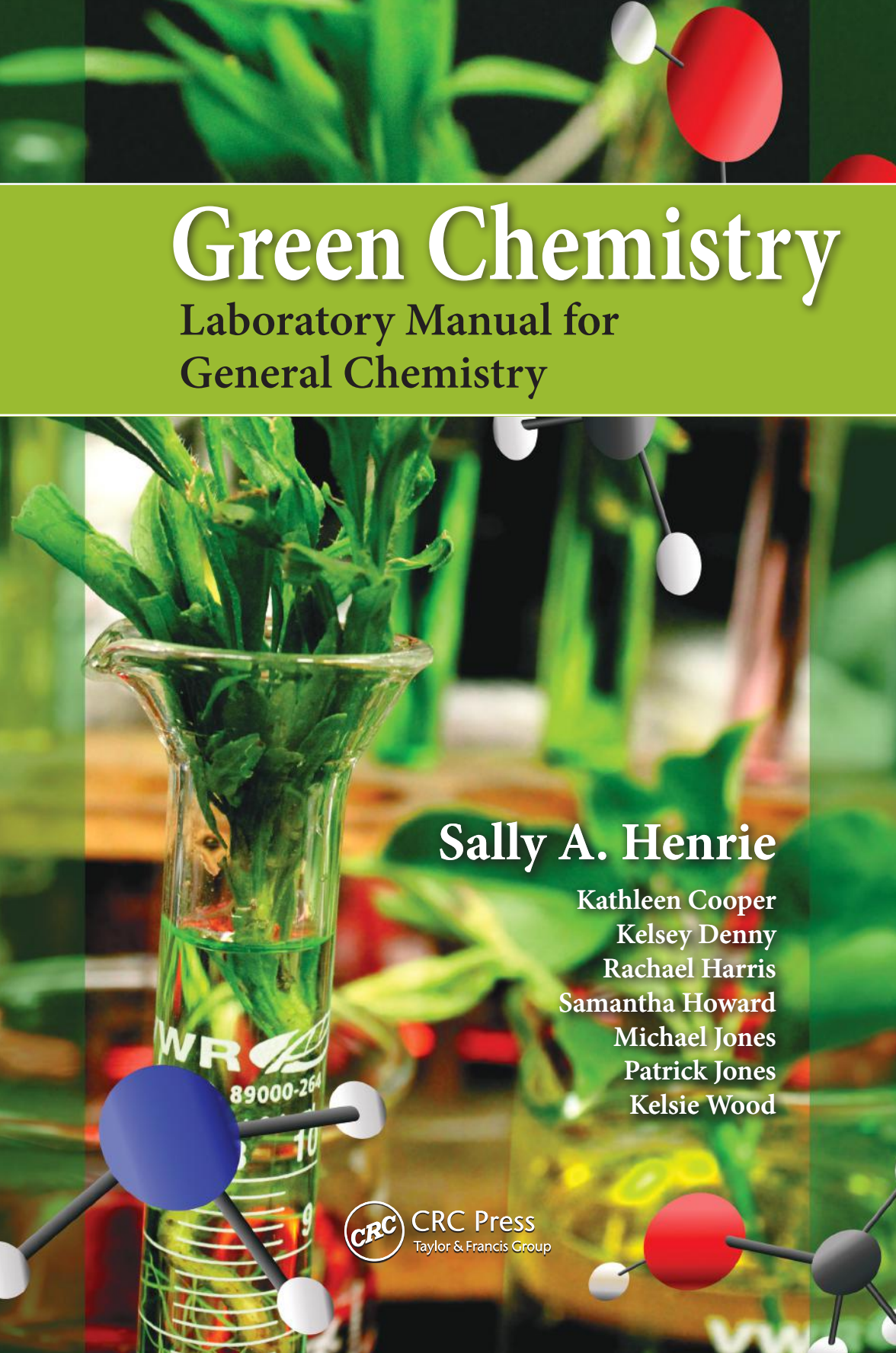
Green Chemistry
Laboratory Manual for
General Chemistry
Sally A. Henrie
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Kelsey Denny
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CRC Press
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CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

Version Date: 20141218

International Standard Book Number-13: 978-1-4822-3021-5 (eBook - PDF)

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Preface

I was impressed by **green chemistry** the very first time I was introduced to it in 2001 by Dr. Mary Kirchhoff at the American Chemical Society National Spring meeting. I was so captivated by it that right after this, I began working with undergraduate students on research to develop manuals that used greener chemicals and methods while still teaching the traditional material typically covered. As the research progressed, I gained a desire to not only develop greener experiments, but also introduce students to green chemistry in a tangible way that challenges them to embrace its vision. I hope that students will become captivated by it like I am as they realize green chemistry is a new way of actually doing chemistry. I want them to grasp that it requires creativity, innovation, and ingenuity to design novel ways to create and synthesize products and to implement processes that will eliminate or greatly reduce the environmental impact, and to be challenged by this. It was with these goals in mind that the *Green Chemistry Laboratory Manual for General Chemistry* was created.

To realize these goals, green chemistry principles are discussed in the introductory material and applied to the experiments that will be performed. After they have completed the procedure and analyzed their results, students are challenged in a **Think Green** inquiry section to consider what principles of green chemistry are positively impacted and to research particular relevant topics. Often in this section they are encouraged to develop a method based on what they learned and then to try their ideas. At the end of each chapter is the **Presidential Green Chemistry Challenge** section. From this, students are able to learn about how the green chemistry principles are actually applied in our world. Students are asked to look up a Presidential Green Chemistry Challenge award that relates to what was studied in the chapter and summarize what was accomplished to receive this award.

But why was the general chemistry laboratory chosen to introduce students to green chemistry principles in this way? The general chemistry laboratory is an excellent place to inspire students to learn to think green.

Many of these students will continue on in science or engineering professions and work in these areas to contribute to society. Teaching them to learn to apply the principles of green chemistry at the start of their college science education will allow them more time to firmly establish a foundation in the principles of green chemistry that they can later use in their future careers.

Acknowledgments

I would like to thank all of the people who worked to create this laboratory manual, and wish I could mention everyone. It could not have been completed without the expertise, contributions, help, and encouragement of many individuals. Most of all, I would like to thank my husband, Ray, and my family for their patience, support, and encouragement. I am especially grateful to all of the research students who have worked diligently with me to develop greener chemistry manuals. Those who worked on this particular manual are Kathleen Cooper, Kelsey Denny, Rachael Harris, Samantha Howard, Michael Jones, Patrick Jones, and Kelsie Wood. I am also appreciative for the help, expertise, and encouragement from my colleagues and students at Union University, especially Dr. Randy Johnston, Dr. Marlyn Newhouse, and Giley Wright. I am most grateful to all of the dedicated and talented people who helped in the production of this manual at CRC Press, Taylor & Francis Group. I am especially appreciative of Hilary Rowe, acquisitions editor, chemistry, for making a way and encouraging me to publish this manual; to Judith Simon, project editor; and Jill Jurgensen, senior project coordinator, for all their efforts to bring this manual to print.

Introduction: Why green chemistry?

> A laboratory procedure you are working on requires you to measure 20.0 ml of concentrated sulfuric acid. Someone bumps you while you are doing this and the acid goes everywhere, including on your skin and clothes. You rush to the safety shower but still end up with some chemical burns, a trip to the emergency room, and totally ruined clothes!

This lab manual has been designed with "greener" procedures so that an accident like the one described above will not happen. Suppose this experiment had been conducted using vinegar instead. You would just rinse off your skin, attempt to dry your clothes with a paper towel, and then spend the rest of the day joking with your friends about how you smelled like Easter egg dye. Or better yet—what if instead the procedure could be modified to use a reusable acid catalyst anchored on a solid?

This green chemistry lab manual was developed not just to prevent accidents and make lab settings safer for you, but *also* to teach you about green chemistry. There are many exciting innovations that have happened because of green chemistry, and even more being developed. While working through the experiments in this manual you will learn about some of them, and hopefully begin to grasp the vision of what thinking as a green chemist really means.

But what exactly is green chemistry? The Environmental Protection Agency defines green chemistry as "the design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment." This means green chemistry is not about just trying to find ways to treat hazardous materials used or produced or to develop better protective equipment. Instead, it seeks innovative ways to *reduce* or even eliminate hazards from the start. The word *reduce* is in italics to make the point that just because a process is greener, it does not mean that all

hazards have been eliminated. But it does mean that they have been significantly reduced in some way.

There was not really a description for green chemistry until the mid-1990s, when Paul Anastas and John Warner created a list of 12 criteria or principles that can be used when designing chemical processes (*Green Chemistry: Theory and Practice*, 1998, Oxford University Press, NY, p. 30). These are known as the *12 principles of green chemistry*. These 12 principles and a brief explanation of each are listed below.

1. **Prevention**: It is always better to prevent hazardous waste than to have to clean it up once it has already been created. It is also better to design a process to be safe instead of having to figure out ways to protect people from toxic chemicals being used or dangerous processes.
2. **Atom economy**: If you build a bookcase, you want to use as much of the wood purchased as possible and not have anything wasted. You may consider different plausible designs and see which one has the least waste and will work the best. Methods of synthesis should be designed in a similar manner—you want as many atoms as possible from the starting materials to be incorporated into the final product.
3. **Less hazardous chemical synthesis**: When you think about chemistry, you may imagine someone in a yellow hazmat suit working with some kind of chemical that has a skull and crossbones on the bottle. Green procedures attempt to eliminate dangerous chemicals like these and use materials that have little or no danger to human health and the environment.
4. **Designing safer chemicals**: If you could design two products that did the same thing—one that could cause cancer and one that would not—which one would you make? The answer to that is obvious—the one that is less toxic! Products of chemical reactions should do what they are designed to, while having minimal toxicity.
5. **Safer solvents and auxiliaries**: Using solvents (liquids used to dissolve other materials), separating agents (chemicals that help two other things separate completely), or other auxiliaries should be cut out of a procedure as much as possible. But, if they are really needed, they need to be as harmless as possible.
6. **Design for energy efficiency**: You're probably very familiar with this principle if you have ever gone shopping for a TV or refrigerator. Most appliances advertise how energy efficient they are, or how much energy you can save by using them. But, you probably have not thought about energy efficiency in the chemistry lab. A chemical reaction should be designed to occur at room temperature and normal pressure, if possible, to save energy. If heating is necessary, it should be designed to be done as efficiently as possible. This could even involve using microwaves for heating!

7. **Use of renewable feedstocks**: We place a higher value on something if it is limited, and try to protect it. This is the same way we should treat our natural resources. Whenever possible, a *renewable* raw material should be used rather than depleting a limited stock of another material.
8. **Reduce derivatives**: Sometimes in chemistry, certain chemicals are used to protect certain parts of a molecule from reacting. Doing this or temporarily modifying a product should be done as little as possible because it generates additional waste.
9. **Catalysis**: A catalyst is something that speeds up the rate of a reaction, but is not used up in the reaction. You can get it back after the reaction has occurred and use it again. A selective catalyst should be used when possible.
10. **Design for degradation**: Some chemicals stick around and build up in the environment, which can cause damage to the ecosystem. The end products of a chemical reaction should break down instead of persisting in the environment.
11. **Real-time analysis for pollution prevention**: Thermostats constantly monitor the temperature of an area to ensure that it stays at just the right temperature. If the room starts to become just a little too hot or too cold, it sends a signal for the heat or air unit to come on. Once the set temperature is reached, it signals it to stop. In the same way, methods involving chemicals should be constantly monitored to prevent the formation of hazardous products, optimize yields, and decrease chemical waste.
12. **Inherently safer chemistry for accident prevention**: Even though safety measures are put in place to prevent accidents, they still happen in the lab—you drop a beaker, a bottle rolls off of the counter, you spill an acid, etc. When an accident occurs, you want it to cause as little damage as possible. This is desired not just for a lab setting, but also for manufacturing that is going on every day that uses chemistry. The chemicals used, all products of the reactions, and the processes should be designed to be as safe as possible and to prevent accidents. This way, even if an accident occurs, it is not as serious as it could have been since the process was designed to make it as safe as possible.

The authors of this manual tried to make labs that would be more interesting to you while incorporating as many of the above principles into each experiment as possible. With all of these steps taken to make the labs safer, they should be completely safe, right? You should be able to do a chemical experiment on the counter, lay a sandwich down on it, and be able to eat it a few minutes later, shouldn't you? Your lab partner can drink what is in a beaker, and nothing should happen to him, right? Wrong!

Many have the misconception that green chemistry experiments are completely without risk. A procedure can be described as green if it makes an improvement in any of the 12 principles. So, conducting procedures in a green way does not make safety precautions irrelevant. Rules such as not eating or drinking in the lab, wearing safety goggles, and avoiding horseplay are still crucial. Once again, even though these experiments are designed to be safer, precautions still need to be observed. Vinegar may be much safer than sulfuric acid, but that does not mean you should be careless when using it!

Green chemistry has often been referred to as preventive medicine for the environment. Heavy metals and other toxic materials have to be put in special containers, sealed up, and taken to special facilities carefully designed to prevent them from entering the environment. If they are not disposed of properly, they can cause illness and environmental disasters. An advantage for you, your instructor, and the environment is that the products of each of these labs normally do not have to be disposed of in this special way. Often it is safe to pour solutions down the drain (with plenty of running water), and solid waste can often be thrown directly in the trash can. Even if the waste does need to be disposed of in a special manner, it will be one used for less hazardous chemicals. This may not seem like such a big deal to you, but if schools across the nation began doing procedures in a green way, it could eliminate tons of hazardous waste and reduce the environmental cost of chemistry education.

Laboratory safety, equipment, and procedures

> A green chemistry laboratory manual means you can't get hurt, right? Wrong!

While this laboratory manual has been designed with greener procedures to cut down on harmful reagents and waste, there are still hazards and risks. Accidents may occur, even using greener procedures. However, if you use appropriate safety practices, a laboratory can be a reasonably safe place. Some common safety procedures you should follow are listed below.

Using glassware

- *Do not use glassware that is cracked*. The glassware may break upon heating or using.
- Clean all broken glassware immediately and dispose of it in the appropriate receptacle.
- *Keep all glassware clean*. Do not store dirty equipment.

Handling laboratory reagents

- *Always be aware of what you are doing*. Study the experiment and know the chemical and other hazards before entering the lab. A good way to find out about a chemical's hazards is to look up and study its (material) safety data sheet ((M)SDS).
- Report hazardous chemical spills to the instructor when they occur. Chemical spills need to be cleaned up immediately and properly.
- Use a fume hood for all chemicals that may produce hazardous or irritating gases or vapors.

- *Keep flammable liquids away from flames or exposed wiring*. If a small fire in a beaker occurs, turn off the source that caused the fire and cover the beaker with a watch glass. Be sure to tell your instructor about it. If a larger fire starts, tell your instructor immediately. Depending on the size of the fire and what is burning, it may be necessary to evacuate immediately.
- Always pour concentrated acids into water, never water into acid. Heat caused by the reaction may cause splattering.
- *Clean up messes when they occur*. If you are unsure of how to properly handle a chemical spill, ask your instructor.
- *Keep reagents pure by not contaminating them through using dirty utensils or glassware*. Not only will your reagents become contaminated, but undesirable reactions, even explosions, may occur.
- *Dispose of waste properly*. Follow the instructions given to you on how to dispose of your chemical waste by your instructor. These vary according to how your lab has been designed to accommodate chemical wastes and your location's regulations.
- If a corrosive liquid or any laboratory chemical used in this manual gets on your skin, immediately rinse the area with water and alert your instructor.
- Do not inhale large quantities of the reagents when checking the odor. Gently waft vapors toward your nose.
- Never eat or drink anything that has been in the lab, including reagents or samples. Eating, drinking, and smoking are not permitted in any laboratory setting.

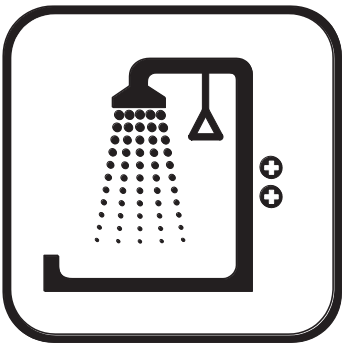
Laboratory attire

- *Wear safety goggles at all times*. It is possible there may be flying debris from glassware breaking and spilled chemicals. If you wear contacts, you should remove them. Splashed chemicals and noxious gases could cause more damage if you are wearing them.
- Long, loose hair should be tied back.
- Wear closed-toe shoes at all times.
- *Wear clothes that give appropriate coverage for protection*. Try to avoid wearing loose-fitting or very flammable clothing.

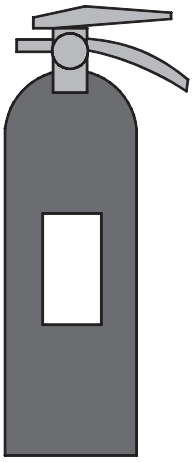
Safety equipment

- Know when to use and how to use all safety equipment.
- Know the location and purpose for all safety equipment, including the eye wash station, safety shower, and fire extinguisher. Illustrations of some common safety equipment are shown below:

Eye wash station



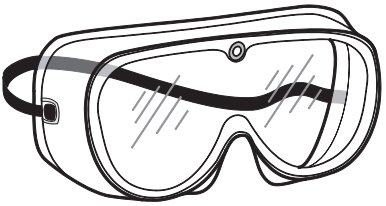
Safety shower with pull chain



Fire extinguisher

Fire blanket

Laboratory fume hood



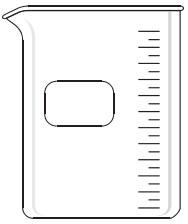
Safety goggles

Common laboratory procedures

- *Pipetting*. Always use a bulb when pipetting; never pipet directly by mouth. When using a pipet, always make sure that the volume of the liquid is greater than the volume of the pipet. Hold the pipet vertically and use a bulb to draw the liquid up until the meniscus is over the etched line. Use your index finger to plug the top of the pipet. Wipe the outside of the pipet with a paper towel and slowly release your index finger pressure just enough to lower the meniscus down to the etched line. Drain the liquid into the receiving container. Allow it to drain for an additional 15 seconds. Do not blow out the liquid that remains in the tip. Instead, just touch the tip of the pipet to the side of the receiving container.
- *Burners*. Make sure that the rubber tubing has no cracks. Turn on the gas and ignite the burner with a striker. The temperature of the flame is controlled by adjusting the volume of gas and air that enters the burner. Gas flow is controlled by rotating the small valve at the base of the burner. Airflow is adjusted by opening or closing the holes at the base of the barrel of the burner. A blue flame with a well-defined inner blue cone is the hottest.
- *Glass tubing*. Always use leather gloves and lubricate glass tubing with glycerol before inserting it into rubber stoppers. Carefully use a gentle twisting motion and avoid using too much force or the glass may break.
- *Measuring with glassware*. Take the measurement at eye level at the bottom of the meniscus, which is the bottom of the curve where the liquid falls.
- *Filtration*. Filter paper used for gravity filtration is most effective when first folded in half, next into fourths, and then one fold opened before placing into the funnel. When filtering by either gravity or vacuum filtration, seat the filter paper using the same solvent your sample is dissolved in. This is not always water. A stir rod can be used to guide the liquid into the funnel. In the case of vacuum filtration, make sure the mechanism is airtight.
- *Centrifuge*. Balance a centrifuge before turning it on. When only one tube containing a sample is to be centrifuged, this is done by placing a tube of equal size filled to the same level with water opposite it. Equally space sample tubes if there is more than one. Unbalanced centrifuges will vibrate and may cause damage to the centrifuge. Turn off a centrifuge and wait for it to stop. Never try to stop it with your hand.

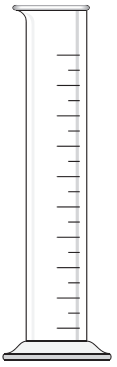
Common glassware

Shown below is some common glassware you will be using. Take a few minutes to learn their names, and try to identify which ones are present in your laboratory drawer or sitting out where you can see them.

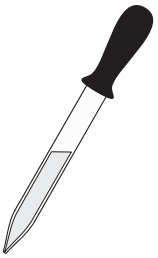


Beaker

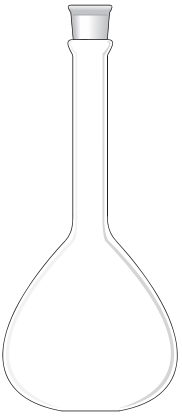
Test tube



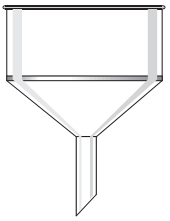
Graduated cylinder



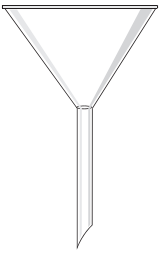
Dropper



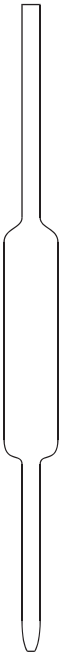
Volumetric flask



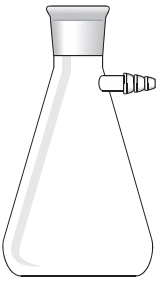
Büchner funnel



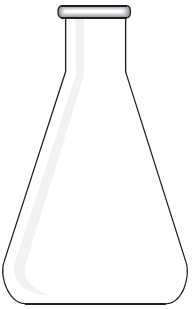
Long-stem funnel



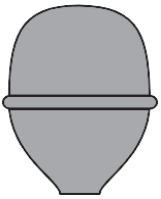
Volumetric pipet



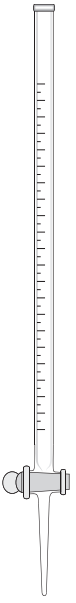
Filter flask



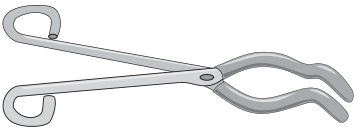
Erlenmeyer flask



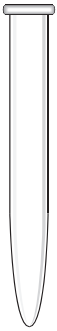
Pipet bulb



Buret

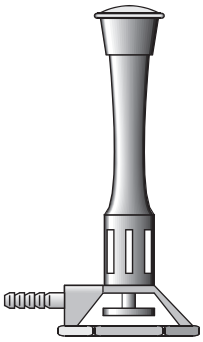


Tongs

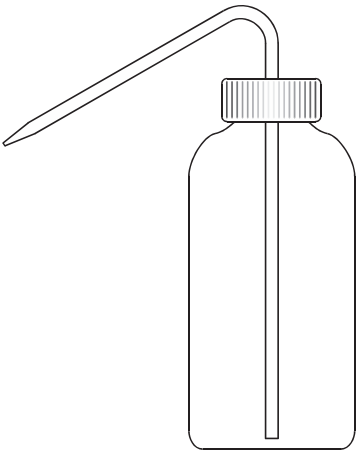


Centrifuge tube

Cuvette

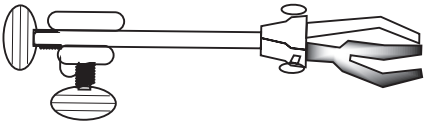


Bunsen burner



Wash bottle

Watch glass



Clamp

About the author

Sally A. Henrie is a professor of chemistry at Union University in Jackson, Tennessee, and has been in chemical education for over 16 years. She earned her BS degree in chemistry from the University of Arizona and her PhD in organic chemistry from South Dakota State University.

Dr. Henrie has taught various courses and laboratories at Union University, including the nonmajors Fundamentals of Chemistry, General Chemistry Laboratory, Organic Chemistry, Organic/Inorganic Synthesis, Survey of Chemical Instrumentation, Advanced Organic Chemistry, and Environmental Chemistry. She is also involved in mentoring undergraduate research students in chemical education and dendrimer research. The *Green Chemistry Laboratory Manual for General Chemistry* is the result of Dr. Henrie mentoring undergraduate students in chemical education research.

Dr. Henrie previously worked as a junior research chemist for Phelps Dodge Corporation, plant chemist for Mount Pleasant Chemical Company, and materials lab supervisor/process engineer for Whirlpool Corporation. While working in industry, she contributed to various environmentally-related projects.

chapter one

Determining the percent of water in epsom salt

> Epsom salt is used in many different ways. It is commonly used as a natural beauty enhancement for exfoliating. Gardeners add it to enrich their soil in magnesium and sulfur. It is even used for home health remedies because bathing in it helps to sooth aches and pains.

Inorganic salts that incorporate water molecules in a fixed ratio in their structure are called hydrates. Heating a hydrate will normally evaporate off water molecules. Not all of the water molecules come off at the same time or even at the same temperature. They become the anhydrous form when all of the water molecules are removed.

The hydrate that will be used in this lab is $MgSO_4 \cdot 7H_2O$, or Epsom salt. Removal of all of the water molecules to form anhydrous magnesium sulfate is shown in Equation 1.1. For this to occur, the temperature must reach at least 225°C.

$$\underset{\text{Hydrate}}{MgSO_4 \cdot 7H_2O} + \text{Heat} \rightarrow \underset{\text{Anhydrous salt}}{MgSO_4} + \underset{\text{Water}}{7H_2O} \qquad (1.1)$$

Once the mass of the magnesium sulfate left behind is determined, the mass of the water heated off can be calculated and used to find the percent of water in the Epsom salt. This relationship is shown in Equation 1.2:

$$\%\ \text{Water} = \frac{\text{Mass of water}}{\text{Mass of hydrate}} \times 100 \qquad (1.2)$$

The percent error is a good way to judge how inaccurate data in an experiment is. To find the percent error, the absolute value of the experimental value subtracted from the theoretical value is divided by the theoretical value and multiplied by 100, as shown in Equation 1.3:

$$\%\ \text{error} = \frac{|\text{theoretical value} - \text{experiment value}|}{\text{theoretical value}} \times 100 \qquad (1.3)$$

Several analytical techniques will be used in this lab, one of which is finding a constant mass. A constant mass is needed for both the accuracy and precision in the results of the experiment. When finding the constant mass, the mass will need to be the same from one reading to the next. In this case, the masses will need to be the same within 0.005 g. If the Epsom salt is not heated to at least 225°C for a long enough time, it will still have some magnesium sulfate monohydrate present. A constant mass can be obtained after all of the water molecules have been removed and proper analytical techniques are used. Proper analytical techniques that are important to obtaining a constant mass include making sure the sample is completely cooled to room temperature before weighing. It is also important not to touch the crucible with your fingers because they may have oils that can add to the mass obtained.

Another analytical technique introduced is the use of a desiccator to cool the hydrate. A desiccator is an airtight jar or container with a lid that has a desiccant, or drying agent, inside to draw or keep moisture from the sample placed inside. It is used in this experiment to ensure that no water is redrawn into the anhydrous magnesium sulfate from the atmosphere after heating because it is hygroscopic. Hygroscopic means it will absorb water from the atmosphere.

Anhydrous magnesium sulfate is an excellent drying agent that is often used to remove water from chemicals that are made or used in an experiment. If instructed to do so, the anhydrous magnesium sulfate you will make can be placed in a collection container so that it can be used later as a drying agent. Using a product from one part of a chemical process to do something in another part improves the overall efficiency. This relates to *atom economy*, the second principle of green chemistry.

Design for energy efficiency is also one of the 12 principles of green chemistry. This means a chemical synthesis needs to be designed so that the least amount of energy possible is used. At times this is done by designing a synthesis that can be performed at or close to room temperature. Other times, designing for energy efficiency is accomplished by using the most energy efficient method. In this lab you will compare the energy efficiencies of two methods used to dehydrate Epsom salt and determine which one of the methods is more energy efficient. One method uses a hot plate and the other a Bunsen burner.

Objective

In this experiment, you are going to determine the percent of water in Epsom salt using two different methods of heating and correct analytical techniques. You will determine which one of the methods is more energy efficient.

Name _____

Prelab questions

1. What is the theoretical value of the percent of water in Epsom salt?

2. If the mass of the Epsom salt before heating is 1.030 g and after heating is 0.510 g, what is the mass of the water that is heated off?

3. If the mass of the Epsom salt before heating is 1.030 g and after heating is 0.510 g, what is the percent of water in Epsom salt?

4. Glassware absorbs small amounts of moisture over time. In this experiment you will dry the crucible and allow it to cool to room temperature in a desiccator before obtaining its mass. If you did not do this, how would it affect your results?

5. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

Part 1: Drying using a Bunsen burner

1. Be sure to wear safety goggles. Inspect the crucible you will use to make sure it does not have cracks or chips. Do not use it if it does!
2. Attach a ring to a ring stand and place a clay triangle on top of the ring. Sit a crucible in the clay triangle. Place the crucible cover on top of the crucible.
3. Place an unlit Bunsen burner under the crucible. Adjust the ring so that it is approximately 2 inches above the Bunsen burner. See Figure 1.1.
4. Light the Bunsen burner and place it directly under the crucible. Adjust the flame so that the tip of the inner blue cone, the hottest part of the flame, is touching the bottom of the crucible.
5. Heat for 3 minutes. The bottom of the crucible will become a dull red. Turn off the Bunsen burner. Allow the crucible to cool to room temperature. ***Caution:*** Do not touch the crucible and its cover until they have cooled to room temperature. The crucible will be hot!
6. Use a mortar and pestle to crush a little over 2.1 g of Epsom salt if there are large crystals.
7. Weigh and record the mass of the room-temperature crucible.
8. Measure out approximately 1.0 g of the crushed Epsom salt into the crucible, weigh, and record the exact mass of the crucible with the Epsom salt in the data section.
9. Sit the crucible containing the Epsom salt back in the clay triangle. Place the probe of an electronic thermometer in the Epsom salt sideways and cover with a crucible lid. *Hint*: You may clamp the thermometer probe on a ring stand and lower it into the Epsom salt.
10. Light the Bunsen burner and record the time. Heat the crucible until the temperature of the Epsom salt reaches at least 225°C. Heat for an additional 3 minutes. The bottom of the crucible will become

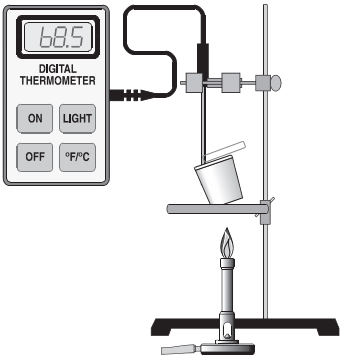


Figure 1.1 Apparatus for drying using a Bunsen burner.

a dull red. Turn off the Bunsen burner and record the time in the data section. Allow the crucible to cool for 2 minutes.
11. Using tongs and an oven mitt, carefully remove the crucible lid and thermometer probe. Then remove the crucible with the sample and place it into a desiccator until it cools to room temperature. ***Caution:*** The crucible, crucible lid, and thermometer probe will be hot!
12. Weigh and record the mass of the crucible and Epsom salt.
13. Repeat steps 10–12 until a constant mass is achieved. This is when less than a 0.003 g difference in the masses is found.
14. Calculate the mass of the water heated off, the percent of water, and the number of water molecules attached to each magnesium sulfate molecule. Also calculate the total time the Bunsen burner was on to heat the Epsom salts.

Part 2: Drying using a hot plate

1. Remove the Epsom salts from the crucible. If you wash it, be sure to flame dry it as you did in Part 1, steps 2–5. Weigh and record the mass of the crucible.
2. Measure out approximately 1.0 g of the crushed Epsom salt from Part 1 into the crucible, weigh, and record the exact mass of the crucible with the Epsom salt.
3. Place the crucible on a hot plate and note the time in the data section.
4. Place the probe of an electronic thermometer in the Epsom salt sideways and cover with a crucible lid. *Hint*: You may clamp the thermometer probe on a ring stand and lower it into the Epsom salt.
5. Increase the temperature until it reaches at least 225°C. Continue to heat the Epsom salt for approximately 10 more minutes at this temperature. Turn off the hot plate and let it cool for a few minutes. Note the time you turned off the hot plate.
6. Using tongs and an oven mitt, carefully remove the crucible lid and thermometer probe. Then remove the crucible with the sample and place it into a desiccator until it cools to room temperature. ***Caution:*** The crucible, crucible lid, and thermometer probe will be hot!
7. Weigh and record the mass of the crucible and Epsom salt.
8. Put the crucible back on the hot plate and repeat steps 5–8, only this time heating the Epsom salt for 3 minutes at 225°C.
9. Repeat steps 5–8 until a constant mass is achieved. This is when less than a 0.003 g difference in the masses is found.
10. Turn off the hot plate and record the time. Determine the amount of time the hot plate was on.
11. Calculate the mass of the water heated off and the percent of water.

Name _____

Data

Part 1: Drying using a Bunsen burner

Table 1.1 Data for Part 1

	Trial 1	Trial 2 (optional)
Mass of crucible		
Mass of crucible and Epsom salt		
Mass of Epsom salt before heating		
Mass of Epsom salt and crucible after first heating		
Total time Bunsen burner was on for first heating		
Mass of Epsom salt and crucible after second heating		
Total time Bunsen burner was on for second heating		
Mass of Epsom salt and crucible after third heating (if necessary)		
Total time Bunsen burner was on for third heating		
Mass of water heated off		
Percent of water		

Total time Bunsen burner was on: _____

Average percent of water (optional): _____

Part 2: Drying using a hot plate

Table 1.2 Data for Part 2

	Trial 1	Trial 2 (optional)
Mass of crucible		
Mass of crucible and Epsom salt		
Mass of Epsom salt before heating		
Mass of Epsom salt and crucible after first heating		
Total time hot plate was on for first heating		
Mass of Epsom salt and crucible after second heating		
Total time hot plate was on for second heating		
Mass of Epsom salt and crucible after third heating (if necessary)		
Total time hot plate was on for third heating		
Mass of water heated off		
Percent of water		

Total time hot plate was on: _____

Average percent of water (optional): _____

Observations

Calculations

Part 1

Calculations for percent water in Epsom salt:

Calculations for percent error:

Part 2

Calculations for percent water in Epsom salt:

Calculations for percent error:

Analysis

1. Was there water still left in the hydrate in Part 1 or Part 2? Why or why not?

2. How do the experimental value and the theoretical value compare for both methods? Which one has the better percent error?

3. Do you consider your percent error acceptable?

4. What if a desiccator was not used in the cooling of the hydrate? How would this affect the outcome of the experimental value of the percent of water found?

5. What if the crucible and sample were weighed before they had cooled to room temperature? How would this affect the outcome of the experimental value of the percent of water found?

Think green

1. How could you attempt to make the procedure for the method you consider to be more green even greener? If there are time and resources available, try your idea(s) and discuss your results.
2. Compare the fuel used to Btus generated for the hot plate and the Bunsen burner methods. If possible, look at the Watts your hot plate used; otherwise, use 950 W in one hour; 1 kW = 3.412 Btu. A small Bunsen burner consumes approximately 3 cubic feet of natural gas per hour and 1 cubic foot = 1.028 Btu. Be sure to consider total time the hot plate or Bunsen burner was on.
3. Compare the greenness of the two methods by considering the green chemistry principles of energy efficiency, renewable feedstock, and safety of the two methods. Which one of the methods used do you consider to be more green? Explain your answer.

Presidential green chemistry challenge

The Environmental Protection Agency (EPA) gave its 2011 Presidential Green Chemistry Challenge Award in the Small Business category to BioAmber, Inc. for research involving using less energy and sequestering CO_2. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners, and write a brief summary about this technology and how it utilizes principles of green chemistry.

chapter two

Determination of the formula of a copper supplement

> If you have ever watched a crime drama on television, you have probably seen a scientist take a sample of unknown substance, run some tests, and return with a report identifying the substance—that is analytical chemistry in action.

Analytical chemists use different experimental techniques to identify compounds, one of which involves the isolation of different elements in the compound and determining the percentage composition of the compound. Percentage composition data can be used to determine the chemical formula. When scientists determine that an unknown sample is 60.66% chlorine and 39.34% sodium, they have identified the unknown sample as common table salt, or by its chemical name, sodium chloride. Every chemical compound has a formula that is unique to that compound. The percentage composition data can be used to determine the chemical formula. An alternative method of determining the chemical formula is to isolate one component of a compound and determine the molar ratios of the elements present in the compound.

How does this relate to green chemistry? *Prevention* and *catalysis* are two of the principles of green chemistry. Catalysts often incorporate a hazardous heavy metal in their structure. Reducing the percent of a hazardous heavy metal in a catalyst or other substance decreases the hazards associated with that particular heavy metal. This experiment uses a compound named copper gluconate. It has a much lower percentage of a heavy metal than the copper compound typically used. The chemical formula of gluconate is $C_{12}H_{22}O_{14}$. Your task is to determine the chemical formula of the compound by isolating the copper and determining the molar ratio of copper and gluconate in the compound. Copper gluconate has a variety of uses and applications, including as an ingredient in the breath mint Certs® and as a source of copper in nutritional supplements.

Example

You are given a sample of compound containing magnesium and chlorine. After isolating the elements from your 5.00 g sample, you discover there are 1.28 g of magnesium and 3.72 g of chlorine.

To determine the molar ratio of each element:

$$\frac{1.28\,\text{g Mg}}{} \left| \frac{1\,\text{mole Mg}}{24.31\,\text{g}} \right. = 0.0527\,\text{moles Mg}$$

$$\frac{3.72\ \text{g Cl}}{} \left| \frac{1\ \text{mole Cl}}{35.45\ \text{g}} \right. = 0.105\ \text{moles Cl}$$

Once you have determined the molar quantities of each element, divide each by the smallest value and round each to a whole number—this will give you the chemical formula for the compound:

$$\frac{\text{Mg}_{0.0527}\text{Cl}_{0.105}}{0.0527\ 0.0527} = \text{MgCl}_2$$

The chemical formula for the unknown magnesium compound is $MgCl_2$; this compound is named magnesium chloride.

To calculate the percentage composition for this compound:

$$1.28\ \text{g Mg}/5.00\ \text{g MgCl}_2 = 0.256 \times 100 = 25.6\%\ \text{Mg}$$

$$3.72\ \text{g Cl}/5.00\ \text{g MgCl}_2 = 0.744 \times 100 = 74.4\%\ \text{Cl}$$

Objective

The purpose of your experiment is to determine the chemical formula for a compound by isolating one component of the compound and determining the molar ratio.

Name _____

Prelab questions

1. Why is it important in this experiment to be accurate in all your measurements?

2. List the measurements you will be taking in this experiment:

3. What wastes are produced in this reaction?

4. Copper gluconate is the copper salt of D-gluconic acid. D-Gluconic acid loses one H to form the gluconate ion that bonds to copper. The gluconate ion has the molecular formula $C_6H_{11}O_7$. What is the molar mass of the gluconate ion?

5. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

1. Weigh 0.500 g of copper gluconate and place in a 50 ml beaker.
2. Add 10 ml 1.0% w/v NaCl to the beaker; stir until all copper gluconate has gone into solution.
3. Lightly sand three small aluminum washers to remove aluminum oxide that has formed and add them to the solution. To increase the speed of the reaction, heat on a hot plate at 60–70°C until the solution loses its bluish color and bubbles stop forming. The solution may be a pale yellow.
4. Remove the beaker from heat carefully and let the solution cool. Decant the clear liquid into a 150 ml beaker. ***Caution:*** The beaker will be hot!
5. When all that remains in the original beaker are the copper-plated washers, rinse with deionized water and decant liquid, being careful not to lose any copper. Repeat this rinsing process three times.
6. Preweigh a clean, dry 50 ml beaker and record its mass in the data section.
7. Carefully remove the first washer and scrape the copper into the preweighed beaker. Rinse the washer to be sure all copper is recovered into the beaker. Add any loose copper that remains in the original beaker into the same beaker. Repeat the process for the second and third washers.
8. Carefully decant off the water. Place the beaker with the copper into a drying oven set at approximately 120°C for 15 minutes. Remove the beaker and allow it to come to room temperature. Weigh and record the mass.

Name _____

Data

Mass of copper gluconate: _____

Mass of beaker: _____

Mass of beaker + copper: _____

Mass of copper: _____

Observations

Calculations

Mass of copper recovered:

Moles of copper recovered:

Mass of gluconate:

Moles of gluconate:

Chemical formula:

Analysis

1. What is the formula of your compound?

2. List two sources of error in your experiment and explain the impact they had on your results.

3. Create a pie chart showing the percentage composition for each element in the compound copper gluconate; clearly label each element and the percentage.

Think green

1. Copper (II) chloride can be used as a source of copper for this experiment, but copper gluconate is preferred due the fact that it is a greener compound. Compare the percent copper in both compounds. Look up the (material) safety data sheet ((M)SDS) for both compounds. In terms of green chemistry, discuss the advantages of using copper gluconate instead of copper chloride in this experiment.
2. Copper (II) sulfate pentahydrate can also be used as a source of copper. Why would the procedure you did not work as it is written? How would you change the procedure so that you could determine its chemical formula? If time and resources permit, test your hypothesis. Determine which of the 12 principles of green chemistry would be negatively impacted by changing to copper (II) sulfate pentahydrate and discuss the reasons for your answer.

Presidential green chemistry challenge

In this experiment you determined the percentage of copper in copper gluconate. The Environmental Protection Agency (EPA) gave its 2009 Presidential Green Chemistry Challenge Award in the Academics category to Professor Krzysztof Matyjaszewski for research that included lowering the percentage of copper in a catalyst. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about this technology and how it utilizes principles of green chemistry.

chapter three

Determination of mass and mole relationships in a chemical reaction

How can the amount of a substance in an unknown be determined? What determines the amount of a desired product that is produced in a chemical reaction?

As a quality control supervisor, a member of your staff has provided you with a sample of calcium chloride solution that did not pass quality standards tests of freezing point depression. The solution is supposed to contain 15% w/v calcium chloride and provide the following levels of freezing point protection: slush free to –53°F and solid at –62°F. The given sample solution did not meet the given level of protection. Upon further investigation, it was determined that the calcium chloride used to prepare the solution was left exposed to the air for 3 hours. Calcium chloride is hygroscopic. Hygroscopic compounds quite literally pull water molecules from the air around them and the water becomes chemically associated with the compound. This can affect the mass of the compound. It is believed the exposure of the calcium chloride to the air led to its eventual failure of quality control tests. You must determine the amount of calcium present in the sample solution utilizing a precipitation reaction with potassium carbonate (K_2CO_3).

Calcium chloride will react with potassium carbonate to form calcium carbonate. The mass of calcium carbonate and the amount of calcium present in the sample solution can be determined using mass and mole relationships.

Before you begin the experiment to determine the amount of calcium chloride present, you must determine the amount of potassium carbonate needed to precipitate the maximum amount of calcium potentially present in the solution. In order to determine this, you must make sure calcium chloride will be the limiting reactant in the reaction. The limiting reactant is the element or compound that controls the amount of product produced in a chemical reaction.

For example, you are given 20 marshmallows, 40 graham cracker squares, and 8 chocolate bars. The recipe for a s'more is 2 graham cracker squares, ½ a chocolate bar, and 1 marshmallow. Following the recipe, how many s'mores can you make? What is the limiting ingredient?

The calculations would look like this:

$$\frac{20 \text{ marshmallows} \mid 1 \text{ s'more}}{\mid 1 \text{ marshmallow}} \rightarrow 20 \text{ s'mores}$$

$$\frac{40 \text{ graham crackers} \mid 1 \text{ s'more}}{\mid 2 \text{ graham crackers}} \rightarrow 20 \text{ s'mores}$$

$$\frac{8 \text{ chocolate bars} \mid 1 \text{ s'more}}{\mid 0.5 \text{ chocolate bar}} \rightarrow 16 \text{ s'mores}$$

Given the ingredients, you can only make 16 s'mores. The chocolate bars limited the number of s'mores you could prepare. It was the limiting ingredient.

A similar situation occurs in chemical reactions. There may be an element or compound that limits the amount of product that can be made in the reaction. It is helpful to know the limiting reactant, especially when you are trying to determine the chemical formula of a compound, or identify how much of a given substance is present in an unknown solution. This will be the case in today's investigation. In order to determine the concentration of calcium chloride present in the solution, it must be the limiting reactant in the equation. An excess of potassium carbonate must be added so that all of the calcium chloride will react to form calcium carbonate. Potassium carbonate is also hygroscopic, so a high excess will be used, but not so much that it will not easily dissolve in water.

Example

In this lab potassium phosphate tribasic could have been used instead of potassium carbonate. How much potassium phosphate tribasic would be needed to fully precipitate all calcium from a 10.00 ml sample of a 10.0% w/v calcium chloride solution?

First, the balanced reaction equation must be written:

$$3CaCl_{2(aq)} + 2K_3PO_{4(aq)} \rightarrow Ca_3(PO_4)_{2(s)} + 6KCl_{(aq)}$$

Next you must determine how many grams of calcium chloride are present in 10.00 ml of a 10.00% $CaCl_2$ (w/v) solution:

$$10.00 \text{ ml} \times 10.00 \text{ g}/100.0 \text{ ml} = 1.000 \text{ g}$$

This must be converted to moles using the molar mass of 110.98 g/mole:

$$1.000 \text{ g} \times 1 \text{ mole}/110.98 \text{ g} = 0.009011 \text{ mole}$$

From the balanced equation, we see it takes 2 moles K_3PO_4 to react with 3 moles of $CaCl_2$.

$$\text{Moles of } K_3PO_4 \text{ needed} = 0.009011 \text{ mole } CaCl_2 \cdot \frac{2 \text{ mol } K_3PO_4}{3 \text{ mol } CaCl_2}$$

$$= 0.006007 \text{ mole } K_3PO_4$$

This needs to be converted to grams using the molar mass:

$$\text{g } K_3PO_4 \text{ needed} = 0.006007 \text{ mole } K_3PO_4 \times 212.27 \text{ g/mole} = 1.275 \text{ g } K_3PO_4$$

Atom economy

The example above uses *stoichiometry*, or mole-to-mole ratios. As you can see, mole-to-mole ratios are very useful because they show how much of each reactant is needed to produce a sufficient amount of product. Green chemistry has another calculation called *atom economy*. It evaluates the atom efficiency of a reaction and looks at all atoms involved. In the above example, the 6 molecules of KCl were not considered, but after the reaction is performed, they are present as waste that needs to be properly disposed. This is uneconomical, especially if the waste is hazardous. You can also think of it as having to buy atoms that you really do not need and will have to get rid of later. A greener reaction has less atomic waste. The general equation for atom economy is as follows:

$$\text{Atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \cdot 100$$

In the above reaction example, the atom economy would be:

$$\text{Atom economy} = \frac{Ca_3(PO_4)_2 \text{ g/mol}}{3CaCl_2 \text{ g/mol} + 2K_3PO_4 \text{ g/mol}} \cdot 100$$

$$\text{Atom economy} = \frac{310.18 \text{ g/mol}}{3(110.98 \text{ g/mol}) + 2(212.27 \text{ g/mol})} \cdot 100 = 40.949\%$$

Atom economy is also valuable when comparing reactions that could be used for a particular application. Although it does not consider

all factors, such as energy efficiency, hazards, excess reactants used, waste disposal costs, or cost of the chemicals, it is still very useful in comparing the atom efficiency of different possible reactions.

Objective

In this experiment, you will investigate the concepts of hygroscopic substances and limiting reactants by determining the percent moisture absorbed by a $CaCl_2$ sample, and determining the mass of calcium chloride present in an unknown through careful precipitation of calcium carbonate.

Name _____

Prelab questions

1. $CaCl_2$ and K_2CO_3 are both hygroscopic. What does this mean and what special precaution needs to be taken when using these chemicals?

2. Write the balanced reaction equation for the precipitation of calcium carbonate from potassium carbonate and calcium chloride and determine the atom economy. How does this compare to the example where K_3PO_4 is reacted with the $CaCl_2$?

3. Using the balanced equation above, determine the limiting reactant if 15 g of $CaCl_2$ was reacted with 15 g of K_2CO_3. Could you use 15 ml of a 15 g/L K_2CO_3 solution to test a solution that is suppose to be a 15 g/L $CaCl_2$ solution? Explain your answer.

4. Determine the mass of anhydrous K_2CO_3 needed to fully precipitate all calcium from a 10 ml sample of 15.0% w/v $CaCl_2$ solution. (*Recall*: This is the supposed concentration of the solution you are testing.)

5. Sometimes an excess is used to make sure the reaction goes to completion. Determine how many grams of anhydrous K_2CO_3 you will need to obtain if you use a 20% excess.

6. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

Part 1: Exploring a hygroscopic substance

1. Weigh a watch glass and record its mass.
2. Place approximately 0.5 g of $CaCl_2$ on it and record the exact mass of the watch glass and the $CaCl_2$. Also record any observations.
3. Let the watch glass sit until the end of the lab period, but make frequent observations. Go on to Part 2.
4. After you have completed Part 2, reweigh the watch glass and $CaCl_2$. Record its mass and determine the amount and percent moisture absorbed.

Part 2: Analyzing a suspect 15% calcium chloride solution

1. Label three 150 ml beakers with Trial 1, Trial 2, and Trial 3. Use a volumetric pipet to add 10.00 ml of the sample $CaCl_2$ solution to be tested into each beaker.
2. Tare a clean 150 ml beaker on a balance and add the amount of anhydrous K_2CO_3 you determined in your prelab calculations question 4 that you will need to precipitate the maximum possible amount of calcium present. Record the exact mass.
3. Use a graduated cylinder to add 25 ml deionized (DI) water to the beaker containing the K_2CO_3. Stir the solution until all of the K_2CO_3 is dissolved. Add this to the beaker labeled Trial 1. Rinse the beaker that contained the K_2CO_3 with two 5 ml portions of DI water and add the rinses to the beaker labeled Trial 1.
4. Stir the solution for approximately 4 minutes. Be sure to rinse off any precipitate that remains on your stirring rod back into the beaker using small portions of DI water. Allow the reaction to sit for 15 minutes to give sufficient time for all $CaCO_3$ to precipitate.
5. For Trial 2, repeat steps 2–4, only use an additional 20% of the amount of K_2CO_3 that you used for Trial 1 and determined in your prelab calculations question 5.
6. For Trial 3, repeat steps 2–4, only use 1.00 g of K_2CO_3.
7. While solutions are precipitating, set up a vacuum filtration apparatus as shown in Figure 3.1.
8. Obtain the appropriate size filter paper (Whatman 40), weigh, and record the mass. Place it in the Büchner funnel and seat it with a small amount of DI water.
9. Label a watch glass Trial 1. Weigh and record the mass.
10. Filter the solution for Trial 1. Use additional DI water and a rubber policeman to ensure the transfer of all solid precipitate into the filtration apparatus and to rinse soluble impurities off of the product.

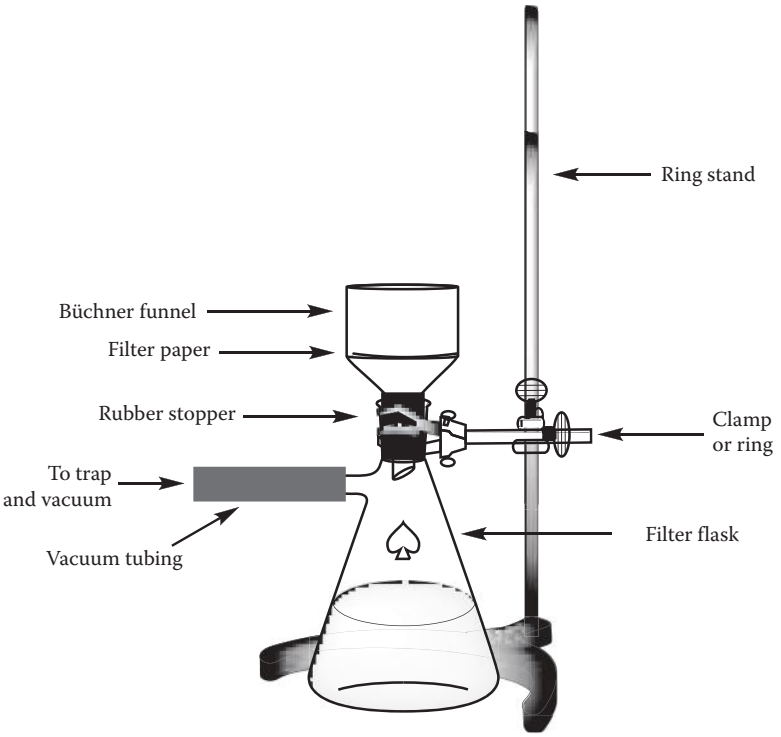


Figure 3.1 Vacuum filtration apparatus.

11. After the solution has been filtered, rinse with approximately 5 ml of ethanol. This will aid the drying process. ***Caution:*** Do not drink! Ethanol used in the lab has poisonous stabilizers added. Also, keep the vacuum going for a few minutes after all of the ethanol has passed through the funnel to aid drying.
12. Carefully, so as not to lose any product, transfer the filter paper and the entire product onto the preweighed watch glass.
13. Allow the product to dry and record the mass of the watch glass, filter paper, and product. If necessary, you can place in a 100°C oven to dry for 5–10 minutes. ***Caution:*** Ethanol is also flammable. Be sure the precipitate and filter paper are almost completely dry before placing them in an oven.
14. Repeat steps 8–13 for Trials 2 and 3.
15. Calculate the mass of the products recovered and the percent $CaCl_2$ in the sample solution for all three trials.
16. Complete Part 1.

Name _____

Data

Part 1: Exploring a hygroscopic substance

Watch glass mass: _____

Watch glass and initial $CaCl_2$ mass: _____

Initial $CaCl_2$ mass: _____

Watch glass and final $CaCl_2$ mass: _____

Final $CaCl_2$ mass: _____

Amount moisture absorbed: _____

Percent moisture absorbed: _____

Part 2: Analyzing a suspect 15% calcium chloride solution

Table 3.1 Data for Part 2

	Trial 1	Trial 2	Trial 3
mL $CaCl_2$			
Mass of K_2CO_3			
Mass of filter paper			
Mass of watch glass			
Mass of watch glass, filter paper, and precipitate			
Mass of precipitate			
% $CaCl_2$ in sample			

Observations

Part 1: Exploring a hygroscopic substance

Part 2: Analyzing a suspect 15% calcium chloride solution

Calculations

Part 1: Exploring a hygroscopic substance

Amount moisture absorbed:

Percent moisture absorbed:

Part 2: Analyzing a suspect 15% calcium chloride solution

Theoretical yield if 15% $CaCl_2$:

Actual yield:

Trial 1:

Trial 2:

Trial 3:

Percent $CaCl_2$ in sample:

Trial 1:

Trial 2:

Trial 3:

Analysis

1. Was there a significant difference between the percent $CaCl_2$ found in Trials 1, 2, and 3? Is this what you expected? Which trial(s) do you think gave more accurate results? Explain your answer.

2. Create a bar graph comparing the supposed percentage concentration and the actual percentage concentration of calcium chloride in the solution.

3. Based on your analysis, how many additional kilograms of anhydrous $CaCl_2$ would need to be added to a 50-gallon drum containing the solution your sample was taken from? Use this conversion factor: 1 gallon = 3.7854 L.

Think green

1. Evaluate the procedure you used in this experiment in terms of atom economy. Determine through calculations if the atom economy could be improved by substituting Na_2CO_3 or $NaHCO_3$ for K_2CO_3? Do you think either of these would be a greener replacement? If time and resources permit, test your hypothesis and discuss your results.
2. Purifying solvent waste obtained from a reaction can be expensive. Potassium chloride is a by-product in this reaction and remains in the wastewater. Research and write a summary regarding how salts are removed from water and the cost to do so.

Presidential green chemistry challenge

The Environmental Protection Agency (EPA) gave its 1998 Presidential Green Chemistry Award in the Academic category to Professor Barry Trost for creating the defined concept of atom economy. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about this technology and how it utilizes principles of green chemistry.

chapter four

Finding ethanol's molar mass using vapor density

> Volatile liquids are used on a daily basis in everyday households. From the gasoline that powers a car to common products stored in the bathroom, like nail polish remover and rubbing alcohol, volatile liquids are everywhere!

The ideal gas law can be used to find the molar mass of volatile liquids. In this experiment, you will use it to find the molar mass of an unknown alcohol. Ethanol is an example of an alcohol. More ethanol is produced than any other alcohol, most of which is used as an ingredient in automotive fuel.

Ethanol is added to gasoline for several reasons, one of which is to help prevent engine knocking. Tetraethyl lead used to be used in gasoline to help prevent engine knocking. It was replaced with methyl *t*-butyl ether (MTBE), which was later replaced with ethanol. Both tetraethyl lead and MTBE did an excellent job preventing engine knocking, but after they were used for a period of time, they were found to have adverse effects on the environment. A greener replacement had to be found and ethanol was chosen.

Another reason ethanol is added to gasoline is that in cold climates, it can keep water from freezing in the fuel system. Small amounts of moisture in the air can be absorbed by gasoline. Water readily separates from gasoline that has not had ethanol added to it. When the weather is cold enough, water present may freeze and cause blockages that will prevent fuel from getting to the engine. But when ethanol is present, it will keep small amounts of water mixed in the gas.

Water present in ethanol must be removed before it is added to gasoline. If too much water is present in gas that has had ethanol added, the ethanol will separate out with the water and cause problems. Chemists often effectively use distillation to purify liquids of different boiling points. In distillation, ideally a pure lower boiling liquid will boil off first, leaving the higher boiling liquid behind. Even though ethanol has a boiling point of 78.3°C and water's boiling point is 100°C, distillation will not remove all of the water from an ethanol/water mixture. This is because a mixture that is 95.6% ethanol and 4.4% water boils at a slightly

lower temperature than pure ethanol, 78.1°C, due to repulsions between the liquids. Liquids that behave like this are called azeotropes. Another method must be used to remove the last 4.4% of water from naturally produced ethanol. Molecular sieves are often used to do this.

Molecular sieves are a type of drying agent that absorbs moisture (water) from solution as well as the atmosphere. This is why the sieves must be dried and then kept in an airtight container. They come in different sizes, and the size used is chosen according to what size is needed to remove the impurity. Water can be removed with a 3 Å molecular sieve, but larger impurities require larger molecular sieves. Because the ethanol used in this experiment contains a certain percentage of water, 3 Å molecular sieves will be used to remove it at the beginning of the experiment. After the molecular sieves are used, they can be dried and reused. Recall that using auxillary substances that can be recovered and reused is a goal of green chemistry since it increases the overall *atom economy*.

After the water is removed from the ethanol, you will use the ideal gas equation (4.1) to determine the molar mass of ethanol. In the ideal gas equation, P is the pressure, V is the volume, n is the number of moles, R is the universal gas constant, and T is the temperature.

$$PV = nRT \tag{4.1}$$

Molar mass (M), simply put, is the number of grams of a substance (g) over the number of moles for a substance (n), or $M = \frac{g}{n}$. By solving for n and substituting into Equation 4.1, the resulting equation (4.2) can be used to calculate the molar mass:

$$PV = \frac{gRT}{M} \tag{4.2}$$

Note that the pressure should be in atmospheres, the volume in liters, and temperature in Kelvin since R is equal to 0.08206 $\frac{\text{liter} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$.

Objective

In this lab, you are going to dry an ethanol sample using molecular sieves and then determine the molar mass of ethanol using the ideal gas equation.

Name _____

Prelab questions

1. How would leaving the molecular sieves container uncapped or in an open beaker for an extended period of time affect the experiment?

2. The barometric pressure is 752.3 mmHg. What is the pressure in atmospheres? Use the conversion factor that 1 atm equals 760 mmHg.

3. Convert 95.8°C to Kelvin.

4. A 3.28 g sample of gas occupies 1.25 L at 293.2 K and 0.997 atm. What is the molar mass?

5. Given the following data, calculate the molar mass.

Barometric pressure	753.1 mmHg
Mass of the flask and foil	80.268 g
Mass of the flask, foil, and condensed liquid	80.615 g
Volume of flask	137.5 ml
Temperature of water bath	99.4°C
Mass of condensed liquid	
Molar mass	

6. If the actual molar mass (accepted value) is 78.3 g/mole, what is the percent error? Use the equation shown below to calculate percent error.

$$\text{Percent error} = \frac{|\text{Accepted value} - \text{Experimental value}|}{\text{Accepted value}} \times 100$$

7. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

Part 1: Preparation of the alcohol

1. Quickly weigh out approximately 4–5 g of 3 Å of molecular sieves into a small vial. Immediately screw the cap back on the vial. *Hint*: Keep the molecular sieves sealed and in a desiccator except when weighing.
2. Measure approximately 8 ml of your ethanol sample into a 10 ml graduated cylinder. Pour it into the small vial containing the molecular sieves. ***Caution:*** Do not drink! Ethanol used in the lab has poisonous stabilizers added. Ethanol is also flammable. Keep it away from flames or exposed wiring.
3. Immediately replace the cap on the vial, and swirl the solution for a few minutes. Let it sit to dry for at least 30 minutes, swirling every few minutes.

Part 2: Experiment

1. While your sample is drying, obtain the barometric pressure and convert it to atmospheres.
2. Bend a 60 mm × 60 mm square of aluminum foil tightly over the top of a 125 ml Erlenmeyer flask. Secure the foil top with a rubber band. Trim the foil closely around the rubber band.
3. Make a pinprick in the center of the foil covering the Erlenmeyer flask. Remove the rubber band.
4. Weigh and record the mass of the 125 ml Erlenmeyer flask with the foil top and pinprick. Carefully remove the foil so as not to tear it and set it aside to use later.
5. After your sample is dry, decant 2 ml of it into a dry 10 ml graduated cylinder. Pour this into the Erlenmeyer flask.
6. Replace the foil top and secure it with the rubber band.
7. Clamp the flask inside a 600 ml beaker filled two-thirds of the way with water. The foil top should be 2 cm above the waterline. The beaker should be sitting on a hot plate, as shown in Figure 4.1.
8. Insert a thermometer in the water bath.
9. Bring the water to a boil and carefully watch until there is no liquid left in the bottom of the flask.
10. As soon as there is no liquid left in the bottom of the flask, immediately record the temperature and remove the flask from the hot water bath. Allow the flask to come to room temperature to condense the vapor.
11. Wipe the flask with a paper towel until it is thoroughly dry. Remove the rubber band and lift up the edges of the foil to ensure no water has condensed under it; if so, wipe it away. Make sure all water is off the flask and foil.

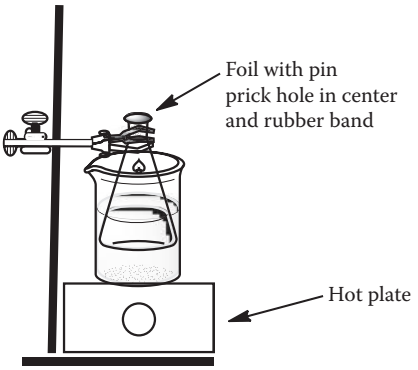


Figure 4.1 Apparatus.

12. Weigh the flask, foil, and condensed liquid and record the mass.
13. Calculate the mass of the condensed liquid and record it.
14. Add another 2 ml of your dry ethanol and repeat the process for another trial.
15. After the second trial is repeated, pour the condensed ethanol into a designated bottle so that it can be reclaimed.
16. Determine the volume of the ethanol vapor by first filling the 125 ml flask with water to the brim. Measure the volume of the water using a 100 ml graduated cylinder. Record the volume.
17. Calculate the molar mass of the ethanol sample using Equation 4.2.
18. Determine your percent error.
19. Decant any leftover ethanol sample into a designated bottle that can be reclaimed. Place the remaining molecular sieves in a designated container located in a hood. They can be dried and reused.

Name _____

Data

Table 4.1 Data for Part 2

	Trial 1	Trial 2
Barometric pressure		
Mass of flask and foil		
Mass of flask, foil, and condensed liquid (step 12)		
Mass of condensed liquid		
Volume of flask		
Temperature of water bath		
Molar mass		

Observations

Calculations

Trial 1 molar mass:

Trial 2 molar mass:

Average molar mass of sample:

Molar mass of ethanol:

Percent error:

Analysis

1. How does the experimental molar mass calculated compare to the expected molar mass of ethanol?

2. If water condensed under the foil on the flask and was not wiped off before weighing, how would the molar mass differ? Why?

3. If the flask were left on the heat after all the liquid had vaporized, how would the molar mass differ?

4. If the flask were taken off before the liquid had vaporized, how would the molar mass differ?

Think green

1. What if your sample was a 95% ethanol/water solution and not all of the water was removed? How would the molar mass differ if some water was still in the ethanol? If there is time, try doing the experiment with a 95% ethanol/water solution and see if you are correct. Discuss your results.
2. Based on the 12 principles of green chemistry, discuss the reasons ethanol was considered a better gasoline additive than MTBE and MTBE was considered to be better than tetraethyl lead.
3. Look up molecular sieves and find some of their uses. What size molecule do different sizes of molecular sieves remove? How would using 5 Å molecular sieves affect your results?

Presidential green chemistry challenge

In this lab you used molecular sieves to purify ethanol. The Environmental Protection Agency (EPA) gave its 2011 Presidential Green Chemistry Award in the Greener Reaction Conditions category to Krafton Performance Polymers, Inc. for an innovative method to purify water. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about this technology and how it utilizes principles of green chemistry.

chapter five

Determining molar volume of a gas at standard temperature and pressure

Why is the air in a hot air balloon heated in order for the balloon to rise?

To answer this question, one must understand the molar volume of a gas. Molar volume is the amount a substance can occupy given 1 mole of the substance. Solids are the easiest to measure, because they do not change shape. Liquids can be measured by observing how much they can fill when poured into a container. However, the molar volume of a gas is more difficult due to the free-flowing nature of gas molecules. The molar volume of a gas can be determined using the ideal gas law. This equation was first introduced by Emile Clapeyron, and despite the fact that most gases are real and not ideal. It can simply be used for almost every gas given the right conditions. The equation for the ideal gas law equation is

$$PV = nRT \tag{5.1}$$

As seen, the molar volume is dependent on the pressure (P), volume (V), and temperature (T). R is also known as the universal gas constant, which is $0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$, and n is the number of moles of the gas being used. Through this it is easy to determine a gas's volume at standard temperature and pressure (STP). Standard temperature and pressure are 0°C (273 K) and 1 atm (760 mmHg). When the equation is solved for the volume of 1 mole of gas at standard temperature and pressure, it is determined that it will occupy 22.4 L. This means that any gas will occupy the same amount of space given the same amount of molecules, the same pressure, and the same temperature.

In this experiment you will determine a gas's volume at standard temperature and pressure and attempt to reach 22.4 L. However, since this experiment is not run at the standard temperature and pressure, another equation that is built off of the ideal gas law must be used. The combined

gas law is where the pressures and volumes of different gases can be used to calculate the molar volume of those gases. The general equation is

$$\frac{P_1 \cdot V_1}{T_1} = \frac{P_2 \cdot V_2}{T_2} \tag{5.2}$$

The combined gas law lets us answer the original question of why the air is heated in a hot air balloon. A hot air balloon can stretch so the pressure remains constant. When it is heated, the volume increases and the air becomes less dense than the air outside it. This provides the lift.

This experiment first uses 5% acetic acid found in vinegar and mixes it with sodium bicarbonate. The reaction first forms carbonic acid, which decomposes into carbon dioxide and water. The abbreviated balanced reaction equation can be written as follows:

$$NaHCO_{3(s)} + CH_3COOH_{(aq)} \rightarrow CO_{2(g)} + H_2O_{(l)} + CH_3COO^-Na^+_{(aq)}$$

Notice that 1 mole of sodium bicarbonate reacts to form 1 mole of CO_2. Knowing this is necessary for the calculation to determine the molar volume of CO_2 at STP, you will also react acetic acid with calcium carbonate and determine the molar volume of CO_2 at STP and compare the results.

Calcium carbonate has many uses and is found naturally in such things as limestone, marble, eggshells, and marine shells. Unpolluted rain is naturally weakly acidic, and over time it will react with calcium carbonate to create a natural buffering system. Acetic acid is a weak acid, which means it will react more slowly than a strong acid. Acid rain contains a dilution of strong acids, which react more quickly with calcium carbonate. Green chemistry addresses acid rain by seeking ways to prevent it through developing processes that reduce or eliminate the creation of gaseous waste that will eventually cause acid rain. This is not the same as seeking ways to deal with it after it is created.

In this lab you will combine the reactants and use the gas produced to force water into a measurement container. The amount of liquid displaced is the volume of gas obtained. Through using this you will solve for V_2 in Equation 5.1 to obtain the volume of CO_2 corrected to STP. To keep track of the variables more easily, the equation can be rewritten as shown in Equation 5.2:

$$V_{STP} = \frac{P_{CO_2} V_{H_2O} T_{STP}}{T_{H_2O} P_{STP}} \tag{5.3}$$

where P_{CO_2} is the pressure of the CO_2, V_{H_2O} is the volume of water displaced, T_{STP} is the standard temperature of 273 K, T_{H_2O} is the temperature of the water, P_{STP} is standard pressure of 1 atm, and P_{CO_2} is the atmospheric

Table 5.1 Water Vapor Pressure at Different Temperatures

Temperature °C	Pressure mmHg	Temperature °C	Pressure mmHg	Temperature °C	Pressure mmHg
15.0	12.8	20.0	17.5	25.0	23.8
16.0	13.6	21.0	18.6	26.0	25.2
17.0	14.5	22.0	19.8	27.0	26.7
18.0	15.5	23.0	21.0	28.0	28.3
19.0	16.5	24.0	22.4	29.0	30.0

pressure minus the pressure of the water the CO_2 is pushing against. It is found using the equation

$$P_{CO_2} = P_{atm} - P_{H_2O} \tag{5.4}$$

The pressure of the water vapor is related to temperature, as shown in Table 5.1, and must be converted to atm by using the conversion factor $\frac{1 \text{ atm}}{760 \text{ mmHg}}$.

Example

An experiment was performed using 0.999 g of sodium carbonate and an excess of acetic acid. The atmospheric pressure was 0.9987 atm and the water temperature was 22.0°C. The volume of CO_2 acquired was 230.0 ml.

To determine the molar volume of the gas, first calculate the pressure of the CO_2 in atm, the temperatures in K, and the volume in L:

$$P_{CO_2} = P_{atm} - P_{H_2O}$$

$$P_{CO_2} = 0.9987 \text{ atm} - 19.8 \text{ mmHg} \cdot \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.9726 \text{ atm}$$

$$T_{H_2O} = 22.0 + 273 = 295.0 \text{ K}$$

$$V_{H_2O} = 230.0 \text{ mL} \cdot \frac{1\text{L}}{1000 \text{ mL}} = 0.2300 \text{ L}$$

The volume of CO_2 corrected to STP can be calculated as shown:

$$V_{STP} = \frac{(0.9726 \text{ atm})(0.2300 \text{ L})(273 \text{ K})}{(295.0 \text{ K})(1 \text{ atm})}$$

$$V_{STP} = 0.207 \text{ L}$$

Next, use the number of moles of your solute to calculate the number of moles of CO_2 that should have been produced. This requires determining the balanced reaction equation:

$$Na_2CO_{3(s)} + 2CH_3COOH_{(l)} \rightarrow 2CH_3COO^-Na^+_{(aq)} + H_2O_{(l)} + CO_{2(g)}$$

$$\text{Moles } CO_2 = 0.999 \text{ g } Na_2CO_3 \cdot \frac{1 \text{ mol } Na_2CO_3}{105.988 \text{ g } Na_2CO_3} \cdot \frac{1 \text{ mol } CO_2}{1 \text{ mol } Na_2CO_3}$$

$$\text{Moles } CO_2 = 0.00943 \text{ moles}$$

Finally, determine the volume for 1 mole of CO_2 at STP:

$$\text{Molar volume} = \frac{V_{STP}}{\text{mol } CO_2} = \frac{0.2070 \text{ L}}{0.00943 \text{ moles}}$$

$$= 22.0 \text{ L/mol}$$

Then, calculate your percent error:

$$\% \text{ error} = \frac{|\text{theoretical value} - \text{experiment value}|}{\text{theoretical value}} \times 100$$

$$\% \text{ error} = \frac{|22.4 - 22.0|}{22.4} \times 100 = 1.79\%$$

Objective

Determine the molar volume of CO_2 gas using the standard temperature pressure and the ideal gas law.

Name _____

Prelab questions

1. Define the combined gas law and its variables.

2. What is standard temperature and pressure?

3. Give two assumptions when using the ideal gas equation that are not true for real gases.

4. Write the reaction equation for the reaction that occurs when acetic acid is added to calcium carbonate.

5. How will vapor pressure play a role in this lab experiment due to the fact that we are using water?

6. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

1. Assemble an apparatus as shown in Figure 5.1. First obtain a single-holed rubber stopper with glass tubing centered in the stopper. The glass tubing should extend approximately 1 inch above and below the stopper. Place it in the mouth of a 125 ml Erlenmeyer flask. Ensure there is a very snug fit between the tubing and the rubber stopper.
2. Fill a 500 ml Erlenmeyer flask to the 450 ml mark with deionized (DI) water, and secure it to a ring stand with either a ring or clamp. Place a double-holed stopper with glass tubing in each hole into the 500 ml Erlenmeyer flask. Let one piece of glass tubing extend nearly to the bottom of the flask and the other extend a small amount past the rubber stopper. Make sure the shorter piece does not touch the water in the Erlenmeyer flask.
3. Place a piece of latex (or Tygon) tubing that is approximately 30 cm long on each of the glass tubes coming out from the top of the rubber stopper in the 500 ml Erlenmeyer flask.
4. Connect the side with the shorter glass tubing to the glass tubing coming out of the top of the 125 ml Erlenmeyer flask.
5. Place a glass tube on the end of the latex tube that is connected to the longer glass tube and clamp it so that water coming through it will run into a 400 ml beaker. Make sure all connections have a very snug fit.
6. Obtain 0.5 g of sodium bicarbonate on a piece of weighing paper. Record the exact mass in Table 5.2.

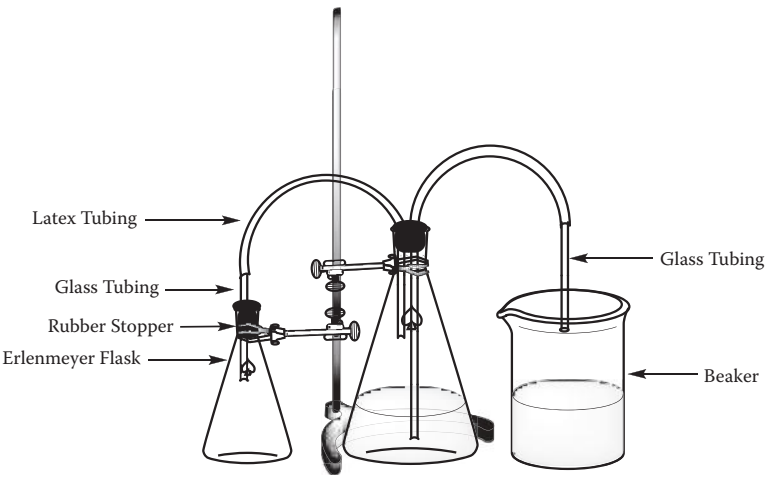


Figure 5.1 Apparatus.

7. Obtain 15.0 ml of 5% acetic acid (or white vinegar), and place into the 125 ml Erlenmeyer flask.
8. Initiate the reaction by quickly adding sodium bicarbonate into the flask containing acetic acid, and immediately place the stopper securely in the mouth of the flask.
9. Gently swirl the flask until no more water is transferred into the 400 ml beaker. If water does not start flowing into the beaker almost immediately, check for leaks and restart the experiment.
10. Determine the barometric pressure and the temperature of the water.
11. Use a 100 ml graduated cylinder to measure the amount of water that was displaced into the 400 ml beaker.
12. Determine how much additional water there was from where the 450 ml of water in the 500 ml Erlenmeyer flask comes up in the glass tube to where it runs into the 400 ml beaker. Use a wash bottle to fill this area with water and then measure the amount using a small graduated cylinder. Add this amount to the amount of water displaced into the 400 ml beaker.
13. Record the total amount of water displaced in Table 5.2.
14. Perform a second trial using the same procedure.
15. Replacing the sodium bicarbonate with calcium carbonate, repeat the experiment. Complete two trials with calcium carbonate.
16. Use your data to calculate the V_{STP}, the theoretical number of moles of CO_2, the volume for 1 mole of CO_2 at STP, and the percent error.

Name _____

Data

Barometric pressure: _____

Table 5.2 Summary of Data and Final Values

Trial	Grams used	mL H_2O displaced (including amount in tubing)	Water temperature K	Molar volume	% Error
Trial 1 $NaHCO_3$					
Trial 2 $NaHCO_3$					
Trial 3 $CaCO_3$					
Trial 4 $CaCO_3$					

Average molar volume for $NaHCO_3$: _____

Average % error for $NaHCO_3$: _____

Average molar volume for $CaCO_3$: _____

Average % error for $CaCO_3$: _____

Observations

Calculations

Trial 1—Sodium bicarbonate

Trial 2—Sodium bicarbonate

Trial 3—Calcium carbonate

Trial 4—Calcium carbonate

Analysis

1. What is the experimental volume/mole calculated based on the experimental data for sodium bicarbonate and calcium carbonate, and how does this compare to the theoretical value?

2. Do you consider your percent error acceptable? List two sources of error in your experiment, what they affected, and explain how they could have been eliminated or diminished.

Think green

1. Hydrochloric acid is commonly used in this experiment. Rewrite the reaction equations using HCl as the acid. Which one of the acids, acetic acid or HCl, do you consider to be more green? Explain your answer considering the 12 principles of green chemistry.
2. The reaction you studied when using calcium carbonate illustrates the effects of acid rain. Research acid rain and discover several negative effects it has on the environment. Identify an industry that has modified its process to reduce the acidity of its emissions. Discuss how it accomplished the reduction addressing principles of green chemistry.

Presidential green chemistry challenge

The reaction you did emits CO_2, a greenhouse gas. The Environmental Protection Agency (EPA) gave its 2012 Presidential Green Chemistry Award to Professor Geoffrey W. Coates in the Academic category for developing catalysts that make biodegradable polymers from CO_2 and CO. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about this technology and how it utilizes principles of green chemistry.

chapter six

Determining the enthalpy change for solvation reactions

> Have you ever twisted your ankle? If you have, you probably put ice on it, or if ice wasn't available, an instant cold pack. In that moment you probably didn't wonder how that cold pack worked, but it has to be some extremely complicated reaction, right? Wrong! Cold packs typically use ammonium nitrate dissolving in water to produce a very cold solution.

Calorimetry studies the amount of heat that flows through a physical or chemical change into its surroundings. What occurs in an ammonium nitrate cold pack illustrates two examples of where a study in the area of calorimetry is relevant. In the first example, a calorimeter is used to measure the heat flow for the process of the solvation reaction of ammonium nitrate and water. The second example involves the specific heat of water.

A reaction's *enthalpy* refers to how much heat a reaction gives off or absorbs if the reaction occurs under constant pressure. Most reactions that you will do in a lab will occur at constant pressure. So typically, you can just say that enthalpy is equal to the heat of the reaction. The formula for the enthalpy of a reaction is shown in Equation 6.1:

$$\Delta H_{sol} = -mc\Delta T \tag{6.1}$$

In Equation 6.1, ΔH is the enthalpy of the reaction, m is the mass of water that is absorbing the heat, c is the specific heat of water, and ΔT is the change in temperature of the water (final temperature – initial temperature).

There are two types of enthalpy reactions: one that releases heat into the environment is referred to as an *exothermic* reaction, while a reaction that absorbs heat from its surroundings is called an *endothermic* reaction.

An example of an exothermic reaction is iron reacting with oxygen to form ferric oxide, more commonly referred to as rust. The formation reaction is shown below:

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3$$

The standard enthalpy for formation of 1 mole of rust, Fe_2O_3, is –824.2 kJ/mole; so, the reaction above releases 1648.4 kJ of heat! The enthalpy value is negative because ΔT is a positive number, making the overall equation negative.

The reaction of ammonium nitrate and water that occurs in a cold pack is a good example of an endothermic solvation reaction:

$$NH_4NO_{3(s)} + H_2O_{(l)} \rightarrow NH^+_{4(aq)} + NO^-_{3(aq)} + H_2O_{(l)}$$

The above reaction absorbs 25.69 kJ of heat for every 1 mole of ammonium nitrate that dissolves in water. This is why a cold pack feels cold—it absorbs heat from the surroundings. Since the ΔT, or change in temperature, is negative, the enthalpy will be a positive number.

A calorimeter is used to measure the heat flow for a process such as the solvation reaction of ammonium nitrate and water. It insulates the heat exchange that is occurring so that only heat exchanged in the process occurring within the calorimeter is measured. Precision calorimeters are used when very exact measurements are required. However, in this lab, you will use a very simple calorimeter composed of two Styrofoam cups nested together. Obviously, some heat will exchange with the Styrofoam cups, but it will be minimal.

Example 1

A student dissolved 8.014 g of NH_4NO_3 in 100.012 g of water in a calorimeter. The temperature changed from 20.9 to 15.2°C. Calculate the enthalpy of solution the student experimentally found in kJ/mole of NH_4NO_3.

$\Delta H_{sol} = -mc\Delta T$

$\Delta T = T_f - T_i = 15.2°C - 20.9°C = -5.7°C$

kJ heat = –(100.012 g H_2O)(4.186 J/g°C)(–5.7°C)(1 kJ/1000 J) = 2.39 kJ

(8.014 g NH_4NO_3)(1 mole NH_4NO_3/80.052 g) = 0.1001 mole NH_4NO_3

ΔH_{sol} = 2.39 kJ/0.1001 mole = 23.8 kJ/mole

Water stays cold a long time, which makes it an excellent choice as a solvent for a cold pack or compress. This is related to a physical property of matter called specific heat. Specific heat is the amount of energy required to raise the temperature of 1 g of a substance by 1°C. Water has a high specific heat value, so it stays colder longer. Since specific heat is a physical property, it can be used to help determine the identity of a substance.

A calorimeter is also used to determine the specific heat of a substance since measuring heat flow is involved.

Fishing sinkers (weights) have traditionally been made of lead since it is dense, fairly easy to cast into the desired shapes, relatively inexpensive, and corrosion resistant. However, concerns over lead poisoning have caused lead-based sinkers to be banned in many places. This relates to the first principle of green chemistry: *prevention*. The need for a greener replacement has initiated the use of various different substances. Steel and different tungsten alloys are common replacements. Neither of these is considered ideal since steel is considerably less dense than lead and tungsten is considerably more expensive, so greener fishing sinkers are still being developed.

Density and specific heat are physical properties that can be used to help identify a metal and determine its purity. In this lab you will use these physical properties to determine whether a green fishing sinker is made from steel or tungsten. Density can be found by obtaining the mass of the fishing sinker and then placing it in water in a graduated cylinder and determining how many milliliters of water are displaced. Dividing the mass by the milliliters of displaced water will equal the object's density.

You will also determine the sinker's specific heat. This is determined by first obtaining its mass, and heating it to a known temperature. The heated sinker is immediately placed in a calorimeter containing a known quantity of water at a predetermined temperature. Heat will flow from the metal to the water until the temperature of the metal and the water is the same. This means the quantity of heat (q) the metal loses must equal the quantity of heat the water gained.

Example 2

A student heated 30.318 g of fishing sinkers to 95.5°C and immediately transferred them into a calorimeter containing 25.023 g of deionized (DI) water whose temperature was 20.5°C. The temperature of the metal and the water reached equilibrium at 23.2°C. Calculate the specific heat of the fishing sinker's metal (s). Use 4.184 J/g°C as the specific heat for water.

$$q = \text{specific heat} \times \text{mass} \times (T_{final} - T_{initial})$$

$$q\text{H}_2\text{O} = -q_{metal}$$

$$\begin{aligned}(4.184\ \text{J/g°C}) \cdot (25.023\ \text{g}) \cdot (23.2\text{°C} - 20.5\text{°C}) \\ = -(S_{metal}) \cdot (30.318\ \text{g}) \cdot (23.2\text{°C} - 95.5\text{°C})\end{aligned}$$

$$s_{metal} = 0.129\ \text{J/g°C}$$

Objective

In this lab, you will use a calorimeter to determine the enthalpy of solvation (ΔH_{sol}) of potassium chloride and determine how much water a sample of calcium chloride contains. You will also use density and specific heat to identify what metal was used to make a greener fishing sinker.

Name _____

Prelab questions

1. Define the variables from the formula $\Delta H_{sol} = -mc\Delta T$:

   ΔH_{sol}:

   c:

   m:

   ΔT:

2. In Part 1 of this lab you will use 0.025 moles of KCl per trial. Calculate how many grams of KCl you will need to obtain for each trial.

3. In Parts 1 and 2 you will need to obtain approximately 15 g of DI water. Water's density at 20°C is 0.9982 $\frac{\text{g}}{\text{mL}}$. Approximately how many milliliters of water will you need to measure out?

4. In Part 2 of this lab you will use 0.0100 mole of $CaCl_2$ per trial. Calculate how many grams of $CaCl_2$ you will need to obtain per trial if you assume the $CaCl_2$ is anhydrous.

5. $CaCl_2$ is hygroscopic. What does this mean and how will you have to handle the $CaCl_2$ because of this?

6. A student dissolved 4.026 g of NaOH in 100.302 g of water. The temperature changed from 20.2 to 30.5°C. Calculate the enthalpy of solution the student experimentally found in kJ/mole of NH_4NO_3. Is this an endothermic or an exothermic reaction?

7. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

Part 1: Finding ΔH_{sol} of potassium chloride

1. Weigh two dry, clean Styrofoam cups that are nested together, and record the exact mass in Table 6.1.
2. Add approximately 15 g DI water to the cups. (Use your calculations from the prelab section.) Record the exact mass of the Styrofoam cups with the DI water in Table 6.1.
3. Weigh out approximately 0.025 mole of KCl into a clean, dry, preweighed 50 ml beaker. (Use your calculations from the prelab section.) Record the exact mass in Table 6.1.
4. Assemble the calorimeter apparatus as shown in Figure 6.1 by clamping a thermometer in a wedged stopper to a ring stand and placing it inside the nested Styrofoam cups. A lid may also be provided. (If an electronic thermometer is used, it can be used to stir instead of a stir rod.) Wait for the temperature to stabilize and record the initial temperature in Table 6.1 to the 0.1°C.
5. Add all of the KCl into the calorimeter, and stir the mixture continually. Tilt the cup slightly if needed to get the thermometer bulb fully immersed in the liquid.
6. Continue to monitor the temperature until a minimum temperature is reached and the temperature has started to definitely increase. Record the minimum temperature obtained to the 0.1°C.
7. Calculate ΔH_{sol} in kJ/mole KCl using the formula $\Delta H_{sol} = -mc\Delta T$.
8. Perform one additional trial, average the kJ/mole KCl values, and compare your experimental value to the literature value of 17.22 kJ/mole. Determine percent error.

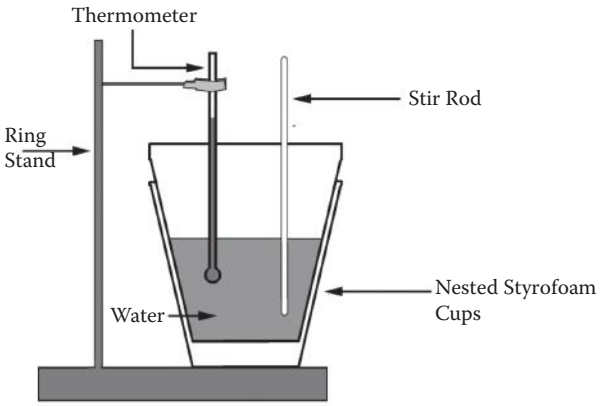


Figure 6.1 Apparatus setup.

Part 2: Finding mass and percent of water in $CaCl_2 \cdot xH_2O$

1. Weigh two clean, dry, nested Styrofoam cups and record the mass in grams in Table 6.2. Add approximately 15 g of DI water to the cups and record the exact mass of the nested Styrofoam cups with the water.
2. Assemble the calorimeter apparatus the same as you did for Part 1. Wait for the temperature to stabilize and record the initial temperature in the data table.
3. In a clean, dry, preweighed small beaker, weigh out approximately 0.010 mole of $CaCl_2 \cdot xH_2O$. (Use your calculations from the prelab section.) Record the exact mass, and cover with a watch glass, in Table 6.2. *Hint*: Perform your measurements quickly for more accurate results.
4. Immediately add the $CaCl_2 \cdot xH_2O$ into the calorimeter, and stir the mixture continually. Tilt the cup slightly if needed to get the thermometer bulb fully immersed in the liquid.
5. Continue to monitor the temperature until a maximum temperature is reached and the temperature has started to definitely decrease. Record the maximum temperature obtained to the 0.1°C.
6. Using the literature value of ΔH_{sol}, –81.3 kJ/mole, and the formula $\Delta H_{sol} = -mc\Delta T$, find the mass of anhydrous $CaCl_2$ present in the drying agent.
7. Calculate the percent of $CaCl_2$ in the sample of $CaCl_2 \cdot xH_2O$.
8. Perform one additional trial and calculate the average percent of $CaCl_2$ in the sample of $CaCl_2 \cdot xH_2O$, as well as the average percent of water in the sample.

Part 3: Finding density and specific heat for fishing sinkers

1. Make a hot water bath by adding approximately 300 ml DI water into a 400 ml beaker and placing it on a hot plate. Heat the water to boiling.
2. While the water bath is heating, weigh at least 20 g of your unknown sample of fishing sinkers and record the exact mass.
3. Place 4 ml water into a 10 ml graduated cylinder. Determine and record the exact volume of water in Table 6.3.
4. Tilt the graduated cylinder almost horizontally and carefully place the sinkers into the graduated cylinder. Slowly tilt the graduated cylinder back up so the sinkers will gradually slide down. If any water splashes out, you will need to start over again after drying your sinkers with a paper towel. Determine and record in Table 6.3 the exact volume the water and sinkers come up to in the graduated cylinder.
5. Remove the sinkers from the graduated cylinder and completely dry them with a paper towel.

6. Place the sinkers in a medium test tube by tilting the test tube and letting them slide down. Use a test tube holder to place the test tube with the sinkers into the hot water bath. ***Caution:*** The water bath is hot! Heat the water for at least 10 minutes after it begins to boil again to ensure the sinkers are the same temperature as the hot water.
7. While the water is heating, weigh two dry, clean Styrofoam cups that are nested together, and record the exact mass in Table 6.3.
8. Add approximately 25 g DI water to the Styrofoam cups. Record the exact mass of the Styrofoam cups with the DI water in Table 6.3.
9. Assemble the calorimeter apparatus the same as you did for Part 1. Wait for temperature to stabilize and record the initial temperature in the data table to the 0.1°C.
10. After the water in the hot water bath has boiled at least 10 minutes, ascertain the initial metal temperature by determining the temperature of the hot water bath to the 0.1°C.
11. Use a test tube holder to remove the test tube containing the sinkers. Carefully and quickly pour the sinkers into the calorimeter. ***Caution:*** The water bath and sinkers are hot! Make sure no water on the outside of the test tube drips into the calorimeter or that any water splashes out of the calorimeter. Turn off the hot plate and let the water in the beaker cool before touching.
12. Stir the mixture in the calorimeter until you have determined the maximum temperature reached. Record the maximum temperature in Table 6.3 to the 0.1°C.
13. Calculate the density and the specific heat for the fishing sinkers. Determine if the sinkers you tested were made from tungsten or steel. Tungsten has a density of 19.35 g/ml at 20°C and a specific heat of 0.133 J/g°C. Steel's density and specific heat vary depending on the type. Its density is usually close to 7.85 g/ml, and its specific heat is close to 0.452 J/g°C.

Name _____

Data

Part 1: Finding ΔH_{sol} of potassium chloride

Table 6.1 Data for Finding Enthalpy of KCl

Trial number	Trial 1	Trial 2
Mass of cups (g)		
Mass of cups + water (g)		
Mass of water (g)		
Mass of KCl beaker (g)		
Mass of KCl + beaker (g)		
Mass of KCl (g)		
Moles of KCl		
Initial temperature (°C)		
Minimum temperature (°C)		
kJ heat		
ΔH_{sol}		
Average ΔH_{sol}		
% error		

Part 2: Finding mass and percent of water in $CaCl_2 \cdot xH_2O$

Table 6.2 Data for Finding Amount of Water in $CaCl_2 \cdot xH_2O$

Trial number	Trial 1	Trial 2
Mass of cups (g)		
Mass of cups + water (g)		
Mass of water (g)		
Mass of beaker (g)		
Mass of $CaCl_2$ + beaker (g)		
Mass of $CaCl_2 \cdot xH_2O$ (g)		
Initial temperature (°C)		
Maximum temperature (°C)		
Mass of $CaCl_2$ (g)		
% $CaCl_2$ in $CaCl_2 \cdot xH_2O$		
Average % $CaCl_2$ in $CaCl_2 \cdot xH_2O$		
Average % of water in sample		

Part 3: Finding density and specific heat for fishing sinkers

Unknown number: _____

Table 6.3 Data for Finding Density and Specific Heat for Fishing Sinkers

	Trial 1	Trial 2 (optional)
Mass of sinkers (g)		
Water reading without sinkers (ml)		
Water reading with sinkers (ml)		
Water displaced (ml)		
Density of sinkers (g/ml)		
Mass of cups (g)		
Mass of cups + water (g)		
Mass of water (g)		
Initial water temperature in calorimeter (°C)		
Final water temperature in calorimeter (°C)		
Hot water bath temperature (°C)		
Specific heat of the sinker		
Metal used to make sinker		

Observations

Part 1: Finding ΔH_{sol} of potassium chloride

Part 2: Finding mass and percent of water in $CaCl_2 \cdot xH_2O$

Part 3: Finding density and specific heat for fishing sinkers

Calculations

Part 1: Finding ΔH_{sol} of potassium chloride

Calculations for ΔH_{sol}:

Trial 1:

Trial 2:

Average and percent error calculations:

Part 2: Finding mass and percent of water in $CaCl_2 \cdot xH_2O$

Calculations for % $CaCl_2$ and % H_2O in sample:

Trial 1:

Trial 2:

Average % $CaCl_2$ and % H_2O:

Part 3: Finding density and specific heat for fishing sinkers

Density of fishing sinkers:

Specific heat of fishing sinkers:

Analysis

1. Evaluate the percent error in Part 1. If the percent error is high, what do you think could have caused this? What could be done to improve the percent error?

2. Based on the average percent H_2O you found in Part 2, how many moles of water and how many moles of $CaCl_2$ would be in a 10.000 g sample?

3. The *x* in $CaCl_2 \cdot xH_2O$ is frequently seen as 1, 2, 4, or 6. Which one is closest to what you found? How do you explain why it is not exactly one of these?

4. How would your results differ if the lid had been left off of the calcium chloride bottle for an hour before the experiment? Why?

Think green

1. Ammonium nitrate is often used for this experiment instead of potassium chloride to demonstrate an endothermic reaction. Look up the (material) safety data sheet ((M)SDS) for both compounds. In terms of green chemistry, discuss the advantages of using potassium chloride instead of ammonium nitrate in this experiment. Determine which of the 12 principles of green chemistry would be negatively impacted by conducting this experiment with ammonium nitrate.
2. The reaction between NaOH and HCl is often used for this experiment instead of calcium chloride and water to demonstrate an exothermic reaction. Determine which of the 12 principles of green chemistry would be negatively impacted by changing to reacting NaOH and HCl, and discuss the reasons for your answer.
3. Reactions used by industry are often exothermic and can increase cooling water temperature. Industries must cool this water before releasing it into streams. Research the effects of releasing water that is a by-product of an exothermic reaction into a stream, paying close attention to how this can affect the aquatic environment.

Presidential green chemistry challenge

In this lab you identified the metal used to make a greener fishing sinker that was developed to replace the traditional lead fishing sinkers. The Environmental Protection Agency (EPA) gave its 2004 Presidential Green Chemistry Award in the Designing Greener Chemicals category to Engelhard Corporation for developing greener pigments to replace its heavy metal-based pigments. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about how this technology utilizes principles of green chemistry.

chapter seven

Spectroscopic determination of food dye in popsicles

> How would you like to eat foods that were dyed with chemicals containing heavy metals like lead and mercury?

Coloring food to make it look more appealing has been around for many centuries. In the past, very toxic chemicals were used at times that sometimes even caused death. Today, food dye is regulated worldwide to prevent toxic food dyes from being used. Food dyes can be synthetically produced or naturally derived. Synthetic food dyes are usually derived from petroleum and are less expensive, easily blended, do not add flavor, and have superior coloring properties. However, some have been associated with health concerns, which has prompted food companies to search for more natural options. For example, because of sensitivities, FD&C Red 40, shown in Figure 7.1, must be clearly indicated on the label as an ingredient.

One of the more popular natural replacements for FD&C Red 40 is carmine, which is extracted from cochineal insects. Unfortunately, it is also known to cause severe allergic reactions. Much research is being done to develop greener natural food colorants that are not only safer, but also stable to heat, light, and pH changes.

Food companies want their food to have consistent color. To do this, they have to be able to quantify how much food dye is present. One method used is UV-visible spectroscopy. Spectroscopic methods rely on the ability of substances to absorb electromagnetic radiation. UV-visible spectroscopy uses the energy, or light, in the UV and visible ranges of the electromagnetic spectrum. This energy is sufficient to promote an electron from a ground electronic state to a higher energy excited electronic state. Only certain wavelengths of light will be absorbed by the electrons in a substance.

To find out how much of a particular substance is in a sample, a spectrum must first be obtained to determine which wavelengths are absorbed. The amount of light absorbed by the sample at different wavelengths is measured by comparing the intensity of the light emitted from the light source to the intensity of the light that emerges from the sample. To do this, focused UV or visible light is shone through a cuvette containing

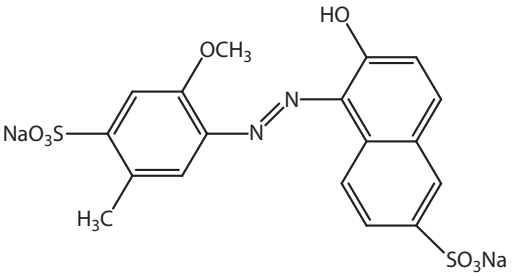


Figure 7.1 Chemical structure for FD&C Red 40 food dye.

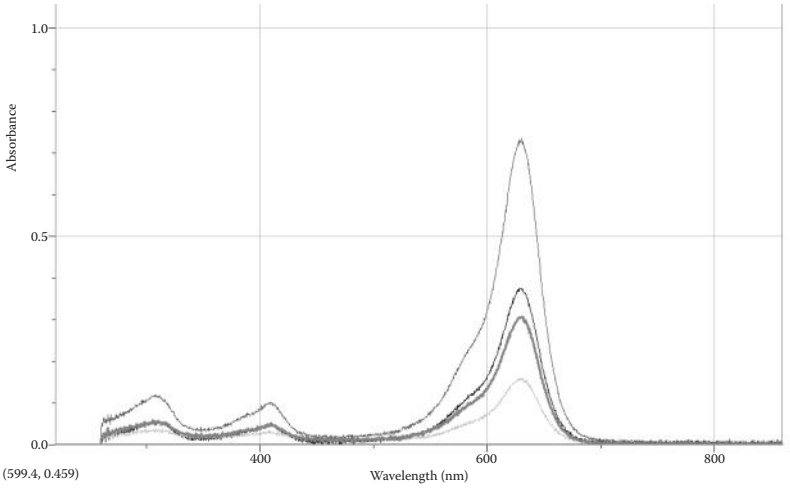


Figure 7.2 FD&C Blue 1 spectrum.

a dilute liquid sample. A prism or diffraction grating separates the different wavelengths of light so a detector can more accurately determine which wavelengths of light have been absorbed. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm. The wavelengths at which absorption occurs and the amount of absorption at each wavelength are recorded. The resulting spectrum is presented as a graph of absorbance (*A*) versus wavelength. An example of the spectrum for FD&C Blue 1 overlaid at different concentrations is shown in Figure 7.2.

From a substance's spectrum a wavelength is chosen to use for quantitation. Often this is the tallest peak, called the λ_{max}, or is close to it, but other wavelengths may be preferred. The wavelength chosen must be where the substance of interest absorbs without a lot of noise or interferences from other components present in the sample of interest.

After the wavelength is chosen, absorbances of progressively more concentrated standard solutions are determined at that wavelength. As the color increases, or becomes more intense, less light is able to reach the detector. Absorbance measurements are found by comparing the amount of light that enters the sample to the amount of light that exits the sample. A sample's concentration is directly related to the absorbance (A). The equation used for this is known as Beer's law, and is shown in Equation 7.1:

$$A = \varepsilon bc \tag{7.1}$$

where ε is the molar absorptivity, b is the path length through the sample, and c is the concentration.

Molar absorptivity is a physical constant characteristic for a particular substance and relates the amount of light a particular substance will absorb per unit of concentration. Different molecules do not absorb light equally. Molar absorptivities may be very large for strongly absorbing chromophores and very small if absorption is weak. A chromophore is the section in a molecule that absorbs or reflects light and determines the color.

To determine the amount of a substance present in a solution, a calibration curve must first be made by graphing the absorbance of the standards versus concentration. If the curve follows Beer's law, it is linear and a trendline equation is generated. A standard curve is shown in Figure 7.3 for FD&C Blue 1 at a wavelength of 630.3 nm.

Most graphs will follow Beer's law for lower concentrations. Usually due to various factors, the line will start to curve at higher concentrations, making it no longer valid to use for quantitation at higher concentrations. Standards are chosen that have concentrations low enough to fall within the linear range. The solution that is to be analyzed should have an absorbance value that falls within the absorbance range measured for

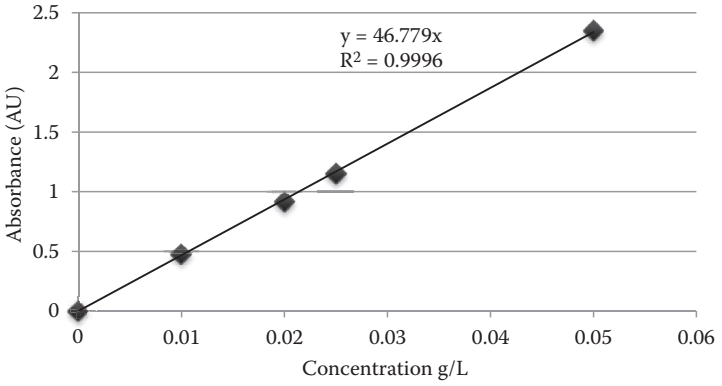


Figure 7.3 Calibration curve example.

the standard solutions. If a sample's absorbance value does not fall within this range, it is diluted to ensure it will fall within the standard range. By using the trendline equation generated from the standard solutions, the absorbance of a sample can be substituted for y, and the resulting x is the concentration of the diluted sample used. The actual concentration can be determined since the amount of dilution is known.

Objective

In this experiment, you will use UV-visible spectroscopy to determine the amount of FD&C Red 40 food coloring in red and pink freezer pops.

Name _____

Prelab questions

1. In this lab, a 1.000 g/L stock solution of FD&C Red 40 will be provided. Fill in Table 7.1 to show how you will prepare the standard solutions listed using only 2.00 and 5.00 ml volumetric pipets and 100.00 and 200.00 ml volumetric flasks.

Table 7.1 Standard Solutions Preparation

Standard	Volumetric pipet size	Volumetric flask size
0.0100 g/L		
0.0200 g/L		
0.0250 g/L		
0.0500 g/L		

2. A standard curve was made for FD&C Blue 1 food dye and the trendline equation was determined to be $y = 56.8x + 0.0498$, where x is given in g/L. A freezer pop sample was found to have an absorbance value at the analyzed wavelength of 1.989 AU, where AU is absorbance units. How many milligrams of FD&C Blue 1 are in a 40.00 ml freezer pop?

3. If the largest standard solution absorbance is 2.590 AU and a red freezer pop gives an absorbance value of 3.056 AU, would the resulting grams of Red 40 calculated be correct? Why or why not?

4. If the absorbance value for the red freezer pop was over the largest standard solution absorbance, explain how you could correct for this.

5. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

1. Set up a UV-visible spectrophotometer according to your instrument's instructions and allow it to warm up.
2. Obtain approximately 20 ml of the 1.000 g/L stock FD&C Red 40 solution provided in a 50 ml beaker. Prepare the standard solutions according to Table 7.1 in the prelab. Mix all standard solutions well.
3. Pour all of the liquid content of an unfrozen pink freezer pop into a 100 ml (or 50 ml) graduated cylinder and record the exact volume.
4. Pour all of the liquid content of an unfrozen red freezer pop into a 100 ml (or 50 ml) graduated cylinder and record the exact volume.
5. Make a 50% dilution of the red freezer pop solution by first pipetting 10.00 ml of the red freezer pop solution into a 50 ml beaker. Rinse the pipet with deionized (DI) water and then pipet 10.00 ml of DI water into the same beaker and mix well.
6. Rinse a cuvette with DI water at least three times and then fill it three-fourths full with DI water. Wipe the sides with a KimWipe™. Run the blank in the UV-visible spectrophotometer between the wavelengths of 400 and 600 nm.
7. Rinse a cuvette with the 0.0200 g/L standard solution at least three times and then fill it three-fourths full with the 0.0200 g/L standard. Obtain a visible spectrum for it between the wavelengths of 400 and 600 nm, and determine the best wavelength to use for the analysis. Record the wavelength chosen.
8. Obtain and record in Table 7.2 absorbance values at the chosen wavelength for each of the standard solutions, making sure to properly rinse the cuvette between standards. Be sure to go from the lowest value standard to the highest value standard.
9. Obtain the absorbance values for the pink freezer pop sample and the diluted and undiluted red freezer pop samples. Make additional dilutions if needed and obtain their absorbance values.
10. Make a standard curve using Microsoft Excel by plotting absorbance (y axis) versus concentration (x axis). Insert a linear trendline and display the equation and R-squared value on your graph. Record the trendline equation.
11. Calculate the milligrams and the number of moles of FD&C Red 40 in the pink and red freezer pops. Use 496.42 g/mole as the molar mass.

Name _____

Data

Wavelength:

Milliliters of pink freezer pop contents:

Milliliters of red freezer pop contents:

Table 7.2 Absorbance Values for Standards and Samples

Solution	Absorbance
Blank	0.000
0.0100 g/L FD&C Red 40	
0.0200 g/L FD&C Red 40	
0.0250 g/L FD&C Red 40	
0.0500 g/L FD&C Red 40	
Pink freezer pop	
50% diluted red freezer pop	
Red freezer pop	

Trendline equation:

Observations

Calculations

Mass of FD&C Red 40 in 1 pink freezer pop (mg):

Moles of FD&C Red 40 in 1 pink freezer pop (mole):

Mass of FD&C Red 40 in 1 red freezer pop (mg):

Moles of FD&C Red 40 in 1 red freezer pop (mg):

Analysis

1. The pink freezer pop contains what percent of the FD&C Red 40 found in the red freezer pop? Does this seem reasonable?

2. Did the calibration curve obey Beer's law? Explain why or why not.

3. Did you use the absorbance value for the undiluted or the diluted sample of the red freezer pop? Explain why this one was chosen.

Think green

1. Food manufacturers are often challenged to find natural food dyes to replace synthetic ones. In terms of the 12 principles of green chemistry, why might using a natural food dye be considered greener? What could prevent them from being evaluated as more green?
2. Betanin is a natural red food dye extracted from beets. Research betanin and decide if it could be a suitable natural replacement for Red 40 in freezer pops. Do you think it would absorb similar wavelengths of light as Red 40? Explain your answers. If time and resources permit, test your hypothesis by making red food coloring from beets and obtaining a UV-visible spectrum of your extract.

Presidential green chemistry challenge

Other industries besides food companies are researching ways to replace petroleum-derived products with naturally derived ones. The Environmental Protection Agency (EPA) gave its 2008 Presidential Green Chemistry Award in the Greener Synthetic Pathways category to Battelle for developing a bio-based laser printer and copier toner. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about how this technology utilizes principles of green chemistry.

chapter eight

Separation of food dyes by paper chromatography

Are green M&M's® made green with blue and yellow food dyes, or is it a green dye? What dye colors are used to make orange M&M's®? These are questions that can be answered through the use of a technique called chromatography.

Chromatography is a method of separating mixtures. It can be used to identify the components of a mixture when the sample is compared to the chromatograph of known substances. Chromatography is utilized in various fields, including forensics, where it is used to identify substances. Another application is in the field of biotechnology, where chromatography is used to isolate proteins. Chromatography can also be utilized to find traces of pesticides in groundwater.

The concept of chromatography is based on two phases: the mobile phase and the stationary phase. The mobile phase is as expected—a moving phase. It can be either a liquid or a gas, depending on the type of chromatography. The stationary phase remains in place, and it can be a solid or a liquid. A good separation results when the components of a mixture have varying levels of affinity for the mobile and stationary phases. Think of the mobile phase as a moving stream and the stationary phase as the streambed. If you were to toss a leaf, very small pebbles, and a large rock into a fast-moving stream, what would happen?

Many things affect the affinity of a substance (the analyte) for the mobile or stationary phase, including polarity, solubility, particle size, and electrical charge. Chemists can use their knowledge of these properties to separate a mixture effectively. Different types of mobile and stationary phases lead to many different types of chromatography, including paper, ion exchange, gas, high-performance liquid, column, affinity, and thin-layer chromatography.

The first objective of this experiment is to determine the best mobile phase for the dyes found in candy-coated M&M's®, keeping in mind that the goal of chromatography is to have a clear separation of the components of a mixture. The method you will utilize is paper chromatography.

The type of paper used determines how fast the mobile phase moves. It is actually the atmospheric water bound to the paper's cellulose that acts as the stationary phase in paper chromatography.

The mobile phase is also known as the eluting solvent. You will conduct multiple tests to determine the best eluting solvent to separate the food dyes. Variants you will investigate include polarity and ionic characteristics through using salt water, water, and isopropanol as eluting solvents. Salt is an ionic substance, water is a polar substance, and isopropyl alcohol is much less polar than water. By changing the concentration of salt, you are changing the ionic characteristics of the solvent. By altering the concentrations of water and alcohol in the solution, you are changing the polarity of the solution.

One way to compare the movement of the analyte (the substance being analyzed) is to calculate the R_f value. The R_f value is determined by taking the distance traveled by the analyte and dividing it by the distance traveled by the mobile phase. An illustration of what a final paper chromatogram will look like and where to take the measurement to calculate an R_f value is shown in Figure 8.1.

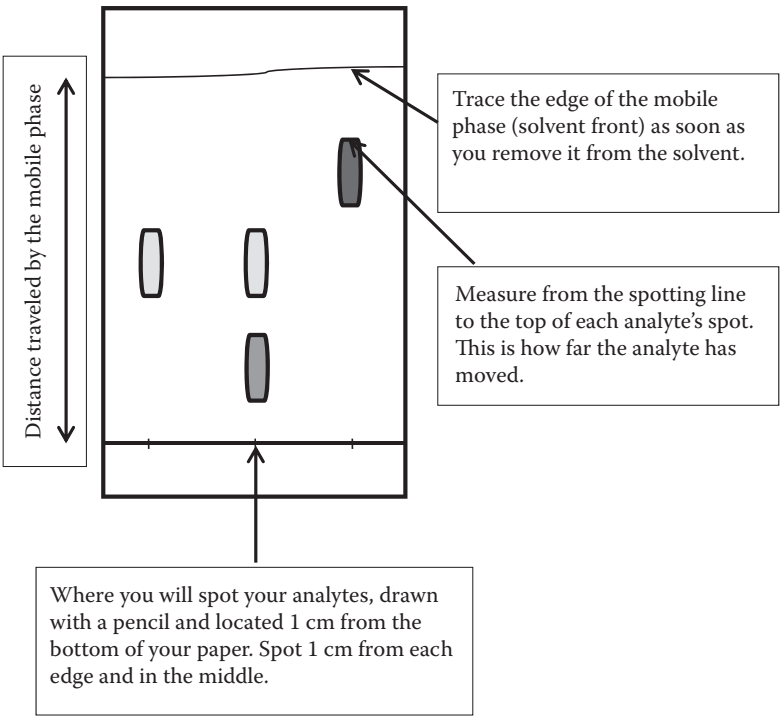


Figure 8.1 Example paper chromatograph.

Example R_f calculation

The red spot moved 5.75 cm, and the mobile phase moved 8.5 cm:

$$R_f = 5.75/8.5 = 0.72$$

When there is more than one dye present, the R_f is calculated and recorded for both spots.

After you have determined the best mobile phase, you will need to identify which dyes are present in your M&M's®. At first it may seem fairly easy to determine what food dyes are present based only on their color, but this is not always possible. If your M&M's® are coated with the traditional synthetic food dyes, a yellow/orange spot could be from either Yellow 5 or Yellow 6, and a blue spot could be from either Blue 1 or Blue 2. If your M&M's® are coated with natural food dyes like they are in the UK, a yellow/orange spot could be from either turmeric or β-carotene. To verify the identifications are correct, standards of these dyes need to be run using the same conditions and a comparison of their R_f values made.

In this lab, you are using three different types of solvents—an ionic solvent, water, and a volatile organic solvent. One of the twelve principles of green chemistry is to *use safer solvents and auxiliaries*, and this is for a very good reason. Most organic reactions involve using volatile organic solvents. This generates large quantities of hazardous and toxic waste that need to be reclaimed or disposed of properly. Several approaches are often considered when changing to a safer solvent, one of which is to eliminate the solvent, and another is to use water, but frequently neither of these approaches will work. Water usually does not dissolve more nonpolar organic molecules. Another promising green solution is to use ionic liquids, and even better, to use ionic liquids made from renewable feedstock. An ionic liquid is a type of salt like the NaCl you will use with a cation and an anion, but it does not have to be dissolved in water since it is a liquid below 100°C. They can be custom designed for a particular application. A major advantage is their lack of measurable volatility, making them much less hazardous and able to be used in microwave synthesis.

Objective

In this experiment, you will investigate the concept of paper chromatography, and attempt to achieve clear separation of food dyes found in M&M's® by varying the eluting solvent (mobile phase). You will also identify the food dyes present in your sample.

Name _____

Prelab questions

1. Rank the following solutions from least polar to most polar:

   50% isopropanol/H_2O

   25% isopropanol/H_2O

   Pure water

   70% isopropanol/H_2O

2. Identify in the procedure the analyte, eluting solvents (mobile phases), and the stationary phase:

   Analyte:

   Eluting solvents:

   Stationary phase:

3. Why would it be important to know which food dyes are in your food?

4. If 70% isopropanol/H_2O and 0.5% NaCl/H_2O worked equally well as eluting solvents for a particular separation, evaluate which would be the greener one to use, and explain your answer.

5. Research and evaluate the hazards for all chemicals you will be using and list them. Study the procedure and look for other possible hazards that exist and list these. What protective equipment will you need to use?

Procedure

Part 1: Determining the best mobile phase

1. Place three regular M&M's® of one color into a 50 ml beaker, and add 1 ml of 70% isopropyl alcohol. Stir gently with a lab scoop until the candy's white undercoating appears. This may take a few minutes. Be sure to get most of the color off of the M&M's®.
2. Quickly decant the liquid into a small test tube or vial. Some white powder may be present in the liquid, but it will not affect the results.
3. Repeat step 1 for two other colors of M&M's®. Be sure to clean your beaker and lab scoop well between colors. Allow the sample solutions to sit and concentrate while the developing chamber and stationary phase are being prepared.
4. Prepare the developing chamber with solvent 1 by pouring deionized (DI) water into a 400 ml beaker (or a developing jar) to a depth of approximately 0.5 cm. Cover with plastic wrap (or a lid).
5. Obtain a piece of chromatography paper that is approximately 5.0 cm wide by 10 cm long.
6. Using a pencil, mark the chromatography paper 1 cm from the bottom, as shown in Figure 8.1. Place small pencil marks 1 cm from both edges and one in the middle. Determine and note where each analyte will be spotted.
7. Dip a small capillary tube into one of the sample solutions. Capillary action will draw solution into the tube.
8. Quickly and lightly touch the end of the capillary tube with the solution on its appropriate mark on the chromatography paper. A small spot of analyte solution should now be present. The spot must be high enough that it will not touch the developing solvent when the spotted chromatography paper is placed in the developing chamber. Repeat for each of the sample solutions.
9. Allow the spots to completely dry. Repeat spotting until colored dots are very visible. This should take 7–10 times and depends on the concentration of your analyte solution. Be sure the spots are dry each time before spotting again. Allow all spots to dry completely.
10. Tape the top of the spotted chromatography paper to a wood splint so that only the top edge has tape on it. Place the spotted chromatography paper in the developing chamber (400 ml beaker) so that it is hanging down from the wood splint about 1 mm above the bottom of the beaker. Be sure it is not touching the glass. Replace the plastic wrap over the beaker's top.
11. Allow the solvent to travel by capillary action to about 1 cm from the top of the chromatography paper. After it has, remove it and mark the edge of the solvent front. Let it dry, and then trace each spot with a pencil.

12. Measure from the spotting line to the top of each spot and record the distance traveled by each spot of color. Some M&M's® colors will have more than one spot. The distance traveled by each spot will need to be measured and recorded in the same cell of the data table.
13. Repeat the procedure using developing solvents 2–4 that are listed in Table 8.1. Also try at least one more developing solvent that you think may give better separation.
14. Calculate and record their R_f values in Table 8.1.

Part 2: Identifying the food dyes present

1. Obtain a piece of chromatography paper that is approximately 6.5 cm wide by 10 cm long. Make sure it will not touch the sides of the developing chamber when placed in it after it is spotted.
2. Using a pencil, mark the chromatography paper 1 cm from the bottom. Determine how many standards you will be spotting, and then place this many evenly spaced pencil marks along the bottom line.
3. Spot the standards until the colored dots are very visible. This should take two or three times since they will be more concentrated. Allow all spots to dry completely.
4. Develop the spotted chromatography paper in the solvent you determined gave the best separation.
5. Measure and record the distance traveled by each spot in Table 8.2. Also calculate and record their R_f values.

Name _____

Data

Part 1: Determining the best mobile phase

Table 8.1 Distance and R_f Values of Sample's Spots

Solvent	Distance solvent traveled (cm)	M&M's® color, distance spots traveled (cm), and R_f		
		Color:	Color:	Color:
Solvent 1: DI water	cm:	cm:	cm:	cm:
		R_f:	R_f:	R_f:
Solvent 2: 70% isopropyl alcohol	cm:	cm:	cm:	cm:
		R_f:	R_f:	R_f:
Solvent 3: 0.20% w/v NaCl solution	cm:	cm:	cm:	cm:
		R_f:	R_f:	R_f:
Solvent 4: 0.50% w/v NaCl solution	cm:	cm:	cm:	cm:
		R_f:	R_f:	R_f:
Solvent 5:	cm:	cm:	cm:	cm:
		R_f:	R_f:	R_f:

Part 2: Identifying the food dyes present

Distance solvent traveled (cm): _____

Table 8.2 Distance and R_f Values of Standard's Spot

Food dye	Distance spot traveled (cm)	R_f

Observations

Calculations

Calculate R_f values for every spot seen for each dye color in all of the solvents. Use the following formula to calculate the R_f values and place them in Table 8.1. Show a sample calculation for the first R_f value listed. *Hint*: All R_f values should be less than 1.

$$R_f = \text{analyte (cm)/solvent front (cm)}$$

Analysis

1. Which solvent provided the best separation?

2. Explain which characteristics of the solvent were used to effectively separate the analytes.

3. Which solvent provided the second-best separation? Predict similarities between the two solvents that could account for the success of separation.

4. What food dyes were present in each of the colors you tested?

5. Some people, especially children, have food allergies or sensitivities to some food colorings, and need to know without a doubt which food dyes are present. Can the analysis you performed definitely tell which food dyes are present? Explain your answer.

Think green

1. Turmeric, β-carotene, and carmine are natural dyes that are substituted at times for yellow, orange, and red. Do you think the same solvent system you used would work to separate food dyes coated with these natural dyes? If time and resources permit, try it for any of these natural food dyes that are available. If the same conditions do not work, attempt to determine a solvent system that does.
2. Which do you think is greener—synthetic or natural food dyes? Justify your answer using the 12 principles of green chemistry.
3. Research ionic liquids and an application where they are being used. Write a summary of what you find.

Presidential green chemistry challenge

One challenge of green chemistry is to find replacements for volatile organic solvents. At times, ionic liquids are suitable alternatives. The Environmental Protection Agency (EPA) gave its 2005 Presidential Green Chemistry Award in the Academic category to Professor Robin D. Rogers of the University of Alabama for developing a way to use ionic liquids to dissolve cellulose, which allows it to then be made into new materials. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about how this technology utilizes principles of green chemistry.

chapter nine

What is the best solution to lower a freezing point?

Have you ever stopped to wonder how salt put on the roads in winter allows them not to freeze? Or how antifreeze keeps the water in your car's radiator from freezing?

Altering the freezing point of solutions is a very common practice. For instance, one of the most common uses is salting roads with NaCl or $CaCl_2$ before or after a winter storm to melt ice by lowering its freezing point. Even though NaCl is considered reasonably safe, some areas that have to use it often are now seeing negative environmental consequences, such as toxic chloride levels to aquatic life in many streams, and damage to roadside vegetation. For this reason different chemicals are being considered, but so far a cost-effective replacement has not been found.

Another example of where freezing point depression is used is adding antifreeze in vehicle radiators to keep the water in them from freezing in cold temperatures. The amount of antifreeze added to the water depends on how cold it gets where the car will be driven. Vehicles driven in very cold climates need a higher percentage of antifreeze in their radiators than those driven in warmer climates.

Glycerol was once used as antifreeze for cars, but was replaced by ethylene glycol since a lower freezing point could be obtained with an ethylene glycol–water mixture. This is especially important in areas that can have very cold temperatures. Unfortunately, ethylene glycol has two major disadvantages over glycerol. The first is that even though it is naturally sweet tasting, it is poisonous if ingested. The second is that it is made from ethylene, and ethylene is made from the lower boiling components of petroleum. The process involves heating to extremely high temperatures that are over 750°C. Glycerol is considered nontoxic and can be produced from renewable resources at much lower temperatures.

The basis for the freezing point depression is due to something known as colligative properties. Colligative properties are properties dependent on the number of solute molecules or ions in a solution, but not their identity or nature. This allows for the substance to have a lower freezing point than normal, which is useful when trying to keep the roads from freezing.

Calculations of colligative properties involve a term called the van't Hoff factor, *i*. It represents how many particles into which the substance separates when dissolved in a solution. For example, $MgCl_2$ has a van't Hoff factor of 3 because it readily dissociates into Mg^{2+} and $2Cl^-$ when dissolved in water. Sucrose is covalently bonded, so it does not dissociate when dissolved in water. It has a van't Hoff factor of 1. Potassium acetate has a van't Hoff factor of 2. It dissociates into potassium ions and acetate ions. Acetate ions are polyatomic ions. Polyatomic ions contain more than one atom, and the atoms making up the ion are covalently bonded to each other. Solutions containing a substance with a larger van't Hoff factor will lower a freezing point more than a solution of the same molarity that has a smaller van't Hoff factor.

In this lab you will use freezing point depression to determine the molar mass of glycerol, sodium chloride, and calcium chloride. The calculation involves two steps. In the first step, you will calculate the molality of the solution. Molality is the number of moles of solute per kilogram of solvent. It is calculated using the equation

$$\Delta T_f = K_f \cdot m \cdot i$$

where ΔT_f is the freezing point of pure solvent minus the freezing point of the solution, K_f is the cryoscopic constant (also called the freezing point depression constant), m is the molality of the solution, and i is the van't Hoff factor.

The cryoscopic constant depends only on the solvent. It is $1.853 \frac{°C \cdot kg}{mol}$ for water since the freezing point of water is lowered by this amount when there is 1.00 mole of nonvolatile solute particles 1 kg of water.

The second step of the calculation uses the calculated molality, the mass of the solute, and the mass of the solvent in kilograms to determine the molar mass. An example is shown below.

Example

When determining the freezing point depression of a solution of 5.00 g of sucrose dissolved in 25.000 g of water, the solution freezes at –1.08°C. Calculate the molar mass of sucrose.

Since water freezes at 0°C, ΔT_f = 0°C – (–1.08°C), or 1.08°C.

Sucrose has a van't Hoff factor (*i*) of 1.

The 25.000 g of water must be converted to kilograms:

$$25.000 g\ (1\ kg/1000\ g) = 0.025000\ kg$$

Using the above values, the molality, *m*, can now be calculated:

$$m = \frac{\Delta T_f}{(i)\left(K_f\right)}$$

$$m = \frac{1.08°C}{(1)\ \ 1.853\dfrac{°C \cdot kg}{mol}}$$

$$m = 0.583 \text{ mole/kg water}$$

To obtain the molar mass, the grams of solute used is divided by the molality that was just calculated times the kilograms of solvent used:

$$\text{Molar mass} = \text{g solute/mole}$$

$$= \frac{5.000 \text{ g}}{0.583 \ \dfrac{\text{mole}}{\text{kg } H_2O} \ \ (0.025000 \text{ kg } H_2O)}$$

$$= 343 \text{ g/mole}$$

The molar mass you obtained experimentally can then be compared to the theoretical molar mass that you should have obtained and a percent error calculated.

The theoretical molar mass for sucrose is $342.3\dfrac{g}{mol}$:

$$\% \text{ error} = \frac{|\text{theoretical value} - \text{experiment value}|}{\text{theoretical value}} \times 100$$

$$\% \text{ error} = \frac{|342 - 343|}{342} \times 100 = 0.292\%$$

In this lab, a solution may enter a state of supercooling. Supercooling is when a chemical remains as a liquid even when its temperature is lower than its freezing point. This is not the same as freezing point depression, where a solute is added to a liquid in order to lower its freezing point. Supercooled water often exists in clouds. Airplanes have to be very careful of this since when they fly through the clouds, they can seed crystallization, which will cause ice to form on their wings and instrument probes. Ice can cause the wing to lose lift and damage

the instrument probes, causing the plane to crash. Fortunately, there are ways to prevent this from happening.

Solutions often supercool in this lab. When this happens, the solution will have to warm up past the point of supercooling to its actual freezing point before it will freeze. Sometimes this can take a long time. To speed things up, a very small seed crystal can be added to a supercooled solution. If this does not work within a few minutes, the solution can be taken out of the ice/salt bath and be allowed to warm up past 0°C. The solution can then be placed back in the ice/salt bath, and when the temperature is just below 0°C, a very small piece of ice can be added.

Objective

The purpose of this experiment is to determine the molar masses of glycerol, NaCl, and $CaCl_2$ by using the freezing point depression of each of the compounds in a solution. The molar masses you determine are then compared to their actual molar masses.

Name _____

Prelab questions

1. What are the colligative properties?

2. What is the K_f value of water?

3. What is the van't Hoff factor, and what happens if it is not used when trying to calculate the molar mass of a substance?

4. What are the van't Hoff factors for glycerol, sodium chloride, and calcium chloride?

5. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

1. Obtain a 400 ml beaker and fill it three-fourths full of crushed ice. Add approximately 40 g of rock salt to the beaker and mix it thoroughly. Determine the temperature using a thermometer. The temperature should eventually reach about –10°C.
2. As this is cooling, pour 15.0 ml of deionized (DI) H_2O into a medium test tube. Clamp the test tube to a ring stand and lower it into the ice/salt bath, making sure all of the water in the test tube is located below the level of the ice.
3. If an electronic thermometer is available, you may use it later to stir the solution in the medium test tube. If it is not available, clamp a wedged rubber stopper equipped with a thermometer to a ring stand. Lower it into the water in the test tube. Also place a stir rod in the DI water in the test tube. See Figure 9.1.
4. Stir the solution until the temperature no longer decreases. Allow the solution to sit undisturbed and observe carefully for the appearance of crystals. If supercooling occurs, the temperature will decrease more than it should, and then start to rise before it freezes. When it freezes, the temperature will level off until it melts. This is the freezing point.
5. Upon the appearance of crystals, record the temperature. This is the experimental freezing point for the water. It should be 0°C. If it is not, you will need to correct the rest of the freezing points for this difference.

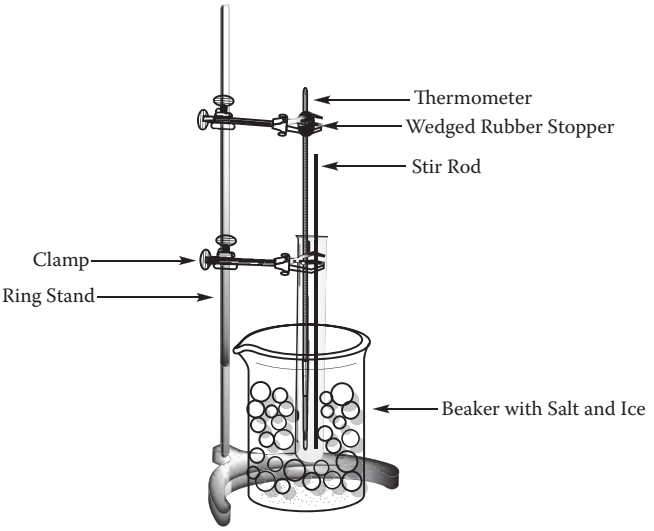


Figure 9.1 Apparatus.

6. Remove the test tube from the ice/salt bath immediately after the freezing point has been determined in order to prevent the breaking of the test tube. Empty the ice and water from the test tube.
7. Obtain and record in Table 9.1 the mass of a 50 ml beaker. Add 3.0 ml of glycerol to it. Obtain and record the mass of the beaker and glycerol.
8. Add 15.0 ml of deionized water. Record the mass of the beaker, glycerol, and DI water. Stir until the solution is well mixed.
9. Ensure the ice/salt bath is still approximately –10°C or lower. If not, add more ice and rock salt and pour out some of the water to adjust the temperature.
10. Pour the glycerol solution into the test tube and place it in the ice bath. Make sure all of the solution in the test tube is below the level of the ice. Place the thermometer in the solution.
11. Stir until the temperature no longer decreases. After the temperature goes below –0.5°C, you can add a small piece of ice as a seed crystal to help prevent supercooling. Be sure to continue to stir until the temperature no longer decreases, even after adding the ice crystal.
12. Allow the solution to freeze and determine the freezing point of the glycerol solution to the 0.1°C. Record the temperature and the corrected temperature (step 5) for when the solution freezes.
13. Repeat steps 7–12 using 0.750 g of NaCl instead of glycerol. Perform another trial using the same procedure with 0.750 g of $CaCl_2$.
14. After determining the freezing points, find the molar mass of all the substances used, and compare them to their theoretical values. Calculate the percent error for each.

Name _____

Data

Experimental freezing point for water (°C): _____

Table 9.1 Data and Results for Molar Mass Determinations

	Glycerol	NaCl	$CaCl_2$
Mass of 50 ml beaker (g)			
Mass of 50 ml beaker and solute (g)			
Mass of solute (g)			
Mass of beaker, solute, and H_2O (g)			
Mass of H_2O (g)			
Experimental freezing point (°C)			
Corrected experimental freezing point (°C)			
Experimental molar mass in g/mole			
Actual molar mass in g/mole			
% Error			

Observations

Calculations

Calculations for the experimental molar mass of each compound:

Glycerol:

NaCl:

$CaCl_2$:

Analysis

1. How do each of these molar masses compare to the theoretical molar masses?

2. Calculate how much NaCl and $CaCl_2$ lower the freezing point per gram. If NaCl and $CaCl_2$ cost the same per gram, which one is the most cost-effective?

Think green

1. Calcium magnesium acetate can be used as an alternative to rock salt. Research the composition of calcium magnesium acetate. Do you think it will lower the freezing point of water more or less per gram than rock salt? If there are time and resources available, try it and see if you are right.
2. Research the environmental impact, effectiveness, and cost for calcium magnesium acetate when it is used for deicing roads. Which of the 12 principles of green chemistry would be positively affected if calcium magnesium acetate replaced rock salt as a road deicer? Which do you consider the best choice to use as a deicer? Justify your answer.
3. Research ethylene glycol and glycerol, including their freezing points, toxicity, and how they are produced. Which of the 12 principles of green chemistry would be positively affected if glycerol replaced ethylene glycol in warmer climates? Which do you consider the best choice to use as antifreeze? Justify your answer.

Presidential green chemistry challenge

The Environmental Protection Agency (EPA) gave its 2006 Presidential Green Chemistry Award in the Academic category to Professor Galen Suppes for a method to make waste glycerol from biodiesel production into ethylene glycol for automotive antifreeze. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about this technology and how it utilizes principles of green chemistry.

chapter ten

Standardization of a sodium hydroxide solution

> As individuals, we compare many things on a daily basis. Would you say that you are tall or short? These comparisons are not accurate unless we have a set height to which we are comparing ourselves. For instance, you are tall compared to a 2-year-old, but short compared to Shaquille O'Neal (who is very tall).

We can easily compare the height of others to the known height of someone else. Let's assume that your laboratory instructor is 5 feet 10 inches. We are told that the girl in the front row is 5 inches shorter than your instructor, while the basketball player is 8 inches taller than your instructor. In each of these cases, the height of the student is being evaluated compared to the height of your instructor. We could then figure out that the girl is 5 feet 5 inches and the basketball player is 6 feet 6 inches without ever measuring the actual height of either student individually. In loose chemical terms, we could say that your instructor is the primary standard, and by knowing the difference, we are able to determine the heights of the students.

This is like a *standard solution* that is used in a chemical analysis. It is a solution in which the concentration is precisely known. One can determine the concentration of a standard solution for a titration analysis by the process of *standardization.* To do this, a *primary standard* is used to accurately determine the molarity of the standard solution. The *primary standard solution* is prepared by first oven drying the primary standard to a *constant mass*, and then dissolving a known amount of it in a known volume of liquid. A primary standard must be very pure, reasonably soluble, stable, nonhygroscopic, and of fairly high molar mass.

If, like the height of your lab instructor, the exact molarity of the primary standard solution is known, then the number of moles can be determined in another solution using a technique known as standardization. A solution can be standardized with a primary standard by carrying out a *titration*. In an acid-base titration, an acid is added to a known quantity of base (or base is added to acid) until the moles of protons donated by the acid equals the moles of hydroxide accepted by the base. This is known as a *neutralization reaction.* When neutralization occurs, the equivalence point of the titration has been reached.

In this lab you will use citric acid, a natural product, as your primary standard. It is commonly used as a primary standard in small soapmaking companies. Using natural products relates to the seventh principle of green chemistry, which is *use of renewable feedstocks*. Citric acid is a triprotic acid, and each molecule is capable of donating up to three protons in an acid-base reaction. A sodium hydroxide solution will be the solution you will standardize in order to determine its molarity.

As previously stated, the primary standard must be dried to a constant mass. Often chemicals will have some moisture present as an impurity, especially if they have been sitting open in a humid environment for a period of time. It is important to know the exact amount of moles of pure substance being used to prepare a primary standard solution. Therefore, all water must be removed from the substance. If water were included in the mass, the concentration of the primary standard would not be accurately known. To ensure all moisture condensed on the chemical is removed, it is dried in an oven below its melting point, cooled in a dessicator, and weighed. This is repeated until all the water is removed and the mass remains the same. This is called a constant mass.

Next, the primary standard solution is prepared by weighing the product and diluting it in water to an accurately known volume. The molarity of the primary standard is then calculated. To do this, first the number of grams weighed out must be converted to moles. The number of moles is then divided by the number of liters of solution made.

Example

Calculate the molarity of a solution where 1.921 g of citric acid is weighed out and diluted to 100.0 ml. Citric acid's molecular formula is $C_6H_8O_7$.

First, the molar mass of the citric acid is determined to be 192.124 g/mole. Next the mass of citric acid weighed out is converted to moles by dividing it by citric acid's molar mass.

$$\text{Moles}_{\text{citric acid}} = \text{g} \cdot \frac{1 \text{ mole}}{\text{molar mass}(\text{g})}$$

$$\text{Moles}_{\text{citric acid}} = 1.921 \text{ g} \cdot \frac{1 \text{ mole}}{192.124 \text{ g}} = 0.1000 \text{ mole citric acid}$$

The molarity, *M*, of the citric acid solution is then calculated by dividing the number of moles of citric acid by the number of liters of solution made:

$$M = \text{Moles/Volume in L}$$
$$M_{\text{citric acid}} = 0.1000 \text{ mole}/(100.0 \text{ ml} \times (1 \text{ L}/1000 \text{ ml}))$$
$$M_{\text{citric acid}} = 0.1000 \, M$$

The standard is placed in a buret, and an exact volume of the solution of unknown molarity that is being standardized is placed into a flask. The primary standard is slowly added to the solution at definitive increments, and the pH is recorded using a pH meter. An example of data obtained in a titration involving a 0.100 *M* citric acid solution and 20.00 ml of a sodium hydroxide solution is shown in Table 10.1, and the data were graphed using Excel in Figure 10.1.

The equivalence point is determined by plotting the volume of primary standard versus the pH of the solution, and then finding the midpoint of the inflection, as shown in Figure 10.1.

The midpoint is found by adding the pH values marked at each line of inflection and dividing that number by 2. It appears that the equivalence point was reached when 6.80 ml of citric acid was added to the solution.

Table 10.1 Titration Data

Milliliters of citric acid added	pH	Milliliters of citric acid added	pH	Milliliters of citric acid added	pH
0.00	11.5	6.20	9.2	7.60	7.6
1.00	11	6.40	9.0	7.80	7.4
2.00	10.6	6.60	8.8	8.00	7.3
3.00	10.3	6.80	8.4	8.20	7.2
4.00	10.1	7.00	8.2	8.40	7.15
5.00	9.9	7.20	8.0	9.00	7.1
6.00	9.5	7.40	7.8	10.00	7.0

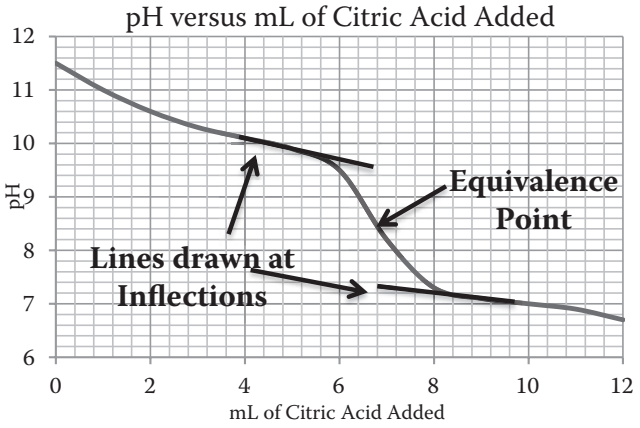


Figure 10.1 pH versus milliliters of citric acid added.

Since citric acid is triprotic, it should have three separate endpoints. Usually the first and second endpoints are not seen since they do not have a fast drop of pH due to a buffering effect.

An equivalence point is easier to see when using a strong acid or a strong base in a titration. A strong acid dissociates almost completely in water and easily gives up H^+ ions. A strong base dissociates almost completely in water to OH^-. Using these makes a sharper titration curve. The example given above uses a strong base and a weak acid. Observe the graphs in Figure 10.2 to note the differences.

Once the equivalence point is found, the molar ratio is used to determine the molarity. To determine the molar ratio, the reaction coefficients of the acid and base are first determined by balancing the reaction equation. The reaction coefficients are the numbers in front of the acid or base in the balanced equation, and these are used to determine the molar ratio of the acid to the base. The molar ratio is found by observing the reaction equation. For example:

$$HO(COOH)(CH_2COOH)_2 + 3NaOH \rightarrow HO(COO^-Na^+)(COO^-Na^+)_2 + 3H_2O$$

In this case, we see 1 mole of citric acid reacting with 3 moles of sodium hydroxide.

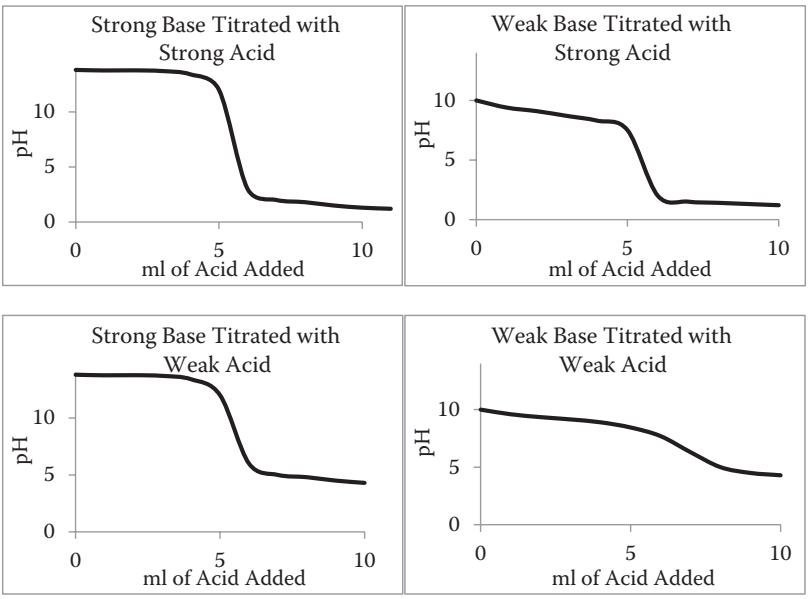


Figure 10.2 Acid-base titration graphs (volume versus pH).

This relationship can be combined with the definition of molarity to obtain a useful and simple equation:

$$b \cdot M_a \cdot V_a = a \cdot M_b \cdot V_b$$

where a = reaction coefficient of the acid, b = reaction coefficient of the base, M_a = molarity of the acid, M_b = molarity of the base, V_a = volume of the acid, and V_b = volume of the base.

Solving for the molarity of the base (M_b), we get

$$M_b = \frac{b \cdot M_a \cdot V_a}{a \cdot V_b}$$

Using this equation, the molarity of the NaOH in the example can now be determined:

$$M_{\text{NaOH}} = \frac{1 \cdot 0.100\ M \cdot 6.80\ \text{mL}}{3 \cdot 20.00\ \text{mL}}$$

$$M_{\text{NaOH}} = 0.0113\ \text{M}$$

Accuracy is important in standardization; therefore, the titration is normally done at least three times. The molarity of the solution is calculated in each trial, and an average is taken to determine the exact molarity.

Objective

In this experiment, you will learn the principle and method of standardizing a solution through titration of a solution of unknown molarity using a primary standard in order to determine the standard solution's accurate concentration.

Name _____

Prelab questions

1. Why is it important that the primary standard chemical be nonhygroscopic and pure? Why is it important to dry the primary standard to a constant mass?

2. Look at Figure 10.2. Which combination of acid and base provides the most distinguishable equivalence point? Which combination is the most difficult to determine an equivalence point for?

3. Potassium hydrogen phthalate (KHP), $KHC_8H_4O_4$, is also a good primary standard that is often used to standardize NaOH solutions. Calculate the molarity of a solution made by weighing out 12.4900 g of dry KHP and then diluting it to 100 ml.

4. 20.00 ml of NaOH was titrated with a 0.600 M $KHC_8H_4O_4$ solution. The data were graphed and the equivalence point was found to be 15.50 ml when standard 0.600 M KHP solution was added. The reaction equation is

$$NaOH_{(aq)} + KHC_8H_4O_{4(aq)} \rightarrow KNaC_8H_4O_{4(aq)} + H_2O$$

   a. What is the molar ratio of NaOH:$KHC_8H_4O_4$?

   b. What is the molarity of the NaOH solution?

5. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

Part 1: Preparation of the primary citric acid standard

1. Weigh a clean, dry 150 ml beaker and record the mass in grams. Place approximately 2.00 g of anhydrous citric acid in the beaker. Record the exact mass of the beaker and citric acid in Table 10.2.
2. If the citric acid has already been dried, proceed to step 4. If it was not, place the beaker with the citric acid in a drying oven set at 110°C for 15 minutes. Remove from the drying oven using oven mitts and place it in a desiccator to cool. ***Caution:*** The beaker will be hot!
3. Once cooled to room temperature, record the mass of the beaker and acid in Table 10.2. Repeat this step until the mass is within ±0.005 g of the mass previously recorded.
4. Add approximately 25 ml of deionized (DI) water and carefully swirl the solution to dissolve the citric acid in the beaker. Pour the dissolved solution through a funnel into a 100 ml volumetric flask. Continue to rinse by adding approximately 15 ml aliquots (or portions) of DI water to the beaker that contained the citric acid and pour the rinse water into the volumetric flask. Do this until the liquid reaches the neck of the volumetric flask. This will help ensure that all of the citric acid is transferred.
5. Remove the funnel and begin to add the DI water with a dropper until the meniscus reaches the 100.00 ml mark on the flask. Figure 10.3 shows a picture resembling a meniscus much like the one you should see in the liquid in the volumetric flask. Be sure that the bottom portion of the curve touches the 100.00 ml mark in order to obtain an accurate volume.
6. Carefully shake the flask to evenly mix the citric acid solution. Be sure to hold pressure against the stopper while you are shaking to keep it from falling out.
7. Calculate the exact number of moles of citric acid that you obtained and divide by 0.10000 L to obtain the molarity of the solution. Label your flask with the correct molarity and name of solution.

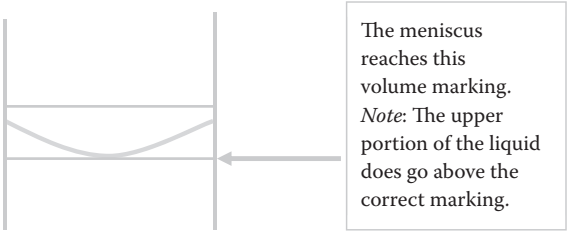


Figure 10.3 Correctly filling a volumetric flask.

Part 2: Titration of the sodium hydroxide solution

1. Pipet 20.00 ml of the sodium hydroxide solution into a 150 ml beaker.
2. Assemble a titration apparatus as shown in Figure 10.4. Do this by clamping a buret clamp to a ring stand and placing a buret in it. Pour approximately 50 ml of your standard citric acid solution into a 150 ml beaker. Place a funnel on top of the buret and a waste beaker below it. Carefully rinse through the buret a few milliliters of the citric acid standard solution. Rinse the buret at least two times.
3. Close the buret stopcock and fill the buret a little over the 0.00 ml mark. Drain the solution into a waste beaker until no air bubbles are present in the tip. You may need to open and close the buret quickly several times to remove air bubbles. If needed, refill the buret slightly over the 0.00 ml mark and slowly drain until the bottom of the meniscus or curve touches the 0.00 ml mark.
4. Calibrate a pH meter according to its directions using pH 7 and 10 buffer standards.
5. Place your pH probe into the sodium hydroxide solution. Swirl for a few seconds and then record the pH in Table 10.3 after it has stabilized. This is the pH at 0.00 ml of citric acid.
6. While swirling the beaker, slowly and carefully begin to add approximately 1 ml aliquots from the buret and record the pH and the total milliliters added of the citric acid solution. Be sure to record the volume to the hundredths place. Continue doing this until you notice the pH begins to drop more noticeably, and then add smaller aliquots (approximately 0.2 to 0.1 ml). Continue until the pH of the solution starts to level back off.

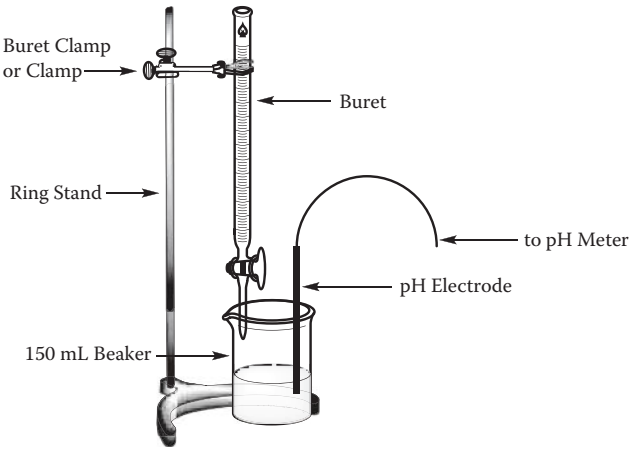


Figure 10.4 Titration setup.

7. Graph your data by plotting the pH versus the amount of citric acid solution added. You can use a graphing program such as Excel. Determine the equivalence point using the graphical data.
8. Repeat the titration at least two more times and record the data in Tables 10.4 and 10.5. Each time graph the data and label the graphs consecutively as Trial 2 and Trial 3.
9. Determine the molarity of the NaOH solution for each trial, and then calculate the average molartiy. Pour this solution into a clean and dry plastic bottle. Label it with the accurately known average NaOH molarity and save it for use in the next experiment.

Name _____

Data

Part 1: Preparation of the primary citric acid standard

Table 10.2 Data for Part 1

Mass of 150 ml beaker	
Mass of beaker and citric acid	
Mass of beaker and citric acid after drying for 15 minutes	
Mass of beaker and citric acid after drying for 15 more minutes (if needed)	
Mass of citric acid	
Molarity of citric acid solution	

Part 2: Titration of the sodium hydroxide solution

Table 10.3 Titration Data Trial 1

Milliliters of citric acid added	pH	Milliliters of citric acid added	pH	Milliliters of citric acid added	pH

Table 10.4 Titration Data Trial 2

Milliliters of citric acid added	pH	Milliliters of citric acid added	pH	Milliliters of citric acid added	pH

Table 10.5 Titration Data Trial 3

Milliliters of citric acid added	pH	Milliliters of citric acid added	pH	Milliliters of citric acid added	pH

Observations

Calculations

Part 1: Preparation of the primary citric acid standard

Molarity of citric acid solution calculation:

Part 2: Titration of the sodium hydroxide solution

Plot each trial in a graphing program such as Excel, and determine the equivalence point for each of the trials:

Trial 1 equivalence point:

Trial 2 equivalence point:

Trial 3 equivalence point:

Determine the molarity of the NaOH solution in each trial:

Trial 1:

Trial 2:

Trial 3:

Average of the NaOH molarities from all 3 trials:

Label the plastic bottle containing the NaOH solution with this accurately known average molarity. Be sure to save this for use in the next experiment in Chapter 11.

Analysis

1. How close were your three trials to each other? Do you consider this acceptable? If not, what do you think you could you have done differently that would have given closer results?

2. If 1.000 g of NaOH were used to prepare 250.00 ml of NaOH solution, what would be the expected molarity of the NaOH solution?

3. How well does the expected molarity compare to the actual average molarity you measured in the standardization?

4. Will it matter when you use your standardized NaOH solution that it is not exactly 0.100 M?

Think green

1. There are many different primary standards that could be used in an acid/base standardization titration. Salicylic acid can be prepared from natural sources. Research salicylic acid and hypothesize if it could be used as a green primary standard. If time and resources permit, try using it to standardize your 0.1 M NaOH and report your results.
2. Potassium hydrogen phthalate (KHP) is often used as a primary standard. It is made from phthalic acid, and phthalic acid is made from naphthalene. Research how naphthalene and phthalic acid are made. Is citric acid a greener standard than KHP? Explain your answer and address the relevant 12 principles of green chemistry.

Presidential green chemistry challenge

The experiment you performed uses a weak acid rather than a strong one. The Environmental Protection Agency (EPA) gave its 1997 Presidential Green Chemistry Award in the Small Business category to Legacy Systems, Inc. for eliminating the use of corrosive strong acid solutions to clean semiconductors. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about this technology and how it utilizes principles of green chemistry.

chapter eleven

Determining the amount of acid in ketchup and hot sauce

> Have you ever eaten something spicy and gotten an awful stomachache afterward? This is because too much acid in your stomach can leave you with an upset stomach. You may decide to take an antacid to help relieve the stomachache, but how much acid will it relieve?

What are some acids and bases you have used within the past week? Initially you may think none; however, you have most likely encountered various acid and base solutions. For instance, orange juice contains citric acid, and many carbonated beverages contain phosphoric acid. Also, many household cleaning agents contain ammonia, which is a base.

What exactly is a base? According to the Arrhenius definition, it is a substance that when added to water increases the amount of OH^- ions present. The pH of a base is above 7. Bases typically taste bitter.

What exactly is an acid? According to the Arrhenius definition, it is a substance that when added to water increases the concentration of H^+ ions present. Acids have a pH that is below 7. Acids are known for tasting sour. This means the more acidic something is, the more sour the taste.

The method used to measure the total amount of acid or base present is an analytical chemistry technique called an acid-base titration. A titration mixes two solutions, one of which is a standard solution whose concentration is precisely known. The other is a solution whose total amount of either acid or base is being determined. To determine the amount of acid in a substance, the acid's chemical formula and how it will react with the standard solution must be known. This information is given in a chemical reaction equation.

The standard solution is added until neutralization occurs. When neutralization occurs, the *equivalence point* of the titration has been reached. This is where the amounts of H^+ and OH^- ions present are equal. The equivalence point is determined by plotting the volume of standard added versus the pH of the solution, and then finding the midpoint of the inflection.

Titrations can be used to calculate how many moles of acid there are per gram of substance. To do this, the following equation is used:

$$\text{Mole}_{\text{acid}} = \frac{a \cdot M_b \cdot V_b}{b}$$

where a = reaction coefficient of the acid, M_b = molarity of the basic solution, V_b = volume of base used in the titration converted to liters, and b = reaction coefficient of the base.

Recall that the reaction coefficients are the numbers in front of the acid or base in the reaction equation.

Example: Calculating the moles of acid in diet cola

If 10.563 g of diet cola required 11.52 ml of 0.100 M Na_2CO_3 to reach the equivalence point, what is the mole per gram of the acid in the cola?

The carbonated beverage contains phosphoric acid, and reacts with the sodium carbonate as shown below:

$$2H_3PO_4 + 3Na_2CO_3 \rightarrow 2Na_3PO_4 + 3CO_2 + 3H_2O$$

Solving for $\text{Mole}_{\text{acid}}$, the equation is rearranged to

$$\text{Mole}_{\text{acid}} = \frac{a \cdot M_b \cdot V_b}{b}$$

$$\text{Mole}_{\text{acid}} = \frac{2 \cdot 0.100\,\text{M} \cdot 0.01152\,\text{L}}{3} = 0.000768 \text{ moles acid}$$

$$\frac{\text{mole}_{\text{acid}}}{\text{gram}} = 0.000768 \text{ moles acid} / 10.563 \text{ g} = 7.27 \times 10^{-5} \frac{\text{moles}}{\text{gram}}$$

Another way solutions are defined in acid-base titrations is to use normality (N). Normality is the equivalents of solute per liter, whereas molarity is the moles of solute per liter. The normality of a monoprotic acid equals its molarity, but the normality of a diprotic acid is twice the molarity. The normality of a triprotic acid is three times the molarity. This is true for bases and their number of hydroxide ions. In this example the standard solution of Na_2CO_3 would be designated as 0.2 N since it has two hydroxide ions to be neutralized. To convert to molarity you would simply divide the normality by 2.

Objective

The objective of this experiment is to determine and compare the moles of acetic acid per gram in a packet of mild taco sauce and a packet of ketchup using acid-base titrations.

Name _____

Prelab questions

1. Define an acid and a base and give a few characteristics of each.

2. Why is it important for the buret to be clean before using?

3. Why are air bubbles in the tip of the buret a possible source of error in a titration experiment?

4. Mild taco sauce and ketchup both contain acetic acid, which reacts with sodium hydroxide as shown below:

$$CH_3COOH + NaOH \rightarrow CH_3COO^-Na^+ + H_2O$$

   What are the reaction coefficients of the acid and the base?

5. If 2.0112 g of ketchup required 9.32 ml of 0.106 N NaOH to reach the equivalence point, what is the mole per gram of acid in the ketchup?

6. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

Titration of mild taco sauce and ketchup

1. Obtain the mass of a clean 150 ml beaker and record it in the data table.
2. Carefully cut the corner of a mild taco sauce packet. Squeeze out one packet of sauce into the preweighed 150 ml beaker, leaving as little as possible in the packet.
3. Weigh the beaker and sauce and record the mass in Table 11.1.
4. Using a graduated cylinder, add 20 ml of deionized (DI) water to the beaker. Stir the solution well using a stirring rod. Rinse the stir rod with about 1–2 ml of DI water in the beaker.
5. Attach a buret clamp to a ring stand. Clamp a 25 ml buret to the buret clamp.
6. Add approximately 50 ml of the standardized sodium hydroxide solution into a clean 150 ml beaker. Place a funnel on top of the buret and a waste beaker below it. Carefully rinse through the buret with a few milliliters of the sodium hydroxide standard solution. Rinse the buret at least two times.
7. Close the buret stopcock and fill the buret a little over the 0.00 ml mark. Drain the solution into a waste beaker until no air bubbles are present in the tip. You may need to open and close the buret quickly several times to remove air bubbles. If needed, refill the buret slightly over the 0.00 ml mark and slowly drain until the bottom of the meniscus or curve touches the 0.00 ml mark.
8. Calibrate a pH meter according to its directions using pH 4 and 7 standards.
9. Place your pH probe into the hot sauce solution. Swirl the solution around for a few seconds, and then record the pH in Table 11.2 after it has stabilized. This is the pH at 0.00 ml of NaOH solution.
10. While swirling the beaker, slowly and carefully begin to add the sodium hydroxide solution to it. Add approximately 1 ml aliquots from the buret and record the pH and the total milliliters of sodium hydroxide solution added. Be sure to record the volume to the hundredths place. Continue until you notice the pH begins to rise more noticeably, and then add smaller aliquots (approximately 0.2 to 0.1 ml). Do this until the pH of the solution starts to level back off.
11. Graph your data by plotting the pH versus the amount of sodium hydroxide solution added using a graphing program such as Excel. From the graph determine the equivalence point and record it in the appropriate data table.
12. Repeat the titration of the sauce two more times using the same procedure, and record the data in the appropriate table.

13. Determine the amount of acid in ketchup using the same procedure, except substitute one-half package (approximately 5 g) of ketchup where mild taco sauce was used.
14. Determine the moles of acetic acid per gram of hot sauce and ketchup for each trial and calculate the average.

Name _____

Data

Table 11.1 Mild Taco Sauce Data

	Mild sauce trial 1	Mild sauce trial 2	Mild sauce trial 3
Mass of beaker in grams			
Mass of sauce and beaker in grams			
Mass of sauce in grams			
Molarity of NaOH standard solution used			
Equivalence point in milliliters			

Table 11.2 Mild Taco Sauce Titration Data Trial 1

Milliliters of NaOH added	pH	Milliliters of NaOH added	pH	Milliliters of NaOH added	pH

Table 11.3 Mild Taco Sauce Titration Data Trial 2

Milliliters of NaOH added	pH	Milliliters of NaOH added	pH	Milliliters of NaOH added	pH

Table 11.4 Mild Taco Sauce Titration Data Trial 3

Milliliters of NaOH added	pH	Milliliters of NaOH added	pH	Milliliters of NaOH added	pH

Table 11.5 Ketchup Data

	Ketchup trial 1	Ketchup trial 2	Ketchup trial 3
Mass of beaker (g)			
Mass of ketchup and beaker (g)			
Mass of ketchup (g)			
Molarity of NaOH solution used			
Equivalence point in milliliters			

Table 11.6 Ketchup Titration Data Trial 1

Milliliters of NaOH added	pH	Milliliters of NaOH added	pH	Milliliters of NaOH added	pH

Table 11.7 Ketchup Titration Data Trial 2

Milliliters of NaOH added	pH	Milliliters of NaOH added	pH	Milliliters of NaOH added	pH

Table 11.8 Ketchup Titration Data Trial 3

Milliliters of NaOH added	pH	Milliliters of NaOH added	pH	Milliliters of NaOH added	pH

Observations

Calculations

Determine the moles per gram of acetic acid in the mild taco sauce or ketchup in each trial.

Trial 1 (sauce):

Trial 2 (sauce):

Trial 3 (sauce):

Average of Trials 1–3 (sauce):

Trial 1 (ketchup):

Trial 2 (ketchup):

Trial 3 (ketchup):

Average of Trials 1–3 (ketchup):

Analysis

1. Which substance contained the most acid per gram?

2. Why was it important to know the exact concentration of the base used in the titration?

Think green

1. If industries directly discharge their acid or base waste into a body of water, it will usually harm the creatures living in the water, especially if it is a strong acid or base. To prevent this, industries treat their waste so their discharge will not cause harm, and it is often more pure than the water they may have initially used from the body of water. In this lab, you used sodium hydroxide, a strong base. How do you think you can you treat your waste so your discharge will not cause harm? How can you find out if your method is effective? If time and resources permit, test your hypothesis.
2. What if instead of treating acid waste, an industry was able to change its process so that no or little strong acid was needed, and any needed could be easily recovered and reused. Determine which of the 12 principles of green chemistry would be positively impacted by making this change and discuss the reasons for your answer.

Presidential green chemistry challenge

The Environmental Protection Agency (EPA) gave its 2012 Presidential Green Chemistry Award in the Greener Reaction Conditions category to Cytec Industries, Inc. for the development of a process that replaces cleaning heat exchangers with sulfuric acid. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about this technology and how it utilizes principles of green chemistry.

chapter twelve

Using an appropriate indicator for acid-base titrations

> Imagine that you are in a wellness center. You walk over to the treadmill, with not a drop of sweat on your body. You place your water bottle in the cup holder and hop on the treadmill. The treadmill band beneath your feet begins to move and you begin to run to keep up. Ten minutes into the run you begin to thirst for water, your forehead is covered in beads of sweat, and your legs start to grow tired. Our bodies have many natural indicators that we witness on a daily basis, such as that of fatigue from running on a treadmill. Much like the way we read our body's indications, we can see a color change in an acid-base titration's solution with the use of the correct indicator.

What is an indicator? There are a huge variety of pH indicators, all of which change color at a different pH. These indicators are usually weak acids that exhibit a different color when they lose an H^+ and form a conjugate base.

In an acid-base titration, pH indicators are used to indicate the point at which the acid and base are mixed in exactly the right proportions so that the acid neutralizes the base. The point at which the indicator changes color is known as the *endpoint* of the titration. If the indicator is correctly chosen, its endpoint will be the same as the *equivalence point*. To better grasp the concept, inspect the titration curve in Figure 12.1. Indicator A changes color around a pH of 12 or 13; therefore, it is not a good indicator for this particular titration because the endpoint of indicator A is not close to the equivalence point of the titration. Indicator B possesses an endpoint around a pH of 7. This is a good indicator for this titration because the endpoint occurs at nearly the same pH as the equivalence point of the acid-base titration. Lastly, indicator C has an endpoint at a pH too low to be used as a good indicator for this titration.

In this experiment you will be provided various indicators and determine the best synthetic indicator and the best natural indicator for a titration. You will then perform a statistical analysis on the results using your

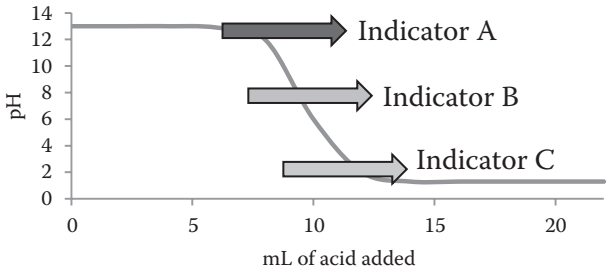


Figure 12.1 Indicators in an acid-base titration.

data and data obtained from others performing this experiment. The statistical analysis you will perform is called a *standard deviation* (σ), and it is often used when doing an analytical analysis. It quantifiably informs the experimenter of the accuracy of his or her experiment by comparing his or her results to a mean. A low standard deviation value is desired. The equation for standard deviation is as follows:

$$\sigma = \sqrt{\frac{\sum (x - \bar{x})^2}{N}}$$

where σ = standard deviation, x = each individual value being used, $\bar{x}$ = the mean of the values, and N = the number of values.

Example

Five students performed the same titration using phenol red as the indicator and the standard deviation was found. The endpoint values they obtained were 7.45, 7.49, 7.41, 7.42, and 7.48 ml, and the mean was determined to be 7.45 ml. The values were then placed into the equation as shown, and the standard deviation calculated.

$$\sigma = \sqrt{\frac{\sum (7.45 - 7.45)^2 + (7.45 - 7.49)^2 + (7.45 - 7.41)^2 + (7.45 - 7.42)^2 + (7.45 - 7.48)^2}{5}}$$

$$\sigma = 0.0316$$

Standard deviation is often utilized to maintain industrial processes. One of the 12 principles of green chemistry is *real-time analysis for pollution prevention*. An industrial process that is continuously monitored and

adjusted to ensure results occur within a very small standard deviation is much more efficient; such a process will result in additional product and reduce wastes.

Objective

In this lab, you will determine the endpoint of several indicators and evaluate which is best for the titration of a borax solution with citric acid. You will also explore the use of natural indicators and standard deviation.

Name _____

Prelab questions

1. What is the difference between an endpoint and an equivalence point?

2. The chart below lists several commonly used indicators, their equivalence points, and the color change that accompanies the reaction.

Indicator	pH range	Base color	Acid color
Methyl orange	3.1–4.4	Yellow	Red
Bromothymol blue	6.0–7.6	Blue	Yellow
Thymol blue	8.0–9.6 (higher pH)	Blue	Yellow

   a. Suppose a titration is performed in which a base of pH 12 is titrated. The equivalence point of the titration is at a pH of 6.8. What indicator should be added to the base solution before the titration is carried out?

   b. What is the color of the basic solution before any acid is added?

   c. What is the color of the solution after the equivalence point is reached at a pH of 6.8?

3. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

Part 1: Getting acquainted with the indicators

1. Retrieve approximately 100 ml of 4% borax solution and approximately 75 ml of 0.500 M citric acid solution in clean and dry beakers for use throughout this lab.
2. Obtain 10.00 ml of 4% borax solution using a 10 ml graduated cylinder, and pour it into a 150 ml beaker. Add 15 ml of deionized (DI) water.
3. Add three or four drops of phenolphthalein indicator solution into the beaker.
4. Properly set up a buret and fill it with 0.50 M citric acid. Do not be concerned about the volume in the buret (this is unimportant for this particular step). Place the beaker under the buret. You will then place a pH probe into the solution.
5. Add the citric acid from the buret slowly, while carefully swirling the solution in the beaker. Pay special attention to the color of the solution. Add the citric acid dropwise when you notice the color of the solution begin to change. You will record the color change in Table 12.1 (state the beginning color of the solution and the ending color of the solution). You will also record in Table 12.1 the pH range at which the color change of the solution occurred, and the pH you would call the endpoint of the titration.
6. Repeat this procedure for phenol red and methyl red indicator solutions. Also try two natural indicator solutions, such as turmeric, red cabbage juice, or grape juice. You may need to use a greater volume of indicator when using the natural indicators. Add until you can clearly see a color change.

Part 2: Titration of borax solution with a pH meter

1. Pipet 20.00 ml of 4% borax solution into a 150 ml beaker.
2. Fill the buret with the 0.500 M citric acid solution so that the meniscus is on the 0.00 ml line of the buret.
3. Place your pH meter in the borax solution. Swirl it around and record the pH. This is the pH at 0.00 ml of citric acid.
4. Begin to add approximately 0.5 ml aliquots from the buret. Record the exact volume to the hundredths place in Table 12.2. Add approximately 0.2 ml aliquots once you notice the pH begins to drop more significantly. Record the data in Table 12.2, or you may use an Excel spreadsheet.
5. Use the recorded data to make a plot of the titration curve.

Part 3: Titration of borax solution using the appropriate indicator(s)

1. Determine which synthetic indicator and which natural indicator show a color change at about the same pH as the equivalence point determined in Part 2.
2. Pipet 20.00 ml of borax solution into a 150 ml beaker.
3. Fill the buret with 0.500 M citric acid solution so that the meniscus is on the 0.00 ml mark of the buret.
4. Place three to five drops of the synthetic indicator determined in step 1 into the beaker. Record the color of the solution.
5. Begin to add 1 ml aliquots from the buret. Refer to Part 2 data to determine about how much citric acid should be released from the buret before adding more slowly. Be sure to swirl the solution often.
6. As the color of the solution begins to change, add smaller aliquots of citric acid until the endpoint is very close. Once very close, add the citric acid dropwise and stir after each drop is added. *Hint*: It is helpful to determine the amount of citric acid added between each drop in case you accidentally go past the endpoint. Add until the color change remains. Record the amount of titrant added to reach the endpoint and the color change of the solution in Table 12.3.
7. Repeat this procedure with the best natural indicator determined in step 1, and record the results. Determine the percent difference from the volume of citric acid needed in Part 2 to reach the equivalence point.
8. Ask at least five other students or groups doing this experiment what volume of citric acid they added to reach the endpoint for both the synthetic and natural indicators. If there are less than five other students doing this experiment, ask everyone. Record these values and determine the standard deviation for each indicator.

Name _____

Data

Part 1: Getting acquainted with the indicators

Table 12.1 Indicator, pH Range, and Color Change

Indicator	pH range	pH endpoint	Beginning color	Ending color
Phenolphthalein				
Phenol red				
Methyl red				

Part 2: Titration of borax solution using a pH meter

Table 12.2 Titration Data

Milliliters of citric acid added	pH	Milliliters of citric acid added	pH	Milliliters of citric acid added	pH

pH of the solution at the equivalence point: _____

Part 3: Titration of borax solution using the appropriate indicator(s)

Table 12.3 Part 3 Data

Indicator	Initial color	Final color	Milliliters of citric acid added	% difference	Standard deviation

Milliliters of citric acid used by other groups:

Observations

Calculations

Percent difference calculations:

Synthetic indicator:

Natural indicator:

Standard deviation calculations:

Synthetic indicator:

Natural indicator:

Analysis

1. In this lab, you selected one indicator, and therefore excluded two other indicators. Justify your decision using pH and equivalence point data.

2. How did the volume of titrant needed to reach the endpoint for the two indicators chosen compare with the volume of titrant needed to reach the equivalence point? Would you consider either or both of them good indicators for this titration? Explain your answer.

3. Evaluate the indicators, considering percent difference, standard deviation, and green chemistry principles. Take into account that phenolphthalein and phenol red are both manufactured from phenol, which is made from petroleum. Which is preferred? Explain your answer.

Think green

1. Many natural indicators such as grape juice are fairly acidic. How will adding an acidic indicator affect acid/base titration results? What can you do to compensate for this? If time and resources permit, try your idea(s) and discuss your results.
2. Automatic titrators are often used in industry. They can be programmed to determine either an equivalence point or an endpoint, set to a defined pH. Research automatic titrators. What problems would be minimized or eliminated if automatic titrators were used instead of indicators? Determine which of the 12 principles of green chemistry would be positively impacted from using automatic titrators and discuss the reasons for your answer.

Presidential green chemistry challenge

In this lab you studied substituting a natural product for a synthetic one. The Environmental Protection Agency (EPA) gave its 1998 Presidential Green Chemistry Award in the Greener Reaction Conditions category to Argonne National Laboratory for developing a synthesis that uses sugars to make organic solvents. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about this synthesis and how it utilizes principles of green chemistry.

chapter thirteen

Preparation and properties of buffer solutions

> A buffer can be thought of as a pH shock absorber; it resists changes in pH when acids or bases are added to a substance. We cannot live without buffers!

Buffers play a significant role in the world around us. For instance, the buffer qualities of soil are important in keeping the pH relatively constant. If the pH were to drop, the organisms living in the soil would not be able to maintain life. This includes plants that are harvested for food! Also, our blood uses buffer systems to maintain a constant pH within our body between 7.35 and 7.45. Even small variations from this range will cause physiological problems.

To understand buffers, we must first understand pH. So what is pH? It is a convenient way to express the concentration of protons (or H^+ ions) in an aqueous solution. pH stands for "potential hydrogen" and is the negative logarithm of the molar concentration of hydrogen ion, as seen in Equation 13.1. Since it is a logarithmic function, even minor changes in pH mean large changes in the hydrogen ion concentration.

$$pH = -\log [H^+] \tag{13.1}$$

Water slightly dissociates to produce equal concentrations of hydrogen and hydroxide ions:

$$H_2O \rightleftharpoons H^+ + OH^- \tag{13.2}$$

The molar concentration of hydrogen ion, $[H^+]$, equals the molar concentration of hydroxide ion, $[OH^-]$, giving a pH equal to 7. Adding an acid increases the H^+ or consumes the OH^-. This causes the $[H^+]$ to increase, which results in a pH less than 7. On the other hand, adding a base increases the OH^- or consumes the H^+. This causes the $[OH^-]$ to increase and results in a pH greater than 7. The pH scale can be summarized as follows:

pH:	1	2	3	4	5	6	7	8	9	10	11	12	13	14
		Acidic				Neutral				Basic				

According to Bronsted and Lowry, an acid can donate a proton (H^+), and a base can accept a proton. After an acid gives up a proton, a species that can accept a proton, a base, is formed from the acid. This base is called the conjugate base of the acid. For example, sodium bicarbonate (HCO_3^-) may lose a proton to become sodium carbonate (CO_3^{-2}). Sodium bicarbonate is the acid, and sodium carbonate is the conjugate base.

Acids and bases can be divided into two broad categories, strong and weak. Strong acids dissociate almost completely in water. Their H^+ cannot handle a + 1 charge, and so it immediately combines with water to form H_3O^+ ions. Strong bases quickly accept protons. Weak acids and bases lose and gain protons with difficulty and dissociate in water much less than strong acids and bases.

What is a buffer? A buffer will resist efforts to change the pH. Buffer solutions contain significant quantities of both partners of a Bronsted-Lowry conjugate acid-base pair. To form a buffer, a weak acid is mixed with its conjugate base, or a weak base with its conjugate acid. Weak acids, instead of strong ones, must be used in buffers so the conjugate bases will have a tendency to react with protons. If a strong acid were mixed with its conjugate base, the conjugate base would have no tendency to react with protons. This would leave the solution vulnerable to attack by protons.

Suppose sodium bicarbonate is mixed with its conjugate base, sodium carbonate. An acid and a base would both be present in the solution that would tend to react with any added acid or base. If a source of H^+ is added, the conjugate base, sodium carbonate, will react as follows:

$$H^+ + CO_3^{-2} \rightarrow HCO_3^-$$

If OH^- is added, the weak acid, sodium bicarbonate, will react as follows:

$$OH^- + HCO_3^- \rightarrow H_2O + CO_3^{-2}$$

In both circumstances, the acid or base introduced will not significantly change the pH of the solution.

How is the pH of a buffer calculated? If a buffer solution is made by mixing equivalent concentrations of any weak acid and its conjugate base, the pH of the solution will equal the pK_a of the weak acid. The pK_a is the acid dissociation constant that is given to you. Knowing this fact allows us to prepare buffer solutions to maintain almost any pH.

The Henderson-Hasselbalch equation provides a mathematical relationship between the pH, the pK_a of a weak acid, and the concentrations of the weak acid and its conjugate base:

$$pH = pK_a + \log([Base]/[Acid])$$

Addition of acids and bases will alter the [Base]/[Acid] ratio and, in turn, change the pH. Since the pH change is related to the *log* of the change in the ratio, the pH change is relatively small.

Example

Calculate the pH of a buffer solution that has an equimolar solution of sodium acetate and acetic acid. The buffer solution contains 10 ml of acetic acid and 13 ml of sodium acetate. (*Note*: The pK_a of acetic acid is 4.75.)

The pH of the buffer solution can be determined using the Henderson-Hasselbalch equation. Since the concentrations of the acid and salt solutions that make up the buffer are **equimolar** (or equivalent) the ratio of milliliters in the equation can be used.

$$\text{pH} = 4.75 + \log (13/10)$$

$$\text{pH} = 4.86$$

What is buffer capacity? The job of a buffer is to keep the pH from drastically changing. However, when all of the available acid or base in the buffer solution has reacted with the acid or base added, the pH will begin to significantly change. The buffer solution will not be able to maintain the pH as more acid or base is added. This is known as the buffer capacity; it is the maximum amount of acid or base that can be added before a significant change in pH will occur.

Buffer capacity explains why acid rain has caused tremendous damage to the environment in some regions. Soil is naturally buffered by different buffering systems. At first, when acid rain falls onto soil, its highest pH buffering system keeps the soil's pH from changing significantly. This can go on for a long time, but if the buffer capacity is reached, the pH will quickly drop to the next buffering system's pH.

In this lab you will make different buffer solutions using acetic acid and sodium acetate. You will obtain the pH for each one and compare it to the calculated pH. Next, you see what happens when you add increasing amounts of diet cola, a weak acid, and borax solution, a weak base, to a buffer solution.

Objective

In this lab you will use the Henderson-Hasselbalch equation to calculate the expected pH and compare these values to experimental ones for acetic acid and sodium acetate solutions. You will also use experimentation to observe buffer capacities.

Name _____

Prelab questions

1. What would you estimate the pH of hydrochloric acid, a strong acid, to be? What is the pH of pure water?

2. One of the buffer systems our body uses to maintain the pH of blood is the carbonate system where H_2CO_3 is the acid and HCO_3^- is the base. Use the Henderson-Hasselbalch equation to calculate the pH of a blood's carbonate buffering system if it has a $[HCO_3^-]/[H_2CO_3]$ ratio of 10 to 1 and the pK_a of H_2CO_3 is 6.37.

3. Our body also uses a phosphate buffering system where $H_2PO_4^-$ is the acid and HPO_4^{2-} is the base. Use the Henderson-Hasselbalch equation to calculate the $[HPO_4^{2-}]/[H_2PO_4^-]$ ratio needed to maintain a pH of 7.41 and the pK_a of $H_2PO_4^-$ is 7.21.

4. Look at Table 13.1 in Part 1 of the procedure portion of the lab. Calculate the expected pH of the buffer solutions (A – E) using the Henderson-Hasselbalch equation. Assume the solutions of acetic acid and sodium acetate are equimolar.

   Buffer solution A:

   Buffer solution B:

   Buffer solution C:

   Buffer solution D:

   Buffer solution E:

5. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist and list them. What protective equipment will you need to use?

Procedure

Part 1: Preparing the buffer solution

1. Obtain approximately 50 ml of 5% white vinegar in a 150 ml beaker to use as your source of acetic acid. Use 0.494 M for the molarity of the acetic acid.
2. Obtain approximately 50 ml of 0.500 M sodium acetate solution in a 150 ml beaker.
3. Label five small (50 – 150 ml) beakers as A, B, C, D, and E. Follow Table 13.1 to prepare buffers A – E. Use volumetric pipets to measure the solutions. Be sure to mix each solution well.
4. Calibrate a pH meter using pH standards of 4 and 7.
5. Obtain the pH of each of the buffer solutions you prepared. Be sure to rinse the pH probe with deionized (DI) water before placing it into a different buffer solution. Record your readings in the appropriate place in Table 13.2.

Part 2: Observing the effects of acid and base on buffer solution

1. Prepare two of the same buffer solutions, F and G, by adding 10.00 ml of both 0.494 M acetic acid and 0.500 M sodium acetate into two 150 ml beakers. A 10 ml graduated cylinder may be used to measure the solutions. Mix well.
2. Use a pH meter to obtain the pH of both buffer solutions. Record these values in the appropriate places in Tables 13.3 and 13.4.
3. A diet cola containing phosphoric acid will be used to observe the effects of an acid on buffer F. If not already done, heat about 50 ml of the diet cola in a 125 ml Erlenmeyer flask in a microwave oven for 30 seconds to release CO_2. Remove the flask using an oven mitt. ***Caution:*** The solution will be hot! (A hot plate may be used if a microwave is not available.)
4. Stir the cola. If bubbles appear, heat the cola in the microwave for additional 30-second intervals until it is flat. Allow the solution to cool to room temperature.

Table 13.1 Preparation of Buffers A–E

Buffer	Milliliters of 0.494 M CH_3COOH	Milliliters of 0.500 M CH_3COONa
A	10.00	10.00
B	10.00	2.00
C	20.00	2.00
D	2.00	20.00
E	2.00	10.00

5. Use a 10 ml graduated cylinder to add 5 ml of the cola to buffer F and mix well. Obtain and record the pH in Table 13.3.
6. Add 5 more ml of the cola to buffer F and mix well. Obtain and record the pH in Table 13.3 (pH with 10 ml of cola).
7. Add 10 more ml of cola to buffer F and mix well. Obtain and record the pH in Table 13.3 (pH with 20 ml of cola).
8. Place approximately 20 ml of DI water into a 150 ml beaker and mix well. Obtain and record the pH in Table 13.3.
9. Add 5 ml of cola into the beaker with 20 ml of water and mix well. Obtain and record the pH in Table 13.3.
10. Obtain about 30 ml of 4% borax solution (w/v) in a small beaker. The borax solution will be used to observe the effects of a base on buffer G.
11. Use a 10 ml graduated cylinder to add 5.0 ml of the borax solution to buffer G and mix well. Obtain and record the pH in Table 13.4.
12. Add an additional 5.0 ml of borax solution to buffer G and mix well. Obtain and record the pH in Table 13.4 (pH with 10 ml of borax solution).
13. Add an additional 10.0 ml of borax solution to buffer G and mix well. Obtain and record the pH in Table 13.4 (pH with 20 ml of borax solution).
14. Place approximately 20 ml of water into a 150 ml beaker. Obtain its pH and record it in Table 13.4.
15. Add 5.0 ml of borax solution into the beaker with 20 ml of DI water and mix well. Obtain and record the pH in Table 13.4.
16. Add an additional 5.0 ml of borax solution to DI water and mix well. Obtain and record the pH in Table 13.4 (pH with 10 ml of borax solution).
17. Add an additional 10.0 ml of borax solution to DI water and mix well. Obtain and record the pH in Table 13.4 (pH with 20 ml of borax solution).

Name _____

Data

Part 1: Preparing the buffer solution

Table 13.2 pH of Buffer Solutions A–E

Buffer	Milliliters of 0.494 M CH_3COOH	Milliliters of 0.500 M $CH_3COO^-Na^+$	pH measured
A	10.00	10.00	
B	10.00	2.00	
C	20.00	2.00	
D	2.00	20.00	
E	2.00	10.00	

Part 2: Observing the effects of acid and base on buffer solution

Table 13.3 Observing Effects of Acid on Buffer F and Water

	pH with 0 ml of cola	pH with 5 ml of cola	pH with 10 ml of cola	pH with 20 ml of cola
Buffer F				
Water				

Table 13.4 Observing Effects of Base on Buffer G and Water

	pH with 0 ml of borax solution	pH with 5 ml of borax solution	pH with 10 ml of borax solution	pH with 20 ml of borax solution
Buffer G				
Water				

Observations

Part 1: Preparing the buffer solution

Part 2: Observing the effects of acid and base on buffer solution

Analysis

1. How do the calculated pH values of buffers A, B, C, D, and E (found in prelab question 3) compare to the actual pH values that you measured in Table 13.1. Hypothesize possible reasons they are not an exact match.

2. Compare the pH of the buffer solutions A, F, and G. Are these results what you would expect? Explain your answer.

3. Did either buffer F or G reach buffer capacity? Explain your answer.

4. What happened when the cola and the borax solution were added to the water? Was there any evidence of buffering? Explain your answer.

Think green

1. Design an experiment to determine how much energy is saved in Part 2 by using the microwave oven you used instead of a hot plate. If there are time and resources available, test your experiment and discuss your results. Use 950 W for the hot plate if the wattage is not shown.
2. Research the various human body blood buffer systems and find out how they work. What happens when blood pH is not in the correct range? Write a summary about what you discover.
3. Research soil buffer systems and find out how they work. How does acid rain affect them? What happens when soil pH is not in the correct range? How does adding lime work? Write a summary about what you discover.

Presidential green chemistry challenge

Soil has a buffering system that acid rain may eventually cause to reach buffer capacity. The Environmental Protection Agency (EPA) gave its 1996 Presidential Green Chemistry Award in the Designing Greener Chemicals category to Rohm and Haas Company for developing a marine antifoulant that is environmentally safe and helps to decrease acid rain by decreasing fuel consumption. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about how this technology utilizes principles of green chemistry.

chapter fourteen

Determination of the rate of reaction and its order

The speed of a car is expressed as the change in the car's position over a certain period of time. This is analogous to a reaction rate.

In chemistry, the rate of a reaction is the change in the concentration of reactants or products per unit of time. Different units may be used, but a common one is molarity over seconds (M/s). The rate of reaction can depend on several different factors, including concentrations of the reactants, temperature, and use of a catalyst.

Catalysis is one of the 12 principles of green chemistry. A catalyst increases the speed at which a reaction occurs by providing an alternative pathway for the reaction to occur at a lower activation energy. This can greatly increase the rate that product is made and significantly lower energy costs. Many catalysts contain hazardous heavy metals in their structure, but they remain in use since they are usually fairly generic and able to catalyze a large number of different reactions. Only very small quantities are needed, and they can usually be regenerated, meaning that little hazardous heavy metal waste needs to be properly disposed. Even though catalyst waste can often be greatly reduced, a large amount of research has been performed to create more environmentally benign catalysts. This is often done by using a less hazardous metal or creating a catalyst that contains a much smaller percentage of a hazardous heavy metal.

Recently, more enzymes are being used as industrial catalysts. Enzymes are large molecules that are naturally used in biological processes to catalyze specific reactions. They have a small, very specific area where only a particular reaction can occur. Since they are so specific, the challenge is to find an enzyme that will work.

Hydrogen peroxide decomposes very slowly over time to form water and oxygen gas. The reaction can be written as

$$2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

A bottle of hydrogen peroxide available for purchase over the counter typically says it is 3%. However, over time it can slowly decompose, so its

concentration needs to be determined. Many catalysts can be used that will speed up this reaction, including the common enzyme catalase. It is found naturally in many things, including carrots, potatoes, yeast, meat, and even dirt. One of the 12 principles of green chemistry is *design for degradation*. This means that like hydrogen peroxide, molecules should be designed to be biodegradable after they are no longer useful.

In the first part of this experiment you will use the catalase in yeast to determine the concentration of hydrogen peroxide in an over-the-counter bottle of hydrogen peroxide. The oxygen produced in the decomposition of H_2O_2 can be collected and the amount determined. The ideal gas law ($PV = nRT$) can then be used to determine its concentration.

Example

If 2.00 ml of a H_2O_2 solution produces 20.00 ml of O_2 at 25.0°C and 1.00 atm pressure, what is the molarity of the hydrogen peroxide?

First, the ideal gas law is rewritten to solve for the number of moles of O_2, n:

$$n = \frac{PV}{RT} \tag{14.1}$$

Next, the pressure (P), volume (V) of O_2 in liters, and temperature (T) in K must be calculated:

$$P = \text{atmospheric pressure} - \text{water vapor pressure}$$

The water vapor pressure at 25°C can be found in a chemical handbook and found to be 24.0 mmHg.

$$\text{Water pressure} = 24.0 \text{ mmHg} \times 1.00 \text{ atm}/760 \text{ mmHg} = 0.0316 \text{ atm}$$

$$P = 1.000 \text{ atm} - 0.032 = 0.968 \text{ atm}$$

$$V \text{ of } O_2 = 20.00 \text{ ml} \times 1 \text{ L}/1000 \text{ ml} = 0.020 \text{ L}$$

$$T = 25.00°\text{C} + 273.15 = 298.15 \text{ K}$$

Since R is the known constant 0.08206 L·atm/mole·K, the moles of O_2 (n) can now be determined:

$$n = \frac{0.968 \text{ atm} \times 0.02000 \text{ L}}{0.08206 \dfrac{\text{Liter} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298.15 \text{K}}$$

$$n = 7.91 \times 10^{-4} \text{ mole of } O_2$$

This is the number of moles that was produced from a 2.00 ml (0.00200 L) sample. Since it takes 2 moles of H_2O_2 to make 1 mole of O_2, the molar concentration of H_2O_2 is

$$M_{H_2O_2} = \frac{7.91 \times 10^{-4} \text{mol } O_2}{0.00200 \text{ L}} \times \frac{2 \text{ mol } H_2O_2}{1 \text{ mol } O_2} = 0.791 \text{ M}$$

In the second part of this lab, you will determine the initial reaction rate of hydrogen peroxide decomposition using potassium iodide to speed up the reaction. One proposed mechanism for this reaction involves two steps, where the first step determines the reaction rate since it is a much slower step than the second step and involves both reactants:

$$H_2O_2 + I^- \rightarrow IO^- + H_2O$$

$$H_2O_2 + IO^- \rightarrow I^- + H_2O + O_2$$

This part studies the initial rate of the reaction's dependence on the concentrations of the hydrogen peroxide and the potassium iodide. A way of studying this effect is through the rate law. The rate law for the reaction you will be completing is shown in Equation 14.2, where *m* is the order of KI and *n* is the order of H_2O_2:

$$\text{Rate} = k[\text{KI}]^m[H_2O_2]^n \tag{14.2}$$

It shows how the rate depends on the concentrations of KI and H_2O_2 for the reaction. The orders are not the coefficients in a balanced equation and must be found experimentally by determining how the rate is affected by changes in the concentration of the reactants. Once these have been found, the rate constant *k* can be calculated. After all variables are known, the rate law can be established for this chemical system.

To experimentally find the orders of KI and H_2O_2, you will first determine the amount of O_2 produced at certain time intervals after KI and H_2O_2 are mixed together. You will next graph your results as product formed versus time and calculate the slope of the line that will be used as the rate. Three experiments will be performed with varying concentrations of each reactant, as shown in Table 14.1. The actual H_2O_2 molarity will be determined in Part 1, and the rate unit will be milliliters of O_2 per second.

As shown, Trials 1 and 3 vary the concentration of the H_2O_2, but not the concentration of the KI. These two trials can be used to find the dependence of the rate of the reaction on the H_2O_2 concentration. You will use

Table 14.1 Concentrations Used of H_2O_2 and KI

Experiment	H_2O_2	KI
1	5 ml of ~0.88 M H_2O_2	10 ml of 0.60 M KI
2	5 ml of ~0.88 M H_2O_2	10 ml of 0.30 M KI
3	5 ml of ~0.59 M H_2O_2	10 ml of 0.60 M KI

these two trials to find the order of the H_2O_2 (n). First, you will create a ratio of the data obtained from these two trials, as shown in Equation 14.3:

$$\frac{rate\ trial\ 1}{rate\ trial\ 3} = \frac{k[\mathrm{KI}]^m_{trial\,1}[\mathrm{H_2O_2}]^n_{trial\,1}}{k[\mathrm{KI}]^m_{trial\,3}[\mathrm{H_2O_2}]^n_{trial\,3}} \tag{14.3}$$

Since the concentration of KI is the same in these two trials, the equation can be simplified to Equation 14.4:

$$\frac{rate\ trial\ 1}{rate\ trial\ 3} = \frac{[\mathrm{H_2O_2}]^n_{trial\,1}}{[\mathrm{H_2O_2}]^n_{trial\,3}} \tag{14.4}$$

To solve this equation, you will take the reaction rate of Trial 1 and divide it by the reaction rate of Trial 3. Next, you will divide the concentration of H_2O_2 of Trial 1 by the concentration of H_2O_2 of Trial 3. These calculations are found in Equations 14.5 and 14.6, respectively:

$$x_{\mathrm{H_2O_2}} = \frac{rate\ trial\ 1}{rate\ trial\ 3} \tag{14.5}$$

$$y_{\mathrm{H_2O_2}} = \frac{[\mathrm{H_2O_2}]trial\ 1}{[\mathrm{H_2O_2}]trial\ 3} \tag{14.6}$$

Finally, taking the log of the result of Equation 14.3 and dividing this by the log of the result of Equation 14.4 will give you the order of H_2O_2, shown in Equation 14.7:

$$n = \frac{\log x_{\mathrm{H_2O_2}}}{\log y_{\mathrm{H_2O_2}}} \tag{14.7}$$

To find the order of the KI (m), you will use the same calculations as H_2O_2, except with the data for the first and second trials since these vary the KI concentration, but not the H_2O_2 concentration. Experiment 1 values are placed in the numerator since this is the higher concentration of KI. The overall order of this reaction is the sum of $m + n$.

The last factor needed for the rate law is the rate constant. For this, the values for each experiment are inserted into the rate law (Equation 14.2) and *k* is found. An average is then calculated. The units for this will be in milliliters of O_2 per second per M.

Objective

In this experiment you will first determine the concentration of the H_2O_2 being used. Next, you will determine the order of the reaction and the rate constant for the reaction of potassium iodide and hydrogen peroxide.

Name _____

Prelab questions

1. What is the molarity of a solution made from taking 10.00 ml of 3.00% H_2O_2 (v/v) and diluting it with deionized (DI) water to 15.00 ml? Use 1.0095 g/ml as the density of 3% H_2O_2. *Hint*: Calculate the molarity of 3.00% H_2O_2 using its density and molar mass. Next, use the equation

$$M_{initial}V_{initial} = M_{final}V_{final}$$

2. When finding the order of H_2O_2, why will Experiments 1 and 3 be used?

3. When finding the order of KI, why will Experiments 1 and 2 be used?

4. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

Part 1: Assembling the apparatus for H_2O_2 concentration determination

1. Assemble an apparatus as shown in Figure 14.1. First, place a single-holed rubber stopper with glass tubing coming out about an inch on the top and the bottom of the stopper into a 125 ml Erlenmeyer flask.
2. Connect one end of a piece of rubber tubing to a U tube and the other to the glass tubing coming out of the rubber stopper in the 125 ml flask.
3. Fill a 400 ml beaker approximately up to the 300 ml mark with DI water, and place it by a ring stand with a clamp. Place a piece of latex (or Tygon) tubing that is about a foot long on the glass tube coming out from the top of the rubber stopper in the 125 ml Erlenmeyer flask.
4. Fill a 25 ml buret with DI water. Place your index finger over the top of the buret in such a way that no water will drain out when the buret is inverted. Invert the buret over the beaker of water and place it a couple of inches into the 400 ml beaker. Carefully place the end of the U tube without the rubber tubing into the buret. Secure the buret with a clamp.

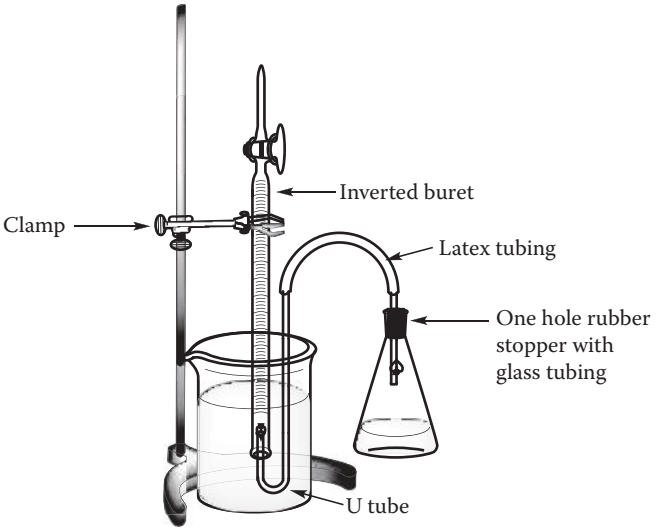


Figure 14.1 Apparatus for finding percent H_2O_2.

5. Carefully and slowly open the buret's stopcock and drain down the water until the volume can be just read. Take a reading of where the water comes up to in the buret and record it in the data section.

Part 2: Determining the H_2O_2 concentration

1. Pour about 40 ml of 3% H_2O_2 into a small beaker for use in Parts 1 and 2.
2. Remove the stopper from the 125 ml Erlenmeyer flask in the assembled apparatus shown in Figure 14.1. Use a volumetric pipet to obtain 2.00 ml of 3% H_2O_2. Add this to the 125 Erlenmeyer flask.
3. Weigh approximately 0.1 g of yeast on weighing paper or in a small beaker.
4. Quickly add the yeast to the 125 ml Erlenmeyer flask and immediately replace the stopper snugly, making sure the seals are airtight. Swirl the Erlenmeyer flask. Oxygen should begin to flow into the buret almost immediately. If it does not, you have a gas leak and need to fix it and begin again.
5. Swirl the flask until no more oxygen goes into the buret. Obtain and record the barometric pressure, the water temperature in the 400 ml beaker, and the milliliters of water left in the buret. Determine the volume of oxygen that went into the buret.
6. Look up the water vapor pressure in a chemical handbook for the water temperature. Calculate and record the molarity of the H_2O_2 for each trial.
7. Repeat this procedure if a second trial is to be done. Average the molarities.

Part 3: Preparation of apparatus for reaction rate determinations

1. Assemble an apparatus as shown in Figure 14.2. First, place a single-holed rubber stopper with glass tubing coming out about an inch on the top and the bottom of the stopper into a 125 ml Erlenmeyer flask.
2. Fill a 250 ml Erlenmeyer flask up to the 200 ml mark with DI water, and secure it to a ring stand with either a ring or clamp. Place a double-holed stopper with glass tubing in each hole into this 250 ml Erlenmeyer flask. Let one piece of glass tubing extend almost to the bottom of the flask and one piece extend just a small amount past the rubber stopper. Make sure the shorter piece does not touch the water in the Erlenmeyer flask.
3. Place a piece of latex (or Tygon) tubing that is about a foot long on each of the glass tubes coming out from the top of the rubber stopper in the 250 ml Erlenmeyer flask.

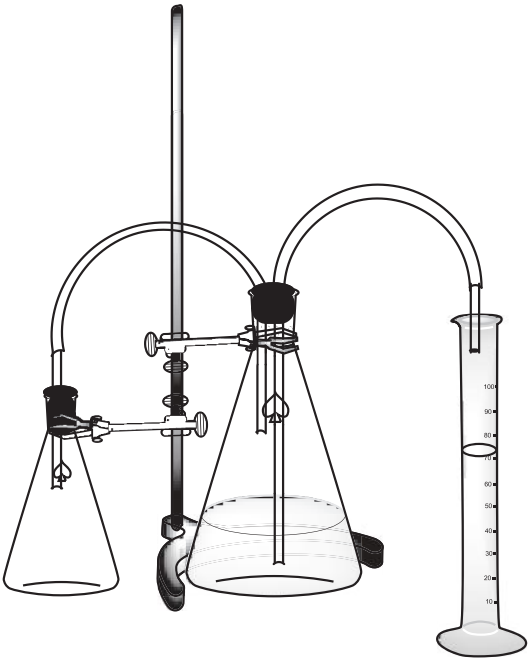


Figure 14.2 Apparatus for reaction rate determinations.

4. Connect the side with the shorter glass tubing to the glass tubing coming out of the top of the 125 ml Erlenmeyer flask.
5. Place a glass tube on the end of the latex tube that is connected to the longer glass tube and clamp it so that water coming through it will run into a tall 25.0 ml graduated cylinder. Ensure that all the seals are airtight.

Part 4: Determining the reaction rate trials

1. Pour 10.0 ml of 3.0% H_2O_2 (mass/volume) into a tall 25 ml graduated cylinder and dilute it with DI water to 15.0 ml. Calculate its actual molarity using the value you determined in Part 1 for the H_2O_2 molarity.

Experiment 1: 0.88 M H_2O_2 and 0.60 M KI

2. Accurately measure 5.00 ml of the H_2O_2 you determined the concentration of in Part 2 into a clean and dry 10 ml graduated cylinder.
3. Remove the rubber stopper and pour the solution into the 125 ml Erlenmeyer flask of the apparatus.
4. Accurately measure 10.00 ml of 0.60 M KI into a 10 ml clean and dry graduated cylinder. Quickly but carefully pour it into the 125 ml

Erlenmeyer flask and immediately replace the stopper. Make sure the seals are airtight.

5. Swirl the 125 ml flask for a few seconds to mix the solutions.
6. Start timing when a steady and constant flow of drops of water are transferring to the graduated cylinder. This may take around 5.0 ml. Record the time in Table 14.2 each time 2.00 ml of water is displaced. Continue until 12.00 ml of water has been displaced since you began timing.
7. Make a scatter graph of the volume of water displaced (y axis) versus time in seconds (x axis) using Microsoft Excel or an equivalent graphing program. Add a linear trendline and display the equation and R^2 value on the graph. Record the slope of the trendline. (*Note*: If you reverse the axes, you will need to use the inverse slope.)
8. Repeat this procedure if a second trial is to be conducted, and average the slopes.

Experiment 2: ~0.88 M H_2O_2 and 0.30 M KI

9. Use the same procedure as Experiment 1, only for the KI solution substitute 10.00 ml of 0.30 M KI instead.

Experiment 3: Diluted H_2O_2 and 0.60 M KI

10. Use the same procedure as Experiment 1, only for the H_2O_2 solution use 5.00 ml of the diluted H_2O_2 instead.

Name _____

Data

Part 2: Determining the H_2O_2 concentration

Barometric pressure: _____

Water temperature: _____

Water pressure: _____

Beginning buret reading for Trial 1: _____

Beginning buret reading for Trial 2: _____

Milliliters of water left in the buret for Trial 1: _____

Milliliters of water left in the buret for Trial 2: _____

Milliliters of O_2 obtained in Trial 1: _____

Milliliters of O_2 obtained in Trial 2 (optional): _____

Average milliliters of O_2 obtained (optional): _____

Part 4: Determining the reaction rate trials

Table 14.2 Rate of Reactions Data for Experiments 1–3

Milliliters of water displaced from when started timing	Experiment 1 time (seconds)		Experiment 2 time (seconds)		Experiment 3 time (seconds)	
	Trial 1	Trial 2 (optional)	Trial 1	Trial 2 (optional)	Trial 1	Trial 2 (optional)
2.00						
4.00						
6.00						
8.00						
10.00						
12.00						

Observations

Part 2: Determining the H_2O_2 concentration

Part 4: Determining the reaction rate trials

Calculations

Part 2: Determining the H_2O_2 concentration

Actual molarity of the 3% H_2O_2 calculation:

Part 4: Determining the reaction rate trials

Actual molarity of the diluted H_2O_2 calculation:

Table 14.3 Reaction Rates for Experiments 1–3

Experiment 1 slopes		Experiment 2 slopes		Experiment 3 slopes	
Trial 1	Trial 2 (optional)	Trial 1	Trial 2 (optional)	Trial 1	Trial 2 (optional)
Average if 2 trials:		Average if 2 trials:		Average if 2 trials:	

Analysis

1. Determine the order of the H_2O_2 in this reaction.

2. Determine the order of the KI in this reaction.

3. Calculate the rate law constant (k) for each experiment and the average rate law constant.

4. What is the overall rate law?

Think green

1. If time and resources permit, expand the experiment to include several more trials with other concentrations of KI and H_2O_2. Evaluate the results. Do they support the original experiment values?
2. In this lab, you used both catalase and KI as catalysts to decompose hydrogen peroxide. There are other catalysts that can be used for this, including PbO_2 and MnO_2. Evaluate these four catalysts in terms of the 12 principles of green chemistry and determine which one is greener. Include risks associated with using these chemicals.

Presidential green chemistry challenge

In this lab you studied reaction rate and reaction order using an enzyme catalyst. The Environmental Protection Agency (EPA) gave its 2012 Presidential Green Chemistry Award in the Greener Synthetic Pathways category to Codexis, Inc. for developing a greener synthesis that uses a biocatalyst to produce Simvastatin, a drug used to treat high cholesterol. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about how using this biocatalyst utilizes principles of green chemistry.

chapter fifteen

Equilibrium constant for ferric ion–salicylic acid complex determination

Businesses are constantly concerned with how to reduce costs and increase revenue. There are two ways this can be accomplished: raising prices, or lowering production costs and increasing yields. Because raising prices tends to have unwanted effects, manufacturers turn to chemists and engineers to help them lower their production costs and increase product yields. Many reactions have some ceiling that cannot be overcome by just adding more reactants, so other factors must be changed to increase yield. One way this ceiling can be described is by the equilibrium constant.

The reactions studied up until now have been perceived as one-way reactions where products don't spontaneously reproduce reactants. In chemical reactions, this full conversion is not usually the case. Reactants constantly form products, but products also form reactants.

Take the reaction of A with B to form C, as shown below:

$$aA + bB \rightleftharpoons cC$$

The arrow in this reaction points both ways! The forward reaction has A reacting with B to form C, while the reverse reaction has C decomposing into A and B. Eventually there will be a point where the forward reaction and the reverse reaction are happening at equal rates. This point is called equilibrium.

At equilibrium, the molar concentrations of products and reactants will be at a fixed ratio. This ratio is ultimately used to describe how much product will be formed in a chemical reaction. The ratio is the equilibrium constant. The equilibrium constant is denoted K_{eq} and can be calculated by raising the molar concentrations of products to their coefficients and

dividing them by the reactant's molar concentrations raised to their coefficients. A general reaction equation and its corresponding equilibrium constant equation can be seen below:

$$aA + bB \rightleftharpoons cC + dD$$

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

From this equation you can see that K_{eq} remains the same at a given temperature even if the molar concentrations change. To calculate an equilibrium constant in the lab, known concentrations of the reactants are reacted until equilibrium is reached. At equilibrium, the concentration of one product is determined, often by UV-visible spectrometry using a standard curve. Knowing the initial concentration of the reactants, the amount of a product formed, and the stoichiometry of the reaction allow for the calculation of how much of the reactants are present at equilibrium.

An ICE chart is often created to assist in determining K_{eq}. ICE is an acronym that stands for "initial change equilibrium," and it records the initial and final concentrations of products and relates those concentrations using a variable of change (x). The amount of change is dictated by stoichiometry. If the initial concentration of the reactants is known and the concentration of one of the products at equilibrium can be determined, then K_{eq} can be calculated.

In this experiment, you will calculate an equilibrium constant for the following reaction first at room temperature and later at varying conditions:

$$Fe^{3+} + C_6H_4(OH)COOH \rightleftharpoons [FeC_6H_4(OH)COOH]^{3+}$$

At the pH you will first make this complex; only one salicylic acid molecule complexes, as shown with one ferric ion. This equilibrium reaction forms 1 mole of a ferric ion–salicylic acid complex, which will be referred to as FeSA. It has a deep purple color that is easily quantifiable by UV-visible spectroscopy.

In the first procedure you will use a UV-visible spectrometer to create a linear calibration curve using standard solutions so the concentration of FeSA at equilibrium can be determined. The calibration curve is made by plotting the absorbances of the standard solutions at a particular wavelength against their concentrations and adding a trendline and its line equation. In the creation of the calibration curve it is important to use a large excess of ferric ammonium sulfate. This drives the reaction almost

to completion, and allows for the assumption that all of the salicylic acid is being converted to the FeSA. Additionally, this procedure is pH dependent. For this reason, the total volume and the reagents are made using 0.002 M HCl.

In the second part of the experiment you will calculate the equilibrium constant at room temperature for this reaction by obtaining the absorbance of a solution made from known concentrations of reactants. To do this, you will create an ICE chart to assist in determining K_{eq}.

Example

A reaction often used for an equilibrium constant lab reacts $Fe(NO_3)_3$ with KSCN to form a red solution containing $FeSCN^{2+}$. It involves the following reaction:

$$Fe^{3+}_{(aq)} + SCN^- \rightleftharpoons FeSCN^{2+}_{(aq)}$$

When doing this experiment, a student mixed 5.00 ml of 1.00×10^{-3} M $Fe(NO_3)_3$ with 4.00 ml of 1.00×10^{-3} M KSCN and diluted to 10.00 total ml using a weak acid solution. A red solution of $FeSCN^{2+}$ was formed, and its concentration at equilibrium was determined to be 1.00×10^{-4} M.

To determine K_{eq}, the initial concentrations of the reactants must first be determined:

$$\text{Initial concentration} = \text{M of reactant} \cdot \frac{\text{L of reactant used}}{\text{L of total volume}}$$

$$\text{Initial } Fe(NO_3)_3 = 1.00 \times 10^{-3}\ \text{M} \cdot \frac{0.00500\ \text{L}}{0.01000\ \text{L}} = 5.00 \times 10^{-4}\ \text{M}$$

$$\text{Initial KSCN} = 1.00 \times 10^{-3}\ \text{M} \cdot \frac{0.00400\ \text{L}}{0.01000\ \text{L}} = 4.00 \times 10^{-4}\ \text{M}$$

The ICE chart in Table 15.1 can then be made and K_{eq} calculated.

Table 15.1 Example ICE Chart

	M of $Fe(NO_3)_3$	M of KSCN	M of $FeSCN^{2+}$
Initial	5.00×10^{-4} M	4.00×10^{-4} M	0 M
Change	-1.00×10^{-4} M	-1.00×10^{-4} M	$+1.00 \times 10^{-4}$ M
Equilibrium	4.48×10^{-4} M	3.48×10^{-4} M	0.52×10^{-4} M

$$K_{eq} = \frac{[FeSCN^{2+}]}{Fe(NO_3)_3\ [KSCN]}$$

$$K_{eq} = \frac{0.52 \times 10^{-4}\ M}{4.48 \times 10^{-4}\ M \times 3.48 \times 10^{-4}\ M} = 334$$

So how does knowing this lower production costs and increase profits? To increase the yield of a reaction, a few things can be done. Le Chatelier's principle says that taking away products will alter the rate of the reverse reaction and cause the position of equilibrium to shift to the right. The opposite is true for reactants. Running the reaction at an optimized temperature or pH can change the equilibrium constant, to improve the amount of product obtained and reduce waste. This utilizes two principles of green chemistry: *atom economy* and *design for energy efficiency*.

Objective

The purpose of this lab is to calculate the equilibrium constant for the reaction forming the iron (III)–salicylic acid complex from ferric ammonium sulfate and salicylic acid by creating a standard curve and utilizing an ICE chart. How the product concentration changes by temperature and pH changes will also be explored.

Name _____

Prelab questions

1. Define the term *equilibrium* and explain the importance of knowing the value of an equilibrium constant.

2. Calculate the molarity of an iron (III)–salicylic acid complex (FeSA) for each of the standard solutions you will use in Part 1 of the procedure to make the calibration curve (Table 15.2). Assume that all salicylic acid is being converted to a 1:1 iron (III)–salicylic acid complex.

Table 15.2 Standard Solutions' Calculated Molarity

Standard	Milliliters of 0.00600 M salicylic acid	Total volume (ml)	Concentration (M) of FeSA
0	0.00	25.00	
1	1.00	25.00	
2	2.00	25.00	
3	3.00	25.00	
4	4.00	25.00	
5	5.00	25.00	

3. Complete the ICE chart for the reaction conditions you will be performing in Part 2 if the iron (III) salicylate concentration was found to be 1.50×10^{-4} M (Table 15.3). (This is different from what you will obtain.)

$$Fe^{3+} + C_6H_4(OH)COOH \rightleftharpoons [FeC_6H_4(OH)COOH]^{3+}$$

Table 15.3 ICE Chart for Iron (III) Salicylate Reaction

	M of ferric ammonium sulfate	M of salicylic acid	M of FeSA
Initial			
Change			
Equilibrium			

4. Write the K_{eq} equation that you will be using showing the substances. Calculate the K_{eq} using the ICE chart created in question 3.

5. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

Part 1: Creation of standard curve

1. If not already done, turn on a UV-visible spectrometer and let it warm up. Set it up according to the instructions for the spectrometer you are using.
2. Retrieve approximately 35 ml of 0.0200 M ferric ammonium sulfate diluted in 0.2 M HCl solution in a 50 ml beaker, and 20 ml of 0.00600 M salicylic acid in a 50 ml beaker.
3. Consecutively label six clean, dry vials or large test tubes 0–5 and place them in order into a test tube rack. Accurately place the amounts of each solution into each vial to make each solution a constant volume of 25.00 ml, as shown in Table 15.4. Place the top on the vial or close off with a small square of parafilm. Mix each solution well.
4. Rinse a cuvette with small amounts of the blank at least three times. Fill the cuvette approximately two-thirds full with the blank. Clean the outside of the cuvette with a KimWipe and place it in the UV-visible spectrometer. Run the blank.
5. Fill the cuvette as you did in step 4 with standard 1 and obtain a spectrum from 400 to 650 nm. Determine the best wavelength to use for a calibration curve. This is often the wavelength with the maximum absorbance and is called the lambda max. However, if too much noise is present for an accurate reading, you may want to choose a different wavelength. If the UV-visible spectrometer does not let you see the spectrum, use 507 nm unless instructed otherwise.
6. Obtain and record the absorbances in Table 15.7 for standards 2 through 5 the same way you did in step 4.
7. Create a graph comparing the absorbance (*y* axis) and concentration (*x* axis) of each sample at the chosen wavelength. Add a trendline of best fit to the graph, and record the trendline equation in the data section.

Table 15.4 Standard Solutions Preparation

Standard	Milliliters of 0.0200 M $NH_4Fe(SO_4)_2$	Milliliters of 0.0060 M salicylic acid	Milliliters of DI water	Total volume
0 (blank)	5.00	0.00	20.00	25.00
1	5.00	1.00	19.0	25.00
2	5.00	2.00	18.0	25.00
3	5.00	3.00	17.0	25.00
4	5.00	4.00	16.0	25.00
5	5.00	5.00	15.0	25.00

Part 2: Calculation of the equilibrium constant for iron (III) salicylate

1. Obtain a little over 10 ml of 0.00400 M $NH_4Fe(SO_4)_2$ in a clean and dry 50 ml beaker.
2. In a vial or test tube, prepare the sample shown in Table 15.5. Mix the solution well, as done in Part 1.
3. Read the absorbance of the solution at the previously chosen wavelength. Calculate the concentration of iron (III) salicylate present using the absorbance and the equation of the standard curve.
4. Create an ICE chart in Table 15.9 for the sample and calculate its equilibrium constant.

Part 3: Effect on absorbance of various factors

1. With the remaining four test tubes, the effects of pH and temperature will be tested. For this, create the samples that are shown in Table 15.6 (ferric ammonium sulfate is labeled FAS and salicylic acid is labeled SA).
2. Obtain and record in Table 15.8 the absorbance of each solution at the previously chosen wavelength.
3. Calculate and record in Table 15.10 the concentrations of iron (III) salicylate present for these solutions using their absorbances and the equation of the standard curve. Compare these values to the value in Part 2.

Table 15.5 Sample Solution Preparation to Determine K_{eq}

Sample	Milliliters of 0.00400 M $NH_4Fe(SO_4)_2$	Milliliters of 0.00600 M salicylic acid	Milliliters of DI water	Total volume (ml)
1	2.00	2.00	21.00	25.00

Table 15.6 Sample Solutions Preparation to Determine Variables' Effects

Sample	Milliliters of 0.0040 M FAS	Milliliters of 0.0060 M SA	Milliliters of DI water	Total volume (ml)	Special addition or condition
1	2.00	2.00	21.0	25.0	Heat 2 minutes in a 60°C hot water bath
2	2.00	2.00	21.0	25.0	Cool 5 minutes in an ice water bath
3	2.00	2.00	16.0	25.0	Add 5 ml 0.01M NaOH
4	2.00	2.00	16.0	25.0	Add 5 ml 0.01M HCl

Name _____

Data

Part 1: Creation of standard curve

Wavelength chosen: _____

Table 15.7 Concentration and Absorbance Values for FeSA

Standard	Concentration (M) of FeSA	Absorbance (AU)
0 (blank)	0 M	
1		
2		
3		
4		
5		

Part 2: Calculation of the equilibrium constant for FeSA

Measured sample absorbance: _____

Part 3: Effect on equilibrium constant for other conditions

Table 15.8 Absorbance for Samples

Sample	Measured absorbance (AU)
1	
2	
3	
4	

Observations

Part 1: Creation of standard curve

Part 2: Calculation of the equilibrium constant for FeSA

Part 3: Effect on equilibrium constant for other conditions

Calculations

Part 1: Creation of standard curve

See prelab question 2 for standard curve molarity values.

Trendline equation from graph:

Part 2: Calculation of the equilibrium constant for FeSA

$$\text{Initial concentration} = \text{M of reactant} \cdot \frac{\text{L of reactant used}}{\text{L of total volume}}$$

Initial M of $NH_4Fe(SO_4)_2$ =

Initial M of salicylic acid =

Trendline equation:

Equilibrium M of FeSA =

Table 15.9 ICE Chart for FeSA Reaction

	M of $NH_4Fe(SO_4)_2$	M of salicylic acid	M of FeSA
Initial			
Change			
Equilibrium			

Calculate the equilibrium constant:

Part 3: Effect on equilibrium constant for other conditions

Calculate the concentration for each listed condition and fill in Table 15.10

Table 15.10 Effect of Other Conditions on Concentration

Sample	Measured absorbance (AU)	Calculated concentration
1		
2		
3		
4		

Analysis

1. Research the chemicals used in the example given in the introduction. What green chemistry principles are explored in this lab? Explain your answer.

2. Why does the standard curve need to be created using a large excess of ferric ammonium sulfate? What would happen if a standard curve was created using stoichiometrically equivalent amounts of both reactants?

3. The effects of slightly varying pH and temperature were tested. Which change was most effective? How effective would slightly changing the concentration of one reactant be?

Think green

1. Evaluate how green the procedure was that you used in this experiment. What are some ways you think this method could be made even greener or could be altered to shift the equilibrium so that more of the product would be produced? If time and resources permit, try your idea(s) and discuss your results.
2. KSCN is often used in equilibrium labs. Although it is highly unlikely in an academic setting, HCN can be formed from KSCN. Research under what conditions this can occur and create a scenario where this would happen in an academic setting from improperly treated waste.
3. If this was a business, how could changing a factor like pH save money in production costs?

Presidential green chemistry challenge

The Environmental Protection Agency (EPA) gave its 2006 Presidential Green Chemistry Award in the Designing Greener Chemicals category to S.C. Johnson & Sons, Inc. for creating a Greenlist™. It is used to evaluate ingredients in its products and reformulate when possible to make them greener. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about this list and explain how it utilizes principles of green chemistry.

chapter sixteen

Determination of amount of ascorbic acid in a vitamin C tablet by redox titration

You have just been hired in quality control at a vitamin supplement company, and on your first day, a potential disaster comes up. Someone forgot to label the containers of vitamin C tablets, and now there is no way to tell which contains 500 mg tablets and which contains 1000 mg tablets! You are tasked with determining just how much vitamin C is in each batch of tablets, and the company has a procedure to do this involving a redox titration. However, this method generates hazardous waste, and due to budget cuts, the company doesn't want to have to pay to dispose of it any longer. So what do you do? A greener method must be developed!

Oxidation is a chemical change involving the loss of electrons that results in an increased oxidation number. This process also includes the loss of a hydrogen atom or gain of an oxygen atom. An example of oxidation is solid zinc losing electrons to go into its ionized form:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$

Reduction is the exact opposite of oxidation. It involves a gain of electrons resulting in decreased or *reduced* oxidation number. Reduction may involve gaining a hydrogen atom or losing an oxygen atom. Aqueous copper gaining electrons to go into its solid form is an example of reduction.

$$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$$

As the name suggests, a redox reaction combines oxidation and reduction. Electrons liberated in the oxidation reaction are used to fuel

the reduction reaction. If the two reactions above are combined, the following net reaction results:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

The above reaction describes using zinc metal to make copper ions come out of solution to form solid copper. But why is this important in green chemistry? One of the purposes of green chemistry is to reduce the environmental impact of chemicals, and that's just what removing copper from the solution does. A solution containing certain copper substances can be dangerous to the environment. But, by plating the copper out of solution, as shown in the reaction above, you form zinc ions and solid copper that normally do not pose as much of an environmental risk.

Now let's get back to the original problem: How do you determine how much ascorbic acid is in the vitamin C tablet? Ascorbic acid is a reducing agent, meaning that it is oxidized in a reaction and causes whatever it reacts with to be reduced. Most typical redox titration reactions use potassium permanganate, a strong oxidizer, to oxidize iron (II) ions into iron (III) ions. So, because this lab is using a reducing agent, you should simply reverse this process and transform iron (III) ions into iron (II) ions. If an unknown amount of ascorbic acid is titrated with a known amount of iron (III) ions, the concentration can be easily determined. The iron (III) (also referred to as ferric) ions can be produced by dissolving ferric ammonium sulfate ($FeNH_4SO_4$) in water.

Salicylic acid is an excellent indicator for this titration. You may be familiar with salicylic acid because it is used to make aspirin and is present in many over-the-counter medicines, such as acne creams. The ferric ions react with salicylic acid to form a ferric-salicylate complex that turns the solution a dark red-purple color (Figure 16.1). However, when no iron (III) ions are present, the solution will be clear.

In the redox titration reaction, ascorbic acid in the vitamin C tablet will be doubly oxidized to form dehydroascorbic acid. The molecular structures are shown in Figures 16.2 and 16.3.

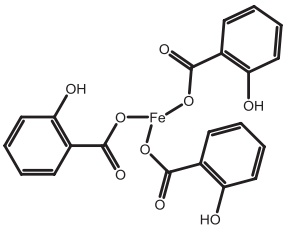


Figure 16.1 Iron (III)–salicylate complex.

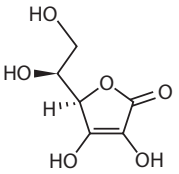


Figure 16.2 Ascorbic acid.

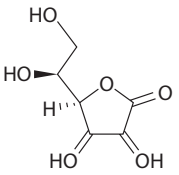


Figure 16.3 Dehydroascorbic acid.

$$Fe^{3+} + \text{Ascorbic acid} \rightarrow Fe^{2+} + \text{Dehydroascorbic acid}$$

In this lab you will prepare a 0.100 M ascorbic acid standard solution and use this to standardize a 0.100 M ferric ammonium sulfate solution that you have also prepared. A salicylic acid solution will be used as the indicator. The calculation is shown below. Note that ascorbic acid is abbreviated to AA.

$$\text{Moles}_{AA} = \text{Total volume}_{AA} \cdot \text{Molarity}_{AA}$$

$$\text{Moles } Fe^{3+} = \text{Moles AA} \cdot \frac{2 \text{ Moles } Fe^{3+}}{1 \text{ Mole AA}}$$

$$\text{Molarity of } Fe^{3+} = \frac{\text{Moles } Fe^{3+}}{\text{Volume } Fe^{3+}} = \text{Molarity of } FeNH_4SO_4$$

Next, you will use your ascorbic acid standard solution to back titrate a solution made from 0.10 crushed vitamin C tablet mixed with excess standardized $FeNH_4SO_4$ solution. A back titration is where an excess of reagent is added, and then the amount of the excess is determined by doing a titration with a second reagent. The second titration shows how much excess of the first reagent was added. This is a back titration since an excess of standardized $FeNH_4SO_4$ is added, and this excess is then titrated with ascorbic acid standard solution. The milligrams of vitamin C in one tablet can now be determined using the calculation shown in the following example.

Example

When determining the milligrams of vitamin C in a tablet, a solution was made by dissolving the mass of a crushed vitamin C tablet in 100 ml of water and filtered. 25.00 ml of this vitamin C solution and 20.00 ml of 0.1000 M $FeNH_4SO_4$ standardized solution were mixed in a 250 ml Erlenmeyer flask and back titrated with 0.1000 M ascorbic acid standard solution. The endpoint was reached after 2.97 ml was added. Calculate the milligrams of vitamin C in one tablet.

$$\text{mmol } Fe^{3+} = M_{Fe^{3+}} \cdot V_{FeNH_4SC_4} \cdot 1000 \text{ mmol/mol}$$

$$\text{mmol } Fe^{3+} = 0.1000 \text{ M}_{Fe3+} \cdot 0.02000 \text{ L} \cdot 1000 \text{ mmol/mol} = 2.000 \text{ mmol}$$

$$\text{mmol AA total} = (2.000 \text{ mmol } Fe^{3+}) \cdot \frac{1 \text{ mmol AA}}{2 \text{ mmol } Fe^{3+}} = 1.000 \text{ mmol}$$

$$0.1000 \text{ M}_{AA} = 0.10000 \text{ mole}_{AA}/\text{L}_{AA} = 0.1000 \text{ mmol}_{AA}/\text{ml}_{AA}$$

$$\text{mmol in AA titrant added} = (2.97 \text{ ml}_{AA})(0.1000 \text{ mmol}_{AA}/\text{ml}_{AA}) = 0.297 \text{ mmol}$$

$$\text{mmol ¼ tablet} = \text{mmol AA total} - \text{mmol in AA titrant}$$

$$\text{mmol ¼ tablet} = 1.000 \text{ mmol} - 0.297 \text{ mmol} = 0.703 \text{ mmol}$$

$$\text{mg AA in 1 tablet} = 4 \cdot 0.703 \text{ mmol ¼ tablet} \cdot \frac{176.12 \text{ mg AA}}{1 \text{ mmol AA}}$$

$$\text{mg AA in 1 tablet} = 495 \text{ mg}$$

Developing a method that replaces potassium permanganate with citric acid and salicylic acid utilizes two of the 12 principles of green chemistry: *prevention* and *use of renewable feedstocks*. Potassium permanganate is a strong oxidizing agent that requires careful storage and use. Citric acid and salicylic acid can both be obtained through natural products.

Objective

The purpose of this lab is to standardize a solution of ferric ammonium sulfate and determine the amount of ascorbic acid in one vitamin C tablet by titration with the standardized ferric ammonium sulfate and back titration with 0.1 M ascorbic acid.

Name _____

Prelab questions

1. Define the terms *oxidation* and *reduction*.

2. Calculate the amount of ascorbic acid needed to produce 100 ml of a 0.100 M solution.

3. Taking into consideration that ascorbic acid ($C_6H_8O_6$) must be oxidized twice to form dehydroascorbic acid ($C_6H_6O_6$), write a reaction equation that balances both elements and electrons.

4. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

Part 1: Preparation of 1.0 M ascorbic acid standard solution

1. Obtain in a 150 ml beaker the correct amount of ascorbic acid to prepare 100 ml of a 0.1 M ascorbic acid using your prelab calculations. Record the exact mass in the data section.
2. Add approximately 50 ml of deionized (DI) water and stir until all the ascorbic acid is dissolved.
3. Use a funnel if needed to carefully transfer the ascorbic acid solution into a 100 ml volumetric flask. Rinse the beaker and funnel with several small portions of DI water and add them to the volumetric flask, making sure not to add past the 100 ml mark. Add DI water until the bottom of the meniscus touches the mark. Stopper the volumetric flask and mix well.
4. Calculate the exact molarity of this ascorbic acid standard solution.

Part 2: Standardization of ferric ammonium sulfate dodecahydrate

1. Obtain in a 150 ml beaker approximately 65 ml of 0.1 M $NH_4Fe(SO_4)_2 \cdot 12H_2O$.
2. Assemble a titration apparatus as shown in Figure 16.4. Use a funnel and fill a 25 ml buret with the 0.1 M ascorbic acid standard solution. Drain some standard solution into a waste beaker until all air bubbles are gone. Fill to the 0.00 ml mark.
3. Label three 125 ml Erlenmeyer flasks 1, 2, and 3 and add 2.00 ml of your 0.1 M ascorbic acid standard solution into each flask from the buret. Record exactly how much 0.1 M ascorbic acid solution you added to each flask in the data table.
4. Add two or three drops of the salicylic acid indicator solution to each flask, and pipet 10.00 ml of 0.1 M ferric ammonium sulfate solution into each one. The resulting solution should be a dark purple.
5. Refill your buret to the 0.00 ml mark. Using proper analytical titration technique, slowly titrate the solution in each Erlenmeyer flask with 0.1 M ascorbic acid standard solution until the solution becomes clear. Record how much titrant was added to each flask in this step in Table 16.1.
6. Determine the total amount of ascorbic acid standard solution that was added. Calculate the exact molarity of the $NH_4Fe(SO_4)_2 \cdot 12H_2O$ solution by first calculating it for each trial and then calculating the average Fe^{3+} molarity.

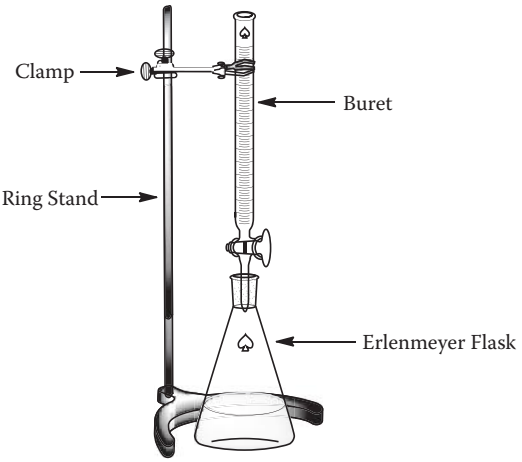


Figure 16.4 Titration apparatus.

Part 3: Titration of vitamin C tablet

1. Obtain three vitamin C tablets, record the mass of each, and calculate the average mass for one tablet. Crush two vitamin C tablets with a mortar and pestle and weigh the average amount of powder that would equal one tablet into a clean and dry 150 ml beaker.
2. Carefully transfer all of the powder into a 100 ml volumetric flask, using DI water to rinse as required. Fill to the mark with DI water and shake well. Filter through Whatman 40 filter paper into a clean and dry 150 ml beaker.
3. Pipet 10.00 ml of the vitamin C tablet solution into three clean 125 ml Erlenmeyer flasks. This is 0.100 of the vitamin C tablet in each flask. Also pipet 10.00 ml of standardized 0.1 M $NH_4Fe(SO_4)_2 \cdot 12H_2O$ solution into each flask. Add two or three drops of salicylic acid indicator solution to each flask. Swirl to mix well and allow it to sit for 5 minutes.
4. Back titrate each flask with the 0.1 M ascorbic acid standard solution, and record the volume added in Table 16.2.
5. Calculate the millimoles ascorbic acid in 0.100 tablet, the average millimoles ascorbic acid in 0.100 tablet and in 1 tablet, and the average milligrams of vitamin C in 1 tablet.
6. After completing the experiment and performing all calculations, check the vitamin C supplement bottle to see the milligrams of vitamin C shown to be in your tablets. Using the information on the bottle, calculate your percent error.

Name _____

Data

Part 1: Preparation of ascorbic acid standard solution

Grams of ascorbic acid: _____

Part 2: Standardization of ferric ammonium sulfate dodecahydrate

Table 16.1 Data for Standardization of Ferric Ammonium Sulfate Dodecahydrate

Trial	1	2	3
Initial volume of ascorbic acid added			
Volume of $FeNH_4SO_4 \cdot 12H_2O$			
Volume of ascorbic acid titrant			
Total volume of ascorbic acid added			
Millimoles Fe^{3+} in solution			
Total millimoles ascorbic acid			
Fe^{3+} solution molarity			
Average Fe^{3+} molarity			

Table 16.2 Data for Titration of Vitamin C Tablet

Trial	1	2	3	Average
Mass of vitamin C tablets				
Volume of $FeNH_4SO_4 \cdot 12H_2O$				
Volume of vitamin C solution				
Millimoles Fe^{3+} in solution				
Volume of ascorbic acid added by titration				
Millimoles ascorbic acid added by titration				
Millimoles ascorbic acid in 0.100 tablet				
Average millimoles ascorbic acid in tablet				
Average milligrams of vitamin C in 1 tablet				
% error				

Observations

Calculations

Part 1: Standardization of ferric ammonium sulfate

Actual ascorbic acid solution's molarity calculation:

Trial 1: Fe^{3+} molarity calculation

Trial 2: Fe^{3+} molarity calculation

Trial 3: Fe^{3+} molarity calculation

Average molarity of Fe^{3+} in ferric ammonium sulfate solution:

Part 2: Titration of vitamin C tablet

Used for all trials:

Trial 1: Calculation for millimoles ascorbic acid in 0.100 tablet

Trial 2: Calculation for millimoles ascorbic acid in 0.100 tablet

Trial 3: Calculation for millimoles ascorbic acid in 0.100 tablet

Average millimoles ascorbic acid in 0.100 tablet:

Average millimoles ascorbic acid in one tablet:

Average milligrams of vitamin C in one tablet:

Actual milligrams of vitamin C in one tablet:

Percent error

$$\% \text{ error} = \frac{|\text{theoretical value} - \text{experiment value}|}{\text{theoretical value}} \times 100$$

Analysis

1. How close were your results to the amount of vitamin C shown on the bottle? Do you consider this acceptable? Explain your answer.

2. Would you expect the pH of the solution to become higher, lower, or stay the same as the ascorbic acid is oxidized?

Think green

1. How would the procedure have to be modified to analyze a 1000 mg vitamin C tablet? If there are time and resources available, try your modified procedure.
2. One standard method uses an iodine titration and a mercury-starch indicator to standardize ferric ammonium sulfate, and another method uses potassium permanganate and strong acids, including sulfuric and phosphoric acids. These chemicals are also typically used in other redox titration labs. Evaluate in terms of the 12 principles of green chemistry why the method utilized in this lab is preferred. Include risks associated with using the chemicals listed in this paragraph.

Presidential green chemistry challenge

Electroplating involves the use of redox reactions. The Environmental Protection Agency (EPA) gave its 2013 Presidential Green Chemistry Award in the Small Business category to Faraday Technology, Inc. for an innovative method for chrome plating using trivalent instead of hexavalent chromium. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about this technology and how it utilizes principles of green chemistry.

chapter seventeen

Qualitative analysis of metal cations and using ion-selective electrodes

> Have you ever wanted to be a detective? Well, regardless of your answer, you are going to become one in this lab by performing qualitative analysis. You're going to investigate how a list of suspects, or metal cations, behave so that you can find out which ones are guilty of being in your unknown solution.

Qualitative analysis is a branch of chemistry dealing with identifying what substances are present in a mixture. In other words, it is like being a chemistry detective. Ions behave in specific ways, and the ways in which they react can tell you which ones are present in a solution of unknown composition.

But, to know if they are in your unknown, you have to be able to see what a positive test looks like. So, you are going to be given a solution containing all five of the following ions: Ca^{2+}, Sr^{2+}, Fe^{3+}, Al^{3+}, and Cu^{2+}. These ions are produced by dissolving mostly their corresponding acetates (compounds that contain the acetate anion—CH_3COO^-) in water.

When compounds dissolve in water, they will typically ionize. Equation 17.1 shows the solvation reaction of calcium acetate dissolving in water:

$$Ca(CH_3COO)_{2(s)} \rightarrow Ca^{2+}{}_{(aq)} + 2CH_3COO^-{}_{(aq)} \qquad (17.1)$$

These ions in solution are free to react with one another to produce another compound. If that new compound is water soluble, it will simply reionize and remain in solution. For example, if a solution containing chloride ions is added to the solution containing calcium ions, calcium chloride would not precipitate out since it is a water-soluble compound.

$$Ca^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)} \rightarrow CaCl_{2(aq)} \rightarrow Ca^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)} \qquad (17.2)$$

However, if the compound is not water soluble, it will precipitate. This is the case when silver ions react with chloride ions:

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)} \quad (17.3)$$

There are solubility rules for ionic compounds that help us know if a compound will precipitate out. A brief summary of these rules is that Group IA, ammonium compounds, acetates, and nitrates, is soluble; most chlorides, bromides, and iodides are soluble; and most carbonates, phosphates, sulfides, and hydroxides are insoluble. Notice that "most" is used for many of the types of compounds. There are exceptions. For example, both Equations 17.2 and 17.3 involve chlorides. One of the solubility rules states that most chlorides are soluble, and yet silver chloride will precipitate. It is one of the known exceptions. In order to minimize side reactions, or reactions that occur in addition to the desired one, most of the compounds used in this lab are acetates.

Throughout this lab, you will see how the ions in solution behave when different chemicals are added—what color changes happen, what precipitates, etc. Flowcharts are very helpful for this type of analysis. A flowchart for this lab is located in the procedure as Figure 17.1. As summarized in this chart, the qualitative identifications are made through three separate sequences. The first sequence confirms the presence or absence of Cu^{2+} and Al^{3+}, the second Fe^{3+}, and the third Sr^{2+} and Ca^{2+}.

In the first sequence, household ammonia is added to the solution being analyzed. If copper ions are present, it will form a complex and turn bright blue. Some of the other ions will precipitate, including Al^{3+}. However, when excess sodium hydroxide is added, the Al^{3+} will redissolve. Equations 17.4 and 17.5 show this reaction sequence:

$$Al^{3+}_{(aq)} + 3NH_{3(aq)} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3NH_4{}^{+}_{(aq)} \quad (17.4)$$

$$Al(OH)_{3(s)} + OH-_{(aq)} \rightarrow Al^{3+}_{(aq)} + 3H_2O_{(l)} \quad (17.5)$$

The solution can be decanted from the precipitate, and when the pH is made weakly acetic using acetic acid, a precipitate will form.

The second sequence confirms the presence or absence of Fe^{3+}. Salicylic acid forms a dark purple complex with iron (III) ions when they are present.

The third sequence begins with a flame test for strontium ion. When strontium ions are present, a flame will have some red around the edges. The presence of strontium ions can be confirmed, as well as determining the presence of calcium ions, by adding a sodium sulfate solution. Strontium and calcium ions will precipitate as sulfates, while copper,

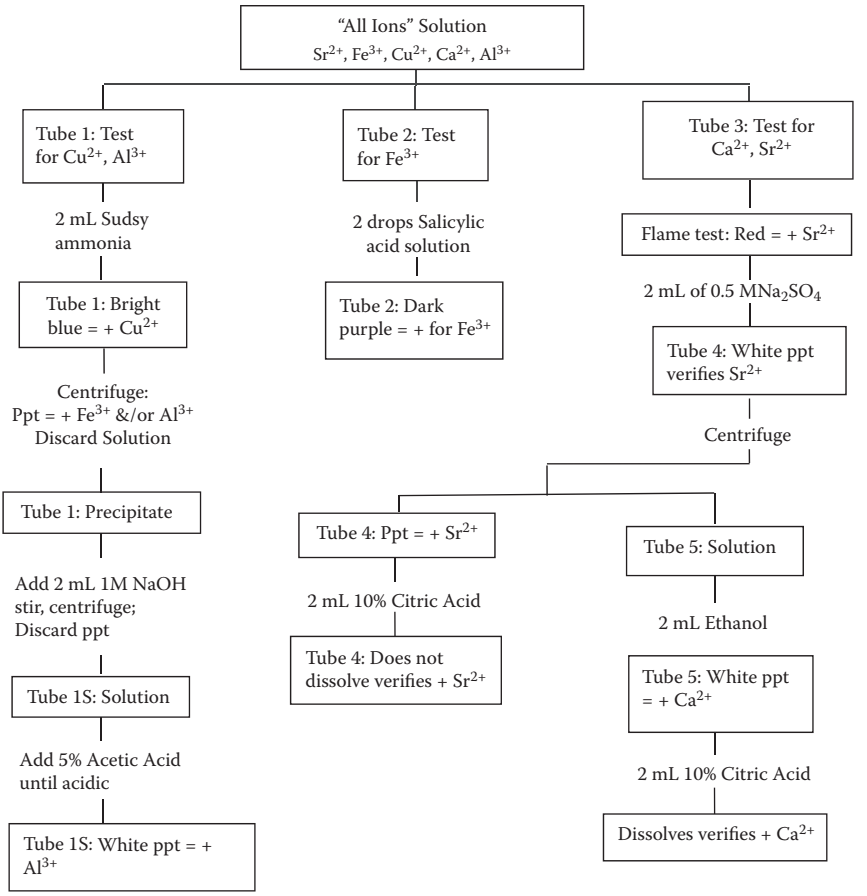


Figure 17.1 Flowchart for known and unknown solutions.

iron, and aluminum ions do not and will remain in the solution. Calcium sulfate is slightly soluble in water, so it will not precipitate out when the sodium sulfate is first added. This allows the strontium sulfate to be separated out first and identified. Calcium sulfate is insoluble in alcohols, so to make it precipitate, you will add ethanol to the solution decanted from the strontium sulfate after it was precipitated. The two sulfates will be further identified by their solubility in acid, specifically citric acid. Calcium sulfate is soluble in citric acid, while strontium sulfate is not.

In this lab, you will first work through the procedure with the known "all ions" solution while referencing the flowchart shown in Figure 17.1. It will be important to record all observations and data and to be as specific as possible on your observations. You should describe the color and consistency of a precipitate, approximately how much there is, etc.

After you have worked through the flowchart with your known sample, you will get an unknown solution that contains some of the ions that were also in your all-ions solution. You will work through the same steps in order to confirm their presence or absence.

As you can see, determining the presence of various ions using a qualitative analysis scheme is not very practical for most applications. This is especially true if a large number of samples have to be analyzed or there has to be continual or regular interval monitoring. For this reason, it is no longer widely used, and has been replaced, for the most part, by chemical instrumentation. There are a large number of chemical instruments available that are designed to perform certain types of analysis. Three instruments that are often used are atomic absorption spectroscopy (AAS), inductively coupled plasma (ICP), and ion-selective electrodes (ISEs). These instruments are also used to determine how much of a particular ion is present.

Flame tests and atomic absorption spectroscopy work on the same principle. They can be used for identification since each element has a unique and distinct set of wavelengths of light that it will absorb. This is due to the configuration of electrons in its outer shell. When an atom receives additional energy from an outside source that is equal to the amount of energy a single electron needs to reach a higher energy orbital or level, the electron will absorb that energy and go to the higher energy level. It then emits the exact amount of energy it absorbed as a wavelength of light that often may be seen as a particular color as it returns to its previous lower energy level.

In a flame test, the energy source is a Bunsen burner. It emits a broad range of energy, but the electrons of the atom being heated will only absorb specific amounts of energy. In AAS the energy source is usually a hollow cathode lamp that emits only the wavelengths for the element being analyzed. The amount of energy absorbed for one specific wavelength is detected. This means AAS can only test for one element at a time. This can be time-consuming if you have a large number of samples that need to be tested for a large number of elements. For this type of analysis, inductively coupled plasma (ICP) is preferred.

When performing an analysis using ICP, sample solutions are introduced into an argon plasma where they are converted into singly charged ions and sent on to be detected and analyzed. There are different types of detectors, including one that incorporates a mass spectrometer (MS). The mass spectrometer sorts the ions by their mass-to-charge ratio (m/z) and sends them on to be detected.

ICP-MS instruments have now been developed to where they can analyze most elements, from lithium to uranium, simultaneously, often down to the parts per trillion level. They can also be used for qualitative analysis and analyze over 80 elements in just a few minutes! For a

qualitative analysis, these ICP instruments mainly require a calibration solution, argon, and electricity. This is definitely a greener method!

Ion-selective electrodes are often used to analyze for specific ions since they are relatively inexpensive, fairly simple to use, and can be portable. This means they can be taken to what needs to be analyzed. ISEs are membrane electrodes that specifically detect a particular ion by measuring the potential of a specific ion in a solution against a reference electrode with a constant potential. ISEs are made for many different ions, including both cations and anions.

One of the 12 principles of green chemistry is *real-time analysis for pollution prevention*. This is often accomplished through the use of ion-selective electrodes. They are frequently used for environmental monitoring and process control, since unlike other methods, they can make in situ (or on-site) measurements. In Part 2 of this lab, you will explore how an ISE can be used to monitor a particular ion by analyzing your all-ions known and your unknown for the calcium ion. ISEs can be sensitive to other ions present, but this is usually to a very small extent. To make sure this is not a problem for your samples, you will check a solution of each ion that may be present first and make sure none of them except the calcium ion solution gives a significant reading.

Objective

You will follow a process to positively identify Cu^{2+}, Al^{3+}, Fe^{3+}, Sr^{2+}, and Ca^{2+} ions; then you will work through the same process to identify which ions are present in an unknown solution. Finally, you will use a calcium ion-selective electrode to determine the presence of calcium in the known and unknown solutions. You will also check to make sure none of the ions present give a significant false reading.

Name _____

Prelab questions

1. What is the difference between *qualitative* and *quantitative* analysis?

2. What are the five ions in the all-ions solution?

3. Prepare a flowchart that shows how you could perform a qualitative analysis on a mixture that could contain Pb^{2+}, Cu^{2+}, and Ca^{2+}. Only Pb^{2+} precipitates as a chloride when dilute HCl is added. Only Pb^{2+} and Cu^{2+} precipitate as sulfides when acidic H_2S is added. Ca^{2+} precipitates when $(NH_4)_2CO_3$ is added.

4. What is an ISE and what is it used for?

5. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

Figure 17.1 shows a flowchart for analysis of known and unknown solutions.

Part 1: Testing for the presence of ions

1. Obtain 10 ml of all-ions solution in a small vial or beaker and a large paper clip or nichrome wire with a small loop at one end.
2. Label six small test tubes 1, 1S, 2, 3, 4, and 5.
3. Continue on through the following procedure while referencing the flowchart in Figure 17.1. Be sure all glassware is clean before use each time. Make observations and record all results in the table provided.

Test for Cu^{2+} and Al^{3+}

4. Place 2 ml all-ions solution in tube 1. In a fume hood add 2 ml sudsy ammonia and stir. Let sit 1–2 minutes and then centrifuge. A blue solution is positive for Cu^{2+}. Discard the solution in the appropriate waste container.
5. Rinse the precipitate with approximately 1 ml deionized (DI) water. Stir and centrifuge. Decant the rinse solution into a waste beaker.
6. Add 2 ml 1 M NaOH and stir well for at least 1 minute. Centrifuge and decant the solution into tube 1S. A precipitate indicates Fe^{3+}. Discard the precipitate.
7. Add 5% acetic acid solution (white distilled vinegar) dropwise until weakly acidic. Test for acidity using pH paper. Stir and make sure it is still showing it is weakly acidic. If not, add more acetic acid solution.
8. Let it sit for 1–2 minutes. Centrifuge if needed to verify the presence of a precipitate. A white gelatinous precipitate is positive for Al^{3+}.

Test for Fe^{3+}

9. Place 1 ml all-ions solution into tube 2.
10. Add 1–2 drops of salicylic acid indicator and mix well. A deep purple solution is positive for Fe^{3+}.

Test for Sr^{2+} and Ca^{2+}

11. Place 2 ml all-ions solution in tube 3. Obtain a nichrome wire that has a loop at one end. If not using a nichrome wire, unfold a large paper clip and make a small loop on one end.
12. Light a Bunsen burner and place the wire's loop in the flame until no or little color is seen. If necessary, clean the loop by dipping it into 2 M HCl and place it in the flame. Repeat until little or no color is seen. Carefully remove the wire from the flame each time. ***Caution:*** The wire loop will be very hot and HCl is corrosive!

13. Dip the wire loop into the all-ions solution and then place it in a Bunsen burner flame. A briefly flickering of red in the flame is a positive indicator for Sr^{2+} ions. Record your observations and results. If the all-ions solution becomes dirty, dispose of it in the proper waste container, clean the test tube, and add 2 more ml of the all-ions solution into tube 3.
14. Add approximately 2 ml of 0.5 M sodium sulfate solution into tube 3. Stir and let sit for 3 minutes to allow it to completely precipitate. Centrifuge. A white precipitate is a positive test for Sr^{2+}.
15. If there is a white precipitate, decant the solution into tube 4. Add 2 ml of 10% citric acid solution into tube 3 and stir. If the white precipitate does not dissolve, it further confirms the presence of Sr^{2+}. Discard the solution and precipitate in the proper waste container.
16. Add 2 ml ethanol to the solution in tube 4 and mix well. ***Caution:*** Do not drink! Ethanol used in the lab has poisonous stabilizers added. It is also flammable and must be kept away from flames. Let the solution sit for 3 minutes to allow it to completely precipitate. Centrifuge. A white precipitate is a positive test for Ca^{2+}. Decant the solution and place it in the appropriate waste container.
17. Add 1 ml of DI water to the precipitate in tube 4 to wash it and stir. Centrifuge, decant off the wash liquid, and discard it.
18. Attempt to dissolve the precipitate in tube 4 with 2 ml of 10% citric acid. Calcium sulfate is soluble in the acid. If the precipitate dissolves, then calcium sulfate is present.
19. Discard the solution and precipitate in the proper waste container. Clean and rinse all glassware used with DI water.
20. Obtain your unknown solution and record its number. Repeat the above procedure with your "unknown" solution and determine which of the five possible ions are present.
21. Dispose of all waste as instructed.

Part 2: Ion-selective electrode test for Ca^{2+}

1. Make a 10% dilution of the all-ions solution. Do this by first measuring 2.5 ml of the all-ions solution in a 25 ml graduated cylinder, and then dilute up to 25 ml using DI water. Pour the solution into a 50 ml beaker. Stir until well mixed.
2. Make a 10% dilution of your unknown solution by placing 2.5 ml of the unknown solution into a clean 25 ml graduated cylinder, and then dilute up to 25 ml using DI water. Pour the solution into a 50 ml beaker. Stir until well mixed.
3. If not already completed, calibrate the Ca^{2+} ion-selective electrode according to the instructions that are given.

4. Place the Ca^{2+} ion-selective electrode into the 10% all-ions solution, making sure the solution comes up far enough to be able to obtain a correct reading. After you have obtained a stable reading, rinse the electrode well with DI water into a waste beaker. Record your observations and results.
5. Place the Ca^{2+} ion-selective electrode into your 10% unknown solution, making sure the solution comes up far enough to be able to obtain a correct reading. After you have obtained a stable reading, rinse the electrode well with DI water into a waste beaker. Record your observations and results.
6. Also test provided solutions containing individual ions for each of the ions present in the all-ions solution. This is to make sure none of them give a significant false positive calcium ion reading. If a false positive result is found, verify that it is not due to contamination by obtaining a fresh solution of that ion and repeat the test. Be sure to rinse the electrode well with DI water into a waste beaker after you have obtained a stable reading for each solution. Record your observations and results.

Name _____

Data

Part 1: Testing for the presence of ions

Table 17.1 Data for Analysis of Known Solution

Ion	Observations	Results
Copper		
Aluminum		
Iron		
Strontium (flame and precipitation tests)		
Calcium		

Table 17.2 Data for Analysis of Unknown Solution

Ion	Observations	Results
Copper		
Aluminum		
Iron		
Strontium (flame and precipitation tests)		
Calcium		

Unknown number: _____

Part 2: Ion-selective electrode test for Ca^{2+}

Table 17.3 Data for ISE Analysis

	Results	Observations
Known solution		
Unknown solution		
Copper		
Aluminum		
Iron		
Strontium		
Calcium		

Analysis

1. What ions did your unknown contain?

2. What compounds are formed when strontium and calcium precipitate? Write balanced equations.

3. What would happen if you decided to add the magnesium ion to the all-ions mixture in the form of magnesium sulfate? What problems would this cause?

4. Did your ion-selective electrode results in Part 2 agree with your Part 1 results? Were there any ions that gave a significant false positive test?

5. Compare the two procedures used to detect the presence of calcium ions. Which one is more useful? Explain your answer.

Think Green

1. Mostly acetates were used to make the all-ions solution. However, there was at least one other anion used. How would you use ion-selective electrodes to determine the other anion present? If there are time and resources available, try your ideas.
2. Why are ions such as calcium and aluminum used in this green lab in place of the cobalt, lead, and silver ions that are used in traditional labs? Why are acetates used instead of nitrate? In terms of green chemistry, discuss the advantages of analyzing for the ions used in this experiment instead of those found in traditional labs.
3. What do you think would happen if you had a copper hollow cathode lamp in an AAS and were analyzing a sample that contained only iron ions? Do you think AAS can be used for qualitative analysis, and if so, how would you do it? If AAS, time, and resources are available, see if you are correct.

Presidential green chemistry challenge

In this lab you used metal acetates instead of more hazardous nitrates. The Environmental Protection Agency (EPA) gave its 2003 Presidential Green Chemistry Award in the Greener Synthetic Pathways category to Süd-Chemie, Inc. for developing oxide catalysts that have no nitrate discharge. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about how these oxide catalysts utilize principles of green chemistry.

chapter eighteen

How to determine the order of an electrochemical series

> How would you like to wake up to a world full of rust, where everything made of iron was coated with a rusty brown layer of iron oxide and disintegrating much faster than normal? Electrochemistry helps keep this from happening!

Rusting is simply a redox reaction between iron and oxygen in the presence of moisture. The moisture can be as little as what is in the air. Since iron and steel products rust quickly, they are often galvanized or coated in some other way to inhibit rusting and eventual deterioration. A galvanized steel product has a zinc coating on the surface to help prevent this reaction from occurring. Unlike other coatings, the zinc does not just put an extra layer between the iron and oxygen like paint does; instead, it sacrificially reacts with the oxygen to form zinc oxide. Since moisture is normally present, it is converted to zinc hydroxide, which will then react with carbon dioxide in the atmosphere to form a layer of zinc carbonate. The zinc carbonate actually forms a protective impermeable layer over the zinc below it. The area of chemistry that studies why zinc is an excellent protective coating for iron is called electrochemistry.

Electrochemistry studies the relationship between electricity and chemical change. There are two major areas of electrochemistry. The first one has to do with using chemical reactions to create electrical energy. A battery providing electrical energy and a battery with cathodic corrosion protection are examples of this section. The second area involves using electrical energy to create a chemical change. Charging a battery and electrolysis are examples of this area. Both of these areas require knowledge about the electrochemical series.

The electrochemical series is simply a list that ranks elements (mostly metals) according to how chemically active they are. *Chemically active* refers to how easily they will lose their electrons. The most reactive will lose electrons more easily and are higher on the list. Elements that tend to hold on to their electrons and lose them with greater difficulty are lower on the list. From this list you can tell how reactive a metal will be to other metals on the list. The greater the separation between two metals on the list, the more likely they will be very reactive when placed in a solution together.

The reactions used to set up this series are called redox reactions, which is short for oxidization-reduction reactions. These are reactions that involve transferring electrons from one substance to another. For example, when zinc metal is placed in a blue copper ion solution, the following reaction occurs, causing the solution to turn colorless:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

As shown, zinc metal is losing its electrons to the copper and dissolving in the solution. This means it is the more active metal since it gives up its electrons more easily. The zinc is being oxidized and is called the reducing agent since it is donating its electrons to another substance in the reaction. Copper ions are gaining the electrons the zinc loses and becoming copper metal. The copper is being reduced and is called the oxidizing agent since it is removing electrons from another substance and taking them on itself.

Corrosion costs the world several trillion dollars annually, in preventing it or repairing or replacing things that have corroded. Prevention is the first listed principle of green chemistry, and it is obviously better to prevent or inhibit corrosion. Several types of corrosion prevention utilize the electrochemical series. Cathodic protection is one example since it controls corrosion by placing (or connecting through a wire) a more chemically active metal on a less active metal that needs to be protected. Electrons flow from the more active metal, the anode, to the less active metal, the cathode. This keeps the protected metal from being oxidized. A magnesium rod is often used as the sacrificial anode, which means it is higher on the electrochemical series list than the metal it is protecting.

In the first part of this lab, you will come up with an electrochemical series of five metals, including copper. To do this, you will use a standard solution of copper (II) sulfate to try to plate copper on four different types of metals: aluminum, iron, tin, and zinc. By determining how much copper is plated on a strip of each of these metals and how quickly they react, you will be able to rank them in order of their reactivity. To get the desired reaction, a small amount of salt will be added to the solution. It acts as an ion channel for the electrons to flow through and makes the reaction faster and more efficient. The amount of salt added depends on the amount of copper in solution.

The procedure you will use is not practical to compare a large number of elements or to use in related calculations. A reliable standard method has been developed to do this. The elements are arranged according to their standard potential when operating at a standard condition of 1 M concentration, gas pressure of 1 atm, and specified temperature that is usually 25°C. The reference electrode used to compare electrode potentials

is a standard hydrogen electrode, and it is assigned a potential of 0.00 V. After you have determined the order of reactivity for the five metals in your series, you will look up their standard potentials in aqueous solutions and see not only if you have them in the correct order, but also if their standard potential differences reflect what you observed.

The second part of this lab relates to the other area mentioned that falls under the umbrella of electrochemistry. This area involves using electrical energy to create a chemical change, and includes electrolysis. In electrolysis, a current is used to cause a nonspontaneous chemical reaction to occur. Electrolysis has many industrial uses, including producing metals from their ores and anodizing metals for corrosion resistance. Aluminum uses both of these examples since it is produced by an electrolytic process and then anodized.

When anodizing, the positive electrode (the anode) is what is being anodized. The oxygen generated at the anode reacts with the aluminum to form the oxide layer. Hydrogen gas is given off at the cathode. The electrochemical reactions are shown below:

$$\text{Anode: } 6H_2O \rightarrow 3O_2 + 12H^+ + 12e^-$$

$$4Al_{(s)} + 3O_2 \rightarrow 2Al_2O_{3(s)}$$

$$\text{Cathode: } 12H^+_{(aq)} + 12e^- \rightarrow 6H_{2(g)}$$

Anodizing provides a fairly benign method for corrosion resistance. This is because it is just increasing the thickness of a naturally protecting oxide layer using a reusable cathode, electricity, and an aqueous electrolyte solution to conduct the electricity that normally can be neutralized. Since mainly oxygen is added to the surface, anodized metals can be more easily recycled than painted or electroplated ones. This significantly lowers energy consumption and greenhouse gas emissions. Acids and bases used in cleaning, pretreatment, and coloring can be neutralized, and use of hazardous heavy metals or toxic organic compounds for coloring is minimal.

In the second part of this lab you will anodize niobium. Jewelry made from niobium uses anodizing to create an array of colors. This works since niobium's color is determined by the thickness of the oxide layer. Applying an increased voltage to the niobium increases the oxide layer and changes the color. The colors seen are the result of constructive thin-film interference of two wavelengths of light. This occurs when two of the same wavelengths of light reflect from two different areas of the niobium, one from the inner metal surface and the other from the outer oxide surface. If their crests match each other, they reinforce each other and provide a bright color.

Objective

In this lab, you will determine an electrochemical series for aluminum, copper, iron, tin, and zinc. You will also study the fairly benign process of anodizing through anodizing niobium metal at different voltages.

Name _____

Prelab questions

1. Define *oxidation* and *reduction*.

2. In the following reaction, identify what is being oxidized, what is being reduced, the oxidizing agent, and the reducing agent.

$$4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$$

   Oxidized:

   Reduced:

   Oxidizing agent:

   Reducing agent:

3. Write the balanced redox reaction equations for each metal that you will be plating in Part 1 of the procedure.

4. Write the electrochemical reaction equations that will occur in Part 2 at the cathode and the anode. Assume Nb_2O_5 is the only oxide that is forming. Identify the electrode where oxidation occurs and the one where reduction occurs.

   Anode:

   Cathode:

5. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist and list them. What protective equipment will you need to use?

Procedure

Part 1: Determining electrochemical series

1. Set up a vacuum filtration apparatus using a 250 ml filtering Erlenmeyer flask and a Büchner funnel.
2. Obtain four watch glasses and label them Al, Zn, Fe, and Sn. Place a piece of Whatman 40 filter paper that will properly fit the Büchner funnel on each one. Obtain and record the mass for each watch glass with filter paper in Table 18.1. Place the filter paper on the Al watch glass in the Büchner funnel, and seat it with deionized (DI) water.
3. Obtain approximately 65 ml of a 0.500 M solution of copper (II) sulfate pentahydrate. Dissolve 0.65 g of NaCl in this solution.
4. Pour 15 ml of this solution into four 20 ml sample vials or medium test tubes that will accommodate a 0.5-inch-wide sample. Label them Al, Zn, Fe, and Sn.
5. Obtain 1.0 × 0.5 inch thin strips of aluminum, iron, tin, and zinc. Lightly sand the surface using medium sand paper to remove the oxidized layer.
6. Place the aluminum strip into its labeled vial or test tube containing the 0.500 M $CuSO_4$/NaCl solution for exactly 30 minutes. If the reaction begins to slow down since the copper metal plated on the aluminum becomes too thick, use a stir rod to gently remove some of the copper while it is still in the solution.
7. After the aluminum metal has reacted for around 15 minutes, place another metal into its vial or test tube and let it react for 30 minutes. Continue to do this for the other two metals, being sure to space them about 15 minutes apart since it will take around 15 minutes to process the samples after they have reacted for 30 minutes.
8. When the aluminum has reacted for 30 minutes, vacuum filter the vial's contents immediately. Use DI water to rinse all of the copper metal into the Büchner funnel. Use forceps or beaker tongs and a spatula to scrape off the copper plated on the aluminum onto the filter paper seated in the Büchner funnel. Remove any aluminum metal pieces.
9. Clean the copper metal by rinsing it with two, 5 ml portions of 1 M HCl. ***Caution:*** 1 M HCl is corrosive. Wash it off immediately if some splashes on you.
10. Rinse several times with DI water followed by 3 ml of ethanol to speed up drying. ***Caution:*** Do not drink! Ethanol used in the lab has poisonous stabilizers added. Allow air to be pulled through the filter paper and sample for a few minutes.
11. Place the filter paper with all of the copper metal on the appropriate watch glass and allow it to dry. Be sure to have this done and

the appropriate new piece of filter paper seated in the Büchner funnel before it is time to filter your next sample.

12. Repeat steps 8–11 for each metal.
13. Place the samples on the watch glasses in an oven set at 120°C and allow them to dry for about 10 minutes. ***Caution:*** Ethanol is flammable. Make sure the filter paper and its contents are almost dry before placing them in an oven.
14. Remove the watch glasses with the copper metal using oven mitts and let them cool to room temperature. ***Caution:*** They will be hot! Do not touch until they have cooled.
15. Obtain and record in Table 18.1 the masses of the copper, filter paper, and watch glass. Calculate and record the mass of the copper.

Part 2: Anodizing niobium

1. Prepare an electrolyte solution by placing approximately 10 g of Epsom salt into a 250 ml beaker. Add approximately 225 ml DI water. Stir until well mixed.
2. Obtain a 5-inch-long piece of 20-gauge Nb wire. Rub it gently with fine sand paper or a wet emery cloth, and then rinse with water. Wipe the surface of the wire with 70% isopropanol to remove any fingerprints.
3. If you are using a commercial anodizing apparatus, proceed as directed by your instructor. If not, obtain two lead wires that have alligator clips on both of their ends, 9 V batteries (six to nine), and a stainless steel lab scoop for the cathode.
4. Assemble your anodizing apparatus as shown in Figure 18.1. Do this by placing a stainless steel lab scoop against the inside of the beaker with the electrolyte solution. To keep it in place, you may use a small piece of duct tape to tape part of the upper portion of the cathode to the outside of the beaker. Make sure it will stay in place in the beaker.
5. Attach one end of a lead wire from the cathode to the negative terminal of a 9 V battery.

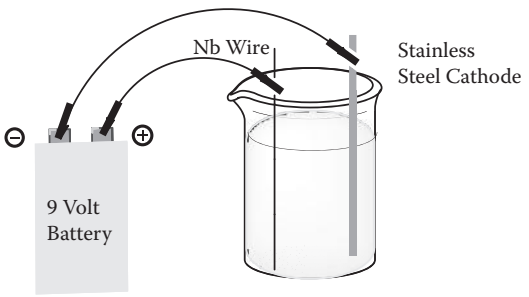


Figure 18.1 Anodizing apparatus using a 9 V battery.

6. Connect the Nb wire to another lead wire and place it in the opposite side of the beaker across from the stainless steel cathode. Do not let it touch the cathode. Submerge the wire into the electrolyte solution as far as it will go while being very careful not to submerge the clip holding the wire.
7. Connect the other end of the lead wire attached to the niobium wire to the positive terminal of the 9 V battery. ***Caution:*** Small electric shock possible. Do not touch any metal parts connected to the batteries, only touch plastic. Be sure to keep the wires, batteries, and your hands dry. Do not let the Nb wire touch the cathode.
8. Leave the niobium wire in the solution connected to the battery for approximately 5–10 seconds in order to form a thin layer of niobium oxide. Disconnect the lead wire from the positive terminal of the battery or turn off the anodizing apparatus.
9. Remove the niobium wire from the solution and dry it with a KimWipe. Observe and record the color of the oxide film that is formed in Table 18.2 of next to 9 V. If the color has not changed, either the battery is dead or the wires were not connected properly. You will need to fix the problem and go back to step 7.
10. If using 9 V batteries, push together the positive terminal of one 9 V battery and the negative terminal of another 9 V battery. Connect the lead wires as before to the correct open battery terminals.
11. Lower the niobium wire into the electrolyte solution again. For a multicolor wire, submerge it approximately ¼ inch less than the first time.
12. Connect the other end of the lead wire attached to the niobium wire to the free positive terminal of the battery assembly or anodizing apparatus. If using an anodizing apparatus, turn it on to 18 V.
13. Allow the wire to anodize for approximately 5–10 seconds as before. Disconnect the lead wire from the positive terminal of the battery or turn off the anodizing apparatus.
14. Remove the niobium wire from the solution and dry it with a KimWipe. Observe and record the color of the oxide film that is formed in Table 18.2 next to 18 V.
15. Continue to anodize your Nb wire by repeating steps 10–14, adding one 9 V battery each time. Use a total of six to nine 9 V batteries. (If using an anodizing apparatus, increase the voltage by 9 V each time.) Remember to not completely submerge the previous area of anodization each time you change the voltage. Also make sure the niobium wire and the cathode do not touch.

Note: Adapted with permission from P. S. Hill, 2005. *Chemistry Collaborations, Workshops and Communities of Scholars*, June 5–10, 2005. Millersville University, Millersville, PA.

Name _____

Data

Part 1: Determining electrochemical series

Table 18.1 Data for Electrochemical Series Determination

Metal	Filter paper + watch glass (g)	Filter paper + watch glass + copper (g)	Copper (g)	Observations
Aluminum				
Iron				
Tin				
Zinc				

Part 2: Anodizing niobium

Table 18.2 Color Obtained from Each Voltage Applied

Voltage (V)	Color	Voltage (V)	Color
9		54	
18		63	
27		72	
36		81	
45			

Observations

Part 1: Determining electrochemical series

Part 2: Anodizing niobium

Analysis

1. Order by increasing strength the series developed from this lab based on the experimental values obtained.

2. Look up and list the standard electrode potential in aqueous solution at 25°C for each metal tested. Use Fe^{2+} for iron. Determine if you have them in the correct order. Do their standard potential differences reflect what you observed? Explain your answer.

3. Use the electrochemical series, including standard electrode potentials, to explain why zinc protects iron and steel.

4. Use Excel or another graphing program to make a bar graph showing the grams of copper plated versus the metals used in Part 1.

5. Explain why increasing the voltage when anodizing the niobium metal created a different color.

Think green

1. In this lab, some copper ions remained in solution, so it cannot be disposed of without further treatment. Copper metal can be recycled. Develop a method to convert the copper ions into copper metal. If time and resources permit, try your idea.
2. Explain how you could compare the corrosion resistance between a galvanized and an ungalvanized nail. If time and resources permit, try your hypothesis.
3. Consider the greenest aspect of using a sacrificial anode. Research how it works and some places it is being used. Write a summary about what you find out, and include which of the 12 principles of green chemistry are positively or negatively affected through the use of sacrificial anodes.
4. Research the benefits of using recycled aluminum instead of creating new aluminum. Which of the 12 principles of green chemistry are positively affected by recycling aluminum? Justify your answer.

Presidential green chemistry challenge

One method used to prevent corrosion on vehicles is to use a cationic electrodeposition primer, which has traditionally been used with toxic heavy metals. The Environmental Protection Agency (EPA) gave its 2001 Presidential Green Chemistry Award in the Designing Green Chemicals category to PPG Industries for developing a less toxic metal primer that uses yttrium. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about how this technology utilizes principles of green chemistry.

chapter nineteen

Voltaic cells and how batteries are made

> You need to send a text message, but you forgot to charge your cell phone. You left the lights on in your car and now your car won't start. We depend on batteries every day, but how do they work?

Electrochemistry plays a key role in producing greener vehicles. Producing greener, lower-cost electric, hybrid, and fuel cell vehicles requires finding ways to make more efficient, longer-lasting, and lower-cost batteries and fuel cells. Batteries are composed of voltaic cells connected together. A fuel cell requires a voltaic cell, but unlike a typical battery, the fuel must be continually replenished. In this lab you will investigate the fundamental principles of how voltaic cells work.

When a strip of zinc metal is placed into a Cu^{2+} solution, a redox reaction occurs that results in copper metal plating out onto the zinc metal. The zinc is losing electrons to the copper ions, so electrons are being transferred, but none of the energy is being harnessed to do beneficial work. Fortunately, there is a way to use this same reaction to get useful energy, and this is through constructing a voltaic, or galvanic, cell. For this reaction, a strip of zinc metal, called a zinc electrode, is first placed into a zinc salt solution and a copper electrode is placed into a copper salt solution, creating two half-cells.

Next, these two half-cells must be connected in such a way that ions can flow between the two half-cells. If only a wire is placed between the two electrodes, there would be a buildup of positive charge and electron flow between the two half-cells would not occur. To keep the electrons flowing and producing an electric current, a salt bridge is inserted from the Zn^{2+} solution in one half-cell to the Cu^{2+} solution in the other half-cell. It allows for the passing of electrons between the solutions, and in turn the passing of the electrical charge. The two half-cell reactions are

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$

Since oxidation occurs at the zinc electrode, it is called the anode. Reduction is occurring at the copper electrode, so it is called the cathode. When the two reactions are added, the voltaic cell reaction becomes

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

In this voltaic cell reaction, the electrons cancel. If they did not, you would need to balance the equation so that they did. The half-cell potentials would not be affected.

This voltaic cell is often depicted as

$$Zn_{(s)}|Zn^{2+}_{(aq)}||Cu^{2+}_{(aq)}|Cu_{(s)}$$

The single vertical line (|)denotes a phase boundary, usually between a solid and a liquid, and the double vertical lines (||) represent the salt bridge. It produces a charge that is moved through the wire from the anode to the cathode. This is called the potential difference and can be measured in volts using a voltmeter. The electromotive force (emf) of a voltaic cell is the maximum this can be and is designated E_{cell}. The electromotive force of a cell is concentration, temperature, and pressure dependent. For this reason, standard electrode (or cell) potentials are obtained for standard conditions where concentrations are all 1 M aqueous solutions, gas pressure is 1 atm, and temperature is usually specified as 25°C and is designated as $E°_{cell}$. This can be calculated by adding the half-cell reaction's emf contributions.

$$E°_{cell} = E°_{oxidation} + E°_{reduction}$$

For this example, they can be calculated using the $E°_{cathode}$ values for zinc and copper ions shown below:

$$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)} \qquad E^\circ = -0.76\,V$$

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \qquad E^\circ = 0.34\,V$$

Since in the voltaic cell the Zn half-reaction is the reverse of what is shown, the negative of the listed value is used since

$$E°_{oxidation} = -E°_{reduction}$$

$$E°_{Zn} = -(-76\ V) = 76$$

$E°_{cell}$ can now be calculated:

$$E°_{cell} = 0.34\ V + 0.76\ V = 1.10\ V$$

Normally the experimental voltage obtained is less than the calculated one. One reason is because energy is expended just moving current through the cell.

As shown in the example voltaic cell, the maximum voltage is 1.10 V when using 1.0 M cathode and anode salt solutions. One way to increase the voltage is to place voltaic cells in series. The lead battery that starts a car is an example of six connected voltaic cells, with each cell producing about 2 V of potential.

Potentials can also be changed by altering the molar concentrations of the cathode and anode salt solutions. When solute concentrations are not 1 M, the Nernst equation can be used to calculate the theoretical measured cell potential. The Nernst equation is

$$E = E° - \frac{RT}{nF} \ln Q$$

where E is the measured cell potential, $E°$ is the standard cell potential, R is the gas constant of 8.314 J/mole·K, T is temperature in K, n is the number of electrons transferred in the balanced reaction equation, F is the Faraday constant of 9.65×10^4 C/mole, and Q is the reaction quotient. In the zinc/copper voltaic cell example n is 2. Q equals $[Zn^{2+}]/[Cu^{2+}]$ or 1.0 M/1.0 M, since in the balanced reaction equation their coefficients are both 1 and the metals are not included. If in the balanced equation an ionic species has a coefficient other than 1, its molarity has an exponent of that coefficient.

The Nernst equation is often simplified to what is shown below through substituting in the constants, converting to base 10 logarithms, and using a temperature of 298 K (25°C).

$$E = E° - \frac{0.0592\ V}{n} \log Q$$

In the first part of this lab you will construct three voltaic cells using iron, copper, and zinc half-cells with 0.10 M metal salt solutions. For the voltaic cells to work properly, you must first sand down the metals to be used as electrodes. This removes the outer oxide layer that forms naturally over time. Once the metals are sanded down, the half-cells are made by placing each metal into its appropriate corresponding ionic solution. Two half-cells will then be connected together through a salt bridge made from chromatography or filter paper strips soaked in KCl solution. After this, a voltmeter will be connected to the two metal electrodes and the voltage obtained. (See Figure 19.1.)

In the second part of the lab, you will connect one of your voltaic cells in series to other students' voltaic cells of the same combination and see

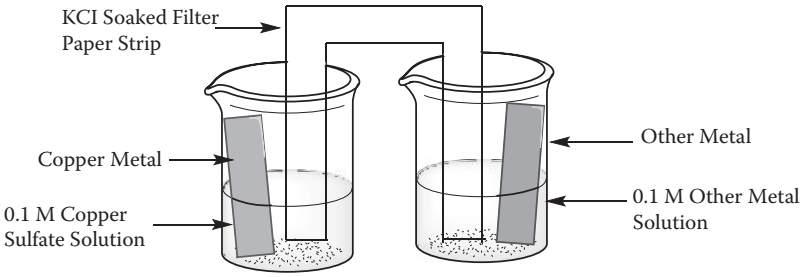


Figure 19.1 Apparatus.

how adding additional voltaic cells affects the voltage obtained. In the final part of the lab, you will see how varying the temperature and the molar concentrations of the cathode and anode metal salt solutions will change the voltage readings. You will use the Nernst equation to calculate *E* for these different molaritites and compare these values to your experimental results.

Objective

In this experiment you will make different voltaic cells by altering half-cell components, their concentrations, and temperature, and compare your experimental voltages to the calculated voltages. You all also connect $Zn_{(s)}|Zn^{2+}_{(aq)}||Cu^{2+}_{(aq)}|Cu_{(s)}$ voltaic cells in series and compare your experimental voltages to the calculated voltages.

Name _____

Prelab questions

1. Define *anode* and *cathode*.

2. Identify the cathode, the anode, where oxidation occurs, and where reduction occurs for a voltaic cell made up of zinc and aluminum half-cells. Use the following half-cell reactions:

$$Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)} \qquad E° = -1.66 \text{ V}$$

$$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)} \qquad E° = -0.76 \text{ V}$$

Cathode:

Anode:

Where reduction occurs:

Where oxidation occurs:

3. Using the information in problem 2, write the balanced cell reaction for a voltaic cell composed of zinc and aluminum half-cells. Also write the notation for this voltaic cell using phase boundary and salt bridge notation. Determine what battery voltage you should get for this voltaic cell at standard conditions. Show your calculations.

   Voltaic cell reaction:

   Voltaic cell notation:

   Battery voltage at standard conditions:

4. Use the Nernst equation to calculate the voltage you would expect to get for a voltaic cell at 25°C, 1 atm pressure, and made up of zinc and aluminum half-cells, using 0.1 M ion solution for both half-cells.

5. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

Part 1: Determining reduction potentials

1. Prepare salt bridges by first cutting eight strips of approximately 1.5 × 12 cm from paper chromatography paper or Whatman 40 filter paper. The piece of filter paper should be long enough to go from the solution in one 50 ml beaker to the solution in another 50 ml beaker while being draped over the middle. (See Figure 19.1.)
2. Place the filter paper strips in the bottom of a 150 ml beaker labeled KCl. Pour in approximately 25 ml of 1 M KCl solution and allow them to soak until they are completely saturated. This should take about 5 minutes. Remove and let them partially dry on a paper towel. They will need to be damp when used.
3. Lightly sand the provided iron, copper, and zinc metal electrodes with sandpaper until they are shiny.
4. Label three 50 ml beakers as Cu, Fe, and Zn. Use a 10 ml graduated cylinder to measure out 10 ml of 0.1 M solution of $CuSO_4$ and pour the solution into the beaker labeled Cu. Also pour 10 ml of 0.10 M $FeSO_4$ and $ZnSO_4$ solutions into their corresponding beakers. Be sure to clean the graduated cylinder before measuring out a different solution.
5. Place the copper electrode in the beaker labeled Cu and lean it against the glass. Lean the iron and zinc electrodes in the same manner in beakers containing their respective solutions. See Figure 19.1.
6. Place the copper and iron half-cells next to each other. Place one end of a KCl salt bridge in the 0.1 M $CuSO_4$ solution and the other end in the 0.1 M $FeSO_4$ solution. Be sure the salt bridge is touching in both solutions. Let it sit for a few minutes to stabilize.
7. Touch the leads of a voltmeter to the copper and iron electrodes so that a positive voltage to the hundredths place is obtained. Wait 1 minute and check the voltage to make sure it has stabilized. Repeat until a stabile voltage is obtained. Record the stable voltage reading in Table 19.1.
8. Remove the leads and the salt bridge. Add a fresh damp salt bridge between the zinc half-cell and the iron half-cell. Obtain a stable voltage reading and record it in Table 19.1.
9. Repeat the process to obtain a voltage reading for a $Zn_{(s)}|Zn^{2+}_{(aq)}||Cu^{2+}_{(aq)}|Cu_{(s)}$ voltaic cell. Be sure to use a fresh salt bridge. Record the voltage reading in Table 19.1.

Part 2: Connecting voltaic cells in series

1. Place yours and another student's $Zn_{(s)}|Zn^{2+}_{(aq)}||Cu^{2+}_{(aq)}|Cu_{(s)}$ voltaic cells next to each other.
2. Connect a wire with alligator clips on both ends from the copper electrode of one of the voltaic cells to the zinc electrode of the other voltaic cell.
3. Touch one lead of a voltmeter to the other copper electrode and the other lead to the other zinc electrode so that a positive voltage to the hundredths place is obtained. Check the voltage every minute until a stable voltage is obtained. Record the voltage in Table 19.2.
4. Continue to add in additional voltaic cells in series in the same way. Take a stable voltage reading each time a voltaic cell is added and record the voltage in Table 19.2.

Part 3: Reduction potentials at different temperatures and ion concentrations

1. Place both half-cells of your $Zn_{(s)}|Zn^{2+}_{(aq)}||Cu^{2+}_{(aq)}|Cu_{(s)}$ in ice baths and let the solutions cool to about 0°C. Place a damp salt bridge between the half-cells. Obtain the stable voltage reading as before. Record the temperature and the voltage reading in Table 19.3.
2. Place both half-cells of your $Zn_{(s)}|Zn^{2+}_{(aq)}||Cu^{2+}_{(aq)}|Cu_{(s)}$ on a hot plate and let the solutions heat to about 50°C. Remove the half-cells using beaker tongs. ***Caution:*** The half-cells will be hot!
3. Place a damp salt bridge between the two half-cells. Obtain the stable voltage reading as before. Record the temperature and the voltage reading in the data section.
4. Make a $Zn_{(s)}|Zn^{2+}_{(aq)}||Cu^{2+}_{(aq)}|Cu_{(s)}$ voltaic cell as before, only instead use 0.001 M $ZnSO_4$ and 0.1 M $CuSO_4$ solutions. Be sure to use a new damp salt bridge. Obtain and record the stable voltage reading in Table 19.3.
5. Make a $Zn_{(s)}|Zn^{2+}_{(aq)}||Cu^{2+}_{(aq)}|Cu_{(s)}$ voltaic cell as before, only instead use 0.1 M $ZnSO_4$ and 0.001 M $CuSO_4$ solutions. Be sure to use a new damp salt bridge. Obtain and record the stable voltage reading in Table 19.3.
6. Make a $Zn_{(s)}|Zn^{2+}_{(aq)}||Cu^{2+}_{(aq)}|Cu_{(s)}$ voltaic cell as before, only instead use 0.001 M $ZnSO_4$ and 0.001 M $CuSO_4$ solutions. Be sure to use a new damp salt bridge. Obtain and record the stable voltage reading in Table 19.3.
7. Pour all of the waste solutions into the appropriate containers as instructed. Be sure to place the copper solutions in a separate container so that the copper can be plated out and recycled.

Name _____

Data

Part 1: Determining reduction potentials

Table 19.1 Measured Reduction Potentials

Voltaic cell electrodes	Measured voltage (V)	Predicted voltage (V)	Percent error
Cu and Fe			
Zn and Fe			
Cu and Zn			

Part 2: Connecting voltaic cells in series

Table 19.2 Series Voltages

Number of voltaic cells	Measured voltage (V)	Predicted voltage (V)	Percent error
2			
3			
4			
5			

Part 3: Reduction potentials at different temperatures and ion concentrations

Table 19.3 Voltages under Different Conditions

Voltaic cell condition	Measured temperature (°C)	Measured voltage (V)	Predicted voltage (V)	Percent error
0°C				
50°C				
0.0010 M $ZnSO_4$ and 0.10 M $CuSO_4$				
0.10 M $ZnSO_4$ and 0.0010 M $CuSO_4$				
0.0010 M $ZnSO_4$ and 0.0010 M $CuSO_4$				

Observations

Calculations

Part 1: Determining reduction potentials

Predicted voltage calculations:

Cu and Fe

Zn and Fe

Cu and Zn

Percent error calculations (show an example calculation):

$$\% \text{ error} = \frac{|\text{theoretical value} - \text{experiment value}|}{\text{theoretical value}} \times 100$$

Part 3: Reduction potentials at different temperatures and ion concentrations

Predicted voltage for 0°C:

Predicted voltage for 50°C:

Predicted voltage for 0.001 M $ZnSO_4$ and 0.1 M $CuSO_4$ cell:

Predicted voltage for 0.1 M $ZnSO_4$ and 0.001 M $CuSO_4$ cell:

Predicted voltage for 0.001 M $ZnSO_4$ and 0.001 M $CuSO_4$ cell:

Analysis

1. In this experiment, 0.1 M instead of 1.0 M metal ion solutions were used in Part 1. According to the Nernst equation, should this cause a significant difference from calculated $E°_{cell}$ values? Do you consider this an acceptable greener substitution? Explain your answer.

2. Do you consider your results for Part 1 acceptable? What factors could have caused a difference between your experimental values and the calculated values? Explain your answer.

3. Do you consider your results for Part 2 acceptable? What factors could have caused a difference between your experimental values and the calculated values? Explain your answer.

4. Did changing the temperature of the voltaic cell significantly alter your voltage readings? Do you think any differences you observed would be considered acceptable for a purchased battery? Explain your answer.

5. Did altering the concentrations of the voltaic cells significantly alter your voltage readings? Is this what was expected? Explain your answer.

Think green

1. Many electrochemical cell experiments use 1.0 M $Pb(NO_3)_2$. Lead (II) nitrate is toxic, and a strong oxidizer. If 1 million general chemistry students each year use just 2 ml of 1.0 M $Pb(NO_3)_2$ to do an electrochemical experiment, how much lead nitrate would end up needing to be processed as toxic waste? If you wanted a standard potential close to Pb^{2+} for an electrochemical lab, what do you think would be a good greener alternative? If time and resources permit, test your hypothesis.
2. Research lithium ion batteries and find out how they work and what makes them rechargeable.
3. Vehicle manufacturers are developing and introducing electric, hybrid, and fuel cell automobiles. Research why these alternatives are considered to be greener than most gasoline engine vehicles? Relate your answer to the 12 principles of green chemistry.

Presidential green chemistry challenge

One of the major difficulties in using fuel cells as a clean energy source to power green vehicles is producing or storing hydrogen. The Environmental Protection Agency (EPA) gave its 2008 Presidential Green Chemistry Award in the Small Business category to SiGNa Chemistry, Inc. for developing a method to stabilize alkali metals that can be used to obtain hydrogen from water for use in fuel cells. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about how this technology utilizes principles of green chemistry.

chapter twenty

Synthesis and chemical analysis of sodium iron (III) EDTA

One, two, three, four bonds! That's all the bonds an atom can make, right? The octet rule is responsible for this belief and works well until the transition metals are reached. Unlike carbon, transition metals form bonds to fill two shells of electrons. As a result, metals can form special bonds called coordination bonds that allow them to bond to more atoms, opening up a whole new type of chemistry: *coordination chemistry*.

The field of coordination chemistry began with Alfred Werner. He noticed that there were different compounds that were only composed of cobalt (III) chloride and ammonia. He noted that it was very hard to remove the ammonia from the compound. He also noticed that adding the same amount of silver nitrate to the different compounds produced different amounts of silver chloride. This suggested that the cobalt and ammonia formed some sort of charged complex with the chloride, and different complexes had different charges. Those complexes would form bonds that were strong enough to keep the complexed chloride from forming silver chloride.

These complexes were found to be possible because of the unfilled *d* orbitals of the central transition metal atom. The metals fill their *d* orbitals by accepting entire electron pairs from other atoms or compounds. The electron pair donators in coordination chemistry are known as ligands. Some ligands donate one pair of electrons and are called monodentate ligands. An example of a monodentate ligand is ammonia. Those that donate more than one pair of electrons are called polydentate ligands. The hexadentate ligand EDTA donates six ligands and is commonly used in coordination chemistry.

The central metal may also be negatively charged. When an anionic center bonds to multiple neutral ligands, a complex ion is formed. This is what happened in the example of cobalt (III) ammonia chloride. In other cases, water molecules will bond to metals. An example of this is the compound ferric ammonium sulfate hexahydrate. In this compound,

a charged complex consisting of six neutral waters and iron (III) is made, which forms ionic bonds to the ammonium and the sulfate.

When comparing the strength of ammonia-metal complexes to water-metal complexes, the ammonia-metal coordination bonds are stronger bonds. Just like replacement reactions with ionically bonded compounds, weak ligands can be removed from complexes by strong ligands. These substitution reactions lead to the formation of more stable complexes.

One useful coordination compound is sodium iron (III) EDTA, and it is shown in Figure 20.1. It has uses as a fertilizer and as an iron supplement for the body. Iron (III) EDTA is a complexion with a charge of –1, so its charge is balanced by the sodium ion. There are multiple ways to make sodium iron (III) EDTA. The direct way of synthesis is to take a source of ferric ions and combine it with a stoichiometrically equivalent amount of EDTA. In this lab, ferric ammonium sulfate is used as a greener source of ferric ions for the reaction. Ferric chloride is commonly used as the ferric ion source. Like other ferric ion sources, they both have a weaker affinity for their water ligands than they do for EDTA.

In this lab you will make sodium iron (III) EDTA using two different processes and compare them in terms of green chemistry. The first uses the direct method previously mentioned. Through this process you will study the green chemistry principle of *real-time analysis for pollution prevention*. Often pollution can be prevented or greatly minimized when a reaction or process is continually monitored. There are various ways this can be done, and what is used depends upon the process. The first reaction can be monitored by pH. Knowing exactly when a reaction is completed prevents waste generated through the use of excess reactants and energy.

In Part 1 you will conduct a small trial run in order to get familiar with the process. The product will not be isolated. An indicator will be used to see the endpoint of the reaction in conjunction with a pH probe. It will be possible to see the endpoint by color change and through monitoring the pH.

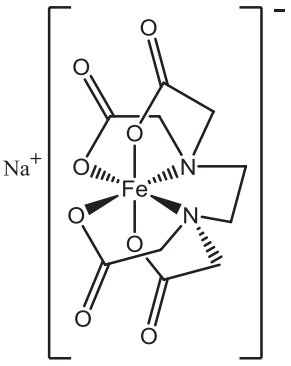


Figure 20.1 Sodium iron (III)–EDTA complex.

The pH will slowly drop while the reaction is occurring, but it will start to increase once it is finished. An example of what a graph of this looks like is shown in Figure 20.2. The arrow shows when the reaction was completed. Although your pH meter may not provide a graph as shown, you should still be able to determine when the pH starts to increase.

After seeing how to determine when the reaction is finished in Part 1, you will synthesize and isolate a larger quantity of sodium iron (III) EDTA in Part 2. While the color indicator you used in Part 1 made the endpoint visually apparent, it also adds a chemical that will later have to be removed. This generates waste, and green chemistry tries to reduce waste. To this end, you will eliminate the indicator since it is possible to note the endpoint of reaction using only a pH probe. This allows for real-time analysis without introducing waste.

In Part 3 you will make sodium iron (III) EDTA by first reacting ferric ammonium sulfate with ammonium acetate to produce the coordination compound ferric acetate. You will then produce sodium iron (III) EDTA by reacting the ferric acetate with EDTA. The acetate ligand forms a stronger bond to the iron than the water ligand, so the waters are replaced in this reaction. The acetate ligands are not stronger than EDTA, however, so when ferric acetate is reacted with EDTA, a replacement reaction will occur, forming sodium iron (III) EDTA.

At first you might wonder why this method is even being considered since it involves an extra step. The reason is that it initially uses a solventless reaction, and less solvent means less waste. Solventless reactions have become an important facet of green chemistry. Generally solventless reactions involve crushing and mixing the reactants together to form another compound.

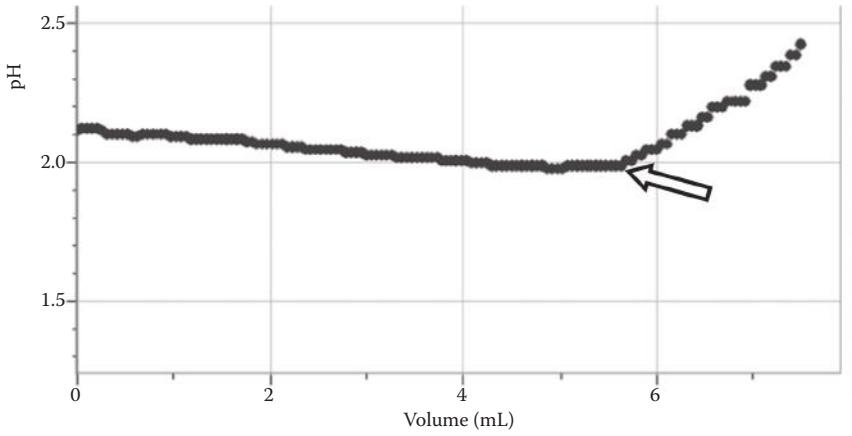


Figure 20.2 Titration of ferric ammonium sulfate with EDTA.

So how can these two very different reactions be compared in terms of green chemistry? Several different calculations have been developed to do this, and in this lab you will use two of them, atom economy and E-factor. Atom economy is calculated by determining the balanced reaction equation and then using the following equation:

$$\text{Atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$

The example already given in Chapter 3 for calculating atom economy illustrates a single-step reaction, like you will do in Part 2, and is shown below:

$$3CaCl_{2(aq)} + 2K_3PO_{4(aq)} \rightarrow Ca_3(PO_4)_{2(s)} + 6KCl_{(aq)}$$

$$\text{Atom economy} = \frac{Ca_3(PO_4)_2 \text{ g/mol}}{3CaCl_2 \text{ g/mol} + 2K_3PO_4 \text{ g/mol}} \times 100$$

$$\text{Atom economy} = \frac{310.18 \text{ g/mol}}{3(110.98 \text{ g/mol}) + 2(212.27 \text{ g/mol})} \times 100 = 40.949\%$$

But how do you calculate the atom economy for a two-step or multi-step reaction like you will do in Part 3? For this, only the reactants of all the steps (not the desired product(s) carried on to the next step or the final step) are added and used in the denominator. For example, to prepare ferric ammonium sulfate, the Fe^{3+} source you will use, the two-step reaction sequence shown below may be used:

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

$$3Fe_2(SO_4)_3 + 3(NH_4)_2SO_4 \rightarrow 6NH_4Fe(SO_4)_2$$

The atom economy is calculated as shown below:

$$\text{Atom economy} = \frac{6NH_4Fe(SO_4)_2 \text{ g/mol}}{6FeSO_4 \text{ g/mol} + 2HNO_3 \text{ g/mol} + 3H_2SO_4 \text{ g/mol} + 3(NH_4)_2SO_4 \text{ g/mol}} \times 100$$

$$= \frac{6(266.01) \text{ g/mol}}{6(151.91 \text{ g/mol}) + 2(63.01 \text{ g/mol}) + 3(98.08 \text{ g/mol}) + 3(132.1 \text{ g/mol})} \times 100$$

$$\text{Atom economy} = 92.36\%$$

Although atom economy is very useful in determining how green a reaction is and comparing it to another reaction, it does omit some things that can make a significant difference, such as solvent and catalyst used. Since you are comparing a solventless reaction to one that uses solvent, the solvent should be considered. For this a different calculation, called the environmental (E) factor, may be used. The E-factor is the ratio of the mass of the total waste generated to the mass of the product obtained. An example, including the equation you will use to calculate the E-factor, is shown below.

Example 1

Calculate the E-factor if 1.456 g of $NH_4Fe(SO_4)_2$ was made using 0.911 g $FeSO_4$, 0.126 g HNO_3, 0.294 g H_2SO_4, 0.396 g $(NH_4)_2SO_4$, and 20.000 g of water that was not reclaimed. How would the E-factor change if the reaction could be done solventless?

$\text{E-factor}_{\text{with } H_2O}$ = total waste (g)/product (g) = 21.727 g/1.456 g = 14.92

$\text{E-factor}_{\text{solventless}}$ = total waste (g)/product (g) = 1.727 g/1.456 g = 1.186

As you can see, doing this example reaction solventless greatly improves the E-factor. A solventless reaction is especially useful when hazardous organic or toxic solvents are used.

In this lab you will calculate the E-factor through weighing the chemicals used and dividing by the product yield. An example is shown below.

Example 2

A student weighed a beaker and then added all of the reactants into it. After the reaction was completed, the mass of the beaker with its contents was obtained. The mass of only the contents was determined to be 25.013 g. The beaker with its contents was heated until the product crystallized out. The product was then isolated through filtration using 5.000 g cold deionized (DI) water to rinse. The product mass was found to be 1.234 g. Calculate the E-factor.

$$\text{E-factor} = \frac{25.013\text{ g} + 5.000\text{ g}}{1.234\text{ g}} = 24.32$$

At the end of the second procedure, you may use a microwave to help grow crystals by heating the solution and to remove excess solvent. Using microwave technology in synthesis not only gives better energy efficiency,

but also has been found to work well for many reactions. Typically the reactions are faster and milder, so often a cleaner product is formed with higher yields.

Reduce derivatives is one of the 12 principles of green chemistry. At times when synthesizing a particular molecule, certain chemicals, called protecting groups, are added to a part of a molecule. They keep that part from reacting while something is done to another part of the molecule. These protecting groups are then removed. Like the second method you will do in Part 3, this requires extra steps, which normally means using extra chemicals, energy, and time, which lowers the atom economy and increases the E-factor. It is better to look for ways to eliminate the need for protecting groups and reduce the number of steps required for the synthesis.

Objective

The purpose of this lab is to synthesize sodium iron (III) EDTA trihydrate from ferric ammonium sulfate and EDTA disodium salt by titration and by reaction with the intermediate ferric acetate formed in a solventless reaction. After successful syntheses, the two methods will be compared.

Name _____

Prelab questions

1. Define the terms *coordination compound* and *coordination bond*.

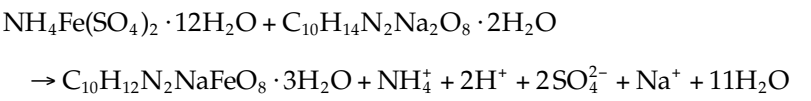
2. How many milliliters of 0.20 M EDTA should it take to titrate 0.0010 mole of ferric ammonium sulfate dodecahydrate? How many milliliters of 0.80 M EDTA should it take to titrate 0.0050 mole of ferric ammonium sulfate?

3. How many grams is 0.0010 mole of $NH_4Fe(SO_4)_2 \cdot 12H_2O$? How many grams is 0.0050 mole of $NH_4Fe(SO_4)_2 \cdot 12H_2O$?

   0.0010 mole $NH_4Fe(SO_4)_2 \cdot 12H_2O$ =

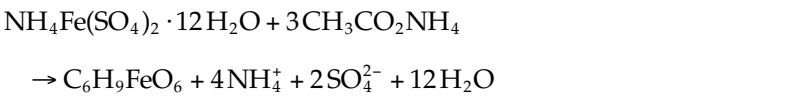
   0.0050 mole $NH_4Fe(SO_4)_2 \cdot 12H_2O$ =

4. Use the following simplified reaction equations to calculate the atom economy for Parts 2 and 3 of the procedure.
   Part 2:

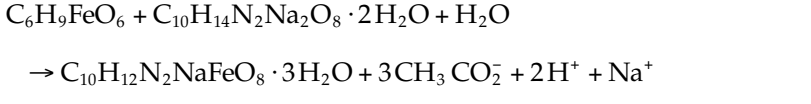


$$NH_4Fe(SO_4)_2 \cdot 12H_2O + C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O \rightarrow C_{10}H_{12}N_2NaFeO_8 \cdot 3H_2O + NH_4^+ + 2H^+ + 2SO_4^{2-} + Na^+ + 11H_2O$$

   Part 3:



$$NH_4Fe(SO_4)_2 \cdot 12H_2O + 3CH_3CO_2NH_4 \rightarrow C_6H_9FeO_6 + 4NH_4^+ + 2SO_4^{2-} + 12H_2O$$



$$C_6H_9FeO_6 + C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O + H_2O \rightarrow C_{10}H_{12}N_2NaFeO_8 \cdot 3H_2O + 3CH_3CO_2^- + 2H^+ + Na^+$$

5. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

Part 1: Sample titration using an indicator

1. Use a mortar and pestle to crush around 5.7 g of $NH_4Fe(SO_4)_2 \cdot 12H_2O$.
2. Clamp a buret to a ring stand. Add a little over 10 ml of 0.20 M EDTA disodium solution into the buret. Check for air bubbles and remove them. Make sure you have at least 10 ml of titrant in the buret. Record your initial reading in Table 20.1.
3. Using your prelab calculations, obtain approximately 0.001 mole of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ and record the exact mass. Place it in a 50 ml beaker, add 10 ml water, and mix until dissolved. A very small amount may not dissolve, but it will not matter at this time. Add two or three drops of salicylic acid indicator, noting the deep purple color!
4. Calibrate your pH meter using pH 4 and 7 buffer solutions. Insert the pH probe into the 50 ml beaker and make sure it is in the solution far enough to be able to register the pH. You may add more water if needed.
5. Keeping in mind your answer to prelab question 2, titrate the ferric ammonium sulfate with 0.20 M EDTA disodium. Add 1 ml aliquots until you are getting close to the expected endpoint, and then add more slowly until the color changes. Be sure to mix well between additions. Record the volume of titrant added and the pH after each addition in Table 20.1.
6. Stop titrating when the solution changes color to a pale yellow and record the pH. Add another 0.5 ml of titrant, mix, and record the titrant volume and the pH. Describe what happened in the observations section.
7. Rinse the pH probe and clean the buret and beaker.
8. Graph your data in a graphing program such as Excel with the pH on the *y* axis and the volume of titrant on the *x* axis. From your graph, determine the lowest pH. This is when the reaction had come to completion. Compare this to the volume when the indicator changed color.

Part 2: Formation of sodium iron (III) EDTA by titration

1. Clamp the buret to a ring stand. This time, fill the buret with 0.8 M EDTA disodium solution. Using a higher molarity will speed up the titration.
2. Obtain and record the mass of a clean, dry 50 ml beaker in Table 20.2. Using your prelab calculations, obtain approximately 0.005 mole

$NH_4Fe(SO_4)_2 \cdot 12H_2O$ (FAS) into the beaker, and record the exact mass. Add 15 ml water and stir until dissolved.

3. Place the pH probe again in the beaker, but this time do not add any salicylic acid indicator! The pH graph will serve as the indication to know when the reaction has ended.
4. Titrate the $NH_4Fe(SO_4)_2 \cdot 12H_2O$ solution using the 0.80 M EDTA disodium titrant. When you are almost to the point where the reaction should end (according to prelab calculations), slowly titrate while mixing. Pay close attention to the pH.
5. Stop titrating immediately when the pH starts to increase. Obtain and record the mass of the beaker and its contents. Calculate and record the content's mass.
6. Heat the solution on a hot plate until a precipitate forms. This will be when the solution is less than 10 ml. Stir occasionally. Note the amount of time the hot plate was turned on and the solution was heated. Allow the sodium iron (III) EDTA to completely precipitate out of solution.
7. Set up a vacuum filtration apparatus using a filter flask and a small Büchner funnel. Preweigh a piece of Whatman 40 filter paper and a watch glass. Place the filter paper in the Büchner funnel and seat it with DI water.
8. Vacuum filter the solution. Rinse with small portions of ice cold water using approximately a total of 5 ml. Also rinse with 2–3 ml cold ethanol. ***Caution:*** Do not drink! Ethanol used in the lab has poisonous stabilizers added. Allow the vacuum to continue to run for a few minutes to help dry the product.
9. Transfer the product and filter paper to the preweighed watch glass, and allow it to dry completely. Obtain and record the mass.
10. Calculate the theoretical yield and your percent yield of sodium iron (III) EDTA trihydrate ($C_{10}H_{12}N_2NaFeO_8 \cdot 3H_2O$).
11. Use the contents mass found in step 5, 5.000 g as the mass of the rinse water, and the product mass to calculate the E-factor. Do not include the water used to seat the filter paper or the ethanol.

Part 3: Formation of sodium iron (III) EDTA in solventless reaction

1. Obtain the mass of a clean and dry 50 ml beaker. Using your prelab calculations, obtain approximately 0.005 mole of your previously crushed ferric ammonium sulfate in the beaker. Record the exact mass used in Table 20.3.
2. Obtain 1.20 g ammonium acetate and place it into the beaker. Record the exact mass used. Make observations of what the solids look like separately.

3. Crush the two solids and mix them together with a stir rod for at least 3 minutes. Note the color change in the reaction and the apparent absorption of waters from the atmosphere forming a wet product.
4. Dissolve the ferric acetate product in 15 ml DI water.
5. Measure out 2.0 g EDTA disodium salt and add it to the beaker. Record the exact mass used. Mix the solution well. The iron should react with the EDTA to form sodium iron (III) EDTA. Obtain and record the mass of the beaker with its contents. Calculate and record the content's mass.
6. Heat the solution in a microwave oven at 15–30 second intervals until a precipitate forms. Use a hot plate to heat the solution only if a microwave oven is not available. Note the amount of time the microwave oven (or hot plate) was turned on and the solution was heated. Let the solution sit to allow the product to completely precipitate out of solution.
7. Set up a vacuum filtration apparatus using a filter flask and a funnel. Preweigh a piece of Whatman 40 filter paper and a watch glass. Place the filter paper in the Büchner funnel and seat it with DI water.
8. Vacuum filter the solution. Rinse with 5 ml ice cold water and 3 ml cold ethanol. ***Caution:*** Do not drink! Ethanol used in the lab has poisonous stabilizers added. Allow the vacuum to continue to run for a few minutes to help dry the product.
9. Transfer the product and filter paper to the preweighed watch glass and allow it to dry completely. Obtain and record the mass.
10. Calculate the theoretical yield and your percent yield of sodium iron (III) EDTA trihydrate ($C_{10}H_{12}N_2NaFeO_8 \cdot 3H_2O$).
11. Use the contents mass found in step 5, 5.000 g as the mass of the rinse water, and the product mass to calculate the E-factor. Do not include the water used to seat the filter paper or the ethanol.

Name _____

Data

Part 1: Sample titration using an indicator

Mass of $NH_4Fe(SO_4)_2 \cdot 12H_2O$: _____

Table 20.1 Initial Titration Using an Indicator

Milliliters of 0.20 M EDTA added	pH	Color	Milliliters of 0.20 M EDTA added	pH	Color
0.00					
1.00					
2.00					

Part 2: Formation of sodium iron (III) EDTA by titration

Table 20.2 Data for Formation of Sodium Iron (III) EDTA by Titration

Mass of 50 ml beaker (g):	FAS used (g):	FAS used (mole):
Calculated (prelab) necessary EDTA (ml):	EDTA used (ml):	Mass of 50 ml beaker plus contents:
Beaker contents mass (g):	EDTA used (mole):	Time hot plate was on:
Filter paper (FP) mass (g):	Watch glass (WG) mass (g):	Product + FP + WG mass (g):
$C_{10}H_{12}N_2NaFeO_8 \cdot 3H_2O$ produced (g):		$C_{10}H_{12}N_2NaFeO_8 \cdot 3H_2O$ produced (mole):
Theoretical yield:		Percent yield:

Part 3: Formation of sodium iron (III) EDTA in solventless reaction

Table 20.3 Data for Solventless Reaction

Mass of 50 ml beaker (g):	FAS used (g):	FAS used (mole):
Ammonium acetate used (g):	EDTA used (g):	
Mass of 50 ml beaker plus contents (g):	Mass of beaker contents (g):	Time microwave (or hot plate) was on:
Filter paper (FP) mass (g):	Watch glass (WG) mass (g):	Product + FP + WG mass (g):
$C_{10}H_{12}N_2NaFeO_8 \cdot 3H_2O$ produced (g):		$C_{10}H_{12}N_2NaFeO_8 \cdot 3H_2O$ produced (mole):
Theoretical yield:		Percent yield:

Observations

Calculations

Part 2: Formation of sodium iron (III) EDTA by titration

Percent yield:

E-factor:

Part 3: Formation of sodium iron (III) EDTA in solventless reaction

Percent yield:

E-factor:

Analysis

1. What green chemistry principles are explored in this lab?

2. From your graph in Part 1, determine the lowest pH. This is where the reaction came to completion. Evaluate and compare this pH to the pH when the indicator changed color.

3. Which lab procedure gave a better percent yield? Did the introduction of an intermediate step in Part 3 lower the yield significantly for the solventless reaction?

4. Which lab procedure has a better atom economy? Which one has a better E-factor? Which method of analysis is a better comparison for how the two procedures performed? Explain your answer.

5. Compare the amounts of time each lab procedure needed to have a hot plate or microwave on. Assuming the watts per hour for a microwave and a hot plate are comparable, which one was more energy efficient? Energy efficiency was not considered in your atom economy or E-factor calculations. How major a factor is this when comparing the two procedures in terms of green chemistry?

Think green

1. Coordination compounds have many uses in a variety of fields, including metallurgy and various biomolecules. Research one coordination compound and describe its uses, how it is generally made, and how much of it is needed in a year.
2. Atom economy calculations are normally done without the consideration of the solvent. One of the reasons for this is that solvents can often be purified and recycled. Research the cost of purifying water. Why might a solventless reaction be considered greener?
3. Different green chemistry metrics have been developed to help evaluate chemical processes, including the two you studied in this lab: atom economy and E-factor. Research different green chemistry metrics. Which do you think would be most effective to evaluate the procedures used in terms of green chemistry? Explain your answer.
4. Research commercially available microwave reactors and how they are used in chemical synthesis. Why might using a microwave reactor be considered greener?

Presidential green chemistry challenge

In this lab you used a solventless reaction. The Environmental Protection Agency (EPA) gave its 2009 Presidential Green Chemistry Award in the Green Synthetic Pathways category to Eastman Chemical Company for developing a solvent-free process to produce esters used in cosmetics and personal care products. Look up information about this award on EPA's website (www2.epa.gov/green-chemistry) under challenge award winners and write a brief summary about how this process utilizes principles of green chemistry.

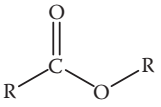
chapter twenty one

Analysis of biodiesel synthesized from canola oil

> Every day, countless amounts of nonrenewable fossil fuels are burned to run vehicles around the world. Finding a renewable energy source may be the most important task presently facing chemists.

Creation of a cost-effective and greener alternative fuel is a major focus of science today. One of the more often used greener fuels is biodiesel. It is made from new or used vegetable oils and animal fats, and is biodegradable and nontoxic. This means it meets the criteria for several of the 12 principles of green chemistry, including the *use of renewable feedstock* and *design for degradation*.

Biodiesel synthesis falls under one of the major subdisciplines of chemistry called organic chemistry. Organic chemistry studies organic compounds that are almost all of the molecules that contain carbon. Organic molecules are classified according to their functional groups. A functional group is simply a specific grouping of atoms that behave in a characteristic manner. In this lab, you will synthesize biodiesel by reacting the organic compounds of methanol and triglycerides. Triglycerides are the main component of animal fats and vegetable oils. Methanol is an alcohol since it has an –OH functional group bonded to its carbon atom. A triglyceride has three ester functional groups, and each one will react with one methanol molecule. A generic ester functional group is shown below:



R is used in organic chemistry to represent a general organic group. It could simply be a $-CH_3$, or it could be a much larger, more complex group. It can even have other atoms besides carbon and hydrogen in its structure, but the atom first bonded in an R group is always carbon. Organic chemists often do not draw every carbon or hydrogen atom. A carbon is represented with two lines coming together at an angle,

as shown in Figure 21.1. It is understood that the correct number of hydrogens that will give the carbon atoms four bonds is present.

The simplest way to produce biodiesel uses what is called a transesterification reaction. In this particular reaction, a base catalyst (KOH) is used to convert the triglycerides into three smaller separate ester molecules, with each one ending in a $–OCH_3$. A molecule of glycerol, a trialcohol, is also formed as a by-product. This is a reversible reaction, so excess methanol is added to drive the reaction toward the product. The reaction is shown in Figure 21.1.

Any water in the process promotes soap making (via saponification) and inhibits transesterification. This means the methanol used must be dry and the KOH weighed out quickly since it is hygroscopic.

On the other side of the ester functional group is a long chain made up of carbon atoms bonded to each other and to hydrogen atoms. This long chain varies between molecules in any oil, so the density and molar mass of the triglycerides in oils and animal fat are averages of many molecules. Figure 21.1 shows a molecule of canola oil undergoing a transesterification using the most common carbon chain found in canola oil.

Additionally, one of the more recent focuses in organic chemistry has been the attempt to make reactions more energy efficient. Most biodiesel syntheses require the use of either a hot plate or a microwave. In this lab, you will see if biodiesel can be made without heating. Instead of heating, you will simply shake the reaction vessel for three 5-minute intervals of time.

Glycerol and methanol have very different densities. Methanol has a low density of 0.79 g/ml and will lie on top of the oil in the beginning of the reaction to make biodiesel, since oil has a density of around 0.92 g/ml. Glycerol is denser at 1.26 g/ml and will settle to the bottom once formed. In this lab, a small quantity of red food coloring is added to the methanol to allow for visualization of the reaction's progress. The coloring is always found in either the glycerol- or methanol-containing layers. As biodiesel

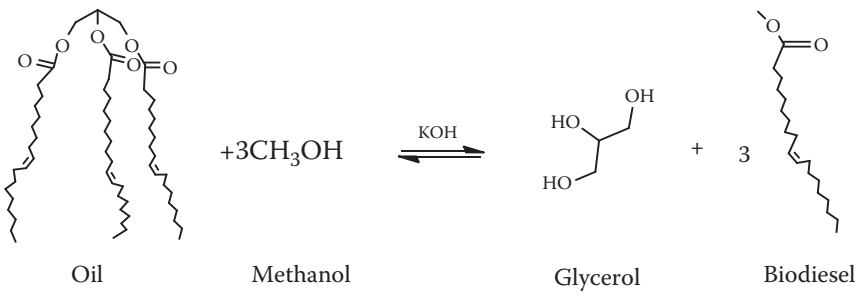


Figure 21.1 Reaction of canola oil with methanol to form biodiesel.

is produced, so is glycerol. This causes some of the red color that begins at the top of the solution to begin to sink to the bottom. By the end of the reaction, the methanol present in the solution is dissolved in the colored glycerol layer at the bottom of the container.

In this lab, you will determine how much oil was converted to biodiesel by two different methods and compare the results. In the first method, you will use the methanol test. It tells how completely the oil was converted to biodiesel. This test takes specified amounts of biodiesel and methanol, mixes the two together, and lets the solution settle into layers for a certain amount of time. Because oil is not soluble in methanol, any unreacted oil will settle within the allotted time to the bottom of the methanol test. From knowing the volume of the unreacted oil, you can calculate the volume and moles of reacted oil.

In the second method you will determine the amount of glycerol formed through measuring the density of the glycerol layer. Since the glycerol layer will consist of unreacted methanol and glycerol, its density can be used to determine how much glycerol is present. To do this, you must prepare a calibration curve for percent glycerol versus density. This will be made by first determining the density of a 50/50 methanol/glycerol mixture. A three-point calibration curve will then be prepared by using the determined density of the mixture and the known densities of methanol and glycerol. The percent glycerol will be determined from the trendline equation. You will then be able to calculate how many milliliters and how many moles of glycerol were made. Since there are 3 moles of biodiesel formed for every 1 mole of glycerol, an approximate percent yield can be calculated.

After the biodiesel is made, it must be rinsed with water to remove the KOH. A strong base in a vehicle's engine will do major damage. The pH of the rinses will be monitored to determine the effectiveness of the rinses. As water flows through the biodiesel and the pH changes, some soap that is present as an impurity may become visible. This is obviously an unwanted contaminant and would need to be removed before the biodiesel could be used.

There are other analytical tests that should be run on produced biodiesel to determine if it is ready for use. The biodiesel produced in this lab would pass some tests, but fail others, so it should not be used in a vehicle!

Objective

The purpose of this lab is to produce biodiesel from methanol and canola oil using a heatless reaction and then to analyze the biodiesel, making use of a methanol test and a calibration curve to determine percent glycerol obtained.

Name _____

Prelab questions

1. Describe what biodiesel is and why the production of biodiesel is significant.

2. Calculate the theoretical yield of biodiesel to be produced in this lab if all 9.50 ml of canola oil is converted into biodiesel. Use 880 g/mole for the average molar mass of a canola oil molecule and 297 g/mole as the average molar mass of a molecule of biodiesel (0.92 g/ml is the average density of canola oil and 0.87 g/ml is the average density of biodiesel).

3. A small amount of red food coloring is added to the methanol/KOH solution. What should happen to the location of the red color over the course of the reaction?

4. Research and evaluate the hazards for all chemicals you will be using. Study the procedure and look for other possible hazards that exist. List all hazards, including ones from chemicals. What protective equipment will you need to use?

Procedure

Part 1: Synthesis of biodiesel

1. Obtain approximately 9.5 ml canola oil in a clean and dry 10 ml graduated cylinder. Record the exact amount of canola oil obtained in Table 21.1. Calculate the number of moles of canola oil this is. Use 880 g/mole for the average molar mass of a canola oil molecule.
2. Add the canola oil into a 15 ml conical plastic centrifuge tube. Be sure to give it adequate time to drain into the centrifuge tube. Use the average molar mass of a canola oil molecule and the average density of canola oil given in prelab question 2 to calculate the grams and moles of canola oil obtained.
3. Acquire 3.50 ml of red methanol/KOH solution in the 10 ml graduated cylinder used to obtain the canola oil. Be sure you obtain 3.50 ml of the red methanol/KOH solution in addition to any residual canola oil. Add this to the centrifuge tube and place the cap securely on the tube.
4. Shake the centrifuge tube vigorously for 5 minutes. Shake it in different ways and directions to avoid catching any of the solution in the tip of the centrifuge tube.
5. Place the centrifuge tube in a centrifuge, and balance it using a counterweight. Run the centrifuge for 30 seconds. Determine and record the volume of the glycerol layer, which is the red bottom layer.
6. Repeat steps 3–5 two additional times. All of the red should be at the bottom of the centrifuge tube. If it is not, repeat steps 3–5 until it is.
7. Carefully pour all of the contents of the centrifuge tube into a 25 ml buret. Allow extra drain time if needed. Let the biodiesel rest for at least 5 minutes to allow it to drain off the sides of the buret and settle into two distinct layers. Determine and record in Table 21.1 the quantity of the top biodiesel layer.

Part 2: Calculation of yield using glycerol calibration curve

1. Carefully drain down the red bottom (glycerol) layer to the end of the tip of the buret. A very small amount of only the red bottom layer may need to be drained into a waste beaker to remove air bubbles. Add this back into the buret and allow it time to settle to the bottom.
2. Obtain a buret reading at the top of the biodiesel to the hundreth's place. Record this value as buret reading 1 in Table 21.2.
3. Obtain and record the mass of a small test tube.

4. Drain approximately 1.0 ml of the red bottom layer into the preweighed test tube. Obtain a buret reading at the top of the biodiesel to the hundreth's place, and record it as buret reading 2.
5. Determine and record exactly how much red bottom layer was drained into the test tube by subtracting buret reading 2 from buret reading 1. Do not get any of the top biodiesel layer into the test tube.
6. Obtain and record the mass of the test tube with the red bottom layer. This can be accomplished by taring a small beaker on the balance and then placing the test tube in it and obtaining the mass. Calculate and record the mass of the contents.
7. Calculate and record the red bottom layer's density.
8. Carefully drain the rest of the red bottom layer into a waste beaker. Obtain and record the volume reading of the biodiesel on the buret as buret reading 3. Subtract this from buret reading 1 to determine the volume of the red bottom layer. Enter this volume under "Total volume of red bottom layer."
9. Obtain and record the mass of another small test tube. Into this test tube drain 2.0 ml of provided 50/50 glycerol/methanol solution located in a buret. Record the exact volume obtained.
10. Obtain and record the mass of the test tube with the glycerol/methanol solution, and calculate the mixture's density in g/ml.
11. The densities of glycerol and methanol are 1.261 and 0.791 g/ml, respectively. Use these densities and the density you determined for the 50/50 glycerol/methanol solution to create a calibration curve that compares percent glycerol to density. Record the equation of the line of best fit.
12. Using the equation of the line, calculate the percent glycerol by volume in the red layer. Do this by inserting the density of the glycerol layer that was calculated in step 7 into the equation.
13. Use the percent glycerol by volume to calculate the milliliters of glycerol present in the red layer. Do this by multiplying the total volume of the red layer by the percent glycerol by volume.
14. Calculate the moles of glycerol produced, using 1.261 g/ml as the density and 92.09 g/mole as the molar mass. From this, determine the moles of biodiesel produced. Next, use this and the moles of canola oil used that was calculated in Part 1 to determine the percent yield. Remember you get 3 moles of biodiesel for every 1 mole of glycerol.

Part 3: Methanol test and product yield by reacted oil

1. Drain a small amount of the biodiesel into the waste beaker to be sure pure product will be used in the methanol test.
2. Drain 1.25 ml biodiesel into a 15 ml plastic centrifuge tube.

3. Add 11.25 ml methanol into the centrifuge tube. Shake vigorously for 30 seconds. Allow the contents of the tube to settle out for exactly 5 minutes.
4. Use the markings on the centrifuge tube to determine as close as possible the amount of undissolved material that collects on the bottom. Record this value in Table 21.3. You may need to look at the markings on an empty centrifuge tube to be able to determine this. For every 0.050 ml that is undissolved, 4.0% of the oil was unreacted. Use this information to calculate how much canola oil reacted in this process.
5. Calculate the yield in moles of biodiesel from the amount of reacted canola oil. Use the density and molar mass values given in question 2 of the prelab. Remember you get 3 moles of biodiesel for every 1 mole of oil. Use this and the moles of canola oil used that was calculated in Part 1 to determine the percent yield.

Part 4: Water rinses

1. Pour 1 ml of deionized (DI) water into the top of the buret and let it settle to the bottom. After the water settles out, drain it into a clean waste beaker. Use pH paper to determine the pH of the rinse water.
2. Rinse the biodiesel four more times with 1 ml portions of DI water. Each time, take the pH of the rinse water as it is draining from the tip of the buret, and not of the mixture of rinses in the waste beaker. If any soap forms, it can be removed later using a spatula.
3. Record the pH of the wastewater for each rinse in Table 21.4.

Name _____

Data

Part 1: Synthesis of biodiesel

Table 21.1 Data for the Synthesis of Biodiesel

Canola oil (ml):	Canola oil (g):
Canola oil (mole):	Volume of biodiesel layer in buret (ml):

Part 2: Calculation of yield using glycerol calibration curve

Table 21.2 Data for Calculating the Yield Using the Glycerol Calibration Curve

Buret reading 1 (ml):	Buret reading 2 (ml):	Volume of red bottom layer in test tube (ml):
Mass of empty test tube in step 3 (g):		Mass of test tube with red bottom layer (g):
Mass of red bottom layer in test tube:		Density of red bottom layer (g/ml):
Buret reading 3:		Total volume of red bottom layer:
Mass of empty test tube in step 9 (g):	Mass of test tube with 50/50 mixture (g):	Mass of 50/50 mixture (g):
Volume of 50/50 mixture (ml):		Density of 50/50 mixture:
Equation of line:		% glycerol by volume in red bottom layer:
Actual volume of glycerol:	Moles glycerol:	Moles biodiesel produced:
Biodiesel yield (g):		% yield of biodiesel:

Part 3: Methanol test and product yield by reacted oil

Table 21.3 Data for the Methanol Test

Volume of undissolved material in methanol test (ml):	% unreacted oil:
Volume of unreacted canola oil (ml):	Volume of reacted canola oil (ml):
Moles of reacted canola oil:	Moles of produced biodiesel:
Yield of biodiesel in grams:	% yield of biodiesel:

Part 4: Water rinses

Table 21.4 Data for the Water Rinses

Table rinses	1	2	3	4	5
pH					

Observations

Calculations

Part 1: Synthesis of biodiesel

Moles of canola oil:

Part 2: Calculation of yield using glycerol calibration curve

Density of red layer:

Percent by volume glycerol:

Volume of glycerol:

Moles of glycerol:

Moles of biodiesel:

Biodiesel yield (g):
(Use 297 g/mol for biodiesel's molar mass.)

Percent yield using glycerol layer density:

Part 3: Methanol test and product yield by reacted oil

Percent unreacted oil:

Volume reacted oil:

Moles of reacted canola oil:

Moles of produced biodiesel:

Biodiesel experimental yield (g):

Percent yield using methanol test:

Analysis

1. What green chemistry principles were utilized in this lab?

2. How similar were the two calculated percent yields? Do you consider this acceptable? Explain your answer.

3. How effective was the water rinse at reducing the pH of the biodiesel? Commercial biodiesel needs to be at a neutral pH. Was the biodiesel made neutral?

Think green

1. How do you think you could improve your yield or make this reaction greener? If time and resources permit, test your hypothesis.
2. Research the difficulties of commercially using the glycerol by-product obtained from biodiesel production. Find common uses for the glycerol by-product, and explain in terms of green chemistry the importance of having a use for the by-products of this reaction.
3. Other alternatives to the fuel crisis exist. Research and write a summary of another potential means of replacing gasoline.

Presidential green chemistry challenge

In this lab you synthesized biodiesel from vegetable oil, a renewable resource. The Environmental Protection Agency (EPA) gave its 2009 and 2010 Presidential Green Chemistry Awards in the Small Business category to Virent Energy Systems, Inc. and LS9, Inc., respectively, for methods to convert natural products into fuels and other chemical products. Look up information about one of these awards on EPA's website (www2.gov/green-chemistry) under challenge award winners and write a brief summary about how this technology utilizes principles of green chemistry.

CHEMISTRY

Green Chemistry

Laboratory Manual for General Chemistry

Green chemistry involves designing novel ways to create and synthesize products and implement processes that will eliminate or greatly reduce negative environmental impacts. The ***Green Chemistry Laboratory Manual for General Chemistry*** provides educational laboratory materials that challenge students with the customary topics found in a general chemistry laboratory manual, while encouraging them to investigate the practice of green chemistry.

Following a consistent format, each lab experiment begins with objectives and prelab questions highlighting important issues that must be understood prior to getting started. This is followed by detailed step-by-step procedures for performing the experiments. Students report specific results in sections designated for data, observations, and calculations. Once each experiment is completed, analysis questions test students' comprehension of the results. Additional questions encourage inquiry-based investigations and further research about how green chemistry principles compare with traditional, more hazardous experimental methods. By placing the learned concepts within the larger context of green chemistry principles, the lab manual enables students to see how these principles can be applied to real-world issues.

Performing laboratory exercises through green experiments results in a safer learning environment, limits the quantity of hazardous waste generated, and reduces the cost for chemicals and waste disposal. Students using this manual will gain a greater appreciation for green chemistry principles and the possibilities for future use in their chosen careers.

K22649

CRC Press
Taylor & Francis Group
an **informa** business

www.crcpress.com

6000 Broken Sound Parkway, NW
Suite 300, Boca Raton, FL 33487
711 Third Avenue
New York, NY 10017
2 Park Square, Milton Park
Abingdon, Oxon OX14 4RN, UK

ISBN: 978-1-4822-3020-8
90000
9 781482 230208

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