solution.
4. Pour solution A into solution B, and pour the resulting solution back into the empty cup to mix them thoroughly. Begin timing as soon as they first mix and continue until there is a color change. Record the time it takes for the color to change.

Green Chemistry

Preventing pollution. Sustaining the earth.

Activity 2. The effect of concentration on the clock reaction

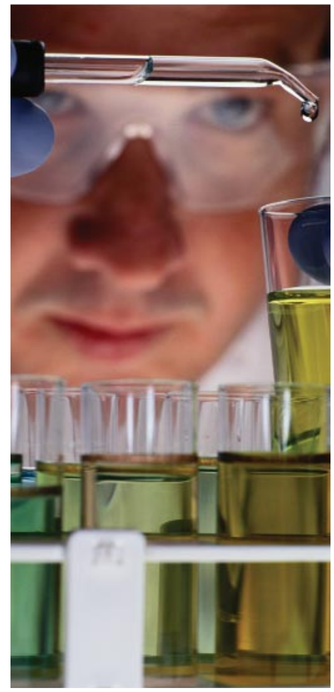
1. Repeat the experiment, but this time use 30 mL of water when preparing solutions A and B. Time the reaction and record the results.
2. Repeat the experiment, but this time use 90 mL of water when preparing solutions A and B. Time the reaction and record the results.
3. Repeat at other concentrations, as directed by your teacher.

Activity 3. The effect of temperature on the clock reaction

1. Repeat the original experiment using 60 mL of water to prepare solutions A and B, but cool the solutions to 15 °C before mixing by placing the containers in an ice bath. Mix as before, timing the reaction and recording the result.
2. Repeat again, this time using a warm water bath to heat the solutions to 25 °C. Mix as before, timing the reaction and recording the result.
3. Repeat again, this time at room temperature. Record the temperature. Mix as before, timing the reaction and recording the result.
4. Repeat at other temperatures, as directed by your teacher.

Questions

1. What is the difference between the clock reaction and other color-changing reactions that you have done prior to this in your studies?
2. *Rate of reaction* is defined as how fast reactants are used up or products appear. What is the relationship between the time it takes for a reaction to occur and the rate of reaction?
3. What appears to be the relationship between the concentration of the reactants and the rate of this reaction?
4. What appears to be the relationship between the temperature of the reactants and the rate of reaction in this experiment?
5. One of the mercury-based clock reactions used approximately 150 mL of 0.01 M $HgCl_2$ solution per experiment for each lab group (2 students per group). For example, assume that all of the approximately 2 million introductory chemistry students in the nation did the safer experiment described in this activity rather than the mercury-based experiment; how much mercury waste would be avoided?
6. What are the advantages of limiting the use of mercury compounds in lab experiments? What are some of the health and environmental problems associated with mercury? Explain why it is desirable to limit the release of mercury into the environment.
7. Suppose a researcher were doing work on mercury compounds and its use couldn't be avoided. What precautions should be taken when disposing of the mercury compounds? Consult a Materials Safety Data Sheet (MSDS) on mercuric chloride or other mercury compound and note the suggestions for disposal.



"Chemistry has an important role to play in achieving a sustainable civilization on earth."

— Dr. Terry Collins, Professor of Chemistry Carnegie Mellon University

Background information

How do we know if a substance is safe or hazardous? Are substances that we call "safe" always safe, or do they pose a risk to health under some conditions? How do we determine risk, and how does risk differ from hazard?

When we consider a substance to be safe, we usually mean it poses little or no risk to us under ordinary conditions of use. The concept of *risk*—defined as the chance of damage, injury, or loss—actually contains two components: *hazard* and *exposure*. A hazard is a source of potential loss or danger. Examples of hazards are a wet floor, a bridge with a weakened support structure, or some chemicals that are highly poisonous or explosive. A risk is the possibility or the chance that the hazard will cause harm. Determination of risk requires that we take into account our level of exposure to a hazard as well as the hazard itself. If we were to state this as an equation, it would look like this:

$$\text{Risk} = f[\text{hazard, exposure}]$$

(Risk is a function of hazard and exposure).

If you refrain from walking across a wet floor, it doesn't pose a risk to you, even though it is a hazard. In other words, without any exposure to the wet floor, you will not be harmed because of it. To determine how great a risk is posed by chemicals, we must also consider both hazard and exposure. Let's look at an example of this involving the toxicity of substances.

It has been said that "the dose makes the poison"; in other words, a substance may be safe in small quantities but deadly in larger amounts.

Some chemicals pose intrinsically greater risks than others because they are harmful even at low exposures. One way to evaluate the toxicity of a substance is to study its effect on animals exposed to varying doses. Substances that have lethal effects even at relatively low doses are considered more hazardous than those that are deadly only at a very high dose. Scientists use the term LD_{50} to refer to the dose that is lethal to 50% of the test animals (usually mice or rats). LD_{50} is typically reported in mg substance/kg body weight. The smaller the LD_{50} value, the more toxic the substance. For example, an oral dose of only 6.4 mg of sodium cyanide per kg of body weight is sufficient to cause death in 50% of a population of rats. In contrast, a dose of 29,700 mg/kg of sucrose (cane sugar) or 3000 mg/kg of sodium chloride (table salt) would have to be fed to rats to cause death in 50% of the population.

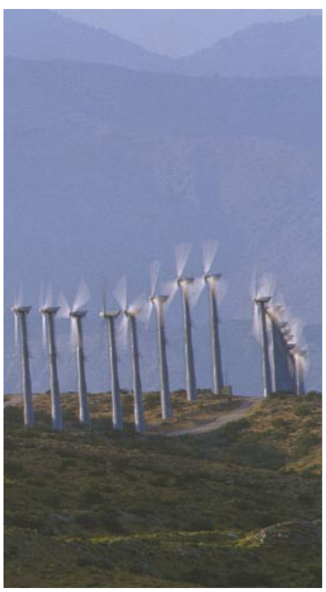
Traditionally, risk management for chemicals has focused on limiting exposure of those who handle them through the use of protective equipment such as gloves, respirators, and fume hoods. These exposure-limiting tools can and do fail. Green chemistry is a much more effective risk management tool because it lowers risk by reducing or eliminating the use of hazardous substances in chemical processes. If substances pose little or no hazard to begin with, then exposure is no longer an issue.

One example of the impact of finding safer starting materials has been demonstrated by the work of Karen M. Draths and John W. Frost at Michigan State University in developing a new way to produce the chemical adipic acid. Very large quantities of adipic acid—$HOOC(CH_2)_4COOH$—are needed every year in the industrial production of nylon-6,6, polyurethane, lubricants, and plasticizers. The typical starting material for making adipic acid is benzene, a cancer-causing agent. In a process aided by biocatalysts (genetically altered bacteria), Frost and Draths have produced adipic acid starting from glucose, a simple sugar found naturally in plants, rather than benzene. Starting with a safe substance like glucose to make adipic acid means that the use of large quantities of benzene can be avoided if new processes such as this one become widely used.

What is a sustainable civilization? We will consider this question from these viewpoints:

The environment and human health.

A stable economy that uses energy and resources efficiently.



Instructional notes

Instructional notes on activity 1. The vitamin C clock reaction

This lab is presented as an example of green chemistry. It introduces an alternative way to do a traditional lab, using safer starting materials. Since your students are new to chemistry, they will not have any experience with the “old” ways. You will need to put this lab into perspective for them by reviewing the older versions of this experiment and discussing what was so bad about them. You might want to do a calculation similar to question 5, only dealing with the amount of formalin used in the formaldehyde clock reactions. (See Reference 2 for this demonstration.)

Although this activity is very popular with students, there are some issues to deal with when you use it in your class. One of the key issues is explaining what is going on in the reaction.

Part of the reaction is easy to explain. When iodine and starch combine, they make a black-blue complex. Students will probably recognize this from their biology class, where iodine is used as a test reagent for starch. The reaction rate being studied is for the following reaction:

$$2H^+_{(aq)} + 2I^-_{(aq)} + H_2O_{2(aq)} \rightarrow I_{2(aq)} + 2H_2O_{(l)}$$

The I^- is produced by adding excess vitamin C (ascorbic acid $C_6H_8O_6$) to household tincture of iodine.

$$I_{2(aq)} + C_6H_8O_{6(aq)} \rightarrow 2H^+_{(aq)} + 2I^-_{(aq)} + C_6H_6O_{6(aq)}$$

When the H_2O_2 is added to the first reaction, it begins to produce I_2. But since the ascorbic acid reacts with the I_2 immediately, it prevents the I_2 from reacting with the starch. The color change occurs only after all the vitamin C is used up. Another issue to talk about is what is meant by the term *rate*. Chemists measure rates of reaction in terms of the rate of appearance of a product or the rate of disappearance of a reactant.

Another issue is that students are measuring time in this lab, rather than rate. The rates would actually be proportional to $1/T$. It is important to convey that as the reaction time gets smaller, the rate is actually larger. If this distinction is not made, students might be thinking the reverse of the proper relationship. It should be noted that this experiment only approximates an authentic rate of reaction. Since the color-change reaction that we are actually seeing is distinct from the reaction rate we are studying, we are only approximating the actual rate. Despite this minor shortcoming, the lab gives students a good concept of rates of reaction.

Instructional notes on activity 2. The effect of concentration on the clock reaction

By lowering the concentration of the reactants (using more dilute solutions), the rate of reaction tends to decrease. If there are fewer molecules in a given volume of solution, then it is reasonable there would be fewer effective collisions and fewer products formed.

Note that the quantitative change in reaction rate brought about by a change in concentration involves a complex interaction. Advanced-level courses consider reaction order and how the reaction mechanism affects rate.

A related extension would be to have students calculate the effect of mixing on the rate of reaction. Students could experiment with different ways of combining the solutions, varying the amount of mixing that occurs.

Instructional notes on activity 3. The effect of temperature on the clock reaction

Be sure to arrange appropriate hot and cool water baths in advance. It is usually easier to set up some central water baths and have all students use them. If you do not have a dedicated water bath, you can always improvise by placing a water-filled metal pan on a hot plate. You will need to replenish the water in these baths during the day. Alternatively, you can have students create their own water baths by using a large beaker at their lab station. Consider grouping students, giving each group a different temperature range to try.

Answers to questions

1. **What is the difference between the clock reaction and other color-changing reactions that you have done previously in your studies?**

   The big difference is that most reactions used in chemistry classes tend to change immediately. This experiment uses a combination of reactions, with the final reaction marking when the reaction series is completed. The analogy is that it is like an alarm clock. The clock runs for a time, and then the alarm sounds. The running clock is like the first reaction above, the "alarm" is like the combination with starch.

2. ***Rate of reaction* is defined as how fast reactants are used up or products appear. What is the relationship between the time it takes for a reaction to occur and the rate of reaction?**

   The rate is the amount of substance reacting per unit of time. Thus the faster (smaller number) the reaction time, the greater (bigger number) the rate.

3. **What appears to be the relationship between the concentration of the reactants and the rate of this reaction?**

   The higher the concentration, the greater the rate of reaction. It should make sense that higher concentration means a greater number of collisions and a greater possibility of effective collisions.

4. **What appears to be the relationship between the temperature of the reactants and the rate of reaction in this experiment?**

   The higher the temperature, the greater the rate of reaction. In this reaction, a higher temperature means greater kinetic energy in the particles and a higher proportion of effective collisions (collisions that lead to reactions). Also, with greater kinetic energy, more collisions will occur.

5. **One of the mercury-based clock reactions used approximately 150 mL of 0.01 M $HgCl_2$ solution per experiment for each lab group (2 students per group). For example, assume that all of the approximately 2 million introductory chemistry students in the**

nation did the safer experiment described in this activity rather than the mercury-based experiment; how much mercury waste would be avoided?

This calculation entails a lot of "what ifs". If 150 mL of solution is used for each pair of students, then

$$2.0 \times 10^{6}\, students \times \frac{0.150\, L}{2\, students} \times \frac{0.01\, mol}{1\, L} \times \frac{271.6\, g}{1\, mol} = 407{,}400\, g$$

This assumes that every classroom in the United States is doing this experiment, which is unlikely. Nevertheless, this single modification would save about 900 pounds of mercury from being used.

6. **What are the advantages of limiting the use of mercury compounds in lab experiments? What are some of the health and environmental problems associated with mercury? Explain why it is desirable to limit the release of mercury into the environment.**

   Elemental mercury is used in hundreds of applications, from electrical switches to street lamps. If mercury gets into the bloodstream and into the brain, it can cause serious damage to the central nervous system. Young people are particularly susceptible to this type of damage. Most mercury pollution is released through the burning of coal and waste incinerators. The dangers of long-term accumulation of mercury in the environment have led to the elimination of most industrial contributions of mercury waste.

7. **Suppose a researcher were doing work on mercury compounds and its use couldn't be avoided. What precautions should be taken when disposing of mercury compounds? Consult a Materials Safety Data Sheet (MSDS) on mercuric chloride or another mercury compound and note the suggestions for disposal.**

   Elemental mercury is not very toxic. Damaging effects occur when it crosses the blood–brain barrier. The compounds of methylmercury are far more toxic. Flinn Scientific suggests that mercury compounds can be safely disposed of by converting them to an insoluble salt and placing them in an approved hazardous materials landfill. Flinn advises that the only safe disposal of mercury metal is to return it to a supplier for recycling.

References

1. Wright, Stephen W. The Vitamin C Clock Reaction. *J. Chem. Educ.,* January **2002**, *79* (1), 41–43.
2. Wright, Stephen W. Tick Tock, a Vitamin C Clock. *J. Chem. Educ.* **2002,** 79, 40A–40B.
3. Shakhashiri, B. Z. *Chemical Demonstrations,* Vol. 4; University of Wisconsin Press: Madison, WI, 1992.