

Laboratory Manual for
General Chemistry



Laboratory Manual
for
General Chemistry

Dale J. Brugh

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Dephlogisticated

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Edition 13.8.26

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Feedback

This laboratory manual is always a work in progress. Constructive feedback to make this manual better for future students can be submitted online at <http://git.dephlo.net/gchemlab/issues> or by email to dale@brugh.co. Submitting feedback online can be anonymous and gives you the ability to track my response. Submitting feedback at the above web address is strongly encouraged.

<http://git.dephlo.net/gchemlab/issues>

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Website

This laboratory manual has a companion website at which you can find pre-lab assignments and other supporting information. A PDF version of this manual is also available for download. Instructors can request a username and password to gain access to instructor notes.

<http://lab.dephlogisticated.net/genchem>

Safety

This manual contains instructions for experiments that can be dangerous. Do not attempt to carry out these experiments on your own; they should be carried out under the supervision of a qualified laboratory instructor.

Every attempt has been made to eliminate errors, but some will inevitably remain. Even in the absence of errors, laboratory conditions sometimes change at the last minute, requiring changes in procedures. The procedures in this manual are no substitute for careful planning and the advice of your laboratory instructor. Always pay careful attention to announced changes in the laboratory procedure.

Acknowledgments

It is difficult to have a completely original idea for a general chemistry laboratory project, and I make no claim that any of these projects are original. I freely admit that I have pilfered the ideas of others. I owe a debt to my colleagues at Ohio Wesleyan University, past and present, who have been writing and refining general chemistry laboratory experiments for our students over many years. Authors who took the time to publish their experiments in the Journal of Chemical Education and elsewhere were also of great help.

While the ideas for these projects may have been taken from colleagues or published works, their presentation in this manual is my own. Several people have contributed to making sure this particular expression of a general chemistry laboratory manual is the best it can be. Any errors that remain are my own.

David Lever provided extensive commentary in the early editions of this manual that greatly improved every project, especially the new ones. Kim Lance provided comments later in the life of this manual that helped progressively improve the quality of the projects, the accuracy of the procedural steps, and the consistency of the educational experience. Most recently, Laura Brice read every page of the manual, marked a disturbingly large number of errors, and provided suggestions for improvement and greater consistency throughout. I am grateful for the time these individuals have dedicated to reviewing this manual. Laura deserves special thanks because her work was uncompensated.

Part I

Laboratory How To

Chapter 1

Staying Safe in Lab

All laboratories are dangerous places. There are things you can do, however, to minimize the danger to yourself and to others during laboratory work. The goal is to leave every lab with no injuries. This is what this chapter is about: how to be safe in the lab.

► Safety protocols are not just about your safety. They are also about the safety of everybody else in lab.

1.1 Basic Safety Equipment

In every chemistry laboratory at Ohio Wesleyan University you will find basic safety equipment, including an eye wash station, a safety shower, and a fire extinguisher. These pieces of equipment should be thought of as last lines of defense against injury. If you have done everything else wrong, you may need to use them.

The eye wash station, safety shower, and fire extinguisher are always located near one of the laboratory doors as shown in Figure 1.1. When you walk into a lab for the first time, take note of where these items can be found.

The eye wash station is used in the event you get something, such as a chemical, in your eyes. Flushing the eyes with plenty of water is normally the first step in dealing with such an accident.

The safety shower is used in the event of a substantial accident in which a person is drenched in hazardous material. For instance, if you spill a large quantity of concentrated acid on yourself, the safety shower may be the only tool capable of diluting the acid fast enough to prevent burns.

The fire extinguisher is to be used in the event of a fire that will not burn itself out without causing damage.



Figure 1.1
Eye wash station, safety shower, and fire extinguisher.

1.2 Protective Clothing

You can reduce the likelihood that the basic safety equipment will be needed by following some basic rules regarding what you wear to lab. Dress for safety and not for fashion. What you wear in lab should be considered part of the first line of defense against injury.

Wear Safety Goggles

You must wear safety goggles at all times while in the laboratory. There are no exceptions. You must wear the safety goggles provided by the Ohio Wesleyan bookstore for this course. Any other goggles, including those from your high school course, are not acceptable.

Each instructor has his or her own policy regarding penalties for not wearing your goggles. For the most part, however, instructors are intolerant of students who persistently refuse to wear their goggles. Wearing goggles is so essential that you should not have to know the penalty for not wearing them. If you like your eyes, you should just wear them all the time.

Consider Clothing Carefully

The clothing you wear can provide a barrier to chemical spills. Because of this, shorts and short skirts are strongly discouraged. You will not be expelled from lab for exposing your legs and arms, but you are warned that this is not a good idea. The building is air conditioned, so it is not uncomfortable to wear something that covers your legs.

Wear Real Shoes

No one will be allowed to carry out laboratory work with bare feet, open-toed shoes, Crocs, or sandals. Wearing socks with sandals or Crocs does not count. You must have a protective covering over your feet. This is not just to protect your feet against chemicals falling to the ground. It is also to protect you from glass which has a nasty habit of following gravity's pull right to your feet. Wear shoes to lab.

Use Gloves

Your laboratory drawer will have a pair of yellow kitchen gloves. Feel free to use these when working with corrosive or toxic chemicals. The gloves are a barrier against injury. Use them.

Use an Apron

There is a drawer in every general chemistry laboratory with an apron. If you feel uncomfortable working with a chemical, feel free to wear one. In some cases, your instructor will recommend that you wear one.

1.3 Sensible Actions

In addition to wearing appropriate clothing, you can take some simple steps in the lab to prevent an accident from happening in the first place. Such sensible actions in lab are part of the first line of defense against injury.

Clean Up Chemical Spills

If chemicals spill while you are in lab, clean them up immediately. Do not leave the chemicals lying around on the bench for somebody to stick their arm or hand into.

Never Heat Sealed Containers

When you heat a sealed container, such as a test tube with a stopper in the top, the pressure increases. This continues until something breaks. If the glass breaks, many people could be injured. Before you heat anything, make sure there is an easy way for the increased pressure to be released.

Never Add Water to Acid

If you add drops of water to concentrated acid, you will discover that the drop of water will rapidly turn into water vapor and spray acid all over. To prevent this, add acid to water if you have to mix the two. A simple mnemonic to help you remember this is “do as you oughtta, add acid to wata.”

Check Instructions and Labels Twice

Read and recheck labels carefully to make sure you mix the proper chemicals. If you can't read a label, ask your instructor for help. If you have any confusion about what a chemical is, ask your instructor for help.

Tie Your Hair Back

If you have long hair, tie it back so that it does not get into chemicals that may have spilled on your work bench. You also do not want your hair to accidentally get into a flame on the few occasions open flames are used.

Practice Good Hygiene In Lab

Do not eat or drink food in lab. While working with chemicals that can injure you, you should never confuse yourself by consuming food or drink. This is not a recommendation; this is a requirement.

You should never taste chemicals or get chemicals anywhere near your mouth for any reason. Stuff in the lab is not for eating. The glassware in lab should also never be placed near your mouth.

You should wash your hands before you leave lab to prevent the spread of chemicals beyond the laboratory door. It is surprisingly easy to get chemicals on your hand and then to rub your eye after leaving lab. The chemical is now in your eye, and that could be nasty. Feel free to wash your hands as many times as you want during lab.

If you must use the bathroom during lab, it is recommended that you wash your hands before going (and after, of course). There are more unpleasant places to get chemicals than your mouth.

► Your parents taught you to wash your hands after going to the bathroom. In chemistry you ought to learn to wash them before going as well.

Use the Hoods

Each general chemistry lab is equipped with many hooded areas that continuously draws air away from the surrounding work area. Try to do as much of your laboratory work as possible in one of these hooded work areas. In the event of a release of a small quantity of noxious fumes (from a beaker or test tube, for example) place the emitting container under the hood.

The individual hoods at the work stations have a limited capacity to remove fumes. If a significant quantity of noxious fumes is released, just leave the room. Notify people why you are leaving on your way out. If you follow the laboratory directions carefully, this should never happen.



Figure 1.2

Broken glassware container.

Clean Up Broken Glassware Properly

If you break glassware in the lab and you are not injured, clean up the glass immediately to prevent others from being injured. Every lab is equipped with a broom and a dust pan. Find them and use them. Always dispose of broken glassware in the proper containers labeled “Broken Glass” as shown in Figure 1.2. Never place broken glassware in the normal trash cans. If you are injured, ignore the broken glass and inform your instructor of your injury.

Let Small Fires Burn Out

In the event of a small fire (contained in a beaker, for example) it may be safest to just let it burn itself out or to smother it with something like a lab notebook. Notify your instructor immediately in the even of a fire.

Walk Away from Large Fires

In the event of a large fire, you should leave the lab immediately, walking calmly to the nearest exit. A large fire is the responsibility of professionals to contain and put out.

1.4 Mitigation of Personal Accident Injury

If you are the victim of an accident, there are things you can do to minimize the injury that could result from that accident. Your actions right after an accident are yet another line of defense against injury.

Chemical Spills

If chemicals are spilled on your clothing or on your skin, wash the chemicals off immediately under cold tap water and then notify your lab instructor so he/she can determine if you need further medical attention.

Cuts

If you are cut, notify your lab instructor immediately so he/she may see that your wound is properly attended to.

Chemicals In The Eyes

If you get a chemical in your eyes, wash them immediately at the eye wash station. Notify your lab instructor so he/she may determine if you need further medical attention.

1.5 Chemical Hazard Information

Working safely and sensibly with chemicals is another line of defense against injury, but this requires that you know the hazards of the chemicals you are using. There are several sources of information regarding the hazards presented by the materials you may encounter in a chemistry laboratory. Chemical containers are often marked with hazard labels such as the NFPA hazard diamond and the EU hazard symbols. These labels communicate a wealth of information about the hazards posed by the chemical. You can obtain additional safety information from material safety data sheets (MSDS), and the NIOSH Pocket Guide. All four of these sources of chemical hazard information are discussed here.

NFPA Hazard Diamond

The National Fire Protection Association (NFPA) is an organization that publishes guidelines to promote fire and health safety. One of their guidelines includes a standard system for labeling chemicals to quickly communicate the hazards of materials. This system is formally called the NFPA 704 Hazard Identification rating system, but it is more commonly referred to as the “NFPA diamond” or the “NFPA hazard diamond.”

The NFPA hazard identification system divides material hazards into four categories: health hazards, flammability hazards, instability hazards, and special hazards. The level of hazard presented by a material in each of the health, flammability, and instability categories is rated on a 5-point scale starting at 0 for minimal hazard and going up to 4 for severe hazard. This information is displayed on a multi-colored diamond background like that shown in Figure 1.3. Each region of the diamond is reserved for a different hazard as indicated in Figure 1.3.

The health hazard rating is indicated on the blue background at the left of the diamond, the flammability hazard rating is shown on the red background at the top of the diamond, and the instability hazard rating is shown on the yellow background at the right of the diamond. The exact meaning of each hazard rating in each hazard category is explained in Tables 1.1, 1.2, and 1.3.

Any special hazard is indicated on the white background at the bottom of the diamond with letter codes. There are three special hazards: oxidizer (OX),

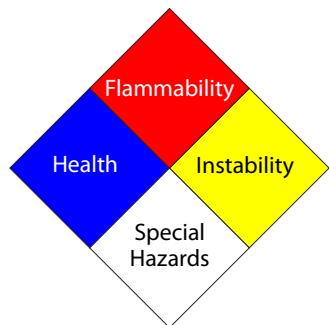


Figure 1.3
NFPA diamond

► The numerical ratings for hazards in the NFPA system always have the following general meanings:

0 =	Minimal Hazard
1 =	Slight Hazard
2 =	Moderate Hazard
3 =	Serious Hazard
4 =	Severe Hazard

► The recognized special hazards and their symbols are:

OX =	oxidizer
SA =	simple asphyxiant
W =	reactivity with water

Table 1.1

NFPA hazard rating descriptions for health hazards.

0	No unusual hazard
1	May be irritating
2	May be harmful if inhaled or absorbed
3	Corrosive or toxic. Avoid skin contact or inhalation
4	May be fatal on short exposure. Protective equipment required.

Table 1.2

NFPA hazard rating descriptions for flammability hazards.

0	Not combustible
1	Combustible if heated
2	Combustible liquid flash point of 100°F to 200°F
3	Flammable liquid flash point below 100°F
4	Flammable gas or extremely flammable liquid

Table 1.3

NFPA hazard rating descriptions for instability hazards.

0	Not reactive when mixed with water
1	May react if heated or mixed with water but not violently
2	Unstable or may react violently if mixed with water
3	Explosive if shocked, heated under confinement or mixed with water
4	Explosive material at room temperature

simple asphyxiant (SA), and unusual reactivity with water (W). The symbols for these special hazards and their meanings are listed in Table 1.4.

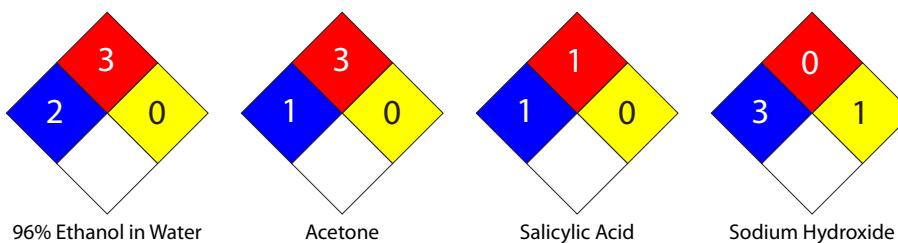
Example NFPA hazard diamonds for chemicals you may encounter in the general chemistry laboratory are shown in Figure 1.4.

It is important to remember that the NFPA system was developed for the purpose of communicating information to fire fighters and other emergency responders. Because of this, there is an emphasis on the material hazards in the

Table 1.4

NFPA special hazards symbols and meaning.

OX	Oxidizer, a chemical which can greatly increase the rate of combustion/fire.
SA	Gases which are simple asphyxiants. Used only for nitrogen, helium, neon, argon, krypton, and xenon.
W	Unusual reactivity with water. This indicates a potential hazard using water to fight a fire involving this material.

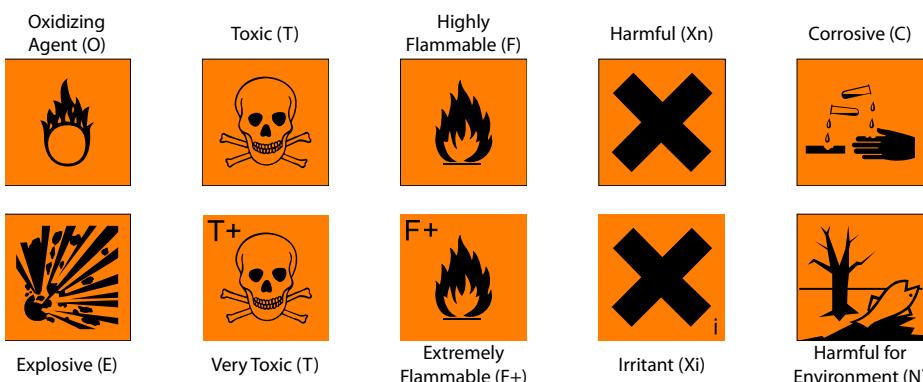
**Figure 1.4**

NFPA hazard diamonds for four chemicals you will encounter in the general chemistry laboratory.

event of a fire. However, chemists usually find this diamond to be helpful in quickly assessing the hazards of a chemical.

EU Chemical Hazard Symbols

Sometimes you will see chemical containers with one or more of the symbols shown in Figure 1.5. Each symbol represents one of the categories of dangerous substances as defined in the European Union Directive 67/548/EEC. This directive specifies the symbols and codes to be used to label substances with these hazards. It is worth familiarizing yourself with these symbols. Even though they are of European origin, they have been widely adopted by the chemical industry because they do business globally.

**Figure 1.5**

European Union hazard labels with their meaning and code.

Material Safety Data Sheets

The NFPA hazard diamond and the EU chemical hazard symbols provide a summary of the hazards posed by a chemical that is quickly recognizable. If you want more detail about the hazards these labels indicate or if you want information about how to intelligently handle and work with a chemical, one of

the first places you might seek this information is the material safety data sheet (MSDS) for that substance.

Material safety data sheets are a common way to catalog the hazards and safe handling procedures for a material. They are provided by the manufacturer of a substance, and their exact format varies from supplier to supplier. Despite this, they typically contain common information. An MSDS normally can be expected to contain information regarding the composition of the substance, hazard identifications (including NFPA ratings), first aid measures, fire-fighting measures, spill handling measures, handling and storage recommendations, personal protection requirements, physical and chemical properties, toxicity (including signs of exposure), ecological impact, and disposal recommendations.

► You can normally obtain physical data such as boiling points and melting points from the substance's MSDS.

The Department of Chemistry saves all manufacturer-supplied MSDS for all chemicals it buys because the U.S. Occupational Safety and Health Administration requires that all employees have access to this information. Our collections of MSDS can be found under the counter in the stockroom. You are welcome to examine the MSDS for any substance used in the general chemistry lab by visiting the stockroom. You can find MSDS sheets from other sources, but generally a fee is required for access. Every employer is required by law to provide MSDS to their employees for free.

You can obtain MSDS sheets directly from the manufacturer of some chemicals, such as ACROS and Sigma/Aldrich. If you look up a chemical in Wikipedia, you will often find a link for the MSDS sheet for that substance.

NIOSH Pocket Guide to Chemical Safety

The National Institute for Occupational Safety and Health (NIOSH) publishes a handbook (*NIOSH Pocket Guide to Chemical Safety*) containing condensed information about the hazards and handling guidelines for a collection of a few hundred substances commonly found in the work environment. Its coverage is not comprehensive, but the information in the *NIOSH Pocket Guide to Chemical Hazards* is easier to read and digest than the MSDS for a substance.

Each entry in the *NIOSH Pocket Guide to Chemical Hazards* contains synonyms and trade names for the substance, physical data, chemical incompatibilities, personal protection advice, and various toxicity data. The section containing synonyms is particularly helpful if you need to know other commonly used names for a substance. This information is typically difficult to find in one location elsewhere.

The *NIOSH Pocket Guide to Chemical Hazards* is available free online at <http://www.cdc.gov/niosh/npg/>. The online version is well organized and easy to search.

1.6 Summary of Dos and Don'ts

Safety is important enough to have some aspects of this chapter repeated. Here is a list of things you should and should not do in lab in the interest of safety.

- Do wear your goggles at all times in the lab.
- Do not wear shorts or short skirts to lab.
- Do not wear open-toed shoes or sandals in lab.
- Do clean up all chemical spills as soon as possible.
- Do clean up all broken glassware as soon as possible.
- Do inform your instructor of any accident.
- Do read chemical labels carefully.

Chapter 2

Checking In and Checking Out of Lab

2.1 Your Laboratory Drawer

You will choose a numbered drawer at the beginning of the semester that will be unlocked for you at the start of each lab period and locked after each lab period. Inside the drawer you will find a collection of laboratory equipment like that illustrated in Figure 2.1.

► Because your lab drawer is locked when you are not in lab, you can safely store your goggles in your drawer so that you never have to remember to carry them to lab.

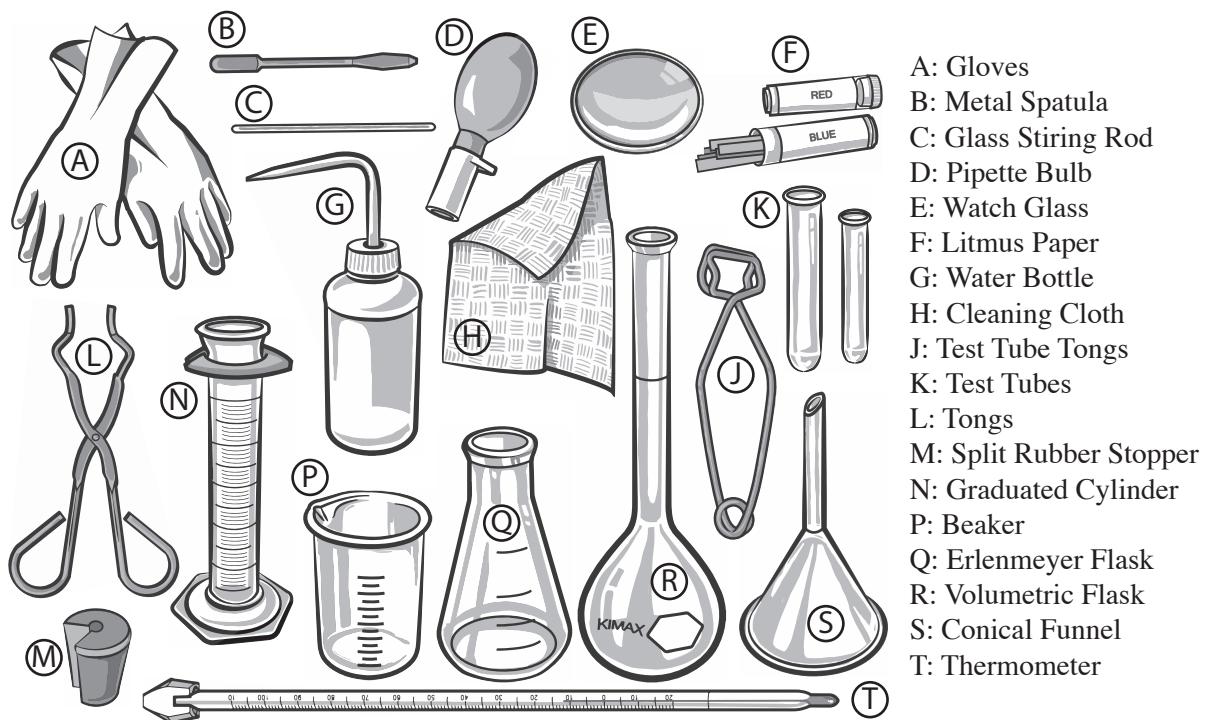


Figure 2.1

Illustrations of items typically found in a laboratory drawer.

Each semester we like to make sure your drawer is stocked with the proper type and quantity of clean and unbroken equipment. Therefore, we ask that you inventory the contents of your drawer at the start and at the end of each semester according to the following procedure.

2.2 Check In Procedure

Follow this procedure at the start of the semester.

1. **Obtain Drawer Inventory:** Before you can inventory the contents of your drawer, you will need a list of what should be in the drawer. This is called the drawer inventory. If a drawer inventory is not at your bench, ask your instructor for one.
2. **Fill Out Information On Drawer Inventory:** Print the laboratory room number, your drawer number, the lab day, the name of your lab instructor, and your name on the drawer inventory where indicated.
3. **Remove All Equipment From Your Drawer:** Remove your drawer from its slot, and place it on your bench. Remove the contents and place them on your bench. If the paper at the bottom of the drawer is dirty, dispose of it and replace it with a new sheet of paper.
4. **Clean All Equipment:** Wash all glassware with soap and water, rinse with deionized (DI) water, and dry thoroughly. Remove all labels. Make sure that all other equipment is clean as well.
5. **Check for Damaged Glassware:** Examine all glassware in your drawer. If you find any glassware that is chipped, broken, or otherwise unusable, dispose of it in the broken glassware receptacle.
6. **Inventory Equipment:** Return the cleaned and undamaged equipment to your drawer one item at a time. As you return each item, place a check mark next to that item on the drawer inventory. If you find any extra equipment that is not on the list, set it aside and do not put it back in your drawer.
7. **Check Gloves:** Check the provided kitchen gloves for fit and condition. If they fit and are undamaged, check them off on the drawer inventory. If they are damaged or do not fit, you will need to get them replaced.
8. **Make List of Needed Equipment:** All the unchecked items on the drawer inventory are the items you need to replace.
9. **Go to Stockroom If Needed:** If you have extra items or need replacement equipment, you will need to go to the stockroom. When you go, take your drawer inventory with you along with any extra items. At the stockroom you will drop off extra items and pick up missing items. If your gloves need to be replaced, take them to the stockroom as well for an exchange.

► New sheets of paper for the bottom of your drawer, if needed, should be available in the front of the lab.

► If you have any question about whether a piece of equipment is usable or not, ask your instructor.

► Do not return broken or chipped glassware to your drawer.

► If you do not know what an item looks like, refer to Figure 2.1 for assistance.

► To minimize the wait at the stockroom window, make sure your list is correct the first time and go to the stockroom only once.

10. **Label Gloves and Goggles:** Using a magic marker, put your name on your goggles and gloves. You can now leave them in your drawer.
11. **Sign Drawer Inventory:** When you are satisfied that your drawer has every item on the drawer inventory and that all of the equipment is undamaged, sign and date the drawer inventory.
12. **Have Instructor Check Drawer:** Have your instructor check your drawer and your drawer inventory form. You should make sure your instructor signs the drawer inventory.
13. **Return Drawer Inventory to Your Instructor:** Return the signed drawer inventory to the front desk in the lab.

2.3 Check Out Procedure

Follow this procedure at the end of the semester.

1. **Obtain Drawer Inventory:** Your drawer inventory from the beginning of the semester should be at your bench. If it is not, obtain it from your instructor.
2. **Remove All Equipment From Your Drawer:** Remove your drawer from its slot, and place it on your bench. Remove the contents and place them on your bench. If the paper at the bottom of the drawer is dirty, dispose of it and replace it with a new sheet of paper.
3. **Clean All Equipment:** Wash all glassware with soap and water, rinse with deionized (DI) water, and dry thoroughly. Remove all labels. Make sure that all other equipment is clean as well.
4. **Check for Damaged Glassware:** Examine all glassware in your drawer. If you find any glassware that is chipped, broken, or otherwise unusable, dispose of it in the broken glassware receptacle.
5. **Inventory Equipment:** Return the cleaned and undamaged equipment to your drawer one item at a time. As you return each item, place a check mark next to that item on the drawer inventory. If you find any extra equipment that is not on the list, set it aside and do not put it back in your drawer.
6. **Make List of Needed Equipment:** All the unchecked items on the drawer inventory are the items you need to replace.
7. **Go to Stockroom If Needed:** If you have extra items or need replacement equipment, you will need to go to the stockroom. When you go, take your drawer inventory with you along with any extra items. At the stockroom you will drop off extra items and pick up missing items.
8. **Sign Drawer Inventory:** When you are satisfied that your drawer has every item on the drawer inventory and that all of the equipment is undamaged, sign and date the drawer inventory.

► New sheets of paper for the bottom of your drawer, if needed, should be available in the front of the lab.

► If you have any question about whether a piece of equipment is usable or not, ask your instructor.

► Do not return broken or chipped glassware to your drawer.

► To minimize the wait at the stockroom window, make sure your list is correct the first time and go to the stockroom only once.

9. **Have Instructor Check Drawer:** Have your instructor check your drawer and your drawer inventory form. You should make sure your instructor signs the drawer inventory.
10. **Return Drawer Inventory to Your Instructor:** Return the signed drawer inventory to the front desk in the lab.
11. **Disposer of Gloves:** Throw your kitchen gloves in the trash. They are contaminated with chemicals and should not be removed from the lab and used for any other purpose.
12. **Take Personal Items With You:** Take your goggles and any other personal items with you as you leave lab.

Chapter 3

Keeping a Laboratory Notebook

Your laboratory notebook is a permanent record of the scientific work you have done and the results you have obtained. It should be accurate and utterly honest. It should be kept in a manner consistent with conventional practice in chemistry and the specific practices of the organization in which you are doing your scientific work. This chapter provides some guidelines for keeping a laboratory notebook in general chemistry at Ohio Wesleyan University.

► Detailed instructions for keeping a laboratory notebook will vary by instructor and employer, but the basic concepts remain the same.

3.1 Purpose of the Notebook

A laboratory notebook has two purposes. First, it provides a record of the research work you have done and the results you have obtained. As a scientific researcher, you will often want to refer back to your previous work to repeat a procedure or to reuse a piece of collected data.

Second, the laboratory notebook must provide a record to others of what work you have done, when you did it, and what results you obtained. A laboratory notebook must communicate information to others, not just to you. It must do so in an unambiguous manner such that others may follow the steps described in your notebook to obtain the same results.

In real life, those who make a scientific discovery are the first who get to claim credit for that work and all the profit that comes from that. Laboratory notebooks are a vital part of establishing the chronology of a discovery. In many instances they become a part of legal battles over who owns the rights to a discovery. Patent battles worth million or billions of dollars are won or lost based on the laboratory notebooks presented to the courts in such battles.

Keeping a good laboratory notebook is an essential part of the practice of science.

3.2 What To Use

For your laboratory notebook, use a bound composition notebook. A bound notebook is used so that pages cannot be inserted or deleted. A bound notebook

► Spiral bound notebooks are not allowed.

gives the reader assurance that nothing has been added or deleted after the original work was done and recorded. This notebook should be dedicated for use as a general chemistry laboratory notebook. It should not be used for lecture notes or for other laboratory courses.

3.3 General Guidelines

Some general rules apply to keeping a laboratory notebook. Follow these guidelines all the time.

1. Always write in the notebook in permanent blue or black ink. Never use pencil or erasable ink. Never use any color of ink other than black or blue.
2. Never rip or cut out pages from your laboratory notebook. The notebook is a record of all things you have done, including the ugly things and the mistakes.

3.4 What to Do First

When you first obtain your laboratory notebook, it will be blank. You should immediately do the following.

1. Print your name on the front cover in blue or black ink.
2. Number each side of each page of your laboratory notebook in blue or black ink, starting with the number 1 on the very first sheet of paper in the notebook. Use one of the outside corners for numbering such as the bottom left and right.
3. Leave pages 1 and 2 blank. On page 3, make a title page by printing the course title and your name. If you have done things correctly, this page should be on the right side of the notebook.
4. Leave page 4 blank. On page 5, write “Table of Contents” at the top. This is where you will list the title of each experiment you perform and the the page number on which each experiment begins.
5. Leave pages 6 through 8 blank for the entries you will make in the table of contents.

3.5 What to Include When Starting a Laboratory Project

New laboratory projects will normally begin with pre-lab work. Therefore, pre-lab work is the first material you will include in your notebook for every project. If you followed the instructions above, the pre-lab work for your first laboratory project should begin on page 9 of your notebook. If you have done

► The fact that you have been asked to number both sides of each page means you should use both sides of each sheet.

things correctly, this will be a page on the right side of your laboratory notebook. Work for every project should begin on a new odd numbered page.

The following list describes in more detail what you should put in your laboratory notebook when starting a new project with pre-lab work. Note that if there is no pre-lab assignment for a particular experiment, you can just move on to the next section.

1. Write the title of the experiment at the top of the starting page.
2. Under this title, write a subtitle for the type of work you are doing. For instance, if you are doing pre-lab work, write “Pre-Lab Assignment” under the experiment title.
3. Write the date next to the title in the ISO standard dating format: 2012-09-15 (Year-Month-Day). This should be the date that you are doing the work, the actual date at the moment you are writing the date. Be completely honest.
4. Do your pre-lab work. Since the pre-lab work is primarily for your benefit, you can organize this material almost any way you want. It must be clear, however, what you were doing and that you made an earnest effort to complete the work asked of you. Much like the rest of the notebook, it should be clear to other readers what you were doing.
5. When you finish pre-lab work for a day, draw a line across the page to indicate where you stopped. If you continue pre-lab work another day, write the current date just below the line you drew and keep doing the work. This will make it clear what work you did on each day.

3.6 What to Include During the Experimental Work

When you come to your laboratory meeting, you should do the following.

1. Write the title of the experiment immediately under the line at the bottom of your pre-lab work.
2. Write the subtitle “Experimental Work” under the title.
3. Write the date next to the title in ISO standard dating format.
4. If you are working with partners, include their names near the title.

These are just organizational details. The real content of the notebook comes next. From the moment you walk into lab until the moment you leave, everything you do gets described in your laboratory notebook. This section gives an overview of the things to be included in your laboratory notebook during an experiment and recommendations for their inclusion. Exact instructions cannot be written for this part. Every experiment is different, and you will have to learn to use your judgment about what is important to include and what is not.

Even experienced chemists sometimes do not have a feel for the relevant information to record in the laboratory notebook. Such an understanding develops with time, and it is our job as instructors to help you develop that understanding.

Procedures

During your experimental work, you should include a detailed description of the procedures you carry out such that your instructor or another student can repeat the experiment from your notebook alone. In some cases, you may want to include diagrams of equipment set-ups because this may be the most effective way to describe what you did or the equipment you used.

These procedures should be written in your own words as you carry out the steps. You should not copy the procedure from the laboratory manual nor should you just reference the laboratory manual. What the manual says to do and what you did may be different, and the laboratory notebook always needs to be a record of what you actually *did*.

Your procedures should be recorded in the past tense. For instance, “added 50.0 mL of DI water to the flask” is appropriate but “add 50.0 mL of DI water to the flask” is not appropriate. The former is a record of what you did. The latter is an instruction.

Data and Observations

Data you collect and observations you make should be recorded directly in your laboratory notebook at the time you collect the data or make the observations. Always include appropriate units for numbers that have them. Make sure all numerical values have the appropriate number of significant figures. For instance, “added 50.00 mL DI water to the flask” means you used a buret to transfer the DI water, but “added 50.0 mL DI water to the flask” probably means you used a graduate cylinder. The number of significant figures matters.

You should also make sure that data are labeled so that a different reader knows what the data refer to. A reader should not, under any circumstances, have to infer what a piece of data is. When a reader comes across a number in your laboratory notebook, it should be transparently obvious what the number refers to. If a reader has to back up a paragraph or two to find out what the number is, you have asked the reader of your notebook to do too much work.

For instance, if you record the mass of a penny, you should write in your laboratory notebook something like this: “Mass of penny: 2.456 g”. You should not just write the number with the assumption you’ll remember what that number is for.

If you organize your data into tables, the table must be labeled so that it is clear what each column represents. It is not necessary (in fact, undesirable) to label each number individually in a table.

Spectra

► Spectra are included with a single fold and a single piece of tape.

If you use an instrument to collect a spectrum, you should include that spectrum

in your laboratory notebook if the spectrum itself is important. The spectrum should be folded in half along the short edge (the 8.5-inch edge) and taped along one of the open short edges to a blank page in your laboratory notebook. Do not put the tape along the fold.

The outside of the spectrum or chromatogram should be labeled with a description of what is on the inside. It should be easy to unfold the spectrum to view the contents, which means you cannot tape the spectrum shut. If you have multiple related spectra or chromatograms to include, you can place several of them on the same page in your notebook by taping them to slightly different positions on the page such that the pages are stacked.

Calculations

Include in your notebook all calculations you must perform. This means that you should actually *do* the calculations in your notebook. Remember, the notebook is a record of all laboratory work, including calculations. If you just include the answers to calculations, I will assume you plagiarized the result.

Graphs

If you are asked to prepare a graph, it should be included in your laboratory notebook in the same manner as you include spectra. The graphs included in your notebook must be labeled on the outside such that it is clear what can be found on the inside. Do not tape your graphs shut, and do not tape them along the fold. If you have multiple related graphs to include, you can include several of them on the same blank page in your notebook by taping them to slightly different positions on the page such that the graphs are stacked.

Line and Signature

When you have finished all experimental work and are prepared to leave lab for the day, draw a line across the page where you finished work and sign on the line. You must then get your instructor to sign on that same line. When your instructor signs on the line, he or she is acting as your witness. Your instructor swears by his or her signature that you did the work above the line on the date specified. In the real world, this can be important.

3.7 What to Include After the Experiment

When you leave your laboratory meeting, you will probably have post-lab calculations to do or questions to answers. This work should all be done in your laboratory notebook. Below the line drawn at the end of your experimental work, write the date. Then start your post-lab work. Show all your work.

Remember, the laboratory notebook is to be independent of the laboratory manual. It should make sense to a reader without the manual. Therefore, make sure it is clear what question you are answering.

For example, if the third post-lab question is “What color was your product?” do not just write “3. Red” as your answer. Instead. Be more descriptive. Write something such as “3. The product was red in color.” This will make your answer independent of the manual. You do not need to re-write the questions in the post-lab assignment.

3.8 What To Do About Errors

► Keeping a laboratory notebook is not a neatness contest. It is about being complete and accurate.

Any error you make in writing down procedures, observations, data, calculations, or answers to questions are to be corrected with a single line through the mistake. Never erase, use white-out, or scratch out errors. Never remove pages from your lab notebook.

You will not be graded on the things you cross out. You are graded on what is not crossed out. However, if you try to hide something or remove it from your laboratory notebook, you will be judged harshly. Again, remember that the laboratory notebook is a record of all things you do in lab, right or wrong.

Chapter 4

Writing an Abstract

An abstract is a concise summary of an experiment. It typically includes a brief description of the experimental problem, the technique used to investigate the problem, and the results obtained in the experiment. This chapter provides details about how to write an abstract for this laboratory course.

4.1 Format of Abstract

There is no single accepted format for an abstract. A practicing scientist must make the format of an abstract match the format required by the journal in which they wish to publish the work. No two journals will agree on a common format; therefore, the format of an abstract has a measure of arbitrariness in it. The one thing all format guidelines have in common is the desire to communicate information concisely to readers.

Being able to follow a set of standards for presenting written ideas is important in any discipline. In this course, you will be expected to follow standards similar to those common for writing an abstract that is to be published in a chemistry journal.

► No, you don't get to pick the format. The department picks the format. You follow that format.

4.2 Style Requirements

The abstract text is to be typed in 12 point Times font using left and right margins that are both 1.25-inch. The top and bottom margins must be 1-inch. The abstract text should be double spaced. Your name, the name of the experiment, and the date of the abstract submission must appear at the top of the document single spaced in bold Times 12 point font. The abstract text must be contained on one page.

To make it easier to conform to this style requirement, a Microsoft Word template for the general chemistry abstract has been provided on the course web site. Download the template and follow the instructions contained within. If you wish to use a word processing program other than Microsoft Word, make sure your document is indistinguishable from the format of the Word template.

► Under no circumstances may the abstract be more than one page.

4.3 Content

► An example abstract can be found on the course website.

If you were writing a complete journal article, the purpose of the abstract would be to convey quickly to the reader the nature and scope of the information presented in the paper. Therefore, the abstract must be brief. However, it must also contain sufficient information for the reader to decide whether or not to read the whole paper. This means it must contain the material that is core to the experiment and the key results but nothing else.

The abstract should be contained entirely within one paragraph. In that one paragraph you should do the following in the order given.

1. State the problem studied or the purpose of the study.
2. Identify the experimental approach by name only.
3. Accurately and concisely summarize the major findings of the study.
4. Concisely state the major conclusions.

The abstract is not to be a list of bullet points. You must write a paragraph in full English sentences. Be certain to use clear, concise, well-constructed sentences. Make sure there are no misspelled words. Use proper grammar throughout.

When writing the abstract, do not use first person, active voice. Instead, use third person, passive voice. Since the experiment has been completed, use past tense. For example, do not say “I heated the reaction mixture for 10 minutes.” Instead, say “The reaction mixture was heated for 10 minutes.” This may seem strange, but it is the custom in chemistry, and you are expected to follow this custom.

Additional Content Warnings

There are a few other things you need to be warned of while writing your abstract.

1. Never begin a sentence with a numerical value. Always find another way to begin the sentence.
2. All numbers less than 1 should either have a leading 0 inserted before the decimal or be written in scientific notation.
3. Never begin a sentence with a chemical formula. You can begin a sentence with a chemical name but not a formula.
4. Be sure each chemical formula with subscripts is displayed with subscripts in the document.
5. Make sure each chemical formula is displayed with proper chemical symbols.
6. Never mention laboratory glassware by name. If you are talking about glassware in the abstract, you are being too detailed.

7. Never refer to the “week” in which part of a laboratory was conducted unless the timing was important for the chemistry involved.
8. Never begin the abstract with the phrase, “In this lab.”
9. Never begin the abstract with the phrase, “The purpose of this lab...”

4.4 Submitting Your Abstract

Many journals and government agencies now require that documents for publication or funding consideration be uploaded as PDF files. Thus, all abstracts in this course must be submitted as PDF files. This means that once you are happy with your abstract in Microsoft Word, or whatever word processing program you use, you must convert the file to Adobe’s PDF format. Your instructor will then give you guidance on how to submit the file. You will either be asked to upload the PDF file to a web site, or you will be asked to email it to your instructor.

The portable document format (PDF) is not an editable document format. This makes it ideal for exchanging documents when you want readers to see exactly what you intended them to see without the possibility that anybody will alter the document. Documents published as PDF are typically smaller in size than the word processing file from which they were generated, and they are readable on all major computing platforms: Mac OS, Windows, and Linux. If your intent is for somebody to read a document and not edit it, you should distribute it as PDF, not in a native word processing format.

There are many ways to generate files as PDF. On the Mac OS, for instance, any file can be converted to PDF by printing it to PDF. Under Windows, producing a PDF file typically requires individual application support. For more detail, see the course web site or contact Information Services.

Please note that changing the extension of the file does not change the format of the document. For instance, changing “.docx” to “.pdf” does not convert a Word file to a PDF file. That conversion has to be done by the software. On all modern operating systems, the file extension indicates the format of the file; it does not change the format of the file.

4.5 Academic Dishonesty

You may consult with others while you are thinking about the abstract, but you must write the abstract on your own. You may not copy or paraphrase (reword) someone else’s work. That is academic dishonesty and will be dealt with according to the policies of your instructor. Some instructors may report your conduct to the Dean and employ other penalties, such as lost points.

Chapter 5

Writing an Experimental Section

An experimental section describes what you did in an experiment with sufficient detail for another researcher with your level of experience to repeat the experiment. This chapter provides some details about how to write an experimental section for this laboratory course.

5.1 Format of Experimental Section

There is no single accepted format for an experimental section. A practicing scientist must typically use the format and style required by the journal in which they wish to publish the work. No two journals will agree on a common format; therefore, the format of an experimental section has a measure of arbitrariness in it.

Being able to follow a set of arbitrary standards for presenting written ideas is important in any discipline. In this course, you will be expected to follow standards similar to those common for writing an experimental section that is to be published in a chemistry journal.

► Even journals for different areas of chemistry have different standards for how to write an experimental section.

5.2 Style Requirements

The text of the experimental section is to be typed in 12 point Times font using 1.25-inch left and right margins with 1-inch top and bottom margins. It should be double spaced. Your name, the name of the project, and the date of submission must appear at the top of the document single spaced in bold Times 12 point font. Under no circumstance should it be more than one page in length.

To make it easier to conform to this style requirement, you can download a Microsoft Word template for the general chemistry experimental section. If you wish to use a word processing program other than Microsoft Word, make sure your document is indistinguishable from the format of the MS Word template when complete.

For this course you are required to limit your experimental section to just one page. There is no general requirement that all experimental sections in chemistry

be so short, but in this course your experimental procedures are not terribly complicated. As a consequence, you are limited to one page to encourage you to sort through all the experimental details to fish out the important ones for inclusion.

5.3 Content

An experimental section should contain all the relevant detail necessary for another expert to reproduce your work. This does not mean that you should reproduce the instructions from your laboratory manual. Instead, you should find the most concise way to communicate what was done. This requires that you understand the important variables in your work. For instance, was the temperature of your solutions important in obtaining your results? If it was, you should report the temperature of the solutions. If the temperature was immaterial to your results, then you should not report it.

This can be confusing early in a scientific career because it may not always be clear what is important and what is not. This is understandable, but you are expected to make some effort to sort through your experiment to find the important facts. This is part of the purpose of asking you to write an experimental section.

In an experimental section, you should do the following.

1. Refer to the source of your procedure, if there is one.
2. State the identity and quantity of reagents used in the experiment.
3. Describe relevant experimental conditions such as temperature, pressure, length of reaction, etc.
4. Identify instruments used by manufacturer and model number.
5. Identify software used by vendor and release version.

As with all scientific writing, you should strive to be concise. However, just because the experimental section is to be concise does not mean you do not have to use full English sentences. You do! Be certain to use clear, concise, well-constructed sentences. Make sure there are no misspelled words. Use proper grammar throughout.

When writing the experimental section, do not use first person, active voice. Instead, use third person, passive voice. Since the experiment has been completed, use past tense. For example, do not say “I heated the reaction mixture for 10 minutes.” Instead, say “The reaction mixture was heated for 10 minutes.” This may seem strange, but it is the custom in chemistry, and you are expected to follow this custom.

► Always use appropriate units.

► Yes, this is an arbitrary choice, and you could write just as effectively in first person. However, here you must conform to the expected standard.

What Not To Include

As a reasonably competent chemist, you should know the name and function of every piece of equipment in the general chemistry lab. Since the experimental section is intended to describe the experiment such that a peer of equal ability could repeat the experiment, your experimental section should never contain

1. descriptions of common glassware used such as flasks, beakers, etc.,
2. descriptions of how to operate equipment or instruments, or
3. descriptions of how to prepare common glassware or instruments.

These things are considered common knowledge. An experimental section does not include common knowledge.

Do not record data that was collected during the experiment unless it characterizes the experimental conditions. For example, the experimental section is not a place to report the volume of titrant used in a titration or the melting point of a solid. It is the place to report the temperature of a water bath used to carry out a reaction. Experimental data is normally reserved for the results section, something you will learn to write in other chemistry courses.

Additional Content Warnings

There are a few other things you need to be warned of while writing your experimental section.

1. Never begin a sentence with a numerical value. Always find another way to begin the sentence.
2. All numbers less than 1 should either have a leading 0 inserted before the decimal or be written in scientific notation.
3. Never begin a sentence with a chemical formula. You can begin a sentence with a chemical name but not a formula.
4. Be sure any chemical formulae with subscripts are actually displayed with subscripts in the document.
5. Make sure chemical formulae are displayed with proper chemical symbols. Microsoft Word will sometimes change the capitalization in chemical formulae, so be careful.
6. Never refer to the “week” in which part of a laboratory was conducted unless the timing was important for the chemistry involved.

5.4 Submitting Your Experimental Section

Many journals and government agencies require that documents for publication or funding consideration be submitted as PDF files. Thus, all experimental sections in this course must be submitted as PDF files. Once you are happy with your experimental section in Microsoft Word, or whatever word processing application you use, you must convert the file to Adobe's PDF format. Your instructor will then give you guidance on how to submit the file. You will either be asked to upload the PDF file to a web site, or you will be asked to email it to your instructor.

The portable document format (PDF) is not an editable document format. This makes it ideal for exchanging documents when you want readers to see exactly what you intended them to see without the possibility that anybody will alter the document. Documents published as PDF are typically smaller in size than the word processing file from which they were generated, and they are readable on all major computing platforms: Mac OS, Windows, and Linux. If your intent is for somebody to read a document and not edit it, you should distribute it as PDF, not in a native word processing format.

There are many ways to generate files as PDF. On the Mac operating system, for instance, any file can be converted to PDF by printing it to PDF. Under Windows, producing a PDF file typically requires individual application support. For more detail, see the course web site or contact Information Services.

Changing the extension of a file does not change the format of the document. For instance, changing “.docx” to “.pdf” does not convert a Word file to a PDF file. That conversion has to be done by the software. On all modern operating systems, the file extension indicates the format of the file; it does not change the format of the file.

5.5 Academic Dishonesty

You may consult with others while you are thinking about the experimental section, but you must write it on your own. You may not copy or paraphrase (reword) someone else's work. That is academic dishonesty and will be dealt with according to the policies of your instructor. Some instructors may report your conduct to the Dean and employ other penalties, such as lost points.

Chapter 6

Melting Point Range Determination

The experimentally measured melting point range of a substance is a physical property that can help confirm the identity and purity of that substance. Determining the melting point range of a substance is a common laboratory activity, and we want you to master this skill. This chapter explains how to measure a melting point range and how to use that information in determining the identity of a substance and in assessing its purity.

6.1 Introduction

What Is a Melting Point Range?

A substance melts when it turns from a solid to a liquid. The temperature at which this happens is commonly called the melting point. This is all fairly straightforward. Given that, what in the world is the melting point range?

The most common and convenient method for heating a substance until it melts does not, technically, measure the melting point of the substance. Instead, it only allows an experimenter to determine the temperature at which a substance begins to melt and the temperature at which it finishes melting. This is a melting point range. No substance will melt at a single temperature (the melting point) using the technique presented here. This will be true no matter how careful you, or any body else, is.

This is a consequence of the design of the devices used to carry out these measurements. It is not a flaw in the equipment owned by Ohio Wesleyan. Instead, all similar equipment behaves the same way. In these devices the temperature of the melting substance is never measured directly. Instead, the temperature of what is around the melting substance is measured. Because of this design, the temperature continues to rise during melting, leading to a melting point range. This, again, is not a flaw. It is the only way to determine the melting point range of small quantities of substance in a quick and efficient manner.

► If we were able to measure directly the temperature of the sample being melted, we would find that the temperature stays constant during melting, leading to a melting point.

Melting a Pure Substance

► A narrow melting point range is evidence that a substance is pure.

Using the technique described in this chapter, pure substances will be observed to melt over a narrow temperature range of between 0.5°C and 2°C . In fact, a narrow melting point range is good evidence that the substance being melted is pure. If the determination of the melting point range is performed carefully, the literature value for the melting point of a substance should fall just below or within the experimentally determined melting point range.

Melting an Impure Substance

► A wide melting point range is evidence that a substance is impure.

If the substance being melted is actually a mixture of more than one substance, the melting point range will not be narrow. The range will typically be greater than 2°C . In fact, the observation of a wide melting point range is good evidence that a substance is not pure.

In addition, impure substances will melt at a lower temperature than the pure substance, providing the level of impurity is low. If the level of impurity is high, the situation is more complicated, and few general statements can be made.

Determining Substance Identity

Let's say you have just measured the melting point range of an unknown compound to be 133°C to 133.5°C . You also know, because your instructor has told you, that the substance must be one of 4 compounds: benzoic acid, 2-naphthol, urea, or trans-cinnamic acid. Can you identify the unknown substance?

First, you know that your unknown substance is probably pure since the melting point range is narrow. Second, if you look up the melting points of the four compounds listed above, you will find that only urea and trans-cinnamic acid are possible matches. These two compounds have known melting points near 132°C while benzoic acid and 2-naphthol have melting points near 121°C .

Since urea and trans-cinnamic acid have the same known melting point and since that melting point is a good match to your unknown substance's observed melting point range, how can you possibly identify your unknown? This is actually easy.

For the sake of argument, let's say that your unknown substance is urea. If you mix a small quantity of urea with your unknown and determine the melting point range of the mixture, you will observe nearly the same melting point range as you did for your unknown alone. However, if you mix a small quantity of trans-cinnamic acid with your unknown and determine the melting point range of that mixture, you will observe a melting point range that is wider than that for the unknown. In addition, the melting for this mixture will begin at a lower temperature than it did for the unknown alone.

6.2 Experimental Procedure

A melting point range is determined by placing a small quantity of the substance to be tested into a glass capillary that is then heated in a Mel-Temp apparatus. This section describes how to carry out this process.

Prepare Sample

- 1. Obtain Melting Point Capillary:** All samples to be melted must be placed into the open end of a glass melting point capillary tube. These capillaries are provided in a plastic tube, as shown in Figure 6.1. Find where these are located and obtain one for each melting point range experiment to be conducted.
- 2. Pulverize Sample If Needed:** Since the open end of the melting point capillary is small (see Figure 6.2), the sample to be melted must be finely divided. Samples such as those shown in Figure 6.3 will easily fit into the melting point capillary. Samples such as those in Figure 6.4 will not and must be pulverized into a fine powder in a mortar and pestle (Figure 6.5) before being placed into the capillary.



Figure 6.3

This sample is a fine powder that will fit into the melting point capillary.



Figure 6.4

A sample in coarse chunks that must be ground up in a mortar and pestle.



Figure 6.1

A container of melting point capillaries.



Figure 6.2

Melting point capillaries, showing the open end (left three) and the closed end (right three).



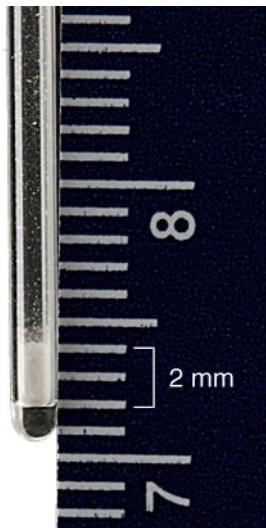
Figure 6.5

A mortar and pestle used to grind samples into a fine powder.

- 3. Place Small Quantity of Sample into Melting Point Capillary:** Push the open end of the melting point capillary into the finely divided sample powder to force a small quantity into the capillary. Invert the capillary and tap the closed end on the lab bench to force the sample to the bottom. You may have to repeat this process to get enough sample into the capillary. In the end, you should have approximately 1 to 2 mm of sample in the tube. Figure 6.6 shows a melting point capillary filled to the proper depth.

- 4. Be Forceful with the Capillary if Necessary:** Sometimes the sample will not go to the bottom of the capillary after tapping the capillary on the lab bench. In these cases, we have a glass “drop tube” about 1 meter in length and open on both ends that will help. Obtain the drop tube, place one end on

► The glass capillary will not break. It will, in fact, bounce off the bench, which is a cool thing to see glass do.

**Figure 6.6**

A melting point capillary filled to the proper depth.

**Figure 6.8**

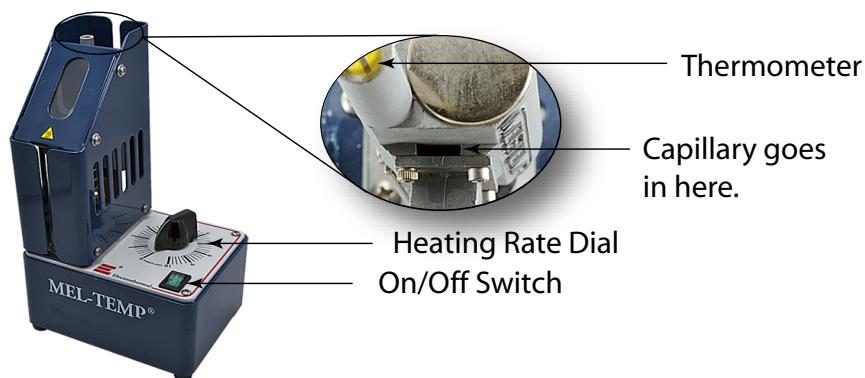
View the sample capillary through this window and lens.

► The more slowly the sample is heated the better your results will be. However, slower heating means that it will take more time to collect the melting point range. You have to make a trade off between time and the quality of your results.

the laboratory bench, and drop the melting point capillary through the top (closed end down). Repeat as necessary.

Melt Sample

- Take Capillary to Mel-Temp:** Take the filled melting point capillary to the Mel-Temp apparatus shown in Figure 6.7. Check the temperature of the Mel-Temp to make sure it is below the melting point of your sample. If you do not know the melting point of your sample, make sure the Mel-Temp temperature is below the lowest melting point you expect to measure. If you are completely unsure of what melting point range you will measure, make sure the Mel-Temp is at a temperature of no higher than 30°C
- Place Capillary Into Mel-Temp:** The melting point capillary fits into a slit in the Mel-Temp that is located just in front and to the right of the thermometer as indicated in Figure 6.7. There are three slots in the slit that can hold the capillary. It does not matter which slot you use for your capillary. Place the capillary into one of these slots.

**Figure 6.7**

The Mel-Temp apparatus with an expanded view of the place where melting point capillaries are inserted.

- Begin Heating Sample:** Turn the heating rate dial on the Mel-Temp (see Figure 6.7) to between 3 and 4 to achieve a heating rate of between 5°C and 10°C per minute. Then turn the on/off switch to the on position. A light should come on in the viewing window, allowing you to see the capillary through the viewing lens as shown in Figure 6.8.
- Monitor Sample:** Continue viewing the sample in the capillary through the viewing lens, and periodically check the temperature and the rate of change of the temperature. If the temperature changes too rapidly (more than 10°C per minute), turn the heating rate dial to a lower number. You can twirl the capillary in its slot from time to time to inspect both sides of the sample.

5. **Record Temperature When Melting Begins:** At some point, you will notice liquid forming in the capillary tube. Record the temperature at the thermometer when you make this observation.
6. **Record Temperature When Melting Ends:** Continue monitoring the sample, twirling the capillary in the Mel-Temp slot to get a good look at the sample from all sides. When you are convinced that all the sample has turned to liquid, record the temperature at the thermometer.

Cleanup

1. **Turn Off Mel-Temp:** When the sample has completely melted and you have recorded the melting point range in your laboratory notebook, turn off the Mel-Temp and remove the sample capillary.
2. **Dispose of Sample Capillary:** Dispose of the sample capillary in the broken glass waste container in the back of the room. Do not attempt to reuse the capillary. Do not throw the capillary into the normal waste container.

► If you need to record a melting point range for the same substance, prepare a new capillary. Never reuse the sample after it has melted.

6.3 Working With a Partner

The Mel-Temp apparatus can hold three sample capillaries. If you can find a partner who also needs to record a melting point range, the two of you can collaborate to obtain both melting point ranges at the same time. To work with a partner, one of you should be designated the temperature recorder and one of you should always observe the samples.

Once you have made that assignment, place both sample capillaries into the Mel-Temp at the same time. The designated sample watcher will call out when each sample begins to melt and when each has completely melted. The other partner will record temperatures.

Besides saving time, it is likely that your melting point ranges recorded in this fashion will be more accurate since you will not have to divide your attention between the thermometer and the sample.

Chapter 7

Boiling Point Determination

The experimentally measured boiling point of a substance is a physical property that can help confirm the identity of that substance. Determining the boiling point of a substance is a relatively rare laboratory activity, but it is a useful skill to practice. This chapter explains one way to measure a boiling point for a liquid that boils at a temperature below 100°C.

7.1 Introduction

Defining the Boiling Point

When you heat a liquid, a temperature is eventually reached at which bubbles begin to form in the liquid along the container's walls. As the temperature continues to increase, the bubbles occasionally break free from the container and rise to the surface. At some temperature, a constant stream of bubbles rises to the surface from the walls of the container and from everywhere else in the liquid. At that point, the temperature of the liquid is observed to remain constant until all the liquid has turned to a gas. This temperature is the boiling point of the liquid.

► The bubbles that form along the walls of the container early in the heating process are usually just dissolved air being forced out of the liquid.

That was an experimental, or empirical, description of the boiling point. It is defined in terms of things we can easily see or measure with just a thermometer. More formally, the boiling point is defined as the temperature at which the vapor pressure of a liquid equals the atmospheric pressure. That may sound cryptic, but the two definitions are consistent with each other.

Measuring a Boiling Point

That leaves us with two ways to determine the boiling point: measure the temperature when bubbles roll out of the liquid and the temperature remains constant or measure the temperature at which the vapor pressure of the liquid equals atmospheric pressure.

The first method sounds more appealing and intuitive. That does not make it a good method, however. Just measuring the temperature when bubbles roll

► For precise results, you cannot determine the temperature of the boiling point by measuring the temperature when many bubbles rise to the surface of the liquid.



Figure 7.1
Ring stand burette clamp.



Figure 7.2
Typical hotplate.



Figure 7.3
Test tube clamped in the burette clamp.



Figure 7.4
Inverted melting point capillary attached to thermometer.

out of the liquid is imprecise because one has to make a decision about when the boiling point has been reached based on the number of bubbles reaching the surface of the liquid. This is subjective. Even if you wait for the liquid to reach a constant temperature you will encounter problems. Near the boiling point the temperature will change very slowly, and unless your container of liquid is large, you will observe temperature fluctuations at the boiling point.

Instead, it turns out that it is much easier (and more precise) to detect when the vapor pressure of the liquid equals the pressure of the atmosphere pushing down on the sample. In other words, from a practical point of view it is easier to employ the formal definition of the boiling point to determine the boiling point. This is what we will do in this procedure description.

7.2 Experimental Procedure

The following procedures describe how to determine the boiling point of a liquid by measuring the temperature at which the vapor pressure of the liquid equals atmospheric pressure as judged by the rise of liquid into a melting point capillary.

Prepare Water Bath and Sample Support

- Obtain Equipment:** Obtain a ring stand, ring stand burette clamp (Figure 7.1), 600 mL beaker, hot plate (Figure 7.2), and a clean and dry 5-inch test tube. Bring all these items to your lab bench.
- Assemble Sample Support:** Attach the burette clamp to the ring stand about three quarters of the way up the pole. Clamp the test tube in the burette clamp at the top of the test tube as shown in Figure 7.3
- Assemble Water Bath:** Place about 400 mL of DI water into the 600 mL beaker and place the beaker onto the hot plate. Make sure the hot plate knobs are all turned to the “off” or the “0” position. Then plug in the hot plate.
- Arrange Parts:** Turn the ring stand and burette clamp such that the test tube is suspended over the 600 mL beaker. Do not place the test tube in the water yet.

Prepare Thermometer and Capillary

- Attach Melting Point Capillary to Thermometer:** Obtain a thermometer from your lab drawer. Obtain a melting point capillary. With the open end of the melting point capillary pointing down, attach the melting point capillary to the bottom of the thermometer with two rubber bands as shown in Figure 7.4
- Attach Split Rubber Stopper to Thermometer:** Obtain the split rubber stopper from your lab drawer and attach it to the thermometer with the top of the stopper just below the 30°C mark.

Prepare Sample

1. **Place Liquid In Test Tube:** Add approximately 3 mL of the liquid to be tested to the 5-inch test tube. Add a single boiling stone to the liquid in the test tube.
2. **Insert Thermometer with Capillary:** Insert the thermometer with attached melting point capillary into the 5-inch test tube containing the liquid to be tested. The split rubber stopper should rest on top of the test tube as shown in Figure 7.5.
3. **Adjust Rubber Stopper As Needed:** When properly adjusted, the thermometer should be approximately 5 mm to 10 mm from the bottom of the test tube as shown in Figure 7.6. Adjust the position of the split rubber stopper on the thermometer to achieve the correct placement of the thermometer.



Figure 7.5

Thermometer inserted into rubber stopper and resting on top of test tube.

Heat Water Bath and Observe Sample

1. **Lower Test Tube Into Water Bath:** Lower the test tube into the water bath by sliding the burette clamp lower on the ring stand poll. The bottom half of the test tube should be immersed in the water. The final setup should look something like that in Figure 7.7.



Figure 7.7

The final setup for a boiling point determination should look something like this.



Figure 7.6

The thermometer and capillary should be about 5-10 mm above the bottom of the test tube.

2. **Begin Heating Water Bath:** Turn the hot plate on and turn the heating dial to a middle position (medium). If after 10 minutes the water temperature has not increased more than 10°C, you might consider increasing the heating rate.
3. **Monitor Sample and Capillary:** Keep monitoring the sample liquid and the capillary until bubbles begin to come out of the open end of the melting point capillary. At first the bubbles will come out slowly and appear to “stick” to the end of the capillary. Wait for the bubbles to come out regularly and without “sticking” to the end of the capillary.

4. **Remove Test Tube from Water Bath:** When the bubbles come out of the capillary regularly, loosen the screw holding the burette clamp to the ring stand poll and raise the test tube completely out of the water. Retighten the clamp's screw.
5. **Look for Liquid Rise in Capillary:** Immediately begin observing the melting point capillary in the liquid. The liquid will eventually begin to rise in the capillary. The instant this begins to happen, record the temperature at the thermometer. This is the boiling point.

7.3 Clean Up

1. **Dispose of Liquid Properly:** Dispose of the liquid according to the proper waste disposal guidelines. If the liquid is an organic liquid, you will likely have to dump it into the appropriate waste containers.
2. **Never Place Boiling Stones In Sink:** Under no circumstances should boiling stones find their way into the sinks. Either dump boiling stones into the trash can or into the waste containers with the liquid sample.
3. **Turn Off Hot Plate and Disassemble Setup:** Turn off and unplug the hot plate. Break down the ring stand and burette clamp and return them from where you obtained them.

7.4 Frequently Asked Questions

What Is the Boiling Stone For?

The boiling stone prevents a particular type of accident that can occur when boiling liquids in a test tube. If the stone were not present, the liquid in the test tube might be ejected from the tube by a particularly large bubble formed as the liquid begins to boil. With the boiling stone, however, the bubbles formed during boiling will always be small.

The boiling stone allows small bubbles of vapor to form (instead of large ones) because it provides a high surface area with many rough edges. Each rough edge or corner provides a place for a bubble of vapor to form. The more rough places there are like this, the more bubbles there will be during boiling and the smaller they will be.

The boiling stone should have no chemical significance as long as it is never reused.

How Does This Method Work?

The bubbles coming out of the melting point capillary are an indication that the vapor inside the capillary is exclusively liquid vapor. When warm liquid vapor enters the capillary from the bottom it immediately begins to rise up the capillary. In doing so it cools and becomes more dense. Eventually it falls back to the

bottom of the capillary, being displaced by warmer vapor. The cooled vapor exits the capillary as a bubble.

When you know there is nothing in the capillary except liquid vapor (when you see bubbles coming out of the capillary), you pull the test tube out of the water bath. Everything begins to cool. As the liquid begins to cool, its vapor pressure decreases. This means the pressure of vapor in the capillary also decreases. When it decreases to just below atmospheric pressure, liquid will begin to rise in the capillary.

Since the boiling point is defined as the temperature at which the vapor pressure of the liquid and atmospheric pressure are equal, the temperature at which the liquid rises in the capillary is a measure of the boiling point.

Are There Any Errors In This Method?

Boiling points listed in the literature are generally quoted at an atmospheric pressure of 1 atm. These boiling points are called normal boiling points.

The obvious problem with the method described here for determining the boiling point of a liquid is that it determines the boiling point at the current atmospheric pressure, which may not be exactly 1 atm. Thus, this method does not give us the normal boiling point of the liquid, which can be problematic if the goal is to compare that experimentally determined boiling point with values from the literature for known compounds.

In Delaware, OH the atmospheric pressure is generally sufficiently close to 1 atm that this technique can be used without correction for qualitative comparison of physical properties.

Chapter 8

Basic Statistical Analysis Of Results

In your study of chemistry you will often need to summarize repeated experimental measurements, and the typical way to do that is to compute the average and standard deviation of the measurements. This chapter describes how to calculate these quantities and provides some insight into their meaning.

8.1 Introduction

If five different people measure your height on the same day using the same measuring device, all five results are likely to be different. Such is the nature of the measurement process. Random errors always conspire to make the results of repeated measurements different. Are all of these results wrong? Are all of them correct? Is there a single correct result?

These are all valid questions. The answer to each question is “no.” No result obtained from measuring your height has any more claim to correctness than any other as long as the measurement technique is appropriate. Instead, each measurement is considered just one sample from the entire universe of all possible values that could be determined for your height using the given measurement process.

If no value is more correct than any other, what is your true height? Do you have a true height? Yes, you have a true height, but you do not know that true height. In fact, some would argue you cannot know your true height because the “true” value is exact with no uncertainty, but all measured quantities have uncertainty. Regardless of your interpretation, what you can always know is the human approximation of your height, which includes an uncertainty.

This human approximation of the truth is obtained by making many measurements of a quantity and then computing the average of the measurements. The average of a set of numbers representing a physical quantity is our best guess of the truth.

To quantify our confidence in the average as a measure of the truth, we often compute the standard deviation of the measurements about the average. This quantity is a direct measure of our uncertainty in determining the average

► The average is also called the mean, and the two terms will be used interchangeably.

► The standard deviation is a measure of the precision of an experimental measurement.

because it reflects the fluctuation in individual measurements due to instrumental or human errors.

- Standard deviation is not a direct measure of the accuracy of an experimental measurement, but it does tell us how confident we are in our knowledge of the truth.

At another level of abstraction, the standard deviation also says something about how well we believe we know the truth. Although the average and the truth may not be equal, one expects the truth to lie no further than the standard deviation away from the average to some level of confidence. If the standard deviation is large, we have little confidence in our knowledge of the truth. If it is small, we have a higher confidence. Of course, the only way to test the accuracy of an experimental result is to know the truth, but you will rarely have this luxury.

Thus, the standard deviation simultaneously serves as a measure of the precision of an experimental measurement and of our confidence in our knowledge of the truth.

8.2 Calculating the Mean

The mean of a set of numbers is a phenomenally easy thing to calculate. It is so easy that you probably already know how to carry out such a calculation. Of course, this is college, which means we want to professionalize our discussion of the average a bit. Thus, part of this discussion will likely be familiar, but some of it will probably be new to you.

Let's say we have measured the length of a table 6 times and have obtained the following lengths in meters: 2.45, 2.40, 2.48, 2.60, 2.33 and 2.40. What is the mean of this set of measurements?

To compute the mean for any set of numbers, just add all the numbers and then divide the total by the number of measurements.

$$\frac{2.45 + 2.40 + 2.48 + 2.60 + 2.33 + 2.40}{6} = \frac{14.66}{6} = 2.44 \quad (8.1)$$

- When adding or subtracting measured values, the final result has the same number of decimal places as there are in the measurement with the fewest number of decimal places.

The value of the mean for this set of measurements is 2.44 m. Note that the final result has been rounded to two decimal places as is required by the rules for working with significant figures in calculations.

That all seems easy enough, but we can generalize this concept a bit and be more professional about it. Let's assign each measured value of the table length to its own variable. For instance, $x_1 = 2.45$, $x_2 = 2.40$, $x_3 = 2.48$, $x_4 = 2.60$, $x_5 = 2.33$, and $x_6 = 2.40$. Again, these are measured values for the table length in units of meters. The mean can now be written as

$$\frac{x_1 + x_2 + x_3 + x_4 + x_5 + x_6}{6} = \frac{14.66}{6} = 2.44 \quad (8.2)$$

Clearly, the result is the same, but we are expressing it with variables instead of numeric values. We can go one step further and call the variable N the number of measurements. In our case, $N = 6$. Thus, the mean can be expressed as

$$\frac{x_1 + x_2 + x_3 + x_4 + x_5 + x_6}{N} = \frac{14.66}{6} = 2.44 \quad (8.3)$$

We can simplify this even further. Since x_1, x_2, x_3 , etc. refer to a succession of measured values, we do not have to refer to them individually. We know the measured values will always start at x_1 and end with x_N because there are always N measured values. In our case, we know there are 6 measured values because $N = 6$; therefore, the measured values will be x_1 through x_6 .

We can therefore describe a mean as “the sum of all measured values x_1 through x_N with the result divided by N .” That’s a concise verbal description of a mean. We now want to translate this into mathematics. Mathematicians have a symbol for the words “sum of,” and it is Σ . Using a mathematician’s terminology, the mean can be expressed as

$$\frac{1}{N} \sum_{i=1}^N x_i \quad (8.4)$$

where x_i stands for any of the measured values. Equation 8.4 means exactly the same thing as Equation 8.3.

Now that we have a compact definition of the mean in Equation 8.4, we need a symbol to represent the mean. A typical symbol used is \bar{x} , or any other variable with the horizontal bar over it.

Calculating The Mean

The mean, \bar{x} , of a set of N values is calculated using

$$\bar{x} = \frac{1}{N} \sum_{i=1}^N x_i \quad (8.5)$$

where i takes on all values from 1 to N in succession. The mathematical definition means the same as the verbal description of the mean “add all measurements and divide the result by the number of measurements.”

8.3 Calculating the Standard Deviation

When you have more than two measured values for a physical quantity, you can calculate the standard deviation of those values about the mean. As discussed in the Introduction, the standard deviation provides a direct measure of the precision of your measured results. It also provides a sense for how well you know the truth, but we will not focus on this latter definition in this section.

For the moment, let’s focus on standard deviation’s role as a measure of precision. Precision refers to the reproducibility of a measurement, how close a succession of measurements are to each other. However, since we already know how to calculate the mean of a set of measurements, we will be interested in how the measured values deviate from the mean. High precision means all measurements are very close to the mean. Low precision means the measurements differ widely from the mean.

► Another way of saying all this is that the standard deviation tells us how our measured values are distributed about the average value (mean).

- The table measured table lengths are (in meters) $x_1 = 2.45$, $x_2 = 2.40$, $x_3 = 2.48$, $x_4 = 2.60$, $x_5 = 2.33$, and $x_6 = 2.40$

We need a way to express this mathematically. We will derive the expression using reasoning similar to that for deriving the expression for the mean in Equation 8.5. We will use the same set of measured table lengths to work through this derivation.

The deviation from the mean for each measured table length can be calculated by taking the difference between each measured value and the mean, \bar{x} . For instance, $(x_1 - \bar{x})$ is the deviation of measurement x_1 from the mean. To be more specific, $(x_1 - \bar{x}) = 2.45 - 2.44 = 0.01$, in units of meters. This is, undeniably, a measure of how much that single measurement deviates from the mean.

We can also carry out this same calculation for all other measured values. The results are in units of meters, of course.

$$\begin{aligned}(x_1 - \bar{x}) &= (2.45 - 2.44) = +0.01 & (x_2 - \bar{x}) &= (2.40 - 2.44) = -0.04 \\ (x_3 - \bar{x}) &= (2.48 - 2.44) = +0.04 & (x_4 - \bar{x}) &= (2.60 - 2.44) = +0.16 \\ (x_5 - \bar{x}) &= (2.33 - 2.44) = -0.11 & (x_6 - \bar{x}) &= (2.40 - 2.44) = -0.04\end{aligned}$$

These values are the deviation of each measured value from the mean. How do we combine them into a single measure of the deviation of the measurements from the mean? You might think that you should average these deviations. This would be a good first guess, but it is incorrect.

The problem with summarizing the individual deviations by averaging them is that normally the average of the individual deviations will turn out to be 0. If the errors in measurement are truly random (as we expect), there will be an equal number of measurements above and below the mean, leading to an average deviation from the mean of 0. Obviously this will not be satisfactory. It would imply that all measurements are perfect!

Instead, we first compute the square of each individual deviation and *then* compute the average of the square of the deviations. Finding the square of each deviation transforms all negative deviations into positive deviations, giving us an all-positive measure of deviation from the mean. This prevents the deviations from averaging to 0.

$$\begin{array}{ll}(x_1 - \bar{x})^2 = +0.0001 & (x_2 - \bar{x})^2 = +0.0016 \\ (x_3 - \bar{x})^2 = +0.0016 & (x_4 - \bar{x})^2 = +0.0256 \\ (x_5 - \bar{x})^2 = +0.0121 & (x_6 - \bar{x})^2 = +0.0016\end{array}$$

Adding up all these values (the square of the deviations) we obtain a value of 0.0426.

The calculation we have just done can be summarized mathematically as

$$\sum_{i=1}^N (x_i - \bar{x})^2 = 0.0426 \quad (8.6)$$

This is the sum of the squares of the deviation of each measurement from the mean. We can now find the average of the deviations, with one small twist. The

- The average of the individuals' deviations of the table length measurements from the mean is 0.00 meters when significant figures are properly accounted for.

- Technically, we do not calculate the average, but that detail will be handled later.

- Some of these results have more than the proper number of significant figures. This is acceptable because these are intermediate results. They are *not* the final result we want.

quantity we want to calculate is

$$\frac{1}{(N-1)} \sum_{i=1}^N (x_i - \bar{x})^2 = 0.00852 \quad (8.7)$$

where N is again the number of measurements. Notice that we have divided by $N - 1$ rather than N to find something I call an “average” of the squares of the deviation from the mean. This is for technical reasons, but for all practical purposes, this is an average. In fact, if you were to make hundreds of measurements, $N - 1$ essentially equals N , and this is truly an average.

Are we there yet? No. This is *not* the standard deviation. Instead, Equation 8.7 is called the variance. The variance is just the square of the standard deviation. The standard deviation is

$$\sqrt{\frac{1}{(N-1)} \sum_{i=1}^N (x_i - \bar{x})^2} = \sqrt{0.00852} = 0.09 \quad (8.8)$$

in units of meters and to the proper number of significant figures.

Of course, we need a symbol for standard deviation. The symbol that is traditionally used for standard deviation is σ .

► We divide by $N - 1$ rather than N because we have lost a “degree of freedom” when we calculated \bar{x} . After we did that, we really only had $N - 1$ unique values left, not N .

► Standard deviations are always reported to one significant figure.

Calculating the Standard Deviation

The standard deviation about the mean, \bar{x} , for a set of N measurements can be calculated

$$\sigma = \sqrt{\frac{1}{(N-1)} \sum_{i=1}^N (x_i - \bar{x})^2} \quad (8.9)$$

where x_i stands for all the measured values from x_1 to x_N , and the symbol Σ means “sum of.” To calculate a standard deviation you must have at least three measured values.

8.4 Interpretation

We have determined that for our measurements of the table length that $\bar{x} = 2.44$ m and $\sigma = 0.09$ m. Notice that both the mean and the standard deviation about the mean have units. We can summarize both results by saying that the length of the table is 2.44 ± 0.09 m. Everything after the \pm is the standard deviation.

► The standard deviation does have units.

With this statement, we are saying that our best guess of the length of the table is 2.44 m and that our measurements are expected to show a deviation from the mean of 0.09 m. When we write 2.44 ± 0.09 m we are also saying that the true value of the table’s length may lie anywhere from 2.35 m to 2.53 m with about 66% confidence.

Note that the value of \bar{x} should never have more decimal places than σ . In fact, σ determines how many decimal places in \bar{x} are significant. This is true regardless of whether the rules for dealing with significant figures in calculations tells you that \bar{x} should have more decimal places.

8.5 Example

► Do not worry about the units if you do not understand them. Just make sure you keep them.

Let us assume you have performed a series of titrations to determine the concentration of calcium in a solution. You obtained the results $[Ca^{2+}] = 0.01104\text{ M}$ for trial 1, $[Ca^{2+}] = 0.01198\text{ M}$ for trial 2, and $[Ca^{2+}] = 0.01157\text{ M}$ for trial 3. What is the average value of the concentration of calcium, $[Ca^{2+}]$, in solution? What is the standard deviation?

The mean is calculated using Equation 8.5 with $N = 3$.

$$\text{Mean} = \bar{x} = \frac{1}{3}(0.01104 + 0.01198 + 0.01157) = 0.01153\text{M} \quad (8.10)$$

The standard deviation is calculated with Equation 8.9. The best way to approach a standard deviation calculation is to make a table showing x_i , $(x_i - \bar{x})$, and $(x_i - \bar{x})^2$. This way you will not forget something. For this example, such a table would look like that in Table 8.1. It is then a simple matter to sum the

Table 8.1

Example table for calculation of a standard deviation.

Trial	x_i	$(x_i - \bar{x})$	$(x_i - \bar{x})^2$
1	0.01104	-0.00049	2.4×10^{-7}
2	0.01198	0.00045	2.0×10^{-7}
3	0.01157	0.00004	1.6×10^{-9}

values in the forth column of Table 8.1 to obtain

$$\sum_{i=1}^N (x_i - \bar{x})^2 = 4.6 \times 10^{-7} \quad (8.11)$$

We can then divide this result by $N - 1 = 2$ and take the square root to obtain $\sigma = 0.0005\text{ M}$. Since the standard deviation reflects the precision of our measurements we report it to one significant figure.

Our final answer for our best guess as to the concentration of calcium ion in this solution is $0.0116 \pm 0.0005\text{ M}$. Note that I have rounded the average to 0.0116 from 0.01157 because the standard deviation tells us that the first uncertain digit is the forth one after the decimal point. Including more digits is meaningless.

Chapter 9

Preparing Acceptable Graphs

Visual presentation of numerical data is a key component of communicating scientific ideas and experimental results. Because of this, you will sometimes be asked to prepare graphs as part of a laboratory project. Learning to do this well takes practice. This chapter provides guidelines for preparing graphs that clearly and honestly communicate the information from which they are generated.

9.1 Software

Many software packages can present numerical data in graphical form. Some of these include Microsoft Excel, Wolfram Mathematica, Apple Numbers, OmniGraphSketcher, Plot, KaleidaGraph, Minitab, IGOR Pro, pro Fit, and gnuplot. Each package has its advantages and disadvantages. In this course, we will use the charting capabilities of Microsoft Excel to present numerical data in graphical form. Microsoft Excel is not the best for this purpose, but it is universally available on campus and easy to learn.

9.2 Preparation Guidelines

The goal of preparing graphs is to create a compact visual object that communicates information clearly and honestly to the viewer. When prepared well, visual representations of data can communicate concepts and ideas faster than the numerical data. In the best cases, visual representations can reveal new ideas or conclusions not imagined from the numerical data alone.

Below you will find guidelines for preparing graphs. In general chemistry, you can consider these to be requirements. As you grow as a scientist, however, remember that these are just guidelines. Sometimes you will want to override the guidelines in the interest of effectively communicating your data.

1. Each graph should have a descriptive, informative, easily understood title at the top of the graph. This title should stand on its own without needing reference to anything else for correct interpretation.

2. Each axis should be labeled with what is plotted on that axis.
3. If a physical quantity is plotted along an axis, that axis must display the units of the values plotted on that axis.
4. Most small data sets are best represented as scatter plots in Microsoft Excel. This is a plot in which each data point is represented by a marker at the appropriate x and y value.
5. All data point markers should be open or closed black circles at a size that does not overwhelm the graph. For most purposes, the size of the data point marker in Microsoft Excel should be near 5 points.
6. Never connect the dots. Never. There are exceptionally few instances in chemistry when you want to connect the dots in plotted data.
7. The data should fill the area of the graph. Adjust the range of the axes so that the data markers fill the graph area.
8. No legend is necessary for simple graphs like the ones produced in general chemistry. Microsoft Excel will insert a legend by default. You should remove it.
9. Most graphs should not have grid lines displayed. They are normally distracting and unhelpful. Microsoft Excel includes grid lines by default. Remove them.
10. Axes should include tick marks at regular intervals along each axis.
11. Graphs for publication will typically have axes drawn on all four sides of the graph. This is not possible in Microsoft Excel. Thus, you do not have to worry about this guideline.
12. The entire graph should appear in black and white. No color and no grays should be used unless it is for communicating something important. In most cases, the use of color is merely aesthetic and should be avoided.
13. Sometimes, Microsoft Excel will create graphs with a gray background. Because of the previous guideline, you will need to change the background to white if Microsoft Excel makes it gray.

9.3 Example Graph

An example of how to prepare a good graph may be more helpful than a list of guidelines. The boiling points and molar masses of the first eight aliphatic aldehydes were collected from Wikipedia and are shown in Table 9.1. These data were then entered into a spreadsheet (Microsoft Excel), and a graph plotting boiling point versus molar mass was prepared. After making adjustments to comply with the guidelines in the previous section, the graph in Figure 9.1

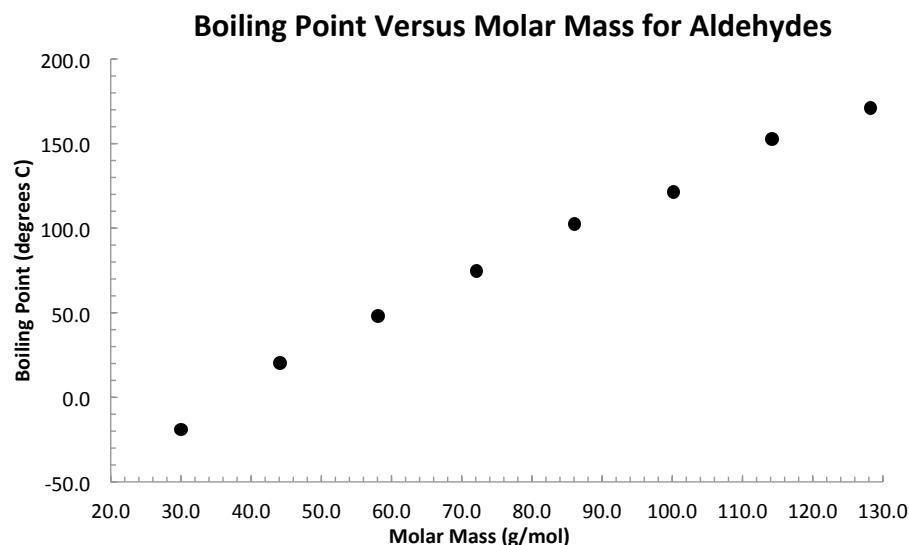
► Fitting data to a straight line is different than connecting the dots. You will fit data to a straight line many times. You will never connect the dots.

Table 9.1

Boiling points and molar masses of the first eight aliphatic aldehydes as collected from Wikipedia.

Formula	Molar Mass (g/mol)	Boiling Point (°C)
CH ₂ O	30.0	-19.0
C ₂ H ₄ O	44.1	20.2
C ₃ H ₆ O	58.1	48.0
C ₄ H ₈ O	72.1	74.8
C ₅ H ₁₀ O	86.1	102.5
C ₆ H ₁₂ O	100.2	121.5
C ₇ H ₁₄ O	114.2	152.8
C ₈ H ₁₆ O	128.2	171.0

was produced. I have omitted the details of how to go from the default graph produced by Microsoft Excel to one like that in Figure 9.1. You can find these details on the course website. For now, just pay attention to the final result.



► For details on how to create and customize graphs in Microsoft Excel, see the course website, ask your instructor, or click around in the software until you make what you want to make.

Figure 9.1

Graph of the boiling point of eight aliphatic aldehydes as a function of their molar mass that illustrates the guidelines for preparing acceptable graphs.

Notice how the graph in Figure 9.1 is very simple. The data markers fill the graph area; the axes are well labeled with units; the only colors are solid black and white. The graph in Figure 9.1 displays the data and enough information to make sense of the data. Nothing extraneous is present. There is nothing in Figure 9.1 to distract the viewer from the data. You should work to prepare graphs of this quality.

9.4 Fitting Data to a Line

In chemistry, and science in general, we are often interested in how well data obey a particular mathematical model. The simplest mathematical model is that of a linear relationship. When two variables are linearly related, they change in a constant proportion to each other. For instance, if one variable doubles when the other doubles, the two variables are linearly related. Likewise, if one variable always decreases by a factor of 3.4 when the other variable decreases by a factor of 1.0, the two variables are linearly related. For a linear relationship to exist, there must be a constant relationship of one variable to the other. Mathematically, this is expressed as

$$y = mx$$

where x and y are variables and m is the slope, the factor that describes how y changes when x changes.

To test how well data obey a linear relationship, we fit those data to a straight line. Technically, this is called a linear least-squares fit. A linear fit finds the straight line that minimizes the square of the difference between the line and the data points. In simpler terms, a linear fit finds the best line that goes through the data. This is called the best-fit line. If the data points fall on or very near the best-fit line, the fit is considered good. If the data points clearly fall off the best-fit line, the fit is considered poor. The quality of the fit can be quantified by a calculated value called R^2 . When R^2 is 1.0, the fit is perfect, meaning that all the data points fall exactly on the best-fit line. The data follow an exactly linear relationship. A smaller value of R^2 indicates a fit that is less good, with more and more data points falling off the best-fit line.

We can examine the data in Table 9.1 to determine if there is a linear relationship between molar mass and boiling point. A quick look at the data in Table 9.1 shows that the boiling point of an aldehyde increases roughly in proportion to the increase in molar mass. The relationship is not exact, but there might be a linear relationship. The graph of the data, shown in Figure 9.1 appears linear. How good is this linear relationship?

Software that can plot data often has the ability to fit data to models such as a straight line. The procedure is different for each software package. When the data in Figure 9.1 are fit to a straight line in Microsoft Excel, the result in Figure 9.2 is obtained.

The fact that the data points in Figure 9.2 lie fairly close to the best-fit line from low molar mass to high molar mass indicates that there is a fairly good linear relationship between molar mass and boiling point for these compounds. The R^2 value is 0.99298, which is a good value, indicated a good fit. The equation of the best-fit line on the graph shows that when the molar mass increases by one unit, the boiling point increases by 1.9°C.

In general chemistry, you should always include the equation for the best-fit line and the R^2 value on the graph if you fit the data to a linear model. These pieces of information are often helpful.

- In Microsoft Excel, fitting data to a mathematical model is called adding a trendline. For details about how to do this, see the course website.

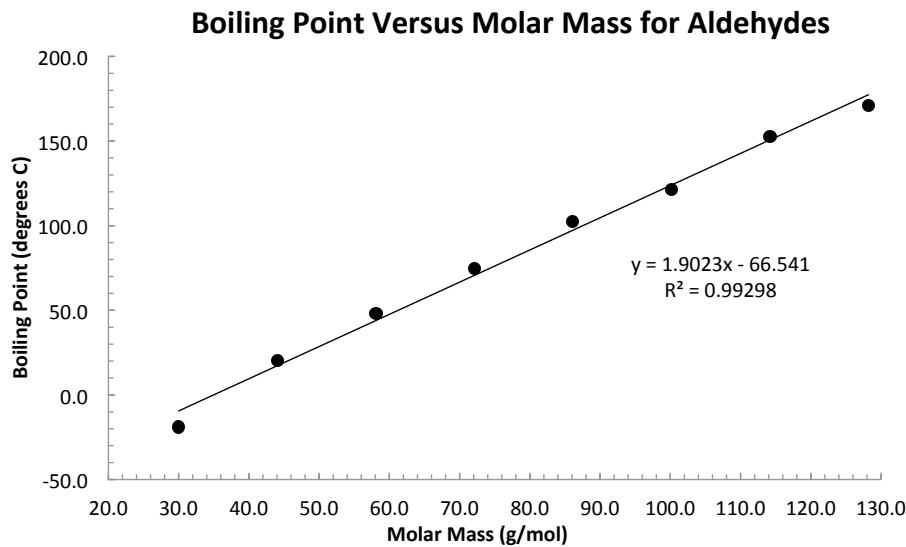


Figure 9.2

Graph of the boiling point of eight aliphatic aldehydes as a function of their molar mass along with the best-fit line. The equation of the line and the R^2 value are shown on the graph.

9.5 Language and Graphs

Scientists need a conventional language to communicate effectively and efficiently. When talking about data and graphs, scientists use the following conventions.

The axis that goes up and down is called the y axis, and this is the vertical direction. The axis that goes side to side is called the x axis, and this is the horizontal direction. In older books and papers the y axis is sometimes referred to as the ordinate axis while the x axis is referred to as the abscissa.

Data pairs consisting of one x value and one y value are plotted in graphs, and we say that the y value is plotted versus the x value. The x value is typically the independent variable, the one that you change as an experimenter to observe the effect. The y value is typically the dependent variable, the one that depends on the value of the x variable.

In Figure 9.1, we would say that the boiling points of the aldehydes are plotted versus their molar masses. In such a plot, we are examining whether the boiling point (the dependent variable) changes in any sensible way when the molar mass (the independent variable) changes.

Part II

Laboratory Projects

Chapter 10

Chemical Information

Common sources of chemical information are used to retrieve chemical and physical data for compounds. These data are analyzed and then summarized in a written report with graphs.

10.1 Introduction

The quantity of chemical information in the world is growing as you read this. By the time you finish this lab, chemical and/or physical data for at least one new molecule will be published in the literature or stored in a database. Where is this information? How is it stored? How do you find it? How do you retrieve the data? How do you know it is reliable data?

As a scientist studying chemistry, it is important to be familiar with how to find and access reliable chemical data in the vast ocean of available chemical information. The number of resources available is large, and we can not cover them all in one lab meeting. Instead, we will start simple. In this project you will search for chemical formulas, physical properties, and uses for particular chemicals in a selection of information sources.

► Examples of physical properties include melting point, boiling point, solubility, density, and appearance.

CRC Handbook of Chemistry and Physics

The *Handbook of Chemistry and Physics*, published by the Chemical Rubber Company (CRC), is a compilation of chemical, physical, and mathematical data. Chemists commonly refer to this handbook as just “the CRC” even though this is technically ambiguous because the Chemical Rubber Company publishes many handbooks. To chemists, however, this is *the* handbook and no further clarification is necessary.

The variety of data contained in the CRC is stunning. In general chemistry, however, we will be concerned with just a few types of information. These will include the chemical and physical data for organic compounds and inorganic compounds. The data for organic compounds are contained in a section of the CRC titled “Physical Constants of Organic Compounds” while the data for

► The index of the CRC cannot be used to look up information for a given chemical. Instead, you have to turn to the correct section first.

inorganic compounds are contained in a section titled “Physical Constants of Inorganic Compounds.”

Data included in these sections consists of the name, formula, molecular or formula mass, color and crystalline form, boiling point, melting point, density, and solubility of various compounds. Looking up a compound is not always intuitive, especially without more training in chemistry. In addition, sometimes the data presented in the tables can be challenging to interpret if you have not used the CRC before.

Your instructor will provide assistance in learning to use the CRC.

Merck Index

Unlike the CRC, the *Merck Index* is a reference handbook focused primarily on the properties of various chemicals and drugs. Also unlike the CRC, the index of the *Merck Index* can be used to look up chemicals.

The index at the back of the *Merck Index* is called “Cross Index of Names.” It lists alternate names for compounds, including brand names for drugs. Next to each name is the monograph number. This number refers to the brief monograph for that compound. No information is given about the page number on which the monograph appears.

NIOSH Pocket Guide

The *NIOSH Pocket Guide to Chemical Safety* was discussed in Chapter 1 on page 1.5. This resource mainly contains information about hazards, but it also contains physical property data as well as a list of common names for substances. It is also available for searching online unlike the CRC and the Merck Index.

Wikipedia

The data on Wikipedia does not qualify as peer-reviewed and authoritative; however, Wikipedia’s own policies require that any data presented on the site have an authoritative source. Wikipedia’s standards for “authoritative source” are not the same as a chemist’s standards. In practice, this means that the chemical and physical data for compounds found on Wikipedia can be used tentatively but should never be relied upon when publishing. In my experience, the data on Wikipedia is sufficiently accurate for all work at the general chemistry level.

Wikipedia is edited collaboratively and can be changed at any time. With many individuals involved in editing Wikipedia, it is unlikely that vandalism of the site will go unnoticed and uncorrected for long, but this can happen. Thus, when you look up data on Wikipedia, be aware that it cannot be assumed to be accurate. Accordingly, citing Wikipedia as a source in any professional journal publication would be considered unacceptable. Only fixed, peer-reviewed sources are considered appropriate.

In this project, we will compare data from the CRC and the *Merck Index* to that from Wikipedia to assess reliability of Wikipedia.

10.2 Safety Considerations

Since all work this week will be carried out in the department of chemistry's student computer lab, not the general chemistry laboratory, there are no unusual hazards.

Goggles

You are not required to bring or wear your goggles because all work will be conducted in the student computer lab this week.

10.3 Experimental Procedure

Organize Yourself

1. **Determine the Compound(s) Assigned to You:** Your laboratory instructor will assign one or more compounds to you when you come to lab. Make sure you know what your assigned compound(s) is (are).
2. **Record Assigned Compound(s) in Notebook:** Write down the name(s) of your assigned compound(s) in your laboratory notebook.
3. **Organize Your Laboratory Notebook:** Before rushing into the next section to look up data for your compounds, make sure your laboratory notebook is organized for the task. Since you know what data you have to look up, you can make a table in your notebook to hold that data. You also know you will have to look up most of the data twice: once in the CRC or Merck Index and once in Wikipedia. Therefore, you might consider making a table in your notebook with properties listed along the left followed by two columns, one for the CRC or Merck data and one for the Wikipedia data.

Look Up Data for Compound(s)

In each step, record your source for each piece of data: the CRC edition number or the *Merck Index* monograph number. Sources are not complete without CRC edition number or the *Merck Index* monograph number.

► Record data directly into your laboratory notebook.

1. **Look Up the Chemical Formula of Your Compound(s):** Using the CRC or the *Merck Index*, look up and record the chemical formula for your assigned compound(s).

► Chemical Formula

2. **Look Up Structural Line Drawing of Your Compound(s):** Search for your compound(s) on Wikipedia and find the structural line drawing that is normally in the upper right-hand corner of the page. Copy this drawing of the compound into your laboratory notebook by hand. Save an image of the structural line drawing to your computer's desktop for inclusion in your report. In rare cases, Wikipedia will not have a structure line drawing of a

► Drawing

compound. If this happens for one of your compounds, search elsewhere on the internet or search the CRC.

► Molecular Mass

3. **Look Up the Molecular Mass of Your Compound(s):** Using the CRC or the *Merck Index*, look up and record the molecular mass for your assigned compound(s) in units of grams/mole. Then look up and record the molecular mass of your compound(s) as reported by Wikipedia.

► Boiling Point

4. **Look Up the Boiling Point for Your Compound(s):** Using the CRC or the *Merck Index*, look up and record the boiling point for your assigned compound(s) in units of Celsius. Then look up and record the boiling point of your compound(s) as reported by Wikipedia.

► Density

5. **Look Up the Density for Your Compound(s):** Using the CRC or the *Merck Index*, look up and record the density for your assigned compound(s). Be sure to record the units. Then look up and record the density of your compound(s) as reported by Wikipedia.

► Use or Occurrence

6. **Look Up the Use or Occurrence of Your Compound(s):** Using the CRC or the *Merck Index*, look up and record the use or occurrence of your assigned compound(s).

► NFPA Diamond

7. **Look Up the NFPA Diamond for Your Compound(s):** Using Wikipedia, look up the NFPA Diamond for your assigned compound(s) and record it in your notebook. Wikipedia will not display an NFPA diamond for all compounds. In these cases, you will have to look elsewhere on the Internet. An alternate source for NFPA data are MSDS sheets. You can search for these with the search term “compound name MSDS”. These will typically not show the NFPA diamond, but they will list the numerical ratings for each portion of the diamond.

Compile Data

1. **Post Your Data:** When you have finished looking up the data for your compound(s), find your compound(s) on the board at the front of the room and fill in the requested data. Always put up the data from the CRC or the *Merck Index*. If the data from Wikipedia agrees with the CRC or *Merck Index* data, put the data on the board in black. If Wikipedia disagrees with the data from the CRC or *Merck Index*, put the data on the board in red. This way we can quickly tell how reliable Wikipedia is.
2. **Copy Data From Board Into Your Notebook:** After you have placed your data on the board, copy the three tables on the board (and all the data in them) into your laboratory notebook. Make sure the tables are labeled properly with the headings on the board: Alkanes, Alcohols, and Acids.

Plot Molecular Mass vs. Boiling Point

For all graphs you are asked to prepare, please adhere to the guidelines for preparing acceptable plots in *Preparing Acceptable Graphs* in Chapter 9 starting on page 49.

1. **Plot Molecular Mass vs. Boiling Point for Alkanes:** Using Microsoft Excel, plot the molecular mass on the x axis and the boiling point on the y axis for all compounds listed in the table labeled “Alkanes.” The phrase “Figure 1” should be part of the graph title.
2. **Fit Alkane Data to Straight Line:** Using the plot prepared in the previous step, fit the alkane data to a straight line. Be sure to add the equation for the line and the R^2 value to the plot.
3. **Plot Molecular Mass vs. Boiling Point for Alcohols:** Using Microsoft Excel, plot the molecular mass on the x axis and the boiling point on the y axis for all compounds listed in the table labeled “Alcohols.” The phrase “Figure 2” should be part of the graph title.
4. **Fit Alcohol Data to Straight Line:** Using the plot prepared in the previous step, fit the alcohol data to a straight line. Be sure to add the equation for the line and the R^2 value to the plot.
5. **Plot Molecular Mass vs. Boiling Point for Acids:** Using Microsoft Excel, plot the molecular mass on the x axis and the boiling point on the y axis for all compounds listed in the table labeled “Acids.” The phrase “Figure 3” should be part of the graph title.
6. **Fit Acid Data to Straight Line:** Using the plot prepared in the previous step, fit the acid data to a straight line. Be sure to add the equation for the line and the R^2 value to the plot.

► See Chapter 9 for information about fitting data to a straight line. See the course website for details about how to fit data to a straight line in Microsoft Excel.

Write Report

1. **Begin Report:** Open Microsoft Word or Apple Pages and begin a new document. In the header, insert your name flush against the left-hand margin and the date flush along the right-hand margin.
2. **Enter Report Title:** On the first line of the document, insert the title “Report for Experiment 1” using a Title style.
3. **Enter Compound Information:** On the next line of the report, create the heading “Compound Information” using a Heading style. Under this heading, list the information you found for your compound(s): compound name, compound formula, molecular mass, boiling point, density, use or occurrence, NFPA rating, and drawing. Be sure to cite your sources. You can drag the drawing you downloaded directly into the word processing document.

- There is a difference between results and conclusions.
4. **Create Results Section:** On a new line, create the heading “Results” using a Heading style. Using full sentences in paragraph form, describe the appearance of the graphs you produced. Refer to the graphs as Figure 1, Figure 2, and Figure 3.
 5. **Create Conclusions Section:** On a new blank line, create the heading “Conclusions” with a Heading style. In this section, comment briefly on the relationship between molecular mass and boiling point seen in the graphs you prepared. In other words, draw a conclusion.
 6. **Include Graphs:** After the last line of text, insert a page break to create a new page. Copy each graph from Microsoft Excel to a separate page of your word processing document. Make sure the pages are labeled appropriately as Figure 1, Figure 2, and Figure 3. Save the your document.

Submit Report

1. **Convert Report to PDF:** Once you are happy with your report, save a copy of it as a PDF document.
2. **Check The PDF:** Open the PDF version of your document and check to be sure it appears exactly the way you want it to appear. If it does not, make changes and generate the PDF again.
3. **Submit Your Report:** Submit your report as your instructor wants: either by email or by electronic upload to a web site.

10.4 Before Exiting Lab

- Update the table of contents in the front of your lab notebook.
- Make sure you have the date next to the start of your experimental work.
- Make sure all pages in your laboratory notebook have been numbered.
- Log out of the workstation you were using.
- Turn in your laboratory notebook.

10.5 Post-Lab Assignments

Once you have submitted your report and turned in your laboratory notebook, your work is complete. There is no further work to do.

Chapter 11

Volumetric Glassware

11.1 Introduction

Early in your chemistry experience you may find the variety of equipment available in a general chemistry lab confusing. For instance, during the first semester of general chemistry alone you will encounter no fewer than six pieces of equipment for measuring the volume of a liquid.

To know which piece of glassware to use, you will need to know what you are trying to accomplish and the precision with which you need to accomplish that. For example, if you need to add 12.5 ± 0.1 mL of acetic acid to a reaction, you will need a piece of equipment capable of measuring volume with a precision of 0.1 mL. This means you must know the precision of all the glassware for measuring volume so that you can make an informed choice.

After you have decided which piece of glassware to use, you will then need to know how to use that glassware.

► Achieving greater precision normally takes more time. Because of this, it is advisable to use a piece of equipment designed for a precision no greater than you require.

Common Glassware

Common glassware for containing liquids and measuring volumes include graduated cylinders, beakers, and Erlenmeyer flasks. Graduated cylinders can measure volumes to an accuracy of about ± 0.1 mL. They are not, however, designed to deliver with such accuracy. With a graduated cylinder, the uncertainty in the volume of liquid you pour out is greater than the uncertainty of the measured volume in the cylinder.

Beakers and flasks are mainly intended for containing liquids used in reactions. They are poor choices for dispensing known volumes of liquids. They have a minimum uncertainty of ± 10 mL.

All of these devices are relatively easy to use. Glassware with greater volume precision is less easy to use.

Volumetric Glassware

Typical volumetric glassware includes volumetric pipets, volumetric flasks, and burettes. Volumetric pipets are designed to deliver a given volume of liquid with a

► Volumetric pipets can also be designed to contain a specific volume of liquid, but you will not use these in general chemistry.

known uncertainty. The volumetric pipets you will use in general chemistry have a typical uncertainty of ± 0.01 mL. Volumetric flasks are designed to contain a given volume of liquid with low uncertainty, typically ± 0.01 mL. Burettes are designed to measure an arbitrary volume of liquid delivered with a precision of ± 0.01 mL.

Volumetric pipets are used when you need to add to a container a certain volume of a liquid with high precision. Volumetric flasks are used when you need to prepare a solution of a known volume. Burettes are used in titrations.

Of all of these, the volumetric pipet is the most difficult to use. It is, however, important to know how to use it, which is why we dedicate an entire laboratory project to its use.

This Project

In this project, you will gain experience using a volumetric pipet by first calibrating your pipet so that you know exactly how much liquid it delivers (along with the correct uncertainty). You will then use your calibrated pipet to determine the density of a solution of unknown density. Along the way, you will gain experience using the top loading balances, another important piece of equipment in the general chemistry laboratory.

Calibration

Calibration is the process of determining the behavior of a piece of equipment. For instance, the manufacturer of the pipets you will use in this project claims that the volume of liquid delivered by the pipet is 10.00 ± 0.01 mL. This may no longer be true. If the pipet was heated at any point in its life, it may not deliver exactly that volume any more. If your technique is not just right, it may deliver a different volume.

Calibration of a pipet is a process by which you figure out the volume actually delivered by your pipet and the uncertainty with which it does that.

11.2 Safety Considerations

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

In this lab, we can pour all waste in the sink. There will be no need to use special waste containers in the hood.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 11.1. Do not use the normal waste baskets for broken glass.

11.3 Experimental Procedure

This section provides procedures for calibrating your pipet and determining the density of the unknown solution.

Prepare Water Reserve

1. **Fill Flask With DI Water:** Clean a 250 mL Erlenmeyer flask, rinse with distilled water three times, and then fill with distilled water.
2. **Set Flask Aside:** Place a thermometer into the flask and set both aside until the temperature of the water stabilizes (does not change any more).

Calibrate Volumetric Pipet with Water

Follow these steps to collect the data that will allow you to determine the actual volume delivered by your pipet. To complete the calibration, you will have to look up the known density of water at the temperature of the water reserve.

You should practice using a volumetric pipet before you use it for this procedure. The practice provides a good opportunity to allow the water in your water reserve to reach a stable temperature.

1. **Rinse 10 mL Pipet:** Rinse a 10.00 mL volumetric pipet thoroughly with distilled water three times.
2. **Document Pipet Used:** In your laboratory notebook, record the information on the stem of the volumetric pipet you are using.
3. **Clean and Dry a 50 mL Beaker:** Clean and dry a 50 mL beaker. After the beaker is dry, handle the beaker as little as possible by hand.
4. **Weigh Empty Beaker:** Weigh the 50 mL beaker and record the mass in your laboratory notebook.
5. **Add 10.00 mL Water to Beaker with Pipet:** Using the volumetric pipet, add 10.00 mL deionized water from your water reserve to the 50 mL beaker.
6. **Weigh Beaker with Water:** Use a balance to find the mass of the beaker with the water in it.
7. **Empty Beaker:** Dump the contents of the 50 mL beaker into the sink.
8. **Repeat:** Repeat steps 3 to 7 three additional times such that you have a total of four mass and volume measurements.



Figure 11.1
Broken glass container.

► This flask of distilled water will be your personal water reserve so that you do not have to use the large laboratory bottles of distilled water as often.

► You never need to dry the inside of the pipet before using it. You should understand why this is true and seek help if you cannot figure it out.

► You do not really know that you are adding 10.00 mL. You only know you have added the volume up to the line.

Determine Density of Unknown Solution

1. **Obtain Solution of Unknown Density:** Solutions of unknown density can be found in bottles in the hoods. Your instructor will assign a solution to you. Record the letter of the unknown in your notebook and then pour about 60 mL of that solution into a clean and dry beaker.
- Rinsing ensures that the pipet contains only the solution of unknown volume.
2. **Rinse Pipette with Unknown Solution Three Times:** Pour about 10 mL of the unknown solution into another small beaker and then suck some of this solution into the pipet to rinse it. Do this a total of three times. Dispose of the waste rinse in the sink.
3. **Clean and Dry a 50 mL Beaker:** Clean and dry a 50 mL beaker. After the beaker is dry, handle the beaker as little as possible by hand.
4. **Weigh Empty Beaker:** Weigh the 50 mL beaker and record the mass in your laboratory notebook.
5. **Add 10.00 mL Solution to Beaker with Pipet:** Using the volumetric pipet, add 10.00 mL of your unknown solution to the beaker.
6. **Weigh Beaker with Solution:** Use a balance to find the mass of the beaker with the solution in it.
7. **Empty Beaker:** Dump the contents of the 50 mL beaker into the sink.
8. **Repeat:** Repeat steps 3 to 7 three additional times such that you have a total of four mass and volume measurements.

11.4 Before Leaving Lab

Before leaving lab for the day, go down this checklist to make sure you have done everything on it.

- Rinse the volumetric pipet with water three times.
- Return the volumetric pipet to the tray in the front of the room.
- Put all of your own glassware back in your drawer.
- Update the table of contents in the front of your notebook.
- Draw a line at the end of your experimental work and sign on the line.
- Have your instructor sign on the line as well.
- Complete all other tasks listed on the blackboard.

11.5 Post-Lab Assignments

Calculations

All calculations should appear in your laboratory notebook. If you make an error, just cross through the error with a single line and then move on. You are strongly advised to carry out as many of these calculations as you can in lab, especially the ones for calibrating your pipet. If you have bad data for calibrating your pipet, you will have no opportunity to redo the experiment after you leave. However, if you do these calculations before you leave, you have the chance to calibrate again.

1. Look up the known density of water at the temperature you recorded for the water reserve. Be sure to record a proper source citation.
2. Convert the literature value for water's density to g/mL if it is not already in those units.
3. For data collected using water to calibrate the volumetric pipet
 - a) Calculate the volume of water delivered in each trial using the literature value of the density of water to convert mass to volume.
 - b) Calculate the average volume of water delivered.
 - c) Calculate the standard deviation of the volume of water delivered.
 - d) Summarize these results in your laboratory notebook by writing the average volume \pm the standard deviation. This is your best determination of the volume delivered by your pipet.
4. For data collected using the solution of unknown density
 - a) Calculate the density of solution for each trial using the calibrated volume delivered by your pipet.
 - b) Calculate the average density of the solution from these measurements.
 - c) Calculate the standard deviation of the solution density from these measurements.
 - d) Summarize these results in your laboratory notebook by writing the average density \pm the standard deviation. This is your best determination of the density of the solution.

► You need to show your work in your notebook. Do not use your calculator's statistical functions.

► You need to show your work in your notebook. Do not use your calculator's statistical functions.

Questions

Write answers to these questions in your notebook. You should not put the answers to these questions in with your experimental work.

1. Compare your value for the calibrated delivery volume of your pipet to that printed on the end of the pipet. How do they compare?

Chapter 12

Compound Identification Using Physical Properties

12.1 Introduction

From one perspective, chemists can be thought of as chemical detectives. Chemists have the skills and knowledge to identify substances of unknown identity using clues about the substance's physical and chemical properties.

In this lab you will take a step toward becoming a better chemical detective by experimentally determining some physical properties for an unknown solid compound and an unknown liquid compound. You will then compare these experimentally determined values to known values for a set of eight compounds. Based on your own experimental work, you will have to properly identify the unknown compounds.

12.2 Safety Considerations

Chemical Hazards

- Flammable Liquids:** Many of the liquids used in this lab, such as ethanol, toluene, and acetone are flammable. Be careful not to spill these or any other liquids on the hot plates when they are hot.
- Vapors:** The vapors released by the solvents in this lab (acetone and toluene) have a distinctive odor and can make some people nauseous in high concentration. High concentrations should never develop in this lab, but you should still do your best to work with all solvents under your bench hood so that the vapors are sucked away.

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.



Figure 12.1
Broken glass container.

Waste Disposal

- Solvents:** The solvents used in this lab (acetone, ethanol, and toluene) cannot be dumped into the sink when you are finished using them. Instead, dispose of all solvents in the appropriate chemical waste containers in the back of the room.
- Unknown Samples:** Any unknown sample that remains at the end of the experiment outside of the original test tube in which it was supplied must be disposed of in the appropriate chemical waste containers in the back of the room.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 12.1. Do not use the normal waste baskets for broken glass.

12.3 Experimental Procedure

This section provides procedures for determining the chemical identity of a liquid and a solid based on their physical properties. You may work with a partner during any step of the procedure. In fact, during some indicated steps you are encouraged to work with a partner. However, you are responsible for identifying your own unknown solid and liquid.

Organize Yourself

► If the identification numbers do not appear in your lab notebook, some parts of your work cannot be evaluated. You may receive no points for those portions of the evaluation.

- Record Identification Numbers:** At your lab bench you will find an unknown solid and an unknown liquid. Each will be in a corked test tube. Each test tube will have a label on it with a number. This number is the identification number that allows your instructor to determine which unknown you were given. Write these numbers down in your lab notebook immediately along with the sample type for each (solid or liquid).
- Determine Which Group You are In:** To avoid long lines at the balances, infrared spectrometer, and Mel-Temp apparatus, students will begin this experiment at different points in the experimental procedure. Your instructor will divide your lab section into groups for this purpose, each with a different starting position in the procedure. Figure out which group you are in and begin with the appropriate experimental procedure.

Determine Solubility of Unknown Solid

- Place Unknown Solid In Test Tubes:** Arrange three clean and dry test tubes in a test tube rack. Place approximately 0.04 g of the unknown solid into each test tube.

⊕ Think about how precisely you have to weigh the solid out. It may be a waste of time to use the balances. For most compounds, 0.04 g is the amount of compound that will fit on the tip of a laboratory spatula.

2. **Add Solvents to Test Tubes:** Add 3.0 mL of water to the first test tube, 3.0 mL ethanol to the second test tube, and 3.0 mL toluene to the third test tube.
3. **Stopper and Shake:** Cork each test tube and shake. Record your observations.

► Be attentive to whether the solid crystals dissolve or not. If they dissolve, the solid is soluble in that solvent. If the crystals do not dissolve, the unknown solid is not soluble in that solvent.

Determine Melting Point Range of Unknown Solid

1. **Determine Melting Point Range:** Follow the procedure in Chapter 6 starting on page 31 to obtain the melting point range for your unknown solid.

⊕ Work with a partner as described on page 35 to save time and obtain better results.

Determine Solubility of Unknown Liquid

1. **Place Unknown Liquid in Test Tubes:** Line up three clean and dry test tubes in a test tube rack. Using an eye dropper, place 15 to 20 drops of your unknown liquid into each of these test tubes.
2. **Add Solvents to Test Tubes:** Add 2 mL water to the first test tube, 2 mL ethanol to the second, and 2 mL toluene to the third.
3. **Gently Agitate:** Gently agitate each test tube for about 30 seconds. Carefully observe the liquid in each test tube and record your observations.
4. **Confirm If Necessary:** If you have a question about whether your unknown liquid is soluble or not, add a few additional drops of the unknown liquid and observe the changes (if any).

► If it appears as though there are two layers of liquid, then your unknown liquid is not soluble in the solvent. If there is just one layer, then your unknown dissolved in the solvent.

Determine Boiling Point of Unknown Liquid

Follow the procedure given in Chapter 7 starting on page 37 to determine the boiling point of your unknown liquid.

Determine Density of Unknown Liquid

1. **Determine Density of Unknown Liquid:** Using the procedure you learned in the laboratory titled “Volumetric Glassware” starting on page 63, determine the density of your unknown liquid. Note that in this experiment you will use a weighing bottle instead of a beaker to hold the liquid.

⊕ Do not dispose of the unknown liquid after determining the density. You can use it for the solubility and boiling point determinations. If you dump the unknown liquid at this stage, you may not have enough to complete the lab, and you will not be given more.

Collect Infrared Spectrum of Unknown Liquid

1. **Place Unknown Liquid on Salt Plates:** Place two drops of your unknown liquid onto a salt plate and then place another salt plate on top of your unknown liquid, ensuring that your unknown liquid spreads between the plates.
2. **Collect Infrared Spectrum:** Obtain the infrared spectrum of your sample according to the instructions given by your laboratory instructor. Print out the collected spectrum and include it in your lab notebook.

► Your instructor will show you how to use the Fourier transform infrared spectrometer.

► Spectra should appear in a lab notebook on a page by itself, taped along one edge, folded, and labeled on the outside.

12.4 Before Exiting Lab

Before leaving lab for the day, go down this checklist to make sure you have done everything on it.

- Return the test tubes containing the unused portions of your unknown solid and liquid samples to the box on the front desk.
- Check to be sure all solid and liquid wastes (other than the unknowns) have been poured into the proper waste container.
- Return the volumetric pipet to the tray at the front of the room.
- Return clamps and rings to the drawers from which you got them.
- Check to be sure all hot plates have been unplugged.
- Check your lab notebook for page numbers on all pages.
- Check your lab notebook to ensure that you have recorded your unknown numbers.
- Update the table of contents in your notebook.
- Draw a line at the end of your experimental work and sign on it.
- Have your instructor sign on the line at the end of your experimental work.

12.5 Post-Lab Assignments

Interpretation of Observations

You may have already carried out these two interpretations of your solubility observations. If you have, then do not write the interpretations for a second time in your notebook. Just move on with the next section.

1. From your observations, determine whether your unknown solid is soluble in water, ethanol, and toluene. If the crystals “disappeared,” the solid is soluble in that solvent. If the crystals did not disappear, the solid is insoluble. If it appears as though the crystals decreased in size but did not completely disappear, then the solid is slightly soluble.
2. From your observations, determine whether your unknown liquid is soluble in water, ethanol, and toluene. If your unknown liquid and the solvent in question formed two layers of liquid when mixed, then your unknown liquid is not soluble in that solvent. If two layers of liquid were not visible after mixing, then your unknown liquid is soluble in the solvent.

Calculations

All calculations should appear in your laboratory notebook. If you make an error, just cross through the error with a single line and then move on.

1. Calculate the density of your unknown liquid from the data you collected. Be sure to do this to the proper number of significant figures.

Questions and Activities

Write your answers to the questions and responses to the activities below in your laboratory notebook. This material should not be mixed in with calculations, procedures, or observations.

1. What is the identity of your unknown solid? Compare all physical properties data for your unknown solid (melting point and solubility) to the data for the possible compounds. Decide what your unknown solid is based on these comparisons. Be sure to justify your conclusion based on your data.
2. Summarize your assignment of an identity to your unknown solid by clearly writing your unknown number again with your identity assignment next to the number. Box the result so it clearly stands out.
3. What is the identity of your unknown liquid? Compare all physical properties data for your unknown liquid (boiling point, density, solubility, and infrared spectrum) to the data for the possible compounds. Decide what the identity of your unknown liquid is based on these comparisons. Be sure to justify your conclusions based on your data.
4. Summarize your assignment of an identity to your unknown liquid by clearly writing your unknown number again with your assignment next to the number. Box the result so it clearly stands out.

Chapter 13

Spectrophotometric Determination of a Copper Salt's Formula Mass

Spectrophotometric analysis is used to determine the percentage of copper by mass in a copper salt of unknown identity. The formula mass of the copper salt is determined from this information.

► This method is based on physical properties; therefore, it is a non-chemical method.

13.1 Introduction

Spectrophotometric analysis in this experiment relies on the absorption of visible light by complexes containing Cu^{2+} . The light absorbed induces no chemical change in the copper compounds. The amount of light absorbed can be related directly to the concentration of copper in solution, which is ultimately the information you need to determine the formula mass of the unknown copper salt.

The instrument that does this work for us is called an ultraviolet-visible spectrophotometer, or UV/Vis spectrometer for short. You will use this instrument in this lab. The particular model you will use was made by Hewlett-Packard (now Agilent).

Standard Curve

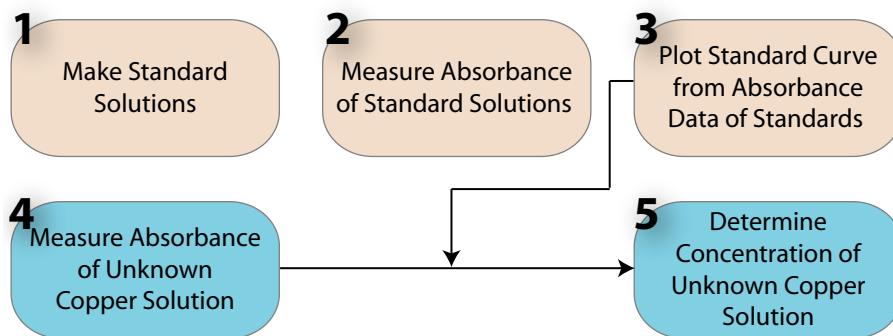
The problem with this technique is that you rarely know exactly how concentration relates to absorption of light for your sample of unknown concentration. Therefore, the first step in an analytical spectrophotometric analysis is normally to prepare something known as a standard curve. A standard curve is a plot showing how the absorbance of light changes as the concentration changes for your unknown species. In other words, preparation of a standard curve tells you exactly how absorption of light depends on concentration.

► Spectrophotometric analysis is almost always a two step process: preparation of a standard curve followed by analysis of your own sample of unknown concentration.

How do you make such a curve if your solution is of unknown concentration? The short answer is that you don't prepare such a curve with your sample of unknown concentration. You first have to prepare other solutions, solutions that are of known concentration. These are called standards. The absorbance of light

Figure 13.1

Overview of the steps you will carry out in this project. Steps 1,2, and 3 are related to producing the standard curve. The standard curve is then used to determine the concentration of your unknown copper sample.



from each of the standard solutions of known concentration is measured. Once this is done, you know exactly how absorbance relates to concentration.

After preparation of the standard curve, you can measure the amount of light absorbed by your sample of unknown concentration. Using the standard curve, it is then possible to obtain the unknown sample's concentration based on its absorbance.

Mathematical Treatment

To make this analysis work, we have to be more mathematical. The concentration of a species in a solution is directly proportional to a measure of how much light is absorbed when it passes through the solution. The exact mathematical relationship is

$$A = \epsilon cb \quad (13.1)$$

which is called Beer's Law. In Equation 13.1, A stands for absorbance, which is a measure of how much light is absorbed. The quantity ϵ is called the molar absorptivity, and it is a measure of how much light is absorbed by each molecule in solution. The quantity c is the concentration of the species in units of molarity, and b is the length of the path the light travels through the solution.

In our case, $b = 1\text{ cm}$ because the cells you will use to record the absorbance of the solutions always have a width of 1 cm. The instrument you will use reports absorbance directly as a unitless number. This is one of the rare cases in which it is appropriate to leave units off of a physical quantity (absorbance).

Summary

This laboratory experiment involves considerable new information that may not be familiar. In particular, the concept of a standard curve and its use in determining the concentration of species in samples of unknown concentration can be confusing. As such, it is easy to get lost in the details of the experimental work which can seem tedious at times.

To help you stay focused, Figure 13.1 shows an overview of the steps you will carry out in this lab. In this figure, the steps highlighted in tan are related to preparation of the standard curve. The steps highlighted in blue are related directly to the determination of the concentration of your unknown copper

► Absorbance is actually the base-10 log of a ratio of two numbers that do have units, but those units cancel. This is why absorbance has no units.

solution. Regardless of the complexity and tedium of the experimental steps, the experiment is just a five step process.

13.2 Safety Considerations

Chemical Hazards

1. **Copper Solutions:** The only chemicals you will be working with today are the copper solutions. These are not hazardous unless consumed in large quantity. However, if you spill these solutions on yourself you should make an effort to wash the affected body part as soon as possible.

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

1. **Copper Solutions:** All copper solutions should be poured into the waste container in the back of the room when you are finished with them. No solutions should be poured down the drain.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 13.2. These containers are in the back of the lab against the outside wall. Do not use the normal waste baskets for broken glass.

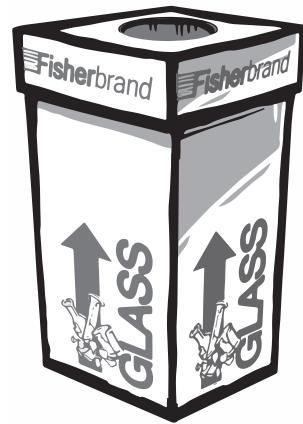


Figure 13.2
Broken glass container.

13.3 Experimental Procedure

Prepare Standard Solutions

The instructions here allow you to complete task 1 in Figure 13.1.

1. **Obtain Five Clean and Dry Beakers:** Obtain five clean and dry beakers of size 150 mL or smaller. Line these beakers up on your work bench and place a single label on each. Label these beakers “Standard A,” “Standard B,” “Standard C,” “Standard D,” and “Standard E.”
2. **Prepare Beaker Labeled “Standard A”:** Pour approximately 50 mL of stock Cu²⁺ solution into the beaker labeled “Standard A.”
► Be sure to record the exact concentration of the stock solution from the reagent bottle.
3. **Obtain 50 mL Volumetric Flask:** Obtain a 50 mL volumetric flask from your laboratory drawer. Obtain a cap or a cork for the flask.

► What is the concentration of this solution?

► This is to make sure no extra copper is transferred to the beaker labeled "Standard C."

► What is the concentration of this solution?

► This is to make sure no extra copper is transferred to the beaker labeled "Standard D."

► What is the concentration of this solution?

► This is to make sure no extra copper is transferred to the beaker labeled "Standard E."

► What is the concentration of this solution?

4. **Prepare Beaker Labeled "Standard B":** Use a 25.00 mL volumetric pipet to transfer 25.00 mL of the Standard A solution into the 50.00 mL volumetric flask. Add DI water to the mark, cap the flask, and thoroughly mix the solution by inverting the flask back and forth ten times. Pour this solution into the beaker labeled "Standard B."
5. **Clean Volumetric Flask:** Rinse the volumetric flask four times with 10 mL portions of distilled water and shake excess water out of the flask.
6. **Clean Volumetric Pipet:** Rinse the volumetric pipet twice with 5 mL portions of the solution in the beaker labeled "Standard B."
7. **Prepare Beaker Labeled "Standard C":** Use a 25.00 mL volumetric pipet to transfer 25.00 mL of the solution in the beaker labeled "Standard B" to the 50.00 mL volumetric flask. Add DI water to the mark, cap the flask, and thoroughly mix the solution by inverting the flask back and forth ten times. Pour this solution into the beaker labeled "Standard C."
8. **Clean Volumetric Flask:** Rinse the volumetric flask four times with 10 mL portions of distilled water and shake excess water out of the flask.
9. **Clean Volumetric Pipet:** Rinse the volumetric pipet twice with 5 mL portions of the solution in the beaker labeled "Standard C."
10. **Prepare Beaker Labeled "Standard D":** Use a 25.00 mL volumetric pipet to transfer 25.00 mL of the solution in the beaker labeled "Standard C" to the 50.00 mL volumetric flask. Add DI water to the mark, cap the flask, and thoroughly mix the solution by inverting the flask back and forth ten times. Pour this solution into the beaker labeled "Standard D."
11. **Clean Volumetric Flask:** Rinse the volumetric flask four times with 10 mL portions of distilled water and shake excess water out of the flask.
12. **Clean Volumetric Pipet:** Rinse the volumetric pipet twice with 5 mL portions of the solution in the beaker labeled "Standard D."
13. **Prepare Beaker Labeled "Standard E":** Use a 25.00 mL volumetric pipet to transfer 25.00 mL of the solution in the beaker labeled "Standard D" to the 50.00 mL volumetric flask. Add DI water to the mark, cap the flask, and thoroughly mix the solution by inverting the flask back and forth ten times. Pour this solution into the beaker labeled "Standard E."
14. **Clean Volumetric Pipet and Flask:** Rinse both the volumetric pipet and volumetric flask with DI water several times.

Measure Absorbance of Standard Solutions

The instructions in this section allow you to complete task 2 in Figure 13.1. Your laboratory instructor or teaching assistant will give you detailed instructions for using the UV/Vis spectrometer to carry out the steps in this section.

1. **Obtain Five Clean and Dry Cuvettes:** In the lab you will find a box with new plastic cuvettes. Bring five of these to your work area.
2. **Obtain Five New Pasteur Pipettes:** Find where the Pasteur pipettes are stored and bring five new ones to your work area.
3. **Fill Cuvettes with Standard Solutions:** Using a new Pasteur pipet for each solution, fill a cuvette with each of the standard solutions you have prepared: Standard A, Standard B, Standard C, Standard D, and Standard E.
4. **Take Cuvettes to Spectrophotometer:** Take the five cuvettes to a spectrophotometer.
5. **Collect Background Spectrum:** Fill a cuvette with DI water and collect a background spectrum.
6. **Record Absorption Spectrum of “Standard C” Solution:** Using the cuvette with Standard C in it, record an absorption spectrum.
7. **Set Spectrometer to Record Absorbance at λ_{max} :** One wavelength in the resulting spectrum will have the highest absorbance. Instruct the UV/Vis instrument to always report the absorbance at that particular wavelength.
8. **Record Absorbance at λ_{max} for “Standard C”:** Write down the absorbance of the solution labeled “Standard C” as reported by the UV/Vis at λ_{max} .
9. **Record Absorption Spectrum of “Standard A” Solution:** Using the cuvette with “Standard A” in it, record an absorption spectrum. Write down the absorbance value reported by the UV/Vis instrument at the previously determined λ_{max} .
10. **Record Absorption Spectrum of “Standard B” Solution:** Using the cuvette with “Standard B” in it, record an absorption spectrum. Write down the absorbance value reported by the UV/Vis instrument at the previously determined λ_{max} .
11. **Record Absorption Spectrum of “Standard D” Solution:** Using the cuvette with “Standard D” in it, record an absorption spectrum. Write down the absorbance value reported by the UV/Vis instrument at the previously determined λ_{max} .
12. **Record Absorption Spectrum of “Standard E” Solution:** Using the cuvette with “Standard E” in it, record an absorption spectrum. Write down the absorbance value reported by the UV/Vis instrument at the previously determined λ_{max} .
13. **Dump Cuvette Contents Into Waste Container:** Pour out the contents of the cuvettes into the waste containers.

► There will probably already be a cuvette near the spectrophotometer with DI water in it. Look for it.

► Yes, this is out of order, but there is good reason for doing this. Really, use Standard C first.

► Be sure to record in your laboratory notebook the wavelength used here.

► Remember that absorbance is a unitless number.

Prepare Solution of Unknown Salt

► Look for a bottle labeled "Cu Unknown Solution A" in your laboratory drawer. If you already have that, do not carry out the steps in this section.

► Without the identification number in your notebook, there may be no way to grade your results, which means no points can be granted.

► If you need to use a mortar and pestle, make sure they are clean and dry before using them.

⊕ Do not waste time making the mass exactly 3.75 g. Get close and record whatever mass you have.

► If some salt sticks to the weighing paper, you can use a squirt of DI water from your water bottle to force it off the paper and into the funnel.

► Be sure not to use too much water. If you fill the volumetric flask past the line you will have to start over.

► Do not rinse the volumetric flask with water and pour into the beaker. This will dilute the solution.

1. **Record Identification Number:** A copper salt sample will be at your bench in a corked test tube. The test tube will have a label on it with a number. This number is the identification number that allows your instructor to determine the true identity of your copper salt. Record this number in your laboratory notebook.
2. **Prepare Salt:** Inspect your unknown salt. If the salt appears in large clumps, you should attempt to grind the salt in a mortar and pestle before weighing it out. Otherwise, you will find it difficult to get the salt to go into the volumetric flask later.
3. **Mass Salt:** Mass out approximately 3.75 g of your copper salt on weighing paper. Knowing precisely how much salt you use is critical for this experiment, but the mass used does not have to be exactly 3.75 g.
4. **Transfer Salt to Conical Funnel:** Insert a conical funnel into a 50 mL volumetric flask. Transfer the salt to the funnel. Be sure all the salt is transferred. Leave none behind. Also, be very careful not to spill any.
5. **Rinse Salt Into Volumetric Flask:** Using your DI water bottle, begin to squirt DI water into the funnel to help force the salt into the volumetric flask. Continue this until all the salt is in the flask.
6. **Rinse Funnel and Remove:** Once the salt has been pushed out of the funnel into the flask, rinse the funnel one more time to be sure all the salt has been rinsed into the flask.
7. **Dissolve Salt in Water:** If you have not done so already, fill the volumetric flask to within 10 mL of the 50 mL mark. Swirl the flask for several minutes to dissolve the salt. Do not proceed to the next step until the salt completely dissolves.
8. **Fill Volumetric Flask To Line:** Using a Pasteur pipet or a clean eye dropper, carefully fill the volumetric flask to the 50 mL line with DI water.
9. **Cap and Mix:** Cap the flask or cork the flask and then invert it several times to be sure it is thoroughly mixed and uniform throughout.
10. **Transfer Solution to Clean and Dry Beaker:** Pour the solution into a clean and dry 100 mL beaker. Label the beaker "Cu Unknown Solution A."
11. **Clean Volumetric Flask:** Clean your volumetric flask.

Prepare Solutions of Unknown Concentration

The instructions in this section allow you to prepare the solutions necessary to complete task 4 in Figure 13.1.

1. **Obtain Three Clean and Dry Beakers:** Obtain three clean and dry beakers of size 150 mL or smaller. Line these beakers up on your work bench and place a single label on each. Label these beakers “Unknown B,” “Unknown C,” and “Unknown D.”
2. **Prepare Beaker Labeled “Unknown B”:** Using a 10.00 mL volumetric pipet, transfer 10.00 mL of “Cu Unknown Solution A” to a 50 mL volumetric flask. Dilute the solution to the 50.00 mL mark with DI water and mix thoroughly. Pour the solution into the beaker labeled “Unknown B.”
3. **Clean Volumetric Flask:** Rinse the volumetric flask with DI water several times.
4. **Clean Volumetric Pipet:** Rinse the volumetric pipet twice with 5 mL portions of the solution in the beaker labeled “Unknown B.”
5. **Prepare Beaker Labeled “Unknown C”:** Using a 10.00 mL volumetric pipet, transfer 10.00 mL of “Cu Unknown Solution B” to a 50 mL volumetric flask. Dilute the solution to the 50.00 mL mark with DI water and mix thoroughly. Pour the solution into the beaker labeled “Unknown C.”
6. **Clean Volumetric Flask:** Rinse the volumetric flask with DI water several times.
7. **Clean Volumetric Pipet:** Rinse the volumetric pipet twice with 5 mL portions of the solution in the beaker labeled “Unknown C.”
8. **Prepare Beaker Labeled “Unknown D”:** Using a 10.00 mL volumetric pipet, transfer 10.00 mL of “Cu Unknown Solution C” to a 50 mL volumetric flask. Dilute the solution to the 50.00 mL mark with DI water and mix thoroughly. Pour the solution into the beaker labeled “Unknown D.”

Measure Absorbance of Unknown Solutions

The instructions in this section allow you to complete task 4 in Figure 13.1. Your laboratory instructor or teaching assistant will give you detailed instructions for using the UV/Vis spectrometer to carry out the steps in this section.

1. **Obtain Four Clean and Dry Cuvettes:** In the lab you will find a box with new plastic cuvettes. Bring four of these to your work area.
2. **Obtain Four New Pasteur Pipettes:** Find where the Pasteur pipettes are stored and bring four new ones to your work area.

3. **Fill Cuvettes with Solutions of Unknown Concentration:** Using a new Pasteur pipet for each solution, fill a cuvette with each of the solutions of unknown concentration: Unknown A, Unknown B, Unknown C, and Unknown D.
4. **Take Cuvettes to Spectrophotometer:** Take the four cuvettes to a spectrophotometer.
5. **Collect Background Spectrum:** Fill a cuvette with DI water and collect a background spectrum.
6. **Set Spectrometer to Record Absorbance at λ_{max} :** Set the spectrophotometer to record absorbance at the wavelength of λ_{max} that was determined when recording the absorbance of the standard solutions.
7. **Record Absorption Spectrum of Solution “Unknown A”:** Using the cuvette with solution “Unknown A” in it, record an absorption spectrum. Write down the absorbance value reported by the UV/Vis instrument at the previously determined λ_{max} .
8. **Record Absorption Spectrum of Solution “Unknown B”:** Using the cuvette with solution “Unknown B” in it, record an absorption spectrum. Write down the absorbance value reported by the UV/Vis instrument at the previously determined λ_{max} .
9. **Record Absorption Spectrum of Solution “Unknown C”:** Using the cuvette with solution “Unknown C” in it, record an absorption spectrum. Write down the absorbance value reported by the UV/Vis instrument at the previously determined λ_{max} .
10. **Record Absorption Spectrum of Solution “Unknown D”:** Using the cuvette with solution “Unknown D” in it, record an absorption spectrum. Write down the absorbance value reported by the UV/Vis instrument at the previously determined λ_{max} .
11. **Dump Cuvette Contents Into Waste Container:** Pour out the contents of the cuvettes into the waste containers.

⌚ Before doing this, be sure that at least one of your absorbance readings falls between 1.0 and the smallest absorbance value recorded for the standard solutions. If not, see your instructor.

Save “Cu Unknown Solution A”

If you have *not* already completed the laboratory project titled “Gravimetric Determination of a Copper Salt’s Formula Mass,” you will need to save your remaining solution and label it “Cu Unknown Solution A.” Otherwise, you can discard it.

1. **Transfer “Cu Unknown Solution A” to Storage Bottle:** Pour the remaining “Cu Unknown Solution A” into a capped storage bottle that will be provided to you. Seal it tightly and label it. Place it in your laboratory drawer until next week.

► You should have about 30 mL of solution remaining.

13.4 Before Exiting Lab

- Thoroughly rinse and return all glassware to the place you originally found it.
- Dispose of plastic spectrophotometer cuvettes in the trash.
- Dispose of unneeded copper solutions in the waste bottle in the hood.
- Put your remaining Cu Unknown Solution A in the waste container in the hood.
- Check your lab notebook for page numbers on all pages.
- Check your lab notebook to ensure that you have recorded your unknown number.
- Update the table of contents in your notebook.
- Draw a line after all your experimental work and sign on that line.
- Have your instructor sign your notebook on the line you just drew below the experimental work.

13.5 Post-Lab Assignments

Prepare Standard Absorbance Curve

This part of the analysis allows you to complete task 3 in Figure 13.1.

1. Calculate the concentration of each of the standard solutions used (A through E) in units of mg Cu²⁺/mL solution.
2. Plot a graph of standard solution absorbance at λ_{max} versus concentration of Cu²⁺ (in mg Cu²⁺/mL solution).
3. Determine the best-fit line (linear least squares line) through these data points and add that to the graph.
4. Add the equation for the best-fit line and the R^2 value to the graph.
5. Tape one short edge of this plot onto a blank page in your laboratory notebook and fold in half. Label it on the outside so that it is clear what is inside.

► Absorbance goes on the *y*-axis, and concentration goes on the *x*-axis.

► See Chapter 9 and your lab notebook for information about fitting data to a straight line. See the course web site for details about how to do this in Microsoft Excel.

Determine Concentration of Unknown Solution A

1. Using the standard absorbance curve you have just produced, select one absorbance reading from the set of solutions of unknown concentration that lies along the line you plotted on the standard curve.
2. Using this absorbance reading, use the standard absorbance curve to determine the concentration of Cu²⁺ in that solution in units of mg Cu²⁺/mL solution.

► There's nothing to be done here except to select the absorbance reading to use in the next step.

3. Calculate the concentration of Cu^{2+} (in g Cu^{2+}/mL solution) in the original unknown solution (Cu Unknown Solution A).
4. If you have several absorbance readings from the unknown solutions that lie along the standard absorbance curve, use them to determine the concentration of copper ions in the Cu Unknown Solution A as well.
5. Calculate the average concentration of copper ions in the Cu Unknown Solution A using all usable absorbance measurements.

► You will use this value in all subsequent calculations.

Calculate Formula Mass of Unknown Copper Salt

All calculations in this section should be done using the average concentration of copper ions in the Cu Unknown Solution A.

1. Using the average concentration of copper ions in Cu Unknown Solution A, calculate the total mass (in units of grams) of Cu^{2+} in the entire original Cu Unknown Solution A. Refer to your laboratory notebook for the original total volume of this solution.
2. Calculate the percent Cu^{2+} in the original copper salt of unknown identity. Refer to your laboratory notebook for the total mass of unknown copper salt originally used.
3. Calculate the formula mass of the original copper salt, assuming only one Cu^{2+} per formula unit.

Chapter 14

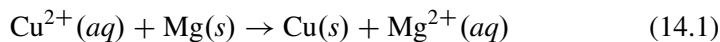
Gravimetric Determination of a Copper Salt's Formula Mass

Gravimetric analysis is used to determine the percentage of copper by mass in a copper salt of unknown identity. The formula mass of the copper salt is determined from this information.

14.1 Introduction

Gravimetric analysis in this experiment relies on precipitating the copper in a salt compound of unknown identity then massing the precipitate. This is a chemical method because it chemically alters the copper ions in solution.

To carry out the gravimetric analysis you will first dissolve the salt in water and then use an oxidation-reduction reaction to convert the copper ions to elemental copper. The elemental copper is not soluble in water and therefore precipitates out of solution. The reaction that takes place is



The $\text{Cu}^{2+}(aq)$ is blue in solution, but $\text{Mg}^{2+}(aq)$ is colorless. As the Cu^{2+} is reduced to $\text{Cu}(s)$ and Mg is oxidized to Mg^{2+} , the solution containing the copper salt will slowly change from blue to colorless.

The solid elemental copper will be at the bottom of the reaction beaker when the reaction is complete, and it can then be collected via gravity filtration. All the copper that is collected by this technique was originally in the copper salt. Thus, the mass of the collected elemental copper is a direct measure of the mass of copper in the original copper salt.

The mass percent of copper in the original salt can easily be calculated as

$$\frac{\text{Mass Elemental Copper}}{\text{Mass Original Salt}} \times 100 \quad (14.2)$$

**Figure 14.1**

Broken glass container.

- The elemental copper is no different than copper wire or a pre-1982 penny. It is therefore safe to dispose of it like normal trash.

14.2 Safety Considerations

Chemical Hazards

1. **Hydrochloric Acid:** The HCl you will use during gravimetric analysis is 6 M. This is concentrated and should be treated with respect. Avoid getting it on your skin. If you do get it on yourself, wash it off immediately.

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

1. **Elemental Copper:** The elemental copper you produce in this experiment should be disposed of in a normal waste basket when you are finished.
2. **Other Liquid Wastes:** All other liquid wastes generated in this lab are dilute and can be dumped down the drain with plenty of water.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 14.1. Do not use the normal waste baskets for broken glass.

14.3 Experimental Procedure

Prepare Solution of Unknown Salt

You only need to carry out the steps in this section if you have not already prepared a solution of your unknown salt in a previous lab period. If you have already completed the laboratory project entitled “Spectrophotometric Determination of a Copper Salt’s Formula Mass,” you should not have to carry out these steps.

- Look for a bottle labeled “Cu Unknown Solution A” in your laboratory drawer. If you already have that, do not carry out the steps in this section.

- Without the identification number in your notebook, there may be no way to grade your results, which means no points can be granted.

- If you need to use a mortar and pestle, make sure they are clean and dry before using them.

1. **Record Identification Number:** A copper salt sample will be at your bench in a corked test tube. The test tube will have a label on it with a number. This number is the identification number that allows your instructor to determine the true identity of your copper salt. Record this number in your laboratory notebook.

2. **Prepare Salt:** Inspect your unknown salt. If the salt appears in large clumps, you should attempt to grind the salt in a mortar and pestle before weighing it out. Otherwise, you will find it difficult to get the salt to go into the volumetric flask later.

3. **Mass Salt:** Mass out approximately 3.75 g of your copper salt on weighing paper. Knowing precisely how much salt you use is critical for this experiment, but the mass used does not have to be exactly 3.75 g.

⌚ Do not waste time making the mass exactly 3.75 g. Get close and record whatever mass you have.
4. **Transfer Salt to Conical Funnel:** Insert a conical funnel into a 50 mL volumetric flask. Transfer the salt to the funnel. Be sure all the salt is transferred. Leave none behind. Also, be very careful not to spill any.

► If some salt sticks to the weighing paper, you can use a squirt of DI water from your water bottle to force it off the paper and into the funnel.
5. **Rinse Salt Into Volumetric Flask:** Using your DI water bottle, begin to squirt DI water into the funnel to help force the salt into the volumetric flask. Continue this until all the salt is in the flask.
6. **Rinse Funnel and Remove:** Once the salt has been pushed out of the funnel into the flask, rinse the funnel one more time to be sure all the salt has been rinsed into the flask.

► Be sure not to use too much water. If you fill the volumetric flask past the line you will have to start over.
7. **Dissolve Salt in Water:** If you have not done so already, fill the volumetric flask to within 10 mL of the 50 mL mark. Swirl the flask for several minutes to dissolve the salt. Do not proceed to the next step until the salt completely dissolves.
8. **Fill Volumetric Flask To Line:** Using a Pasteur pipet or a clean eye dropper, carefully fill the volumetric flask to the 50 mL line with DI water.
9. **Cap and Mix:** Cap the flask or cork the flask and then invert it several times to be sure it is thoroughly mixed and uniform throughout.
10. **Transfer Solution to Clean and Dry Beaker:** Pour the solution into a clean and dry 100 mL beaker. Label the beaker "Cu Unknown Solution A."

► Do not rinse the volumetric flask with water and pour into the beaker. This will dilute the solution.
11. **Clean Volumetric Flask:** Clean your volumetric flask and return it to your drawer. You will not need it again this lab period.

Prepare Reaction Beakers

1. **Pipet "Cu Unknown Solution A" to Beakers:** Pipet 10.00 mL of Cu Unknown Solution A into a 100 mL or 150 mL beaker. Label this beaker "Reaction 1." Pipet another 10.00 mL of Cu Unknown Solution A into a different 100 mL or 150 mL beaker. Label this beaker "Reaction 2." Add about 20-30 mL of distilled water to each beaker.

► This solution can either be prepared following the procedure in the previous section or by retrieving the bottle labeled "Cu Unknown Solution A" from your lab drawer.
2. **Add Magnetic Stir Bar:** Obtain a magnetic stir bar for each beaker and drop one into each beaker.
3. **Place Beakers Onto Stir Plate:** Place each beaker onto its own stirring hot plate. Make sure the heating element is turned off on both stirring hot plates. We only want to stir.
4. **Begin Stirring Solutions:** Turn on the stirring portion of the stirring hot plate so that the solutions are stirred at a low but steady rate.

5. **Add Magnesium Turnings:** Add 0.15 g of magnesium turnings to each beaker.

Monitor Reactions

For each reaction mixture, you need to do the following.

1. **Make Sure Stirring Continues:** Make sure the stir bar continues to stir the reaction mixture continuously. If the stirring stops, adjust the position of the beaker on the stirring hot plate or adjust the knob controlling the rate of stirring until stirring is returned to normal.
2. **Add HCl If Needed:** If the solution turns cloudy white or yellow-brown, add 6 M HCl drop-wise until the solution clears.
3. **Scrape Coating Off Mg If Needed:** Observe the magnesium turnings in the solution. If they become completely coated with a yellowish-brown material, use a glass stirring rod to scrape or poke the debris off as well as you can.
4. **Add Mg As Needed Until Solution Is Clear:** If nearly all the Mg dissolves and the solution is still blue, add an additional 0.15 g magnesium turnings.
5. **Dissolve Remaining Magnesium:** When the reaction mixture is colorless, all the copper has precipitated and the reaction is finished. If Mg turnings remain in solution, you must add 6 M HCl to the solution to dissolve the excess magnesium. You will know that no magnesium remains in solution when you see no bubbles being evolved from the reaction mixture.

Prepare Watch Glass and Filter Paper

You can carry out the steps in this section while you are waiting for the copper to precipitate in the reaction beakers. This will save time.

1. **Obtain Watch Glasses:** Retrieve two watch glasses from your laboratory drawer. Make sure they are clean and dry.
2. **Label Watch Glasses:** Obtain two adhesive labels and write “Reaction 1” on one of them and “Reaction 2” on the other in pencil. Attach one to each watch glass.
3. **Place Filter Paper on Watch Glass:** Obtain two pieces of filter paper and place one on the watch glass labeled “Reaction 1” and the other on the watch glass labeled “Reaction 2.”
4. **Weigh Watch Glass and Filter Paper:** Weigh the watch glass and filter paper combination for the watch glass labeled “Reaction 1.” Do the same for the watch glass labeled “Reaction 2.”

► The bubbles are hydrogen gas.

► Do not use pen or wax pencil to write on the labels. You need to use normal pencil, which will not melt when heated.

► Do not write on the filter paper.

► Do not mix up the filter papers. They must remain with the watch glass they were weighed with.

Suction Filter Elemental Copper

1. **Set Up Suction Filtration Apparatus:** Set up the suction filtration apparatus as described by your instructor.
2. **Filter “Reaction 1” Product:** Place the filter paper from the watch glass labeled “Reaction 1” into the bottom of the Buchner funnel. Pour the reaction mixture (liquid and copper precipitate) out of the beaker labeled “Reaction 1” and onto the filter paper in the suction filtration apparatus.
3. **Rinse “Reaction 1” Beaker:** Rinse the beaker labeled “Reaction 1” several times with DI water from your DI water bottle. Pour each rinse into the filtration apparatus. Be sure to remove all copper from the beaker.
4. **Rinse Copper with Water:** Rinse the copper in the Buchner funnel several times with 5-10 mL portions of DI water from your water bottle.
5. **Rinse Copper with Acetone:** After a few minutes of suction filtration, rinse the copper in the filtration apparatus with two 5-10 mL portions of acetone.
6. **Remove Filter Paper from filtration Apparatus:** Carefully remove the filter paper from the suction filtration apparatus. You may have to work your spatula under the filter paper to lift the filter paper out. Place the filter paper and copper back onto the watch glass labeled “Reaction 1.”
7. **Allow Product to Dry in Air:** Place the watch glass and product for “Reaction 1” under the hood at your bench and allow it to dry while you filter the product from the beaker labeled “Reaction 2.”
8. **Filter Product from Beaker Labeled “Reaction 2”:** Repeat steps 2 to 7 for the beaker and watch glass labeled “Reaction 2.”

④ You can do this step while you are waiting for copper to precipitate.

► This helps to remove water present.

Dry and Mass Product

1. **Weigh Watch Glass Labeled “Reaction 1”:** Weigh the watch glass labeled “Reaction 1” and its contents after the copper on it has dried in the hood for 10 minutes.
2. **Dry Product in Oven:** Place the watch glass labeled “Reaction 1” and its contents into an oven at 110°C for 10 minutes.
3. **Cool Watch Glass Labeled “Reaction 1”:** After 10 minutes in the oven, remove the watch glass labeled “Reaction 1” and allow it to cool to room temperature.
4. **Weigh Watch Glass Labeled “Reaction 1”:** Weigh the watch glass labeled “Reaction 1” with its contents.
5. **Repeat Until Mass Remains The Same:** Repeat steps 3 to 4 until you no longer observe a change in mass.

6. **Repeat Process for Watch Glass Labeled “Reaction 2”:** Repeat steps 1 to 5 for the watch glass labeled “Reaction 2.”

Save “Cu Unknown Solution A”

If you have *not* already completed the laboratory project titled “Spectrophotometric Determination of a Copper Salt’s Formula Mass,” you will need to save your remaining solution and label it “Cu Unknown Solution A.” Otherwise, you can discard it.

► You should have about 30 mL of solution remaining.

1. **Transfer “Cu Unknown Solution A” to Storage Bottle:** Pour the remaining “Cu Unknown Solution A” into a capped storage bottle that will be provided to you. Seal it tightly and label it. Place it in your laboratory drawer until next week.

14.4 Before Exiting Lab

- Place the solid copper product in the normal trash can. This is not a special chemical waste. This is just like throwing out copper wire or a penny.
- Return the test tube containing the unused portion of your unknown to the box in the hood.
- Make sure all equipment that does not belong in your personal lab drawer has been returned to its designated spot.
- Check your lab notebook for page numbers on all pages.
- Update the table of contents in your notebook.
- Draw a line in your notebook at the end of your experimental work. Sign on that line.
- Have your instructor sign your notebook on the line.

14.5 Post-Lab Assignments

Calculations

All calculations should appear in your laboratory notebook. If you make an error, just cross through the error with a single line and then move on.

1. Calculate the total mass of copper present in each reaction beaker (Reaction 1 and Reaction 2).
2. Calculate the total mass of copper in the entire original 50 mL of “Cu Unknown Solution A” using data from each reaction beaker independently.

3. Calculate the percent copper in the original copper salt you weighed out in step 3 on page 87. Use data from each reaction beaker independently.
4. Calculate the formula mass of the original copper salt, assuming only one Cu^{2+} per formula unit. Do this using data from each reaction beaker independently.

► Be sure to use proper units and significant figures.

Chapter 15

Survey of Chemical Reactions

This experiment provides hands-on experience with five classes of chemical reactions: metathesis, acid-base, redox displacement, redox decomposition, and redox combination. After you have finished this lab you will have a better feel for the types of transformations matter can undergo and have a better ability to write chemical reactions that describe what you observe in the laboratory.

15.1 Introduction

One of the objectives of General Chemistry is to learn to predict chemical reactions and write chemical equations. No other aspect of chemistry has such overriding importance in all branches of the science, primarily because virtually all chemical problems have their basis in some type of chemical transformation.

Chemical reactions are all around us: the combustion of gasoline in your car, the neutralization of excess stomach acid with an antacid, and the fermentation of grape juice. Our very existence is dependent upon countless chemical reactions occurring in our bodies every day. Anyone working in technical areas such as engineering, medicine, geology, biology, physics, or chemistry can benefit from a basic knowledge of chemical reactions.

Even if one does not work in a technical area, the prevalence of chemicals in modern society means that we all can become better citizens with some awareness as to the reaction properties of these chemicals.

This experiment is designed to allow you to experience a wide variety of reactions. We will divide the experiment into general reaction types and ask that you observe the changes that occur within each example and, in some cases, verify the nature of the products by means of simple chemical tests.

Reaction Classification

There are a variety of ways of classifying chemical reactions, most of which are equally acceptable. The classification used here will enable you to quickly acquire the ability to predict and write chemical reactions. The classifications used are:

1. Metathesis Reactions
2. Acid-Base Reactions
3. Redox: Displacement Reactions
4. Redox: Decomposition Reactions
5. Redox: Combination Reactions

We will deal with all five in this experiment.

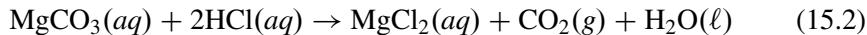
Metathesis Reactions

A metathesis reaction is characterized by two soluble ionic substances exchanging ion partners. The result of such an exchange is often the formation of a precipitate, the evolution of a gas, or the formation of a weak electrolyte. For example, the reaction between barium chloride and sodium sulfate is a metathesis reaction.



Both barium chloride and sodium sulfate are soluble in water; however, barium sulfate is not. Thus, the precipitate $\text{BaSO}_4(s)$ forms in this reaction.

Another example of a metathesis reaction is that between magnesium carbonate and hydrochloric acid in which a gas (carbon dioxide) and a weak electrolyte are formed.



In reaction 15.2 some students are confused about where the carbon dioxide came from on the product side. Because of this, it can sometimes be difficult to see how reaction 15.2 is a metathesis reaction.

You have to keep in mind that when $\text{CO}_3^{2-}(aq)$ is mixed with excess acid (HCl), $\text{H}_2\text{CO}_3(aq)$ will form. However, $\text{H}_2\text{CO}_3(aq)$ is unstable and will almost immediately decompose into carbon dioxide and water. That is where the carbon dioxide came from in reaction 15.2.

Knowledge of solubility rules (from your text and lecture materials) is essential to the predictions of the course of these reactions.

Acid-Base Reactions

Acid-base reactions are a special type of metathesis reaction, but a very important one. For our purposes here, we shall consider acids to be substances donating protons and bases as substances donating hydroxide ions. The reaction between an acid and a base, termed a neutralization reaction, produces water and a salt (an ionic compound produced in an acid-base reaction).

For example, consider the reaction between potassium hydroxide and nitric acid shown in reaction 15.3.



Here, you can see that the base potassium hydroxide donates the hydroxide ion (OH^-) while the acid donates a proton (H^+) to yield water and the potassium nitrate salt.

Redox Displacement Reactions

A displacement reaction occurs when an atom in its elemental state displaces an ion from a salt. For example, a metal atom can react with the salt of another metal to give the salt of the first metal and the second metal in a free elemental form. An example of this is the reaction between metallic sodium and the salt zinc chloride.



Sodium started as a pure element with an oxidation state of 0, but it ended up with an oxidation state of +1 in a salt (sodium chloride). Zinc, which started out in the salt with an oxidation number of +2 ended up as a free metal with oxidation number 0. Zinc has been displaced from the salt by the metal sodium.

Keep in mind that this is a redox process with the species losing electrons being oxidized and the species gaining electrons being reduced. In the above example each of the two sodium atoms lost an electron and was oxidized; a Zn^{2+} ion gained two electrons and was reduced.

Because this is a redox process, it depends on the propensity of an atom of one element to give up an electron to an ion (or atom) of a second element. That is, some elements are more able than other elements to give up electrons. This means that just mixing an element with a salt does not guarantee that a redox displacement reaction will occur. The two elements must differ in their ability to give up electrons.

As an example of a redox displacement that will not occur, consider the reaction between iron metal and magnesium chloride.

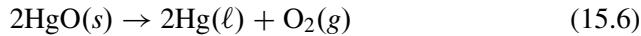


There is no reaction between these species because iron is just not able to give up its electrons to a Mg^{2+} ion to produce magnesium atoms and an Fe^{2+} ion. That is to say that Fe atoms have less ability to give up electrons than do Mg atoms.

► The activity series of metals may help you predict the outcome of redox displacement reactions. Search for this in your textbook.

Redox Decomposition Reactions

Many compounds, when heated strongly, will break down (decompose) to give elements or simpler compounds as products. Frequently, a gas is generated in a decomposition. For example,

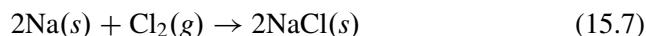


is a decomposition reaction. Since the oxidation numbers of the elements involved in this reaction have changed from reactants to products, this is a redox reaction.

Redox Combination Reactions

When two or more reactants come together to form a single compound, the reaction is called a combination reaction. If one or more of the reactants is a free element, the reaction must be a redox reaction.

If a metal and a nonmetal react in a combination reaction, the metal invariably is oxidized to form a positive ion, and the nonmetal undergoes reduction to an anionic species. For example,



are both redox combination reactions in which a metal and nonmetal combine to produce a single compound. In both cases, the metal has a positive oxidation state and was therefore oxidized in the reaction.

Combination reactions involving oxygen are among the most important. Metal oxides are formed by the direct combinations of metals with oxygen. It is a property of these resulting compounds that they form basic aqueous solutions. For example, if sodium metal reacts with oxygen, sodium oxide ($\text{Na}_2\text{O}(s)$) is formed. If this solid is then placed in water, the reaction



will take place, yielding excess hydroxide and a basic solution. This provides a way for you to test if a metal oxide has been formed in a combination reaction.

15.2 Safety Considerations

Chemical Hazards

- Silver Nitrate:** You will use silver nitrate (AgNO_3) in this experiment. If you get this on your hands it will leave a brown or black stain that will remain for several days. If you wish, use rubber gloves when handling the silver nitrate.
- Acids In Test Tubes:** When you are asked to shake a test tube containing an acid, make sure you cover the tube with a cork and not your finger or thumb.

Experimental Precautions

In this lab you will heat metal and a test tube in a flame. In all cases, this work should be performed in a hood. When heating test tubes, always point them away from you and anybody else in the room.

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

You will generate waste in this lab that cannot be thrown down the drains or into the trash can. Please adhere to all disposal policies. When in doubt, ask your lab instructor.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 15.1. Do not use the normal waste baskets for broken glass.



Figure 15.1
Broken glass container.

15.3 Experimental Procedure

In all of the following experimental steps, you are to record your observations as clearly as possible. Ultimately, you will have to explain your observations with a balanced reaction. Even though you are not asked to produce a balanced reaction until after all the experimental steps are complete, you might think about what reaction is relevant as you carry out the experimental steps.

Reaction Set 1

1. **Mix Copper Wire and Silver Nitrate:** Clean a piece of copper wire with steel wool. Place the copper wire in a test tube and add 5 mL of $\text{AgNO}_3(aq)$ solution. Allow the test tube to stand 30 minutes. Observe the results after this 30 minute period.



Do not get silver nitrate on your hands. It leaves ugly brown stains that will not come off for days. Use gloves if desired.

Reaction Set 2

1. **Mix Copper Wire and Nickel Sulfate:** Clean a piece of copper wire with steel wool. Place the copper wire in a test tube and add 5 mL of a $\text{NiSO}_4(aq)$ solution. Allow the test tube to stand for 30 minutes. Observe the results after this 30 minutes period.

Reaction Set 3

1. **Mix Barium Chloride with Sulfuric Acid:** Dissolve a spatula-full of BaCl_2 in about 5 mL of distilled H_2O in a test tube. Add about 2 mL of 1 M H_2SO_4 to the solution.

Reaction Set 4

1. **Add Nickel Nitrate to Water in Test Tube:** In a test tube, dissolve a spatula-full of $\text{Ni}(\text{NO}_3)_2$ in 5 mL of DI water.
2. **Add Sodium Carbonate to Water in Test Tube:** In a separate test tube, add and dissolve a spatula-full of Na_2CO_3 in 5 mL of water.
3. **Mix The Two Solutions:** Mix the aqueous nickel nitrate and aqueous sodium carbonate solutions by dumping one into the other.
4. **Add Hydrochloric Acid To Mixture:** Slowly add 6 M HCl to the mixture of aqueous nickel nitrate and sodium carbonate until the reaction ceases.

Reaction Set 5

Make a table in your laboratory notebook to record the observations for this reaction set in tabular form.

- Long range pH paper is not the same as litmus paper.
- A pH less than 7 indicates an acidic solution; a pH greater than 7 indicates a basic solution.

1. **Test pH of 1 M HCl:** Put 5mL of 1 M HCl into a clean and dry beaker. Determine the pH of the solution with long range pH paper.
2. **Add Sodium Hydroxide and Test pH:** Add 1 mL of 1 M NaOH to the HCl solution and mix thoroughly. Determine the pH of the mixture with long range pH paper.
3. **Repeat Step 2 9 Times:** Repeat the procedure in step 2 9 more times until you have added a total of 10 mL NaOH.

Reaction Set 6

1. **Mix Copper Sulfate Solution and Sodium Hydroxide:** Put 5 mL of $\text{CuSO}_4(aq)$ solution in a test tube. Add several drops of a 1 M NaOH solution to the same test tube.
2. **Add Sulfuric Acid:** To this mixture, add 1 M $\text{H}_2\text{SO}_4(aq)$ until a homogeneous solution results.

Reaction Set 7

1. **Mix Zinc and Hydrochloric Acid:** Place a small amount of zinc metal in a test tube. Add 5 mL of 6 M HCl solution.
2. **Test for Presence of Hydrogen:** After a reaction begins in the test tube with the zinc and HCl, bring a lighted wooden splint to the mouth of the test tube. If you hear a “pop” sound when you bring the lighted splint to the test tube, hydrogen was present.

Reaction Set 8

1. **Mix Copper and Hydrochloric Acid:** Put a piece of copper wire in a test tube. Add 5 mL of 6 M HCl.

Reaction Set 9

1. **Place Potassium Chlorate in Test Tube:** Place a couple of spatulas full of $\text{KClO}_3(s)$ in a test tube. Attach a test tube holder to the test tube so that you don't have to hold the test tube directly.
2. **Prepare Wooden Splint:** Light a wooden splint and have it ready as you carry out the next step.
3. **Heat Test Tube:** Heat the test tube with potassium chlorate in a flame until the solid melts and a blanket of gas rises to the top of the test tube.
4. **Bring Glowing Splint to Test Tube Mouth:** Stop heating the test tube and blow out the burning wooden splint. Immediately place the glowing splint into the middle of the test tube.
5. **Add Water and Silver Nitrate to Test Tube:** After the test tube has cooled, add 5 mL of DI water to dissolve the residue. Then add several drops of $\text{AgNO}_3(aq)$ solution.

► Working in pairs will be particularly effective here. One of you can heat the test tube while the other prepares the wooden splint.



Heat the test tube in a hood with the tube opening pointing away from people.

► If oxygen is present, the splint will glow more brightly.

Reaction Set 10

1. **Burn Magnesium Metal in Flame:** With a pair of tongs, grab a piece of magnesium metal. Ignite the metal in a flame.



Exercise extreme caution when burning magnesium. The flame is bright and hot. Do all work in a hood.

15.4 Before Exiting Lab

Before leaving lab for the day, go down this checklist to make sure you have done everything on it.

- Place all liquid waste into the waste container marked "liquid waste" located in the hood in the back of the room.
- Return all reagent bottles to the tray at the center of your lab bench and put all your laboratory equipment back into your drawer.
- Scrupulously clean your laboratory bench area.
- Check your lab notebook for page numbers on all pages.
- Update the table of contents in your notebook.
- Draw a line at the end of your experimental work and sign on that line.
- Have your instructor sign on the line.

15.5 Post-Lab Assignments

Activities and Questions

Respond to these questions and activities in your laboratory notebook after all observations have been recorded. Answers to questions and responses to activities should not be mixed in with calculations, procedures, or observations.

► Your reactions must be consistent with your observations. Do not write reactions based on what you think *should* have been observed. Write them based on what actually was observed.

1. For each reaction set, write all the balanced reactions necessary to explain what was observed. Your reactions must be balanced, have proper phase indications (aq, s, g), and must use standard notation for chemical element symbols.
2. For each reaction in each reaction set, classify the reaction as metathesis, acid-base, redox displacement, redox decomposition, or redox combination.

Chapter 16

What Is the Heat of Formation of MgO?

16.1 Introduction

Chemical reactions can either absorb energy when they take place (endothermic reactions) or release energy (exothermic reactions). The magnitude of this energy change is determined by the chemical participants in the reaction and the quantity of product formed.

The energy absorbed or evolved by a chemical reaction as heat when carried out at constant pressure is called the enthalpy of reaction and is given the symbol ΔH . Sometimes it is symbolized by ΔH_{rxn} to emphasize that it represents an enthalpy change for a reaction. ΔH is often expressed in units of kJ/mole, where the “mole” refers to the amount of a specific reactant or product. To make sense of ΔH_{rxn} , the reaction must be specified.

► Enthalpy of reaction is sometimes referred to as heat of reaction.

In this experiment, you will measure the enthalpy changes accompanying several exothermic reactions utilizing a simple calorimeter. This calorimeter consists of an insulated vessel, a thermometer, and a lid. This constitutes an open system because the calorimeter is not truly isolated from its surroundings. Matter and energy can therefore be transferred between the system and the surroundings. A styrofoam cup will be used as the insulated vessel in this experiment to help retain the heat. The energy given off by any reaction carried out in the calorimeter is absorbed by both the calorimeter and the solvent (water). This causes an increase in the temperature of the calorimeter and solvent that can be measured. The heat, q , that is absorbed by the calorimeter and solvent is calculated from the equation

$$q_{\text{calorimeter}} = C\Delta T \quad (16.1)$$

where C is the heat capacity of the calorimeter and solvent, and ΔT is the change in temperature of the water (the solvent) in the calorimeter. Heat capacity is defined as the amount of energy required to raise the temperature of an object by 1°C . In this experiment, the vessel and the amount of solvent remain constant, so C is a constant as long as you use the same calorimeter throughout the experiment.

Enthalpy is an extensive quantity. As a consequence, the amount of heat generated by the reaction is given by

$$q_{\text{reaction}} = n \Delta H \quad (16.2)$$

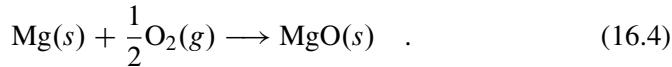
where n is the number of moles of a specific reactant or product and ΔH is the enthalpy change of the reaction in kJ/mol.

Since the energy of the universe is conserved in any process, the total energy change of the system (the reaction) and surroundings (calorimeter and solvent) is equal to zero. Equations 16.1 and 16.2 can be combined with the conservation of energy to give

$$q_{\text{calorimeter}} + q_{\text{reaction}} = C \Delta T + n \Delta H = 0 \quad (16.3)$$

From Equation 16.3 you can derive an expression that will give you C as a function of the enthalpy change for a reaction. This is what you will need to do when you calibrate the calorimeter (determine C). You can also rearrange this equation to give the enthalpy change as a function of the temperature change. This is what you will need to do when determining the unknown heats of reaction.

As you may recall, a heat of formation (ΔH_f) is a specific type of enthalpy change. It is the enthalpy change in a reaction that forms one mole of a species from the elements in their standard states. For MgO, the balanced equation for this reaction is



It would be very difficult to measure the enthalpy change for this reaction directly. It can be determined by indirect methods, however.

Hess's Law tells us that we can obtain the enthalpy change for any reaction by measuring and adding the enthalpy changes for any series of reactions that add up to give the reaction we are interested in. This is what we will do in this experiment.

The formation reaction for solid MgO can be obtained by adding the reactions corresponding to the formation of water, the reaction of solid Mg with HCl, and the reaction of solid MgO with HCl. The details of doing this will not be spelled out for you here. Instead, you will be expected to write and add these equations on your own.

16.2 Safety Considerations

Chemical Hazards

You will work with acids in this lab. As always, if you spill acid on your skin be sure to wash it off immediately with plenty of water.

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

All waste containing magnesium must be poured into the appropriate waste container. Waste that does not contain magnesium can be poured down the drain with plenty of water.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 16.1. Do not use the normal waste baskets for broken glass.



Figure 16.1
Broken glass container.

16.3 Experimental Procedure

Calibrate the Calorimeter

- Obtain Cups and Lids:** Select two styrofoam cups, and place one inside the other. Select a tight-fitting lid, and place it on the top cup. This is now your calorimeter.
- Record NaOH and HCl Concentrations:** On the tray of reagents you should find a bottle of NaOH and a bottle of HCl that are both approximately 1.0 M. Record the exact concentration of both solutions in your notebook.
- Clean Graduated Cylinder:** Rinse a 50 mL graduated cylinder with deionized water several times and then rinse it twice with about 3 mL of the 1.0 M NaOH solution, being sure to roll the NaOH over the entire inside surface of the cylinder. Discard the rinses.
- Add NaOH to Calorimeter:** Using a graduated cylinder, transfer 50.0 mL of the 1.0 M NaOH solution into the calorimeter. Measure the temperature of the NaOH solution using a thermometer.
- Remove and Clean Thermometer:** Remove the thermometer from the calorimeter and rinse the thermometer with deionized water. The DI water rinse should *not* go into the calorimeter.
- Clean Graduated Cylinder:** Rinse the graduated cylinder with deionized water several times and then rinse it twice with about 3 mL of the 1.0 M HCl, being sure to roll the HCl over the entire inside surface of the cylinder. Discard the rinses down the sink.
- Prepare and Measure Temperature of HCl Solution:** Measure 50.0 mL of the 1.0 M HCl into the graduated cylinder. Measure the temperature of the HCl solution in the graduated cylinder.
- Add HCl to NaOH Solution:** Add the HCl solution quickly into the NaOH solution in the calorimeter and start the timer. Replace the lid on the calorimeter with the thermometer in place. Immediately begin collecting and recording

► Be sure to record the temperature of the solution and all remaining temperatures to one decimal place.

► Be careful not to tear, rip, puncture, or otherwise mutilate your calorimeter from this point forward. If you do, you can repeat steps 1 through 8 above on a new calorimeter.

temperature readings at 30-second intervals for 7 minutes. Swirl the calorimeter to mix the reactants well with the thermometer and lid in place.

9. **Clean Calorimeter:** When data collection is complete, pour the contents of the calorimeter down the drain and rinse the calorimeter with distilled water. Dry the calorimeter as completely as possible.

React Mg with HCl

1. **Add HCl to Calorimeter:** Using a clean 50 mL graduated cylinder, add 100.0 mL of 1.0 M HCl to the empty calorimeter.
2. **Weigh Out Magnesium:** Weigh out a sample of magnesium about 0.15 g in mass on the electronic balance.
3. **Record Temperature of HCl:** Record the initial temperature (T_{initial}) of the 1.0 M HCl in the calorimeter. Be sure to rinse your thermometer after taking the temperature reading.
4. **Add Magnesium to HCl:** Quickly add the magnesium to the calorimeter and start the timer. Replace the thermometer and lid and begin swirling the reaction mixture. Immediately record the temperature. Record the temperature at one-minute intervals until a definite linear decrease in temperature is noted.
5. **Clean Calorimeter:** When data collection is completed, pour the contents of the calorimeter into the appropriate waste container. Rinse the calorimeter with distilled water and dry as completely as possible. The rinses can go down the drain.

► About 7 or 8 points during the definite temperature decrease are necessary to make an extrapolation.

React MgO with HCl

1. **Add HCl to Graduated Cylinders:** Add 50.0 mL of 1.0 M HCl to each of two clean 50 mL graduated cylinders. Do not pour this into the calorimeter yet.
2. **Add MgO to Calorimeter:** On an electronic balance, transfer approximately 1.6 g of MgO to a weighing boat. Determine the mass of the MgO and the weighing boat on the balance and record the data. Transfer the MgO to the dry calorimeter.
3. **Determine Mass Of Weighing Boat:** Record the mass of the weighing boat after the transfer.
4. **Record Temperature of HCl:** Record the initial temperature (T_{initial}) of the 1.0 M HCl solution in the graduated cylinders. If you have allowed them to stand for a few minutes, they should both be at the same temperature and thus measuring the temperature in one is sufficient.

5. **Add HCl to Calorimeter:** Add the 100.0 mL of 1.0 M HCl to the calorimeter containing the MgO and start the timer. Replace the lid and insert the thermometer. Begin swirling the mixture and immediately record the temperature. Record the temperature at one-minute intervals in the same manner described above in the reaction of Mg with HCl.
6. **Be Sure to Swirl:** In this reaction all the MgO should react since HCl is used in excess. However, if the solid MgO is allowed to sit on the bottom or sides of the cup it will not dissolve and hence it will not react. Make sure it dissolves by constantly and gently swirling and/or stirring the solution during the reaction process.
7. **Check That All MgO Has Dissolved:** Before discarding this solution, check to see that all of the MgO has reacted. If solid MgO remains, the results from this portion of the experiment are not accurate. If any solid is present, this portion of the experiment must be repeated.
8. **Clean Calorimeter:** When data collection is completed, pour the contents of the calorimeter into the waste container at the front of the lab. Rinse the calorimeter with distilled water and dry as completely as possible. The rinses can be poured down the drain.

16.4 Before Exiting Lab

- Check your lab notebook for page numbers on all pages.
- Update the table of contents in your notebook.
- Draw a line at the end of your experimental work for the day. Sign your notebook at the line.
- Have your instructor sign your lab notebook before you leave the lab. This helps verify where you stopped lab work for the week.

16.5 Post-Lab Assignments

Calorimeter Calibration

1. The initial temperature, T_{initial} , will be defined as the average temperature of the two solutions that were mixed for the calibration experiment. Calculate this value and record it in your notebook.
2. Using graph paper that has been provided, make a plot of temperature versus time for your calibration data. Temperature should go on the y -axis, and time should go on the x -axis.
3. This graph should show a region where the temperature decreases linearly with time. Using a ruler, draw a line extrapolating the linear portion of the graph back to time=0.

4. Read the temperature off the graph at this time=0 extrapolation. This is the T_{final} for the calorimeter calibration.
5. Compute the heat capacity of the calorimeter using the above temperature change and the value of ΔH_{rxn} for Reaction D that you determined in your pre-lab assignments. Be sure to attach appropriate units.

Reaction of Mg with HCl

1. The initial temperature, T_{initial} , will be defined as the temperature of the HCl in the calorimeter before the Mg is added.
2. Using the graph paper that has been provided, make a plot of temperature versus time for your collected data.
3. From this graph and using a ruler, extrapolate back to time=0 that portion of the graph showing a linear decrease in temperature.
4. Read the temperature off the graph at this time=0 extrapolation. This is the T_{final} for the reaction of Mg with HCl.
5. Using the calorimeter heat capacity that was determined above, calculate ΔH for this reaction (Reaction B) and label it ΔH_b . This number should have units of kJ/mol.

Reaction of MgO with HCl

1. The initial temperature, T_{initial} , will be defined as the temperature of the HCl in the calorimeter before the Mg is added.
2. Using the graph paper that has been provided, make a plot of temperature versus time for your collected data.
3. From this graph and using a ruler, extrapolate back to time=0 that portion of the graph showing a linear decrease in temperature.
4. Read the temperature off the graph at this time=0 extrapolation. This is the T_{final} for the reaction of Mg with HCl.
5. Using the calorimeter's heat capacity that was determined above, calculate ΔH for this reaction (Reaction C) and label it ΔH_c . This number should have units of kJ/mol.

Heat of Formation of MgO

1. Using the values for ΔH_b , ΔH_c , ΔH_f (water), and the balanced equations for the reactions corresponding to these enthalpy changes (Reaction B, Reaction C, and Reaction A), determine the heat of formation of MgO(s), $\Delta H_f(\text{MgO})$. This number should have units of kJ/mol.

Chapter 17

Nickel Dimethylglyoxime Formation Stoichiometry

The reaction between nickel and dimethylglyoxime in ethanol is examined to confirm the stoichiometry and to calculate the percent yield. The concept of limiting reagent is illustrated.

17.1 Introduction

In this experiment you will examine the stoichiometry of the reaction between nickel(II) nitrate and dimethylglyoxime to form nickel(II) dimethylglyoxime.

A solution of nickel(II) nitrate contains nickel(II) ions and nitrate ions while a solution of dimethylglyoxime contains dimethylglyoxime in molecular form as shown in Figure 17.1. When the solutions are mixed, the nickel ions and dimethylglyoxime react to form nickel(II) dimethylglyoxime. This compound, shown in Figure 17.2, is a water-insoluble molecule that precipitates out of solution when formed. The net ionic reaction is shown in Figure 17.3.

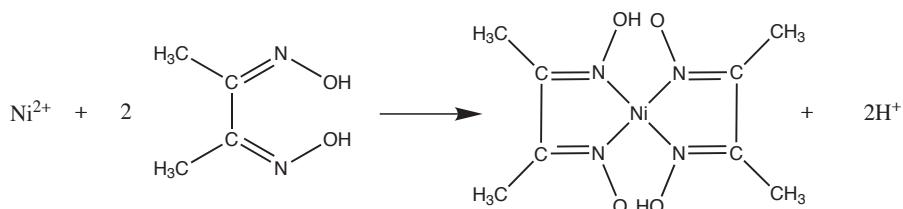


Figure 17.3

The net ionic reaction for the formation of nickel(II) dimethylglyoxime.

The amount of nickel(II) dimethylglyoxime that forms depends on the quantities of nickel(II) ions and dimethylglyoxime originally mixed together. In this experiment you will determine whether Ni^{2+} or $\text{C}_4\text{H}_8\text{N}_2\text{O}_2$ is the limiting reactant, how much nickel(II) dimethylglyoxime should theoretically form, and how much nickel(II) dimethylglyoxime actually does form.

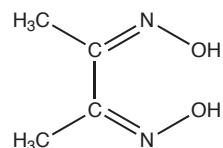


Figure 17.1

Dimethylglyoxime is a reagent used in the formation of NiDMG.

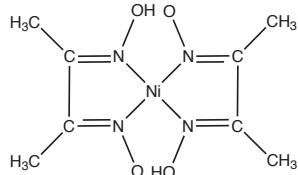


Figure 17.2

Nickel(II) dimethylglyoxime (NiDMG) is the main product of interest in this lab.

17.2 Safety Considerations

Chemical Hazards

- nickel(II) dimethylglyoxime:** The nickel(II) dimethylglyoxime you will precipitate in this experiment is a deep red color. If it gets on your hands, it will stain them for several days. If it gets on your clothing, it will likely stain them for life. Wear gloves and an apron if you wish to be cautious.

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.



Figure 17.4

Broken glass container.

Waste Disposal

You will generate waste in this lab that cannot be thrown down the drains or into the trash can. Please adhere to all disposal policies. When in doubt, ask your lab instructor.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 17.4. Do not use the normal waste baskets for broken glass.

17.3 Experimental Procedure

Prepare Nickel(II) Solution

⌚ You can save yourself time in lab by doing this calculation before lab.

- Mass Out Nickel Nitrate:** Using a top loading electronic balance, mass out on weighing paper sufficient $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to make 50 mL of an approximately 0.050 M Ni^{2+} solution.
- Dissolve Nickel Nitrate in Ethanol:** Add the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to a clean and dry 50.00 mL volumetric flask. Add about 40 mL ethanol to the flask to dissolve the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Shake and swirl the flask until the nickel compound is dissolved.
- Fill Flask to the Mark:** Fill the volumetric flask to the 50 mL mark with ethanol using an eyedropper to achieve a volume of 50.00 mL.

Prepare Reaction Mixtures

- Prepare Beakers for Reactions:** Obtain a 100 mL beaker and a 150 mL from your drawer. Make sure they are thoroughly clean and dry.

► This solution will be referred to as the Ni^{2+} stock solution.

2. **Label Beakers:** With a wax pencil, label one beaker as “Reaction 1” and the other beaker as “Reaction 2.” It does not matter which beaker receives which label.
3. **Add Nickel(II) Stock Solution to Beakers:** Using a graduated cylinder, add 20 mL of the Ni^{2+} stock solution to both beakers: the one labeled “Reaction 1” and the one labeled “Reaction 2.”
4. **Clean and Dry Graduated Cylinder:** Thoroughly rinse the graduated cylinder with water three times and then with ethanol twice. It is essential that you get rid of all traces of Ni^{2+} .
5. **Add Dimethylglyoxime to “Reaction 1” Beaker:** Using a graduated cylinder, add 20 mL of the dimethylglyoxime (DMG) solution to the beaker labeled “Reaction 1.”
6. **Add Dimethylglyoxime to “Reaction 2” Beaker:** Using a graduated cylinder, add 10 mL of the DMG solution to the beaker labeled “Reaction 2.”

► Failure to thoroughly clean the graduated cylinder before the next step will result in the formation of a red mess in the cylinder.

► The DMG solution is ethanol that is approximately 0.130 M in dimethylglyoxime. Record the actual concentration from the reagent bottle.

Allow Reaction To Take Place

1. **Clean Stirring Rods:** Obtain two stirring rods from your drawer. Thoroughly clean and dry them. Assign one of them to the beaker labeled “Reaction 1” and the other to the beaker labeled “Reaction 2.”
2. **Stir Beakers Occasionally:** Allow both beakers to sit for at least 10 minutes, stirring occasionally with separate glass rods.
3. **Allow Precipitate to Settle:** Allow the precipitate to settle to the bottom of the beakers for about 10 minutes without stirring or otherwise disturbing the beakers.

④ While the precipitate settles to the bottom of the flask you can prepare the watch glasses for massing (next section).

Prepare Watch Glass and Filter Paper

1. **Obtain Watch Glasses:** Retrieve two watch glasses from your laboratory drawer. Make sure they are clean and dry.
2. **Label Watch Glasses:** Obtain two adhesive labels and write “Reaction 1” on one of them and “Reaction 2” on the other in pencil. Attach one to each watch glass.
3. **Place Filter Paper on Watch Glass:** Obtain four pieces of filter paper and place two on the watch glass labeled “Reaction 1” and the other two the watch glass labeled “Reaction 2.”
4. **Weigh Watch Glass and Filter Paper:** Weigh the watch glass and filter paper combination for the watch glass labeled “Reaction 1.” Do the same for the watch glass labeled “Reaction 2.”

► Do not use pen or wax pencil to write on the labels. You need to use normal pencil, which will not melt when heated or dissolve in ethanol.

► Do not write on the filter paper.

► Do not mix up the filter papers. They must remain with the watch glass they were massed with.

Suction Filter Product of Reactions

1. **Prepare Ice Bath:** Place a scoop-full of crushed ice into an ice bath pan and then add about 200 mL DI water.
2. **Cool Ethanol in Ice Bath:** Place about 40 mL of ethanol into a 50 mL beaker and immerse the bottom of the beaker into the ice bath to cool the ethanol.
3. **Set Up Suction Filtration Apparatus:** Set up the suction filtration apparatus as described by your instructor.
4. **Filter “Reaction 1” Product:** Place the filter papers from the watch glass labeled “Reaction 1” into the bottom of the Buchner funnel. Pour the reaction mixture (liquid and precipitate) out of the beaker labeled “Reaction 1” and onto the filter paper in the suction filtration apparatus.
5. **Rinse “Reaction 1” Beaker:** Rinse the beaker labeled “Reaction 1” with two 5-10 mL portions of cold ethanol. Pour each rinse into the filtration apparatus.
6. **Rinse with Acetone:** After the ethanol has drained away, rinse the precipitate in the filtration apparatus with two 5 mL portions of acetone.
7. **Remove Filter Papers from Filtration Apparatus:** Carefully remove the filter papers from the suction filtration apparatus. You may have to work your spatula under the filter papers to lift them out. Place the filter papers and product back onto the watch glass labeled “Reaction 1.”
8. **Allow Product to Dry in Air:** Place the watch glass and product for “Reaction 1” under the hood at your bench and allow it to dry while you filter the product from the beaker labeled “Reaction 2.”
9. **Filter Product from Beaker Labeled “Reaction 2”:** Repeat steps 4 to 8 for the beaker and watch glass labeled “Reaction 2.”

► This helps to remove additional ethanol and any water present.

Dry and Weigh Product

1. **Weigh Watch Glass Labeled “Reaction 1”:** Weigh the watch glass labeled “Reaction 1” and its contents after the precipitate on it has dried in the hood for 10 minutes.
2. **Dry Product in Oven:** Place the watch glass labeled “Reaction 1” and its contents into an oven at 110°C for 10 minutes.
3. **Cool Watch Glass Labeled “Reaction 1”:** After 10 minutes in the oven, remove the watch glass labeled “Reaction 1” and allow it to cool to room temperature.
4. **Weigh Watch Glass Labeled “Reaction 1”:** Weigh the watch glass labeled “Reaction 1” with its contents.

5. **Repeat Until Mass Remains The Same:** Repeat steps 2 to 4 until you no longer observe a change in mass.
6. **Repeat Process for Watch Glass Labeled “Reaction 2”:** Repeat steps 1 to 5 for the watch glass labeled “Reaction 2.”

17.4 Before Exiting Lab

- Combine your DMG precipitate and liquid waste from the filtration and pour them into the container marked “liquid and solid NiDMG waste” located in the hood at the back of the room.
- Clean your filtration apparatus thoroughly with water. If it is still stained red, use dilute HCl to clean it. Pour all HCl waste from cleaning into the waste container at the back of the room.
- Rinse the filtration apparatus one final time with water and dry the filtration apparatus thoroughly.
- Make sure your work area is scrupulously clean. The compound NiDMG has a habit of being difficult to clean up. Use Softscrub if necessary. Clean your bench and your hands several times.
- Check your lab notebook for page numbers on all pages.
- Update the table of contents in your notebook.
- Draw a line in your notebook where your experimental work ends. Sign on this line.
- Have your instructor sign your notebook on the line at the end of your experimental section.

17.5 Post-Lab Assignments

Calculations

All calculations should appear in your laboratory notebook. If you make an error, just cross through the error with a single line and then move on.

1. From your data, calculate the actual experimental mass of product collected for the reaction in the beaker labeled “Reaction 1.”
2. From your data, calculate the actual experimental mass of product collected for the reaction in the beaker labeled “Reaction 2.”
3. Calculate the theoretical yield expected for the reaction in the beaker labeled “Reaction 1.”
 - a) Write a balanced reaction.

- b) Determine the number of moles of Ni^{2+} added to the beaker labeled “Reaction 1.”
 - c) Determine the number of moles of DMG added to the beaker labeled “Reaction 1.”
 - d) Identify the limiting reagent.
 - e) Calculate the mass of NiDMG product expected.
4. Calculate the theoretical yield of NiDMG expected for the reaction in the beaker labeled “Reaction 2.”
- a) Write a balanced reaction.
 - b) Determine the number of moles of Ni^{2+} added to the beaker labeled “Reaction 2.”
 - c) Determine the number of moles of DMG added to the beaker labeled “Reaction 2.”
 - d) Identify the limiting reagent.
 - e) Calculate the mass of NiDMG product expected.
5. Calculate the percent yield for the reaction in the beaker labeled “Reaction 1.”
6. Calculate the percent yield for the reaction in the beaker labeled “Reaction 2.”

Chapter 18

Synthesis of Aspirin and Oil of Wintergreen

18.1 Introduction

One of the activities commonly associated with chemists is the making of new compounds and materials. Synthesis, as this is otherwise known, is integral to our modern way of life. Many of the items we depend on every day are, in fact, synthesized by chemists from compounds that may be very different. Aside from the practical benefits of synthesis, the ability to carry out complex transformations of matter from one form to another is a great intellectual achievement for humans.

In this project, you will get to try out synthesis. Specifically, you will make two compounds with different chemical and physical properties from the same starting molecule. You will synthesize aspirin, which can be used to relieve pains, and you will synthesize oil of wintergreen, which can be used to flavor foods. You will not be expected to understand how these transformations take place, but you will be expected to develop the laboratory skills required to carry out a simple synthesis and to isolate the synthesized material.

The Starting Material

Both syntheses in this project will start with salicylic acid, which is shown in Figure 18.1. Salicylic acid consists of a ring of alternately single and double bonded carbon atoms with groups of attached atoms that have names. The $-\text{OH}$ group of atoms shown on the right side in Figure 18.1 is known as a hydroxyl group. The $\text{HO} - \text{C} = \text{O}$ group of atoms shown at the top of Figure 18.1 is known as a carboxylic acid group.

Salicylic acid is one member of a group of analgesic compounds known as salicylates. Salicylates are structurally diverse, but they are all built from the same basic structure shown in Figure 18.1 for salicylic acid. In fact, one can think of salicylates as modifications of the structure of salicylic acid. In this project you will modify salicylic acid in two difference ways to synthesize two different salicylates.

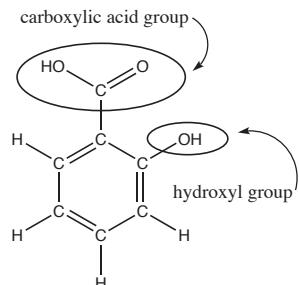
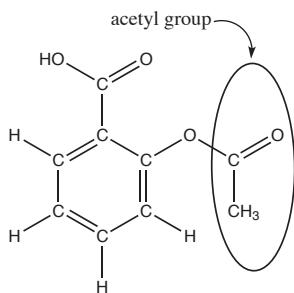


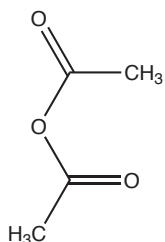
Figure 18.1

Salicylic acid, the starting material for the synthesis of aspirin and oil of wintergreen.

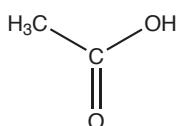
► An analgesic is a substance that helps relieve pain.

**Figure 18.2**

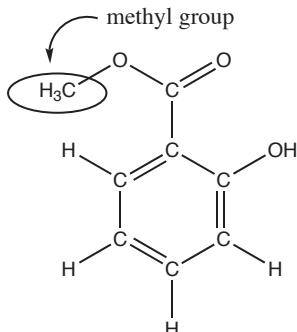
Aspirin, also known as acetylsalicylic acid.

**Figure 18.4**

Acetic anhydride, one of the reagents in the synthesis of aspirin.

**Figure 18.5**

Acetic acid, one of the products in the synthesis of aspirin.

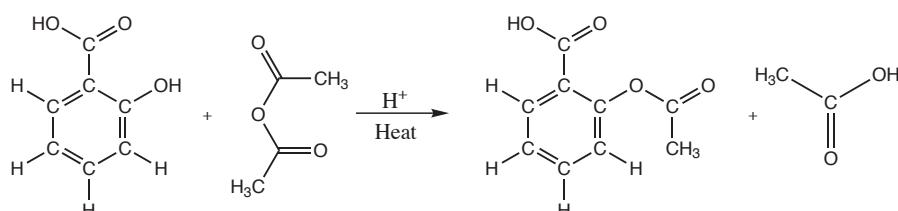
**Figure 18.6**

Methyl salicylate, also known as oil of wintergreen.

About Aspirin and Its Synthesis

Aspirin, also known as acetylsalicylic acid, is a common drug used to combat pain, fever, inflammation, and the recurrence of heart attacks. Like salicylic acid, it is just one example of a salicylate, but it is commercially the most important member of this group of compounds. Aspirin can be synthesized from salicylic acid by replacing the hydrogen atom (H) of the hydroxyl group ($-OH$) with an acetyl group ($O = C - CH_3$). The result of this substitution is shown in Figure 18.2, where the acetyl group has been circled.

Aspirin can be synthesized according to the reaction shown in Figure 18.3. In this reaction salicylic acid (Figure 18.1) is mixed with acetic anhydride (Figure 18.4) in the presence of a catalytic amount of sulfuric acid. The products of this reaction are aspirin (Figure 18.2) and acetic acid (Figure 18.5).

**Figure 18.3**

The overall reaction for the synthesis of aspirin, also known as acetylsalicylic acid.

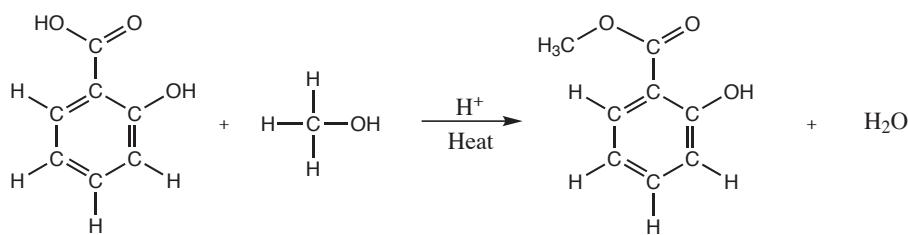
About Oil of Wintergreen and Its Synthesis

Oil of wintergreen, also known as methyl salicylate, is yet another member of the group of compounds known as salicylates. Methyl salicylate is used as a rubefacient in such products as Bengay and other analgesic heat rubs. Its wintergreen smell contributes to the characteristic odor of such products. Oil of wintergreen is also used to flavor gum and candy, notably Lifesavers.

Methyl salicylate, shown in Figure 18.6, can be synthesized by modifying the carboxylic acid group ($HO - C = O$) of salicylic acid (Figure 18.1) to replace the hydrogen atom (H) in the group with a methyl group ($-CH_3$). This can be carried out by reacting salicylic acid with methanol (CH_3OH) in the presence of an acid catalyst. This reaction is shown in Figure 18.7.

18.2 Experimental Design Considerations

Most experiments are simple in concept. The execution is often more challenging. This section contains some information about the experimental details you will have to worry about while working through this project.

**Figure 18.7**

The overall reaction for the synthesis of oil of wintergreen, also known as methyl salicylate.

Isolating Product

In many syntheses, the product you are trying to produce will not be the only substance in the reaction vessel when you decide the reaction is complete. Other products (call byproducts) are often present, and sometimes some of the reagents are still present. Synthesis is a messy business, and isolating the product of interest can sometimes be complicated. Many of the experimental details in this project are driven by the need to effectively isolate the product of interest. The following sections explain why some of these decisions were made.

Isolating Aspirin

Isolating aspirin is relatively easy. Aspirin is a solid at and below room temperature, and it is not very soluble in water. Therefore, if we add a reaction mixture containing aspirin to water in an ice bath, solid crystals of aspirin should form. However, the reagent salicylic acid is also a solid at room temperature, and it also has low solubility in water. If any salicylic acid remains at the end of the reaction, it will crystalize with the aspirin, giving impure product.

To guard against this possibility, we have designed the project such that the acetic anhydride is present in excess. This means that if the reaction is carried out for long enough, there should be no salicylic acid left in the reaction vessel. Through experience, we know that heating the reaction mixture for 6 minutes is “long enough.”

Because acetic anhydride is present in excess, there will be some of this left at the end of the reaction. However, acetic anhydride reacts rapidly with water to produce acetic acid. This is why we have you pour the reaction mixture into water when you are done heating the mixture. Acetic acid, in turn, is very soluble in water. When you filter your product crystals, the liquid, which contains the acetic acid, will simply fall away into the filter flask. The result is an effective isolation of aspirin, assuming you actually made any aspirin.

Isolating Oil of Wintergreen

Isolating oil of wintergreen is somewhat more challenging because it is not a solid at room temperature. However, the same principals apply as when isolating

a solid. Steps must be taken to ensure that only the desired product is present.

In this synthesis, salicylic acid will remain at the end of the reaction. To remove this excess reagent, you will pour the reaction mixture into water, which will cause the salicylic acid to form a white solid. This solid can be filtered out of the reaction mixture. What remains should be a mixture of methanol, oil of wintergreen, and water. It will mostly be water.

► This process is called extraction.

To further isolate the oil of wintergreen, you will add small amounts of dichloromethane to your product liquid. Oil of wintergreen is much more soluble in dichloromethane than in water or methanol. This means it will move into the dichloromethane. Because dichloromethane and water do not mix, it is possible to then remove the dichloromethane and put it in a separate container. If this is repeated several times, the result will be a quantity of dichloromethane with oil of wintergreen in it.

► Decision You Make

When you add the dichloromethane to your reaction mixture, two layers of liquid will form. You want to remove the dichloromethane after the extraction. To do this, you will have to decide which layer is dichloromethane. To make this decision, look up the density of water and of dichloromethane. The liquid with the lower density will float on top of the liquid with the higher density.



Figure 18.8
Acetic anhydride: Corrosive (C).

18.3 Safety Considerations

Chemical Hazards

- Acetic Anhydride:** Acetic anhydride is a volatile and corrosive chemical. It should be treated with respect. You may want to wear gloves while transferring it. See Figure 18.8 for the EU hazard symbol. If you spill this on yourself, wash immediately with water.
- Methanol:** Methanol is flammable. Be sure not to spill it on a hot plate because it may burst into flames. Methanol flames are difficult to see, which means this is a particularly dangerous hazard. Methanol has EU hazard classifications of F for highly flammable and T for toxic. Dispose of methanol in appropriate waste containers.
- Dichloromethane:** You will work with small quantities of dichloromethane in this project. You should minimize exposure to this compound by working with it in your hood as much as possible. Dichloromethane has an EU hazard classification of Xn for harmful. Dispose of dichloromethane in appropriate waste containers.

Goggles

You are expected to wear goggles at all times in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

No liquid or solid waste may be poured down the drain in this lab unless you are specifically instructed to do so. Everything must be disposed of in the waste containers in the hoods.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 18.9. Do not use the normal waste baskets for broken glass.



Figure 18.9

Broken glass container.

18.4 Experimental Procedure

Aspirin Synthesis

Set Up Boiling Water Bath

You can set up a water bath with another student who is also carrying out the synthesis of aspirin because there will be plenty of room in the water bath for two test tubes.

1. **Obtain Hot Plate:** Obtain a hot plate and plug it in near your work area. Be sure the hot plate is under a hood so that fumes evolved during heating are pulled away by the hood.
2. **Fill Beaker with Water:** Fill a 600 mL beaker about two-thirds full of tap water and place it on the hot plate.
3. **Heat Water to Boiling:** Begin heating the water in the water bath so that it boils.

⌚ Continue work in the next section while the water boils.

Set Up Iced Water Bath

1. **Obtain Ice Bath Pan:** From a drawer in the back of the laboratory, obtain a metal pan in which to make an ice bath.
2. **Add Ice to Pan:** Add one scoop of crushed ice to the pan from the styrofoam container in the back of the room.
3. **Add Water to Bath:** Add 50 to 100 mL of tap water to the pan.
4. **Obtain Clean and Dry Beaker:** Obtain a 150 mL beaker from your laboratory drawer. Make sure it is clean and dry.
5. **Add DI Water to Beaker:** Add about 50 mL DI water to the beaker.
6. **Place Beaker In Ice Bath:** Place the beaker in the ice bath.

Prepare Reaction Mixture

1. **Mass Salicylic Acid:** Mass approximately 2 g of salicylic acid on a piece of weighing paper using a top loading electronic balance. Do not waste time achieving an exact mass of 2.000 g. Obtain a mass of 1.8 - 2.2 g salicylic acid and record the actual mass to the nearest 0.001 g.

► The 8-inch test tube is not one you have in your drawer. You will have to obtain one from the front of the room.

 Acetic anhydride is a volatile, corrosive chemical with an unpleasant odor. Do all work with acetic anhydride under your hood. If you spill some of it on your hands, wash it off with water.

2. **Add Salicylic Acid to Test Tube:** Transfer the salicylic acid to an 8-inch test tube and attach a label with your name to the top of the test tube.

3. **Add Acetic Anhydride:** Using a 10 mL graduated cylinder, measure out 5 mL of acetic anhydride and add it to the test tube.

4. **Add Sulfuric Acid:** Add 3 drops of 6 M H_2SO_4 to the test tube.

5. **Stir Contents of Test Tube:** Stir the contents of the test tube with a glass stirring rod to thoroughly mix the contents.

Heat Reaction Mixture

1. **Attach Test Tube To Ring Stand:** Secure the 8-inch test tube to a ring stand with a single burette clamp.

2. **Suspend Test Tube Over Water Bath:** Orient the ring stand and burette clamp on the ring stand such that the test tube can be easily lowered into the water bath.

3. **Place Reaction Mixture In Boiling Water Bath:** Lower the test tube containing the reaction mixture into the boiling water bath and leave it there for 6 minutes.

4. **Remove Test Tube from Boiling Water Bath:** After 6 minutes have passed, raise the test tube out of the boiling water. Observe any changes that have taken place.

Crystallize Product

1. **Pour Reaction Mixture into Cold Water:** Pour the contents of the test tube into the DI water that has been cooled in the 150 mL beaker immersed in the iced water bath.

2. **Rinse Test Tube Into Cold Water:** Rinse the test tube with several milliliters of DI water, adding rinse to reaction mixture.

3. **Swirl Beaker Contents:** Gently swirl the flask to aid in the mixing of the solution for about 30 seconds.

4. **Reheat Mixture:** Remove the boiling water bath from the hot plate and place the 150 mL beaker containing the reaction mixture onto the hot plate. Wait for the reaction mixture to achieve a gentle boil and then immediately remove it from the hot plate.

► Wait for the water to boil before placing the test tube in the water bath.

► Leave the beaker with boiling water on the hot plate until later.

► Any unreacted acetic anhydride reacts with water to form acetic acid.

► Once you have finished with this step you may turn off and unplug the hot plate.

5. **Wait for Crystals to Form:** Allow the entire mixture to cool on your bench until crystals form. This may take 30 minutes or more.

► Slow cooling facilitates the formation of crystals.

Prepare Watch Glass and Filter Paper

1. **Obtain Watch Glass and Filter Paper:** Obtain a clean and dry watch glass from your laboratory drawer. Obtain a piece of filter paper from the reagent tray at your bench. Place the filter paper on the watch glass.
2. **Mass Watch Glass and Filter Paper:** Determine the mass of the watch glass and filter paper using an electronic top loading balance.

► You do this now so that you can determine the mass of aspirin isolated.

Suction Filter Product

1. **Set Up Suction Filtration Apparatus:** Set up the suction filtration apparatus as described by your instructor.
2. **Filter Product Crystals:** Place the filter paper from the watch glass into the bottom of the Büchner funnel. Pour the reaction mixture (liquid and crystals) out of the beaker onto the filter paper in the suction filtration apparatus.
3. **Dry Crystals for Several Minutes:** Allow air to be pulled over the crystals for several minutes to help dry them.
4. **Remove Crystals from Büchner Funnel:** Carefully remove the crystals and filter paper from the funnel and place them on the watch glass.
5. **Store Crystals in Laboratory Drawer:** Once you have returned all items to your laboratory drawer, carefully place the watch glass with product crystals in your drawer to be stored until next week.

► You may have to use your spatula to lift the edge of the filter paper.

Oil of Wintergreen Synthesis

Set Up Hot Water Bath

You can set up a water bath with another student who is also carrying out the synthesis of oil of wintergreen because there will be plenty of room in the water bath for two test tubes.

1. **Obtain Hot Plate:** Obtain a hot plate and plug it in near your work area. Be sure the hot plate is under a hood so that fumes evolved during heating are pulled away by the hood.
2. **Fill Beaker with Water:** Fill a 600 mL beaker about two-thirds full of tap water and place it on the hot plate.
3. **Heat Water:** Begin heating the water in the water bath so that it reaches a constant temperature of 75°C. It is important that the water not boil.

⌚ Continue work in the next section while the water heats.

Set Up Iced Water Bath

1. **Obtain Ice Bath Pan:** From a drawer in the back of the laboratory, obtain a metal pan in which to make an ice bath.
2. **Add Ice to Pan:** Add one scoop of crushed ice to the pan from the styrofoam container in the back of the room.
3. **Add Water to Bath:** Add 50 to 100 mL of tap water to the pan.
4. **Obtain Clean and Dry Beaker:** Obtain a 50 mL beaker from your laboratory drawer. Make sure it is clean and dry.
5. **Add DI Water to Beaker:** Add about 10 mL DI water to the beaker.
6. **Place Beaker In Ice Bath:** Place the beaker in the ice bath.

Prepare Reaction Mixture

1. **Mass Salicylic Acid:** Mass approximately 0.5 g salicylic acid on a piece of weighing paper using a top loading electronic balance. Do not waste time achieving an exact mass of 0.500 g. Obtain a mass of 0.4 - 0.6 g salicylic acid and record the actual mass to the nearest 0.001 g.
2. **Add Salicylic Acid to Test Tube:** Transfer the salicylic acid to a 5-inch test tube and attach a label with your name to the top of the test tube.
3. **Add Methanol:** Using a 10 mL graduated cylinder, measure out 3 mL methanol and add it to the test tube.
4. **Add Boiling Stone:** Add a boiling stone to the test tube.
5. **Add Sulfuric Acid:** Add 10 drops of 18 M H₂SO₄ to the test tube.
6. **Stir Contents of Test Tube:** Stir the contents of the test tube with a glass stirring rod until the bulk of the salicylic acid dissolves.

Heat Reaction Mixture

1. **Attach Test Tube To Ring Stand:** Secure the 5-inch test tube to a ring stand with a single burette clamp.
2. **Suspend Test Tube Over Water Bath:** Orient the ring stand and burette clamp on the ring stand such that the test tube can be easily lowered into the water bath.
3. **Place Reaction Mixture In Hot Water Bath:** Lower the test tube containing the reaction mixture into the water bath and leave it there until the volume of the reaction mixture has decreased to half its original volume.

► Be sure the water bath is at a temperature near 75°C but not above.

4. **Remove Test Tube from Hot Water Bath:** After the volume of the reaction mixture has decreased by 50%, raise the test tube out of the hot water. Observe any changes that have taken place. Gently waft air near the top of the test tube to your nose and note what you smell.

► Leave the beaker with hot water on the hot plate until later.

Extract Product

1. **Add Cold DI Water to Reaction Mixture:** Pour 5 mL of the cold DI water into the 5-inch test tube containing the reaction mixture.
2. **Gravity Filter Reaction Mixture:** Insert a funnel into your smallest Erlenmeyer flask and filter the reaction mixture through filter paper in the funnel. It may take 10 minutes for all the liquid to drain into the flask.
3. **Pour Collected Liquid into Conical Centrifuge Tube:** Obtain a conical centrifuge tube with cap and pour the collected liquid from the gravity filtration into the centrifuge tube.
4. **Add Dichloromethane:** Add about 1 mL dichloromethane to the conical centrifuge tube using either an eye dropper or Pasteur pipet. Cap the tube and shake for about 30 seconds.
5. **Remove Appropriate Layer:** You should see two separate liquid layers in the conical centrifuge tube. Use a pasteur pipette to remove the appropriate layer. Place the removed liquid into a small test tube.
6. **Repeat Extraction Twice More:** Repeat steps 4 and 5 two more times, each time adding the removed liquid to the same small test tube.
7. **Add Sodium Sulfate to Test Tube:** Add an appropriate quantity of sodium sulfate, as specified by your instructor, to the test tube with the liquid from the previous step.
8. **Gravity Filter Contents of Test Tube:** Pour the contents of the test tube through filter paper in a funnel and collect the filtrate in a 4-inch test tube for storage. This will filter out the sodium sulfate particles.
9. **Seal Test Tube with Product:** Place a cork in the test tube containing the extracted, dried, and filtered liquid. Wrap parafilm around the cork and top of the test tube to prevent evaporation of the liquid.
10. **Store Test Tube with Product Liquid:** Store the test tube with the product liquid as directed by your instructor.

► You will have to figure out how many drops there are per milliliter.

► This was a decision you were to make before coming to lab.

► Sodium sulfate acts as a drying agent. it helps remove water.

18.5 Before Exiting Lab

- Pour the waste from the suction filtration down the drain. This waste is just vinegar, so this is safe.

- Return clamps and rings to the drawers from which you got them.
- Make sure all hot plates have been unplugged.
- Clean all glassware before returning to your drawer.
- Check your lab notebook for page numbers on all pages.
- Update the table of contents in your notebook.
- Draw a line in your notebook at the end of your experimental work and sign on that line.
- Have your instructor sign on the line as well.

18.6 Post-Lab Assignments

At the end of this lab there are no post-lab assignments. Once you have produced product and cleaned up your work area, there is nothing else to do.

Chapter 19

Characterization of Synthesized Aspirin and Oil of Wintergreen

In this experiment you will carry out a number of analyses on the products you previously synthesized from salicylic acid. These tests are intended to characterize the identity and purity of the product.

19.1 Introduction

Analyzing Product of Aspirin Synthesis

You should have already carried out the synthesis shown in Figure 18.3 on page 114. This reaction indicates that aspirin and acetic acid are the only products. The acetic acid should have dissolved in water and been flushed away during filtration of the product. Therefore, your product should be exclusively aspirin, right?

Just because the reaction in Figure 18.3 says that your product should be aspirin alone does not mean that it is. Even if most of your product is aspirin, it is not likely that it is pure. Some of the original salicylic acid may remain in the product because it did not react. Thus, characterization of the product of a synthesis serves two purposes: to confirm the identity of the product and to ascertain the level of purity of the product. After a synthesis, you must always characterize your product using appropriate tests.

To characterize the product of the aspirin synthesis you will perform a chemical test to identify any salicylic acid present in your product, obtain a melting point range for your product, carry out thin layer chromatography of your product, and collect an infrared spectrum of your product.

The chemical test for salicylic acid is a test of purity. The melting point range of your product will help quantify purity. It can also help confirm identity as long as the sample is pure. When carried out properly, the thin layer chromatography test can help confirm identity and purity. Of all of these tests, however, the infrared spectrum will be the most conclusive in determining the identity of your product.

Chemical Test for Salicylic Acid

Many phenols (aromatic rings with an -OH group attached) form colored complexes with the Fe^{3+} ion. Salicylic acid is a phenol, but aspirin is not. This makes it possible to test your product to see if any salicylic acid is present in the white solid which you isolated in the experiment.

Analysis of Product of Oil of Wintergreen Synthesis

You should have already carried out the synthesis of oil of wintergreen shown in Figure 18.6 on page 114. As in the synthesis of aspirin, it is not likely that the only product of the oil of wintergreen synthesis and subsequent isolation is oil of wintergreen. Unlike with the aspirin synthesis, we will not be concerned about the purity of the product in this synthesis.

Instead, we will only be interested in confirming that oil of wintergreen is present. You have probably already noted that the smell of your product indicates the presence of oil of wintergreen, but we would like more conclusive evidence. To obtain this evidence you will collect an infrared spectrum of the product. With any luck, this will confirm the presence of oil of wintergreen.



Figure 19.1

Broken glass container.

19.2 Safety Considerations

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 19.1. Do not use the normal waste baskets for broken glass.

19.3 Experimental Procedure

The characterization tests described in the following sections can be performed in any order. To help make efficient use of equipment and time, your instructor will probably tell different individuals to start with different characterization tests. Be attentive for this announcement.

Test for Salicylic Acid

This section describes how to test the product of the aspirin synthesis for salicylic acid.

1. **Obtain Three Test Tubes:** Obtain three test tubes from your laboratory drawer and line them up in a test tube rack at your work area. Make sure they are clean and dry.
2. **Add Salicylic Acid to Test Tube:** Add a few crystals of pure salicylic acid to one of the test tubes.
3. **Add Product to Test Tube:** Add a few crystals of your aspirin synthesis product to another test tube.
4. **Add Aspirin to Test Tube:** Add a few crystals of authentic (pure) aspirin to the last test tube.
5. **Add DI Water to Test Tubes:** Add 1 mL of DI water to each of the test tubes.
6. **Add Ferric Chloride Solution to Test Tubes:** Add 2 drops of a solution that is 1% in ferric chloride. ► Ferric chloride is FeCl_3

Thin Layer Chromatography

This section describes how to perform thin layer chromatography of the aspirin synthesis product.

Prepare Solutions for Thin Layer Chromatography

1. **Obtain Three Test Tubes:** Obtain three clean and dry test tubes from your drawer. Line them up in a test tube rack.
2. **Add Samples to Test Tubes:** Place about 1 mg of your aspirin synthesis product in one test tube, about 1 mg of authentic (pure) aspirin in another test tube, and about 1 mg of pure salicylic acid in the third test tube.
3. **Add Ethanol/Ethyl Acetate Solution to Test Tubes:** To each test tube add 20 drops of a solution that is 50% ethanol and 50% ethyl acetate by volume. Agitate the test tubes to dissolve the samples in the solvent.

Prepare TLC Jar

1. **Obtain a TLC Jar:** Find where the TLC jars are located and retrieve one. Make sure it has a lid. ► TLC is short for thin layer chromatography.
2. **Add Developing Solvent to TLC Jar:** Add about 10-15 mL of the developing solvent to the TLC jar. ► In this lab the developing solvent is 30% hexane and 70% ethyl acetate.
3. **Check Depth of Solvent:** Using a ruler, measure the depth of the solvent in the jar. You can do this from outside the jar. The ruler does not have to be immersed in the jar. Be sure the depth is no more than 7.5 mm. Adjust if necessary.

4. **Cover TLC Jar with Lid:** Place the lid on the TLC jar and allow it to stand while you proceed to preparing the TLC plates.

Prepare TLC Plate

1. **Obtain a TLC Plate:** Obtain a TLC plate from your instructor. Be sure to always handle the TLC plate by its edges. Never touch the surface with your fingers.
2. **Mark TLC Plate:** Using a pencil, lightly draw a very narrow and faint line across one short side of the TLC plate about 1 cm from the bottom. Lightly mark three equally spaced X marks on the line. The marks on the outside should be at least 0.5 cm from the left and right edges.
3. **Obtain Three Micropipettes:** Locate the micropipettes and bring three of them back to your work area.
4. **Spot TLC Plate:** Using a different micropipette for each solution, spot each of the three solutions you prepared onto its own X on the TLC plate. Be sure to write down in your lab notebook which solution is on which X.
5. **Verify Spots on TLC Plate:** After applying all three solutions to the TLC plate, verify that enough of each sample has been spotted on the plate. This is confirmed by checking that a dark spot exists on each X when the plate is viewed under UV light. Spot more solution on the plate if needed.

Develop TLC Plate

1. **Develop TLC Plate:** Place the TLC plate in the TLC jar prepared earlier and place the lid on the jar. Make sure the end containing the spotted samples is placed in the bottom of the jar. Also be sure the spots are not submerged by the developing solvent. If they are, you will have to start over.
2. **Monitor TLC Plate Development:** Let the developing solvent rise to within 0.5 to 1.0 cm of the top of the plate. When the solvent has reached that height, remove the TLC plate from the TLC jar.
3. **Allow TLC Plate to Dry:** Set the TLC plate on a paper towel face up. Allow it to dry in air for a few minutes.
4. **Outline Spots on TLC Plate:** After the solvent has evaporated from the plate, expose the plate to UV light and outline all spots in pencil.

Melting Point

This section describes how to determine the melting point of the aspirin synthesis product. Be sure to refer to *Melting Point Range Determination* in Chapter 6 starting on page 31 for detailed information about how to collect a melting point. Only brief instructions are given here.

⊕ It will be helpful if you work with a partner as described in Section 6.3 on page 35.

1. **Obtain Melting Point Capillaries:** Find where the melting point capillaries are located and retrieve three of them. Take these back to your work area.
2. **Obtain Weighing Paper:** Obtain three pieces of weighing paper and bring them back to your work area.
3. **Obtain Samples To Be Melted:** Pour a few milligrams of authentic (pure) aspirin onto one piece of weighing paper. Pour a few milligrams of pure salicylic acid onto another piece of weighing paper. Finally, pour a few milligrams of your aspirin synthesis product onto the last piece of weighing paper.
4. **Pack Capillaries with Samples:** Pack each melting point capillary with one of the samples you just poured out. Each capillary should have enough sample to bring the sample depth to a few millimeters as shown in Figure 6.6 on page 34.
5. **Collect Melting Point Range of Samples:** Using the Mel-Temp apparatus, determine the melting point range of these three samples.

Infrared Spectrum

Your instructor or your laboratory assistant will provide considerable help in collecting the infrared spectrum of the products from the aspirin synthesis and the oil of wintergreen synthesis.

1. **Take Product to FTIR:** When one of the infrared spectrometers is available, take your product to that instrument. Make sure an instructor or teaching assistant is there to help you.
2. **Prepare Sample:** Place some of your product sample onto salt plates in the manner described by your instructor.
3. **Collect Spectrum:** Collect an infrared spectrum of your product. Be sure to print out a copy of the spectrum for inclusion in your laboratory notebook.
4. **Perform Library Search for Spectrum:** Using the instrument software, search for spectra that match the spectrum of your product. In your laboratory notebook write down the three compounds whose spectra most closely match your product spectrum.

19.4 Before Exiting Lab

1. Place all of your aspirin synthesis product in the jar labeled “aspirin” located in the hoods in the back of the room.
2. Place all used developing solvent in the bottle labeled “used developer” in the hoods in the back of the room.

3. Check your lab notebook for page numbers on all pages.
4. Update the table of contents in your notebook.
5. Draw a line at the end of your experimental work and sign on it.
6. Have your instructor sign on the line at the end of your experimental work.

19.5 Post-Lab Assignments

Questions

1. What does the melting point range data tell you about the identity and purity of the aspirin synthesis product?
2. What does the thin layer chromatography tell you about the identity and purity of the aspirin synthesis product?
3. What does the ferric chloride test tell you about the identity and purity of the aspirin synthesis product?
4. What does the infrared spectrum of the aspirin synthesis product tell you about its identity and purity? If you have performed molecular modeling of the vibrations in aspirin, compare the infrared spectrum predicted by the modeling software to the infrared spectrum you obtained for your actual product.
5. What does the infrared spectrum of the oil of wintergreen synthesis product tell you about its identity and purity? If you have performed molecular modeling of the vibrations in oil of wintergreen, compare the infrared spectrum predicted by the modeling software to the infrared spectrum you obtained for your actual product.

Chapter 20

Molecular Modeling of Infrared Absorptions

20.1 Introduction

In this laboratory project we will use molecular modeling techniques to investigate the infrared absorption spectra for a series of molecules to learn how infrared spectroscopy can be used to identify and distinguish molecules based on common structural features. Along the way, you will learn how the atoms in a molecule move when exposed to infrared light. This project is relatively straightforward to carry out, but it requires some background information on spectroscopy, molecular modeling, and how we describe molecular structure.

Molecular Structure

You will learn more about how molecules are put together when you cover Lewis and VSEPR theories, but for now we need to know just a few things. Atoms in a molecule are attached by bonds, which are normally represented as lines in drawings of molecules. For this project, the nature of these bonds is unimportant. You just need to know that bonds are the connections between atoms in a molecule that allow the atoms to remain fixed in number and fixed in place for a given molecule.

Figure 20.1 shows a drawing of a single molecule of water, which consists of one atom of oxygen and two atoms of hydrogen. Two common parameters are used to discuss the structure: bond length and bond angle. Bond length is the distance between two atoms in a molecule. The oxygen to hydrogen bond length is shown in Figure 20.2. Bond angle is the angle made by any three atoms in a molecule. The H-O-H bond angle is indicated in Figure 20.3 with a red asterisk at the vertex of the bond angle.

Water is simple, but every molecule, no matter how complicated, has a set of bond lengths and bond angles that describe the relative placement of the atoms. For instance, codeine is shown in Figure 20.4, and a few bond lengths and bond angles have been indicated on the drawing.

► These common structural features are called functional groups.

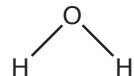


Figure 20.1
Molecular drawing of water.

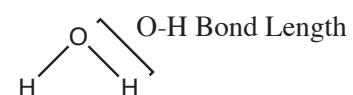


Figure 20.2
O-H bond length in water.

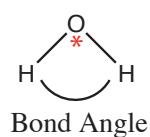


Figure 20.3
H-O-H bond angle in water.
The red asterisk marks the vertex of the bond angle.

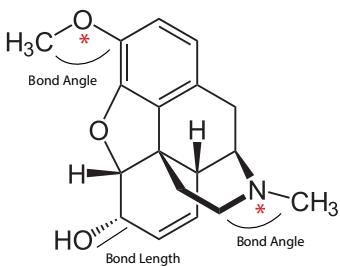


Figure 20.4
Codeine with a bond length and two bond angles marked.

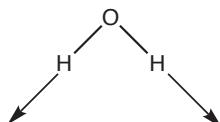


Figure 20.5
Displacement arrows for a stretch in water.

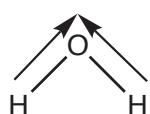


Figure 20.6
Displacement arrows for a stretch in water.

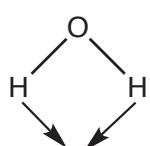


Figure 20.7
Displacement arrows for a bend in water.

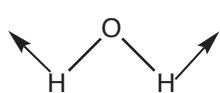


Figure 20.8
Displacement arrows for a bend in water.

Molecular Vibration

When we draw diagrams of molecules, such as those in Figures 20.1 and 20.4, we get the impression that the atoms are stationary. This is never true. The atoms in all molecules are constantly in motion, and these motions are called vibrations because the motions occur in a regular and repeating pattern. If you have a physics background, you might call this periodic motion. The atoms do not move by much, but they are always moving relative to one another. The subject of molecular vibration is complicated, and its detailed exploration is well beyond the scope of this project. For this project, all you need to understand is that there are two basic types of vibration: stretches and bends.

A stretch is a type of vibration in which the length of a bond changes. If the two atoms defining the ends of a bond get further apart, the bond is undergoing a stretching vibration. Because vibrations are regular and repeating, the lengthening cannot continue forever. It eventually stops and becomes compression. That eventually stops, too, and becomes lengthening again. In other words, in a stretching vibration, the two atoms defining a bond move away from each other and then toward each other in a repeating pattern.

A bend occurs when atoms move in such a way to increase or decrease a bond angle in a regular and repeating manner. So, for instance, when the two hydrogen atoms in water in Figure 20.1 move closer together, the H-O-H bond angle changes. This is a bending type of vibration.

Indicating Vibrations with Displacement Arrows

Words become too cumbersome when discussing vibrations. Therefore, chemists use a short hand notation to indicate the type of vibration. Chemists use arrows on atoms to show which way they move in a vibration. Arrows that move directly along a bond indicate stretches as shown in Figure 20.5. The arrows on the hydrogen atoms in Figure 20.5 indicate stretches of the H-O bond. This same stretch could be indicated with arrows going the other way as shown in Figure 20.6. Either is acceptable.

When indicating a bend with arrows, the arrows are typically close to being at a right angle to the direction of a bond. If a chemist wanted to indicate the bending motion of water, the arrows in Figure 20.7 or Figure 20.8 would be acceptable. Each shows the same bend. In all cases, the arrows placed on the molecule to show the type of vibration are called displacement arrows because they indicate which way the atoms displace during a vibration.

Atomic Spectroscopy

In lecture you have seen that hydrogen atoms exposed to electromagnetic radiation (light) will absorb specific wavelengths of that light to produce an absorption spectrum. You have also learned that these absorptions result in hydrogen's electron moving from one stable orbit to another stable orbit. When the energy of the light exactly matches the energy difference between two stable orbits of the electron, the atom will absorb that wavelength. All other wavelengths of light

are not absorbed; they are transmitted. When light is absorbed by hydrogen, we say that it has undergone a transition. All atoms can undergo transitions when exposed to the right wavelength of light.

Every atom has a different absorption spectrum. In fact, the absorption spectra for atoms are so unique that they can be used to identify the elements present in a sample. Another way of saying this is that the absorption spectrum of each element serves as a fingerprint for that element. It is a unique identifier. Of course, experimental realities complicate this somewhat, but it is largely true.

Molecular Spectroscopy

Molecules can also undergo transitions in which electrons move from one “orbit” to another, and you will learn about these transitions in later laboratory projects that involve ultraviolet/visible spectroscopy. For now, however, we want to focus on another type of transition that can take place for molecules that is called a vibrational transition. In this type of transition, the atoms in a molecule begin to move relative to each other in response to being exposed to a particular wavelength of light. Vibrational transitions can typically be caused by light in the infrared region of the spectrum. When molecules are exposed to infrared light and the absorptions are recorded, the result is an infrared absorption spectrum.

These vibrations involve atoms getting closer together and further apart in a repeated manner, much like a mass oscillating on the end of a spring or a clock pendulum moving back and forth. Vibrational transitions can involve stretches or bends. An infrared absorption spectrum is characteristic of a molecule in the same way an atomic absorption spectrum is characteristic of an atom because the number and type of vibrations in a molecule are unique to that particular molecule. This can be used to identify molecules.

► Yes, clocks used to have pendulums. The motion of the pendulum is so regular that it can be used to . . . keep time.

Vibrational Spectra

So far, I have almost exclusively talked about the wavelength at which molecules or atoms absorb light. However, most chemists do not talk about the wavelength at which molecules absorb infrared light to excite molecular vibrations. Instead, most chemists will talk about such transitions as occurring at a particular wavenumber. This means we need to understand what a wavenumber is.

A wavenumber is a unit that is directly proportional to energy and to frequency. It is not equal to either, but it can be used like them because it is directly proportional to both. A wavenumber is defined as $\frac{1}{\lambda}$, where λ is the wavelength of the light. It is given the symbol $\tilde{\nu}$. So, in mathematical form,

$$\tilde{\nu} = \frac{1}{\lambda} \quad . \quad (20.1)$$

Molecular Modeling

Molecular modeling involves predicting the properties of molecules, including their spectra, using nothing but mathematical models. These models can some-

times be quite complicated, and the details of how these models work are well outside the scope of this course. However, thanks to modern computers, we can easily use these models to obtain meaningful predictions about the behavior of molecules without understanding every detail of how the models work. In this project you will use known models to predict the spectra for a set of molecules and to obtain information about how the atoms vibrate after each absorption.

Transition versus Absorption

A vibrational transition is a change in how a molecule vibrates in response to exposure to light. So, for instance, if exposure to the right frequency of light causes the O-H bonds in water to begin stretching more or the H-O-H bond angle to increase more, we say that the molecule has undergone a vibrational transition.

When these transitions take place, light is removed from the beam of light that hits the molecules, and the result is an absorption. What happens if two transitions take place at nearly the same frequency? They will appear at nearly the same wavenumber in the observed infrared spectrum. They may be so close that the two transitions appear to lie right on top of each other. In this case, you will see just one absorption.

Absorptions are the observed features in an infrared spectrum. Transitions are the changes in molecular motion that take place when the molecule interacts with light. A single absorption may correspond to one or more transitions, depending on how similar in energy the transitions are.

20.2 Safety Considerations

This project requires you to use computer workstations to model the behavior of a collection of molecules. There are no chemical hazards, there is no need to wear your goggles, and there is no need to be concerned with waste disposal.

20.3 Experimental Procedure

This section contains suggested procedures for an investigation employing the molecular modeling software Scigress.

Assigned Molecules for Group Analysis

Your instructor will assign four molecules to you. These molecules will be drawn on a sheet of paper and labeled with their names. You are to predict the infrared absorption spectrum for each and then obtain the transition wavenumber for the indicated stretches and bends in these molecules. Follow the instructions in this section to obtain these values.

1. **Change Background Color to White:** Using help provided by your instructor, change the background color of all windows to white.

2. **Draw Molecule in Scigress and Save:** Draw one of your assigned molecules in Scigress, valence beautify it, and then save the file with the name of the molecule.
3. **Set Up Computational Experiment to Predict Spectrum:** Set up a new experiment in the Scigress software by selecting New from the Experiment menu. In the Experiment window that appears, select *IR Transitions* next to Property and *MOG PM5 FORCE* next to Using. Leave the setting next to Property of: at the default setting of *chemical sample*.
4. **Start Computational Experiment to Predict Spectrum:** Start the computational experiment by clicking the Start button on the Experiment window. When the experiment has successfully completed, close the Experiment Status window and the Experiment window.
5. **Change How Molecule is Displayed:** Go to the View menu and select Lines.
6. **Display Computed Infrared Spectrum:** Select IR Transitions from the Analyze menu to display the spectrum that was computed by Scigress for the molecule you drew.
7. **Change How Spectrum Is Displayed:** Select the entire spectrum by pressing CTRL-A on the keyboard. The entire spectrum should turn red. Then select Transition Attributes... from the View menu. In the window that displays, enter 20 for the width and click the OK button.
8. **Tile Spectrum and Molecule Windows:** Select Tile from the Window menu so that the spectrum and the molecule windows are displayed side by side. Make sure only the two windows you want to tile are open when you select the tile command.
9. **Find Transition for Each Assigned Molecular Stretch:** Click the triangles below each absorption in the spectrum to reveal each transition and the molecular motion that gives rise to that transition. Examine the displacement arrows on the molecule for each transition until you find the one that predominantly results in a stretching and/or compression of the bond or bonds indicated in your assigned molecule.
10. **Record Wavenumber of Each Assigned Stretch:** When you find a transition that corresponds to an indicated stretch, double click on the triangle for that transition (or select Transition Attributes... from the View menu) and record the wavenumber of that transition to one decimal place. Close the Transition Attributes window when finished.
11. **Find Transition for the Assigned Molecular Bend:** Click the triangles below each absorption in the spectrum to reveal each transition and the molecular motion that gives rise to that transition. Examine the displacement arrows on the molecule for each transition until you find the one that predominantly results in the bending of the bond angle indicated by the red asterisks (*) on your molecule.

► Property of: chemical sample
Property: IR Transitions
Using: MOG PM5 FORCE

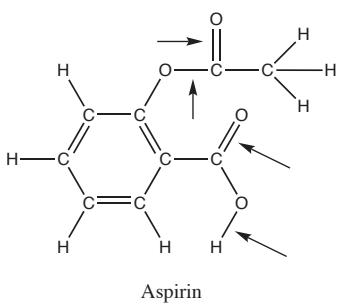
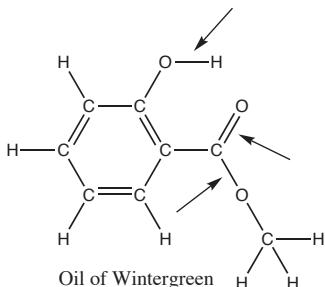
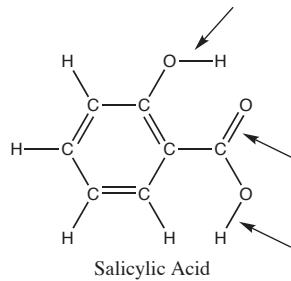
► This makes the displacement arrows easier to see.

► This makes the appearance of the spectrum more realistic and should be done prior to analyzing any computed spectrum.

► This makes analyzing the spectrum easier.

► The red asterisk is on the atom at the vertex of the angle that changes during the bend.

12. **Record Wavenumber of Assigned Bend:** When you have found the transition that corresponds to the indicated bend, double click on the triangle for that transition (or select Transition Attributes... from the View menu) and record the wavenumber of that transition to one decimal place. Close the Transition Attributes window when finished.
13. **Provide Data To Class:** When you have collected the absorption wavenumber for each indicated stretch and bend in all your assigned molecules, provide the data to the class in the manner indicated by your instructor.
14. **Record Conclusions Drawn from Class Data:** Your instructor will comment on the meaning of the class data when all the data are submitted. You should record in your laboratory notebook the major conclusions to be drawn from the class data.



Aspirin, Oil of Wintergreen, and Salicylic Acid

After your instructor has helped you see what the group data implies, you are to predict the infrared absorption spectra for salicylic acid, oil of wintergreen, and aspirin. The procedure presented below is a condensed version of the more detailed procedure enumerated in the previous section. You should fill in the detailed procedure from your previous experience.

1. **Predict IR Absorption Spectrum of Salicylic Acid:** Draw salicylic acid in a new Scigress window and predict its infrared absorption spectrum using MOG PM5 FORCE with the procedure you previously employed. Salicylic acid is shown at the top of Figure 20.9.
2. **Print Computed IR Spectrum of Salicylic Acid:** Print the predicted spectrum for salicylic acid so that you can annotate it as indicated in the next step. This spectrum should be included in your notebook. Be sure to change the background of your spectrum to white before printing.
3. **Find and Record Wavenumber of Molecular Stretches:** Click the triangles below the predicted infrared absorptions until you find transitions corresponding to the stretching and/or compression of the bonds indicated with arrows in Figure 20.9. Record the wavenumber of these transitions and then mark their location on the spectrum along with the bond that is stretching for that absorption. Make note of whether the transitions can be distinguished as separate absorptions in the spectrum.
4. **Predict IR Absorption Spectrum for Oil of Wintergreen:** Draw oil of wintergreen in a new Scigress window and predict its infrared absorption spectrum using MOG PM5 FORCE with the procedure you previously used. Oil of wintergreen is shown in the middle in Figure 20.9.
5. **Print Computed IR Spectrum of Oil of Wintergreen:** Print the predicted spectrum for oil of wintergreen so that you can annotate it as indicated in the

Figure 20.9

Molecules to be investigated in this section.

next step. This spectrum should be included in your notebook. Be sure to change the background color of your spectrum to white before printing.

6. **Find and Record Wavenumber of Molecular Stretches:** Click the triangles below the absorptions until you find transitions corresponding to the stretching and/or compression of the bonds indicated with arrows in Figure 20.9. Record the wavenumber of these transitions and then mark their location on the printed spectrum along with the bond that is stretching for that absorption. Make note of whether the transitions can be distinguished as separate absorptions in the spectrum.
7. **Predict IR Absorption Spectrum for Aspirin:** Draw aspirin in a new Sci-gress window and predict its infrared absorption spectrum using MOG PM5 FORCE with the procedure you previously used. Aspirin is shown at the bottom of Figure 20.9.
8. **Print Computed IR Spectrum of Aspirin:** Print the predicted spectrum for aspirin so that you can annotate it as indicated in the next step. This spectrum should be included in your notebook. Be sure to change the background color to white before printing.
9. **Find and Record Wavenumber of Molecular Stretches:** Click the triangles below the absorptions until you find transitions corresponding to the stretching and/or compression of the bonds indicated with arrows in Figure 20.9. Record the wavenumber of these transitions and then mark their location on the printed spectrum along with the bond that is stretching for that absorption. Make note of whether the transitions can be distinguished as separate absorptions in the spectrum.

20.4 Before Leaving Lab

Before leaving lab for the day, go down this checklist to make sure you have done everything on it.

- Work through as many of the Post-Lab Assignments as you can before the end of the lab period so that you can take advantage of your instructor's help.
- Log out of the computer workstation you were using.
- Push your chair in so that others do not trip on it.
- Update the table of contents in the front of your notebook.
- Draw a line at the end of your experimental work and sign on the line.
- Have your instructor sign on the line as well.

20.5 Post-Lab Assignments

Questions

All the work you have done in this project leads to four question that you should answer in your laboratory notebook.

1. For a given bond in a molecule, does it take more energy to stretch that bond or to carry out a bend involving that bond? You should be able to answer this question based on the data you gathered today. Cite specific evidence from your work today to support your answer.
2. Is it possible to distinguish salicylic acid from oil of wintergreen based on their infrared absorption spectra? If so, cite obvious and specific differences in their spectra that allow the two to be distinguished. Focus on the differences brought about by the stretching motions indicated in Figure 20.9.
3. Is it possible to distinguish salicylic acid from aspirin based on their infrared absorption spectra? If so, cite obvious and specific differences in their spectra that allow the two to be distinguished. Focus on the differences brought about by the stretching motions indicated in Figure 20.9.
4. Is it possible to distinguish oil of wintergreen from aspirin based on their predicted infrared absorption spectra? If so, cite obvious and specific differences in their spectra that allow the two to be distinguished. Focus on the differences brought about by the stretching motions indicated in Figure 20.9.
5. Compare the infrared spectra predicted by the modeling software for aspirin and oil of wintergreen to the infrared absorption spectra you have collected for your synthesized aspirin and oil of wintergreen.

► Answer this question only if you have not already completed the project in which you should have collected infrared absorption spectra of synthesized aspirin and oil of wintergreen.

► Answer this question only if you have already completed the project in which you should have collected infrared absorption spectra of your synthesized aspirin and oil of wintergreen.

Chapter 21

Examining Molecules with Molecular Modeling

This lab introduces the use of molecular modeling software to visualize molecular structure and to calculate molecular properties. The structure of H_2SO_4 and SO_4^{2-} are investigated and compared to their Lewis structures. The series of molecules H_2 , HF, LiF, and NaF are investigated to observe the effect electronegativity differences have on the ionic nature of a bond.

21.1 Introduction

Molecular Modeling

Humans are terrific at making models that have predictive capacity. For instance, if you know about gravity and the nearly circular orbits of the planets around the sun, you can predict what stars and planets can be seen in the sky at any time of year.

This image of the planets traveling around the sun is a model. It is mostly correct, and it gives you the ability to make predictions. You can physically build this model from some balls and wire or you can simply make it in your head. As long as you apply the rules of the model (Newton's Law of Universal Gravitation) fairly, you will obtain reasonably correct predictions.

Plants and stars are huge objects. In chemistry we are interested in modeling incredibly small things such as atoms and molecules. Chemists have traditionally modeled molecules as consisting of balls (the atoms) connected by sticks (the bonds). Such stick and ball models of molecules has great predictive power. Once the structure of a molecule is known, a great deal can be said about its functions.

This is not an easy process, however, because the model of how atoms are held together is quite complex. You have already learned a little about this model that is called quantum mechanics. By comparison, gravity is simple.

But, fortunately, we live at a time when computers can make complex tasks easy. What once took trained chemists and physicists years to do by hand can today be done by a general chemistry student in a few minutes.

The Department of Chemistry has computer software that applies the rules of quantum mechanics (with some approximations!) to atoms in a molecule and generates a prediction of what a molecule will look like. You will use this software in this lab to explore the structure of several molecules.

Computer Aided Chemistry with Scigress

It is important to understand that the rules of quantum mechanics (the rules of bonding) are not dependent on a computer program. These rules existed long before the first computer was invented. The computer is simply used to do complex calculations rapidly so that you can develop insight quickly.

The particular piece of software that the Department of Chemistry owns to carry out these calculations is called Scigress, and it is produced by Fujitsu Corporation. It is just one of many programs that are capable of nearly the same thing.

Precision and Accuracy of a Computer

Before you go too far, it is important to understand that a computer is not perfect. Just because a machine spits out an answer does not mean it is “correct.” Humans built computers, and humans wrote the software with certain assumptions and goals in mind. It is important to critically analyze the results before just blindly accepting them.

Perhaps the most important point to make in this area is that computers, like your calculators, can produce more decimal places than are valid. You, the chemist, must make a judgment as to how many decimal places to keep.

If you have studied significant figures then you probably have a good feel for how to do calculations while keeping the right number of significant figures. With the computer and software in this lab, however, there are a tremendous number of calculations that are completely invisible to you. How do you know how many significant figures to keep in this case?

Well, about the only thing you can do at this level is accept the advice of somebody else. For the purpose of this lab, you should trust bond lengths to two decimal places and bond angles to one decimal place. If the software gives you a result with more significant figures, round until you have the appropriate number of significant figures.

21.2 Safety Considerations

There are no special cautions or warnings this week. Working at a computer is a relatively safe endeavor.

Goggles

There is no need to wear goggles this week because all your work will be in the computer lab with no chemicals or glassware.

21.3 Experimental Procedure

Structure of Sulfuric Acid

One of the many reagents you will use in general chemistry is sulfuric acid. In this experiment you will probe its three dimensional structure.

1. Open the Scigress molecular modeling program and using the Drawing tool draw H_2SO_4 in a manner consistent with the most likely Lewis structure.
2. After drawing the molecule, push the Select tool button and then click anywhere in the blue background to make sure the entire molecule is selected.
3. Go to the Beautify menu and select Comprehensive.
4. Go to the Experiment menus and select New.
5. The default options in the window that pops up are all appropriate. Simple click the Start button.
6. You will be prompted to save the molecule. You need to save it so select Yes and then give it a name.
7. The experiment will run after you save the molecule. When the computer tells you that it is done calculating, close the calculation windows and look at the results.
8. Measure all the S-O bond lengths. Why are they different?
9. Measure the O-S-O angles.
10. Now, delete the hydrogen atoms by selecting them one by one and pushing the delete key.
11. Select the oxygen atoms to which these hydrogen atoms were connected and change their charge to -1.
12. Select Beautify → Comprehensive again.
13. Run another experiment in the same manner as before.
14. Measure the S-O bond lengths and the O-S-O bond angles again. Can you explain what has happened?

Ionic Versus Covalent Species

In this experiment you will observe how electrons are distributed in four molecular species: H_2 , HF, LiF and NaF. You will be asked to explain the trends you observe.

1. Draw each of these molecules in the Scigress program. You can draw only one per window.

2. Select Experiment → New.
3. When prompted, save the file with a name of your choice.
4. From the experiment window that pops up, pull down the “Property” list and scroll down until you see “electrostatic potential on electron density.” Select this option.
5. Next pull down the “Using” list and scroll down until you see “PM5 geometry using PM5 wavefunction” and Select this option.
6. Push the “Start” button to begin the experiment.
7. When the computer has finished, show the surface and describe the results in your laboratory notebook.
8. Repeat this procedure for all the molecules in this list and then explain the trend that you observe.

21.4 Before Exiting Lab

No hazardous waste is generated during this laboratory period so there is nothing to clean up. Please make sure, however, that you have logged out of your computer before leaving the computer lab.

- Make sure page numbers appear on all the used pages of your laboratory notebook.
- Make sure you have updated your notebook’s table of contents.
- Log out of the computer workstation you used.
- Draw a line at the end of your experimental work and sign on it.
- Have your instructor sign on the line below your experimental work.

21.5 Post-Lab Assignments

1. Explain the results you obtained for the bond lengths in H₂SO₄. Is it what you expected?
2. Explain the results you obtained for the bond lengths in SO₄²⁻. Is it what you expected?
3. Explain the trend observed in the “electrostatic potential on electron density” surfaces for the experiments on H₂, HF, LiF and NaF.

Chapter 22

Molecular Mass by the Dumas Method

22.1 Introduction

If you know the mass of a sample of molecules and the quantity of molecules in that sample, it is a relatively simple matter to compute the molar mass of the molecules in the sample: just divide the mass (in grams) by the quantity of molecules in units of moles. That gives a value with units of molar mass, g/mol. Any experiment that allows you to independently determine the mass of a sample and the moles of substance present in the sample provides a way to determine the molar mass of the substance. In this project we will use this method to determine the molar mass of a liquid.

The Dumas Method

You can easily measure the mass, volume, and temperature of a liquid. The mass of the liquid provides half the information needed to determine the molar mass of the liquid. Unfortunately, there is no way to convert the volume and temperature of the liquid into moles of liquid. This means the molar mass of a liquid cannot be easily determined from the volume, temperature, and mass of the liquid. Ultimately, this is because there is no simple relationship between moles of liquid and the volume and temperature of the liquid.

However, if the liquid can be converted to a gas, the ideal gas law would apply. The ideal gas law provides a relationship between volume, temperature, and moles, allowing the moles of sample to be determined and thereby allowing molar mass to be computed. The ideal gas law is the basis for the Dumas method for the determination of the molar mass of a liquid.

In the Dumas method, a volatile liquid is placed in a container of known volume with a small hole in the top. The container is heated to a known temperature above the boiling point of the liquid so that the volatile liquid completely vaporizes and fills the container. Excess vapor flows out of the hole in the container. When all the liquid has vaporized, the container is cooled and massed. The mass of the container is subtracted, and what remains is the mass of liquid that had, just a moment before, completely filled the container as a gas.

► A volatile liquid is one that can be easily vaporized.

When the liquid was a vapor filling the container as a gas, its volume, temperature, and pressure were known. Using the ideal gas law,

$$PV = nRT \quad , \quad (22.1)$$

the moles of gas present can be computed. Because the mass of liquid is already known, it is simple to determine the molar mass of the substance. In Equation 22.1, P is the pressure of the gas, V is the volume occupied by the gas, n is the moles of gas particles, R is the Universal Gas Constant, and T is the temperature of the gas.

22.2 Experimental Design Decisions

Most experiments are simple in concept. The execution is often more challenging. This section contains some information about the experimental details you will have to worry about while working through this project.

In particular, this section provides information to help you make four critical decisions during the experiment. These decisions will impact the quality of your results. These decisions are shown in Table 22.1 and are discussed in detail in this section.

We will give you some advice about how to answer question 2 in Table 22.1. For the remaining three decisions, we will not tell you what to do. Instead, we will provide data that should help you make these decisions on your own.

Table 22.1

Decisions you must make before you can effectively carry out this experiment. Help in answering each question is provided in this section.

-
-
1. What volume of unknown liquid should be used?
 2. When is the unknown liquid completely vaporized?
 3. When should the flask be removed from the water bath?
 4. When should the flask be massed?
-
-

The Container

The container you will use in this laboratory experiment is a 125 mL Erlenmeyer flask with a rubber septum on top as a cap. You will insert a syringe needle through the septum to provide a small hole as the vent for excess vapor. The flask will be immersed in boiling water to heat the liquid in the flask. When you remove the flask from the boiling water, you will have to be very careful to make sure you dry off all water, even the water that condenses around the septum cap.

You will need to know the volume of this container, and it is not 125 mL. The gas will fill the flask to the top (to the septum), but the 125 mL mark is well below the top of the neck of the flask. You will have to come up with a way to determine the volume of the flask.

Pressure

To use the ideal gas law (Equation 22.1) to compute the moles of vapor present in the flask, you must also know the pressure of the the gas in the flask. When a liquid boils, the vapor pressure of the liquid is equal to the current atmospheric pressure. Therefore, the pressure of liquid vapor inside the flask when all the liquid has just finished boiling will be the current atmospheric pressure. All you need is a current reading from a barometer

Decision 1: Volume of Unknown Liquid to Use

The volume of unknown liquid added to the flask at the start of an experiment will influence the outcome. Rather than tell you what volume of liquid to use, we provide the data in Table 22.2 from previous experiments by other students with two liquids. We can benefit from what they learned in these experiments.

► First decision from Table 22.1.

Table 22.2

Mass of flask plus liquid after experiment when the initial volume of liquid is varied from 2 mL to 5 mL.

Initial Volume (mL)	<i>cis</i> -1,2-dichloroethylene	1,1,1-trichloroethane
2	67.2702	67.6169
3	67.2723	67.5929
4	67.2735	67.5953
5	67.2705	67.5909

The data in Table 22.2 show how the volume of liquid introduced to the flask at the start of the experiment influences the final mass of the flask plus liquid when the experiment is complete. These data provide enough guidance for you to determine the volume of liquid that should be introduced at the start of the experiment.

Decision 2: How to Determine When All Liquid Has Vaporized

The most obvious way to determine when all the liquid has vaporized is to look into the flask to see when the liquid is gone. Discerning the quantity of a colorless liquid through water and glass is not simple, however. A more reliable measure of the quantity of liquid remaining is needed.

► Second decision from Table 22.1.

As the flask is warmed in the hot water bath, the unknown liquid will begin to vaporize. The vapors of the liquid will begin to fill the flask and then spill out through the top of the flask. Because the vapor of the unknown liquid has a different index of refraction than air, you will see “swirls” at the top of the flask as the vapors of the unknown escape. Technically, these swirls are known as a Schlieren pattern.

When all of the unknown liquid has vaporized, the flask will be full of the unknown liquid’s vapor, and the vapor will stop being pushed out the top of

the flask. Therefore, the Schlieren pattern will disappear. When the Schlieren pattern disappears, all the liquid has vaporized.

Decision 3: When to Remove Flask from Water Bath

► Third decision from Table 22.1.

After you have determined that all the liquid has vaporized, when should you remove the flask from the hot water bath? Immediately? After a few minutes? Does it matter when you remove the flask?

The data in Table 22.3 show the final mass of the flask plus liquid for experiments with two compounds when delaying the removal of the flask from the water bath by an increasing time. Pay attention to how the final mass changes as the time interval increases, and then make a decision about how long you will leave the flask in the water bath after the liquid has vaporized.

Table 22.3

Mass of flask plus liquid when the flask is removed from the water bath after an increasing time following the vaporization of all liquid in the flask.

Time (sec)	cis-1,2-dichloroethylene	1,1,1-trichloroethane
5	67.2731	67.5890
30	67.2720	67.5870
60	67.2715	67.5863
90	67.2712	67.5859
120	67.2703	67.5854
180	67.2689	67.5850
240	67.2534	67.5837

Decision 4: How Long to Let Flask Cool

► Fourth decision from Table 22.1.

After you withdraw the flask from the boiling water and thoroughly dry the outside of the flask, you have to mass it. When should you mass it? Immediately? After a few minutes? After a half hour? Does it matter?

You can use the data in Table 22.4 on page 145 to help you decide how long the flask should cool after removing it from the water bath. Table 22.4 presents data from previous experiments for two different compounds in which a flask plus liquid is allowed to cool for increasing amounts of time after being withdrawn from the hot water bath. You should use these data to make a decision about how long to cool the flask before massing.

22.3 Safety Considerations

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Table 22.4

Mass of flask plus unknown after cooling for the indicated time.

Time (min)	cis-1,2-dichloroethylene	1,1,1-trichloroethane
2	66.1023	67.7231
5	66.5515	68.4742
10	66.5525	68.4745
15	66.5528	68.4747
30	66.5525	68.4749
120	66.5393	68.4748
240	66.5129	68.4571

Using the Hoods

The work you do today will cause vapors of toxic substances to be emitted into the air. To help avoid exposure, try to carry out all your work, including the heating of your flask, under your personal bench hood.

Waste Disposal

All chemical wastes have their appropriate receptacles in the large hoods in the back of the laboratory. The volume of liquid waste remaining after your experiments will be small, but it should still be poured into the appropriate waste container.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 22.1. Do not use the normal waste baskets for broken glass.

22.4 Experimental Procedure

This section provides a suggested procedure for determining the molar mass of a volatile liquid by the Dumas method.

- Set Up Boiling Water Bath:** Fill a 600 mL beaker about half full with water and place it on a hot plate. Add a few boiling stones and begin heating the beaker quickly until the water boils. Turn down the heat until the water boils gently but constantly.
- Secure Rubber Septum to Flask:** Place rubber septum on top of a 125 mL Erlenmeyer flask as illustrated by your instructor.
- Weigh Container with Septum:** Measure the mass of the flask with the septum in place.



Figure 22.1
Broken glass container.

► Add water as needed during the lab period, but never add water during an experimental trial.

4. **Attach Flask to Ring Stand:** Attach the flask to a ring stand with a single burette clamp.
5. **Record Atmospheric Pressure:** Record the atmospheric pressure as read from a barometer or as provided by your instructor.
6. **Insert Needle Through Septum:** Obtain a syringe needle and insert it through the septum. This will serve as one of two vents.
7. **Add Unknown Liquid Sample to Container:** Add the appropriate amount of unknown liquid to the flask through the septum cap by injecting the liquid through the septum with a syringe. When the injection is finished, remove the syringe from the needle, but leave the needle inserted in the septum.
8. **Immerse Flask in Boiling Water:** Immerse the flask into the boiling water bath as deeply as possible with the clamp attached. Avoid allowing water to touch the septum.
9. **Monitor Liquid in Flask and Schlieren Pattern:** Continually monitor the liquid level in the flask and the Schlieren pattern of “swirls” coming out of needle.
10. **Remove Flask from Water Bath:** When you are convinced the liquid in the flask has completely vaporized and the Schlieren pattern has disappeared, remove the flask from the water bath after the time interval you previously determined.
11. **Allow Flask to Cool:** Allow the flask to cool for the time period you previously determined. While cooling, you can take the flask out of the clamp.
12. **Thoroughly Dry Flask:** Dry the outside of the flask as completely as possible, including areas close to the bottom of the septum.
13. **Mass the Flask:** After the cooling period you previously determined, mass the flask. Be sure to remove the needles from the septum before weighing the flask.
14. **Complete Two Replicate Trials:** Repeat steps 6 to 13 twice more. There is no need to replace the septum or remove the liquid that is already in the container.
15. **Pour Remaining Liquid into Waste Container:** Remove the septum cap and pour the remainder of the liquid in the appropriate waste container.
16. **Determine the Volume of Your Flask:** Using an appropriate technique, determine the volume of the flask you used for this experiment.

► The volume of unknown liquid to add was a decision you were to make on your own as described on page 143.

► There should now be two needles in the septum.

► How long to leave the flask in the boiling water after the Schlieren pattern disappears was a decision you were to make on your own as described on page 144.

► How long to let the flask cool was a decision you were to make on your own as described on page 144.

22.5 Before Leaving Lab

Before leaving lab for the day, go down this checklist to make sure you have done everything on it.

- Put all of your own glassware back in your drawer.
- Update the table of contents in the front of your notebook.
- Draw a line at the end of your experimental work and sign on the line.
- Have your instructor sign on the line as well.

22.6 Post-Lab Assignments

Calculations

All calculations should appear in your laboratory notebook. If you make an error, just cross through the error with a single line and then move on. To make things easier to read, you may want to present your final results in tabular form.

1. Compute the mass of liquid remaining in the flask after each experimental run.
2. Compute the moles of liquid remaining in the flask after each experimental run. For this, you will have to know the volume of the flask, the atmospheric pressure, and the temperature of the flask. The temperature of the flask is the temperature of the boiling water, but recall that the temperature of the boiling water will not be 100°C unless the atmospheric pressure is exactly 760 mmHg.
3. Compute the molar mass of the liquid for each experimental run.
4. Compute the average molar mass of the liquid along with a standard deviation.

Chapter 23

Identification of an Unknown by Freezing Point Depression

The molar mass of an unknown compound is determined by measuring the freezing point depression it induces in cyclohexane. The unknown compound's molar mass and melting point are used to identify the unknown compound from a list of candidates.

23.1 Introduction

Freezing Point Depression

When a solute is dissolved in a solvent, the freezing point of the solution is lower than that of the pure solvent. This is called freezing point depression. It is typically given the symbol ΔT_f and is defined as the normal freezing point of the pure solvent minus the freezing point of the solution. The value of ΔT_f is always positive, and it is understood that it refers to the amount by which the freezing point of a pure solvent is lowered by addition of a solute.

Freezing point depression is directly proportional to the molal concentration of solute particles. The identity of the solute particles does not matter. The constant of proportionality that relates the molal concentration of solute particles to ΔT_f is the freezing point depression constant. It is normally given the symbol K_f . It is unique for each solvent. This verbal description of freezing point depression can be expressed mathematically as

$$\Delta T_f = K_f m \quad (23.1)$$

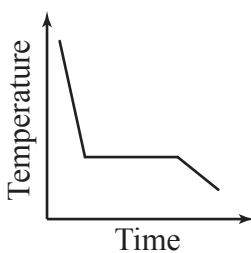
where m is the molal concentration of the solute particles and the other symbols have their previously defined meanings.

The value of m must be the molality of solute particles and not the molality of the solute. For instance, if one mole of sodium chloride is dissolved in one kilogram of water, the molality of solute particles is 2 molal and not 1 molal because the sodium chloride breaks into two ions in solution. If the solute is, instead, a non-electrolyte, the molality of the solute is expected to equal the molality of solute particles. All substances in this project are non-electrolytes.

► Molality of solute particles is defined as the moles of solute particles divided by the kilograms of solvent.

► The value of m must reflect the total concentration of particles. If a solute breaks into ions, m will not be the molal concentration of the solute alone.

► Because all solutes in this project are non-electrolytes, the molality of solute is the molality of dissolved particles.



Measuring a Freezing Point

It might be difficult to understand how an unknown solute can be identified using freezing point depression when ΔT_f does not depend on the identity of the solute. This is possible because the molar mass of a solute can be determined by measuring the freezing point depression of a solution composed of a known mass of solute and a known mass of solvent. Molar mass by itself may not be enough to identify an unknown compound, but it can be helpful when used in combination with other physical or chemical data.

Figure 23.1

Idealized cooling curve for pure solvent. The temperature remains constant while freezing.

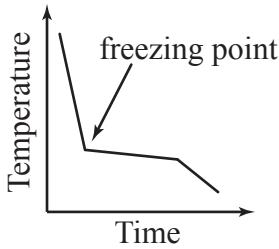


Figure 23.2

Idealized cooling curve for a solution. The temperature is never constant. The freezing point is the temperature at which the slope of the cooling curve changes dramatically.

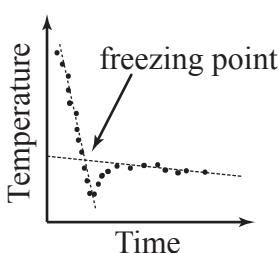


Figure 23.3

Experimental cooling data extrapolated to find the intersection between the low-slope and high-slope regions.

In this project you will measure the freezing point depression of cyclohexane when a known mass of an unknown compound is dissolved in a known mass of cyclohexane. You will compute the molar mass of the compound from the freezing point depression. You will use this in combination with a measured melting point to suggest the most likely identity of the compound from a list of candidates.

To measure the freezing point of pure cyclohexane you will place the liquid in a test tube which you will immerse in an ice water bath. You will record the temperature of the cyclohexane at regular intervals. The temperature will fall as the cyclohexane cools. The temperature is expected to fall rapidly until it reaches the freezing point; it will then remain constant as it freezes. An idealized cooling curve showing what to expect is provided in Figure 23.1. The freezing point is read from a cooling curve like that in Figure 23.1 by looking for the data points that show zero slope. Extrapolating these data points back to the temperature axis provides the freezing point.

Solutions of cyclohexane and a solute are expected to behave differently in the same experiment. The temperature of a solution is expected to fall rapidly and then cool more slowly as the solution begins to freeze; the temperature is not expected to remain constant while freezing. An idealized cooling curve showing what to expect is provided in Figure 23.2. The freezing point of the solution is determined from a cooling curve like that in Figure 23.2 by looking for the temperature at which the slope of the cooling curve changes dramatically. That point is marked with an arrow in Figure 23.2.

Your experimental data will not look like the idealized cooling curves because you will not be able to stir the cyclohexane such that energy is distributed uniformly at all times. This will result in fluctuations in the temperature as the experiment proceeds. You will have to do your best to find the region of constant temperature in the case of cooling pure solvent and, in the case of cooling the solution, the region of intersection shown in Figure 23.2.

When cooling a solution, you may record temperatures that go down but then go back up as illustrated in Figure 23.3. If you encounter this, the freezing point is not the lowest point on the graph. Instead, you can determine the freezing point by extrapolating the data points in the high-slope region and those in the low-slope region until the extrapolations intersect. This intersection is the freezing point. The region where the temperature goes down before going back up is results from not thoroughly stirring the solution.

Collecting Quality Data

The temperature data you collect must start before freezing begins and continue until everything is frozen. This provides the best chance of distinguishing the high-slope from the low-slope region in the cooling curves. To be sure you have usable data, you will be asked to measure the freezing point of the solution three times. After collecting your data and before leaving the lab, you should plot your data to be sure it has the expected appearance. You can check with your instructor to be sure the data look usable. If the data are not acceptable, you can collect more before leaving lab.

Plotting Data

You will have to plot the temperature versus time data to finish your analysis. You will most likely plot these data using a piece of software such as Apple Numbers, OpenOffice, or Microsoft Excel. Regardless of the application you use, the plots need to be constructed so that temperatures can be read from the vertical axis with a precision of $\pm 0.1^\circ\text{C}$. This can be accomplished by changing both the range of the vertical temperature axis and the spacing of the tick marks on the axis.

The vertical axis range should be set to something only slightly larger than the temperature range of your actual data points so that no space is wasted. Wasted space pushes tick marks closer together and makes the temperature scale more difficult to read. We want to avoid this by spreading the data out as much as we can. Most software packages will ask you enter a minimum and a maximum temperature to specify the axis range.

The interval for tick marks is also important. Major tick marks should be placed every 1.0°C , and minor tick marks should be placed every 0.2°C . This will provide you with a graph that can be read to a precision of $\pm 0.1^\circ\text{C}$.

► It will also be helpful to plot your data so that the temperature scale is along the long side of a piece of paper. This will require that you rotate the plot to be portrait and not landscape. It is not sufficient (or helpful) to print the graph in the portrait orientation without also rotating the plot. The goal is to spread out the temperature axis as much as possible.

23.2 Safety Considerations

Chemical Hazards

Some of the compounds used in this lab may be irritants. You are advised to wear gloves while working with the chemicals in this project. If you spill any chemical on your skin, wash it off immediately with plenty of water.

Goggles

You are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

All waste in this lab must be poured into the appropriate waste containers. No waste can be poured down the drain.



Figure 23.4
Broken glass container.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 23.4. Do not use the normal waste baskets for broken glass.

23.3 Experimental Procedure

Organize

- Find a Partner:** It will be essential to work with a partner during this project. Find a partner or take the partner assigned by your laboratory instructor.
- Record Unknown Number:** At your lab station you will find a test tube or vial containing an unknown solid compound. Record the number of this unknown in your laboratory notebook.
- Set Up Ice Water Bath:** Fill a 400 mL beaker about half full of tap water and add ice so that the beaker is nearly full.
- Obtain Test Tube:** Obtain a 150 mm (6-inch) test tube from the table in front of the lab. This is not one of the test tubes in your drawer.
- Obtain Test Tube Clamp:** Obtain a test tube clamp from the appropriate drawer in the lab. You will use this to secure the 150 mm test tube to a ring stand so that it can be lowered into and raised out of the ice water bath.

Measure Melting Point of Unknown

⌚ You can measure the melting point at any time during your laboratory period. You do not have to do it first. Wait until the lines are short.

Using the procedures described in Chapter 6, determine the melting point of the unknown solid assigned to you. The unknown is expected to be pure, which means the melting point range should be narrow.

Measure Freezing Point of Cyclohexane

- Weigh Test Tube in Beaker:** Place the 150 mm test tube in a small beaker and find the mass of both together.
- Add Cyclohexane to Test Tube:** Measure out 10 mL of cyclohexane using a graduated cylinder and pour it into the 150 mm test tube.
- Weigh Test Tube with Cyclohexane:** With the test tube containing the cyclohexane in the same beaker used previously, find the mass of the beaker, test tube, and cyclohexane.
- Clamp Test Tube to Ring Stand:** Using a test tube clamp, secure the test tube containing cyclohexane to a ring stand. Place the ice water bath under the test tube so that it can be lowered into the ice bath.

► Do not lower the test tube into the ice bath yet.

5. **Place Thermometer into Split Stopper:** Carefully place a thermometer through a split rubber stopper so that when placed into the test tube the bulb of the thermometer is a few millimeters above the bottom of the test tube.
6. **Allow Cyclohexane to Thermally Equilibrate:** Insert the thermometer into the test tube and rest the split rubber stopper on top of the tube. Be sure the thermometer does not touch the bottom of the test tube. Let this apparatus stand for about five minutes to be sure the temperature has stabilized.
7. **Prepare Notebook for Data Collection:** Make a table in your notebook to record temperature data at 10 second intervals for about 5 minutes.
8. **Lower Cyclohexane Into Ice Bath:** Lower the test tube apparatus into the ice bath, making sure the top of the cyclohexane is below the surface of the ice bath. Immediately start a stop watch and begin stirring the cyclohexane gently with the thermometer.
9. **Record Temperature Data:** One partner (the observer) should stir the cyclohexane and monitor the temperature continually during the experiment. The other partner (the recorder) should monitor the stopwatch and record data. Every ten seconds, the recorder should say “now”, and upon that prompt the observer should read out loud the current temperature to the nearest 0.1°C . Continue collecting data for about 5 minutes overall or until the temperature has remained constant for 2 minutes.
10. **Remove Cyclohexane from Ice Bath:** Raise the test tube apparatus containing the cyclohexane out of the ice bath. Allow the cyclohexane to melt and to return to room temperature. Do not remove the thermometer from the test tube. If you do, you will lose cyclohexane.
11. **Repeat Measurement:** Repeat the measurement of the cooling curve of pure cyclohexane two more times using the same procedure as above.

► This part of the experiment is a bit intense. If you miss a temperature reading, just move to the next one.

Measure Freezing Point of Cyclohexane Solution

1. **Add Unknown to Cyclohexane:** Add approximately 0.20 g of your unknown to the cyclohexane already in the test tube. With your thermometer, carefully stir to dissolve all added solute. It is important that the solute dissolve completely.
2. **Prepare Notebook for Data Collection:** Make a table in your notebook to record temperature data at 10 second intervals for about 5 minutes.
3. **Lower Cyclohexane Solution Into Ice Bath:** Lower the test tube apparatus into the ice bath, making sure the top of the cyclohexane solution is below the surface of the ice bath. Immediately start a stop watch and begin stirring the cyclohexane solution gently with the thermometer.

⊕ Do not waste time massing out exactly 0.200 g. Get close and just record the mass of what you have.

► This part of the experiment is a bit intense. If you miss a temperature reading, just move to the next one.

4. **Record Temperature Data:** One partner (the observer) should stir the cyclohexane solution and monitor the temperature continually during the experiment. The other partner (the recorder) should monitor the stopwatch and record data. Every ten seconds, the recorder should say “now”, and upon that prompt the observer should read out loud the current temperature to the nearest 0.1°C. Continue collecting data for about 5 minutes.
5. **Remove Cyclohexane Solution from Ice Bath:** Raise the test tube apparatus containing the cyclohexane solution out of the ice bath. Allow the cyclohexane solution to melt and to return to room temperature. Do not remove the thermometer from the test tube. If you do, you will lose cyclohexane solution.
6. **Repeat Measurement:** Repeat the measurement of the cooling curve for the cyclohexane solution two more times using the same procedure as above.

Check Data

Before disassembling your experimental setup and leaving the lab, you should plot your temperature versus time data for the cooling of pure cyclohexane and the cyclohexane solution. You should check that the data look roughly like the expected idealized curves shown in Figures 23.1 through 23.3. If your data do not look usable, you should go back to the lab and collect more data. You can check with your instructor if you wish.

To visualize your data, the minimum you need is a computing device with access to Google Drive. A computing device with a native spreadsheet application will probably make things easier. Using the application of your choice, plot your data and assess its quality. In this visualization step you do not have to produce beautiful graphs; you just have to examine the data.

23.4 Before Exiting Lab

- Check your data to be sure you do not need to collect more.
- Dispose of the cyclohexane solution in the appropriate waste container.
- Clean and dry the 150 mm test tube. Return it to the table at the front of the lab.
- Return the test tube for vial with the unknown compound to the front of the room.
- Clean up your work area so that it is scrupulously clean.
- Check your lab notebook for page numbers on all pages.
- Update the table of contents in your notebook.

- Draw a line at the end of your experimental work for the day. Sign your name on the line.
- Have your instructor sign your lab notebook before you leave the lab.

23.5 Post-Lab Assignments

Follow These Graphing Guidelines

In the next two subsections you will be asked to plot your data. For all plots you should make sure to do the following.

- Set the range for each axis to utilize all the space on the paper.
- Set major tick marks on the temperature axis to be placed at 1°C intervals.
- Set minor tick marks on the temperature axis to be placed every 0.2°C .
- Orient the graph so that the vertical temperature axis is along the long side of the paper onto which it will eventually be printed. This will spread out the temperature axis as much as possible. This must be done in the plotting application.
- Be sure you follow all other guidelines for preparing graphs as discussed in Chapter 9.

► It is not sufficient to print the plots in the portrait orientation unless the temperature axis extends for the entire length of the long side of the page.

The only guideline for preparing graphs that you can violate in preparing graphs for this project is the one regarding grid lines. These graphs are not for presentation of data to an external audience. Instead, they are “working” graphs for the purpose of allowing you to extract freezing temperatures. Grid lines may help in this.

Analyze Cooling Curves for Pure Cyclohexane

1. Plot the cooling curve data for cooling pure cyclohexane. Plot each cooling curve on a separate graph.
2. For each cooling curve for pure cyclohexane, determine the freezing point.
3. Compute an average freezing point for pure cyclohexane.

Analyze Cooling Curves for Cyclohexane Solution

1. Plot the cooling curve data for cooling the cyclohexane solution. Plot each cooling curve on a separate graph.
2. Using a ruler, draw the best single line you can through the high-slope region early in time. Do the same for the low-slope region. Do this for each cooling curve.

3. Find the temperature at which these lines intersect on each cooling curve. This temperature is the freezing point. Record this value for each cooling curve.
4. Compute the average freezing point for the solution using the data from all cooling curves.
5. Compute the freezing point depression, ΔT_f , for the solution using the average freezing points.

Identify the Unknown Compound

1. Using the freezing point depression constant for cyclohexane, K_f , determine the molality of your cyclohexane solution.
2. Compute the molar mass of the unknown compound you were assigned.
3. In conjunction with the melting point you determined for the unknown, select the most likely identity of the unknown from the list of candidates.

Chapter 24

What Are the Kinetics of the *t*-Butyl Chloride Hydrolysis?

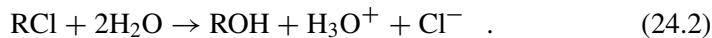
The rate law, rate constant, and activation energy of the hydrolysis of *t*-butyl chloride are determined.

24.1 Introduction

In this experiment we will examine the kinetics of the hydrolysis of tertiary-butyl chloride, $(\text{CH}_3)_3\text{CCl}$. Tertiary-butyl chloride is often abbreviated as *tert*-butyl chloride or *t*-butyl chloride. Its molecular structure is shown in Figure 24.1. The hydrolysis reaction we will study is given by the equation



The molecule *t*-butyl chloride is a member of a group of organic compounds called alkyl chlorides. They differ in composition by the hydrocarbon group attached to the chlorine. All alkyl chlorides undergo a hydrolysis reaction similar to that in Equation 24.1. Only the hydrocarbon portion is different. Because these reactions are so similar, it is common to write the hydrocarbon portion of the formula of alkyl chlorides as R, where R can be any alkyl group. This allows the hydrolysis of any alkyl chloride to be written as



If R is *t*-butyl, Equation 24.2 is the same as Equation 24.1. To save space and to be consistent with common practice in chemistry, *t*-butyl chloride will be abbreviated as RCl. The alcohol produced will be abbreviated as ROH.

Determining [RCl] at Various Times

How do we experimentally follow the rate of the reaction in Equation 24.2 in the simplest way possible? Monitoring the disappearance of the reactant RCl or the appearance of products ROH or Cl^- could be difficult. We also do not have the equipment to monitor the concentration of RCl, ROH, or Cl^- as a function of

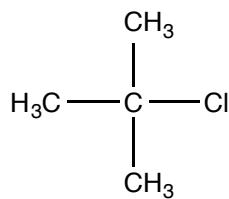


Figure 24.1

Drawing of tertiary-butyl chloride.

► An alkyl group is a collection of carbon and hydrogen atoms that are all singly bonded. Symbolizing alkyl groups with R is common throughout chemistry.

time. Monitoring the disappearance of H₂O would be impossible, considering that the reaction mixture will be about 50% H₂O.

Following the appearance of H₃O⁺ as a function of time is the only remaining method of determining the rate of the reaction. This can be accomplished in several ways. The pH of the reaction mixture could be measured at various times as the reaction proceeds, but pH meters are too expensive for us to supply one to everybody. Another way to monitor the appearance of H₃O⁺ is to titrate the hydronium ion present at any given time. This is the approach we will take.

How do we titrate a reaction that is constantly producing more H₃O⁺? We can not. Instead, we will add excess NaOH to the reaction, along with some phenolphthalein, and allow the reaction to titrate itself. Essentially, we will titrate past the end point and allow the continual production of H₃O⁺ by the reaction to bring the titration to the end point. A color change will tell you when the excess NaOH has been consumed and the end point has been reached. This is probably the easiest titration you will ever perform because, technically, you are not doing it.

► This summary is very important. Be sure you understand it.

► Every time the color of solution changes from pink to clear you have collected one more concentration versus time data point. You need many of these, and the only way to obtain another is to add more NaOH.

► You should write an equation showing the reaction between hydroxide and hydronium ion.

This can be difficult to grasp, so think about this some more. We need to know [RCl] as a function of time. We cannot measure this concentration directly. Instead, we will measure the moles of H₃O⁺ produced as a function of time. We will do this by adding enough OH⁻ to consume all H₃O⁺ for a short period of time as it is produced by the reaction. The solution will be pink so long as OH⁻ is present in excess. As soon as the solution turns clear, we will know that the reaction has produced exactly a number of moles of H₃O⁺ equal to the moles of OH⁻ we added. Then you will do it again: add excess hydroxide and wait for the color to change from pink to clear. You will keep doing this until you have sufficient time data.

The amount of RCl present at any time can be calculated with a little stoichiometry. It will always be true that the moles of RCl remaining in the reaction will be the initial moles of RCl minus the moles RCl used up (reacted). This can be expressed mathematically as

$$\text{moles RCl}_{\text{remaining}} = \text{moles RCl}_{\text{initial}} - \text{moles RCl}_{\text{used up}} . \quad (24.3)$$

We know the stoichiometric relationship between moles RCl used and moles H₃O⁺ formed. It is one to one. We also know the stoichiometric relationship between moles H₃O⁺ produced and moles OH⁻ added. It is also one to one. This information allows us to write

$$\text{moles RCl}_{\text{remaining}} = \text{moles RCl}_{\text{initial}} - \text{moles OH}^-_{\text{used to titrate}} . \quad (24.4)$$

Concentrations can then be calculated using the known volumes of solution.

Each time you observe a change in the solution color from pink to clear, the total moles of hydronium ion produced by the reaction equals the total moles of sodium hydroxide added to the solution. We need to know the total moles of RCl remaining at many times. This means you will have to add excess and watch the color change many times.

24.2 Safety Considerations

Chemical Hazards

You will work with t-butyl chloride in this lab. Do not dispense this chemical yourself. Ask your laboratory instructor or your teaching assistant to do it for you.

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

All waste in this lab can be poured down the drain with plenty of water.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 24.2. Do not use the normal waste baskets for broken glass.



Figure 24.2

Broken glass container.

24.3 Experimental Procedure

Setup Equipment for Experiment

- 1. Setup Water Bath:** Fill an 800 mL beaker with about 300 mL of tap water that is close to room temperature. Allow this beaker to reach room temperature, unless you were assigned a reaction temperature that is above room temperature (see next step).
- 2. Place Water Bath on Hot Plate:** If you belong to the part of the lab that will carry out this experiment at an elevated temperature, place your water bath on a hot plate and begin gently heating the water bath until your assigned temperature is reached. Maintain this elevated temperature within $\pm 1^{\circ}\text{C}$. Control the temperature by taking the beaker off the hotplate as necessary.
- 3. Obtain 250 mL Flask and Stopper:** Obtain a 250 mL flask and make sure it is clean and dry. Find a cork to fit the flask.
- 4. Fill Flask with Solvent:** Using a graduated cylinder, add 100 mL of a 50:50 v/v isopropanol-water mixture to the flask and quickly stopper it.
- 5. Place Flask in Water Bath:** Place the flask into the water bath, but do not allow it to touch the bottom of the beaker. You may consider securing the flask in the water bath with a clamp attached to a ring stand.

► It is very important that you regulate the temperature in your water bath to within $\pm 1^{\circ}\text{C}$. This means you will have to suspend a thermometer in the water bath to constantly monitor the temperature.

► The NaOH is about 0.25 M but you need to record the precise value which appears on the bottle.

6. **Prepare Buret:** Obtain a buret and buret holder, and bring them back to your work area. Rinse the buret twice with 5 mL aliquots of the standardized NaOH in isopropanol-water solution. Place buret in the buret holder and carefully add about 30 mL of the standardized NaOH solution to the buret. Do not completely fill buret.

Carry Out and Monitor Reaction

It is important to get as many points as you can early in the reaction. If you do not collect two data points within the first few minutes, you will not be able to properly evaluate your data. Therefore, you need to read these instructions and understand them before you begin. If you have to refer to the following instructions while you are carrying out the experiment, you are moving too slowly.

1. **Add Phenolphthalein to Flask:** Add 10-15 drops of phenolphthalein to the flask containing solvent. Quickly stopper the flask again.
2. **Add t-Butyl Chloride:** When you are ready to begin the reaction, quickly remove the flask from the water bath and take it to the hood where the *t*-butyl chloride is dispensed. Your instructor will then add 1.00 mL of *t*-butyl chloride to your flask. Stopper and swirl the flask to dissolve the *t*-butyl chloride. Start a stop watch or write down the clock time as soon as the *t*-butyl chloride is dissolved. Return the flask to its water bath as quickly as possible.
3. **Add Sodium Hydroxide to Flask:** Record the initial buret reading in your notebook. **Room T:** Add about 0.5 mL of NaOH solution (or enough to make the pink color persist) from the buret to the solution in the flask and mix well by swirling the flask. Record final buret reading. **For T=26°C:** Add about 0.75 mL of NaOH solution (or enough to make the pink color persist) from the buret to the solution in the flask and mix well with a stirring rod. Record final buret reading. **For T=30°C:** Add about 1.0 mL of NaOH solution (or enough to make the pink color persist) from the buret to the solution in the flask and mix well with a stirring rod. Record final buret reading.
4. **Monitor Reaction Flask:** Watch the flask carefully and record the clock time at which the solution fades to colorless. Record *all* buret readings (initial and final) that correlate with the clock times at which the end points are reached. These constitute *essential* data!
5. **Continue Adding Sodium Hydroxide:** After each fade to colorless, add another aliquot of sodium hydroxide appropriate for the temperature of your reaction mixture. Record the clock time at which the solution fades to colorless. Do this as quickly as you can without rushing. Continue this until the time between the last two additions of NaOH is about 4 times as long as the time between additions at the beginning of the reaction. You should obtain at least 20 data points.

► The moment the *t*-butyl chloride is added is $t = 0$. Start a stop watch or record the clock time in your notebook.

► All clock times should be recorded to the nearest 5 seconds.

6. **Experimental Note 1:** If your solution (at either temperature) turns colorless as soon as you swirl it, add another aliquot of base appropriate for the temperature of your reaction flask. If enough base has been added, the solution will stay pink after swirling.
7. **Experimental Note 2:** There is no harm in allowing the solution to remain acidic while you record your data. This will simply be included in your next reading.
8. **Experimental Note 3:** The time of fading can be adjusted by adjusting the amount of base added. If you miss the time of fading, just add a little base and record the time and final buret reading only for the fading you observe.

Clean Up Work Area

1. **Clean Buret:** Drain the contents of the buret into the sink and rinse the buret once with about 5 - 10 mL 1 M HCl. Flush this down the sink. Rinse the buret twice with DI water then fill with DI water and cork. Return the buret to the drawer from which you obtained it.
2. **Dump Reaction Mixture:** Discard the contents of the reaction flask down the sink with plenty of water.
3. **Unplug Hot Plate:** Unplug the hot plate and allow it to cool. Then return it to the shelf.

24.4 Before Exiting Lab

- Check your lab notebook for page numbers on all pages.
- Update the table of contents in your notebook.
- Draw a line at the end of your experimental work for the day. Sign your notebook at the line.
- Have your instructor sign your lab notebook before you leave the lab. This helps verify where you stopped lab work for the week.

24.5 Post-Lab Assignments

Assignments 1, 2, and 3 must be completed before you turn in your lab notebook. All remaining post-lab assignments will actually be completed during our normal lab meeting time the week after you complete the experimental part of this experiment.

1. Compute the number of moles of t-butyl chloride you added to your reaction flask.

2. Calculate the initial concentration of t-butyl chloride in your reaction flask in units of molarity. We will call this quantity $[RCl]_0$.
3. Prepare a data table in your notebook with the following columns: total time, total mL NaOH added, total moles NaOH added, moles RCl remaining, and total volume of solution (L). This table with five columns should appear in your notebook. You should then make entries for each data point you collected
4. Enter all the values you just computed into a spreadsheet. Add three additional columns to that spreadsheet: $[RCl]$, $\ln[RCl]$, and $\frac{1}{[RCl]}$. You can use the spreadsheet to compute these three columns based on the data you have entered in the previous four columns.
5. Using the data in the spreadsheet you have just created, make a plot of $[RCl]$ versus time. Add a linear trend line and make sure the equation for the line appears on the graph. Print out the graph and include it in your notebook.
6. Using the data in the spreadsheet you have just created, make a plot of $\ln[RCl]$ versus time. Add a linear trend line and make sure the equation for the line appears on the graph. Print out the graph and include it in your notebook.
7. Using the data in the spreadsheet you have just created, make a plot of $\frac{1}{[RCl]}$ versus time. Add a linear trend line and make sure the equation for the line appears on the graph. Print out the graph and include it in your notebook.
8. From all the information you have just processed, determine the order of this reaction and find the rate constant, k .
9. Pool the class data for the rate constant, k , at the three different temperatures and make an appropriate plot to determine the activation energy of this reaction. Print out the plot and include it in your notebook.

► The total time is the time since $t = 0$, not the time between the fading of the pink. Total mL NaOH is the total added since $t = 0$.

► We will do this and all subsequent assignments together during lab the week after the experiment. Do not do these steps on your own.

Chapter 25

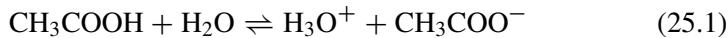
How Can We Alter the Extent of a Reaction?

25.1 Introduction

Extent of Reaction

One of the complexities of chemistry is that reactions do not always go to completion. For instance, if you place acetic acid (CH_3COOH) in water, some of it will dissociate into acetate ions (CH_3COO^-), producing hydronium ions in the process. However, the bulk of the acetic acid will not dissociate. In other words, the reaction does not go to completion.

The process described above can be written as the equation



where the double-headed arrow between reactants and products explicitly indicates that the reaction is reversible, which means that this equation represents an equilibrium process. To indicate that most of the acetic acid remains undissociated we would say that the equilibrium lies far to the left. There is nothing in the equation itself that tells us to which side the equilibrium lies. This has to be determined computationally or experimentally.

Any discussion of a reaction that does not convert all reactants to products must be discussed in the context of equilibrium and reversibility. This is why we normally include the double-headed arrow in equations describing such reactions. However, you should keep in mind that just because a reaction is reversible does not mean it does not go to completion. Technically, all reactions are reversible, but many still go to completion.

A reaction that is known not to go to completion implies a reversible reaction and an equilibrium process. However, reversibility does not imply that a reaction does not go to completion.

The degree to which a reaction goes to completion is called the extent of reaction. We would say that acetic acid dissociation in water has a small extent of reaction. If your business is to produce large quantities of a product, such as some anti-cancer drug, then you want to force all reactions involved in the synthesis of that product to have a large extent of reaction. If you are in the

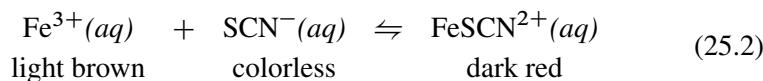
business of minimizing the impact of an environmental toxin, you want to force all reactions leading to biological harm to have the smallest possible extent of reaction.

It is worth noting that increasing the extent of a reaction is referred to as shifting an equilibrium system to the right. Likewise, decreasing the extent of a reaction is referred to as shifting an equilibrium to the left. These are just terms, but they need to be learned.

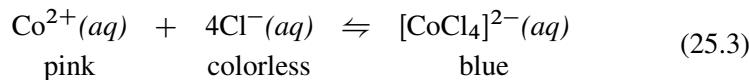
In either case, it is useful to know how to alter the extent of a reaction, whatever that reaction may be. This is what this lab is about.

Equilibrium Systems in This Lab

In this experiment, you will establish two equilibrium systems, make changes to these systems, and observe the results. From your observations you will determine if the extent of reaction has changed. You will then write equations to describe your observations and conclusions. The two equilibrium systems you will study are



and



In both of these equilibrium systems, any change in extent of reaction can be monitored by color changes. In the first equilibrium system, a change in color from brown to red indicates a greater extent of reaction. A change from red to brown indicates a reduced extent of reaction. In the second equilibrium system, a change in color from pink to blue indicates an increase in the extent of reaction. Likewise, a change from blue to pink indicates a decrease in the extent of that reaction.

Predicting Changes in Extent of Reaction

According to Le Chatelier's Principle, when changes are made to a system at equilibrium, the system alleviates, or minimizes, those changes by shifting the position of its equilibrium. In other words, the system responds by altering the extent of reaction.

More specifically, addition of a reactant normally increases the extent of reaction and the removal of a reactant normally decreases the extent of reaction. Likewise, addition of a product to an equilibrium system normally decreases the extent of reaction and removal of a product normally increases the extent of reaction.

The addition or removal of heat can also affect the extent of a reaction. The influence of heat on the extent of a reaction can be predicted by considering heat to be a reactant if the reaction is endothermic and considering heat to be

► Add reactant, shift right. Remove reactant, shift left.

► Add product, shift left. Remove product, shift right.

a product if the reaction is exothermic. Therefore, when heat is added to an endothermic reaction, the extent of reaction increases because you are essentially adding a reactant. Likewise, when you add heat to an exothermic reaction you are adding a product to the equilibrium system and therefore decreasing the extent of reaction.

Using Your Observations

The first step in successfully completing this lab is to accurately record your observations. Do this without any regard for what you think “should” happen. Just record what you see. After this, use your observations to determine if the extent of reaction changed. This can be done based on the color change that was observed, if any. Based on the observed color changes, you can determine if the extent of reaction increased (equilibrium shifted to the right) or decreased (equilibrium shifted to the left).

After you have determined how each change affected the equilibrium, you can attempt to write an equation to describe that change. Remember, if a change in the extent of reaction was observed, then the change you induced in the system must have caused a change in reactant or product concentrations (including heat).

For instance, if you observe that a change results in a shift in equilibrium to the right, either a product concentration must have been reduced by your change or a reactant concentration must have increased. After you determine the direction of change, you must determine how that change was made and then describe it with an equation.

25.2 Safety Considerations

Chemical Hazards

- Concentrated HCl:** You will use 12 M HCl in this lab. Concentrated HCl is corrosive and will cause burns if you get it on your skin. It will also damage clothing. If you get concentrated HCl on your skin, wash the affected area immediately with plenty of water.

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

No liquid or solid waste can be poured down the drain in this lab. Everything must be disposed of in the waste containers in the hoods.

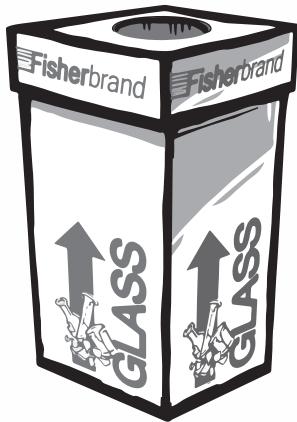


Figure 25.1
Broken glass container.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 25.1. Do not use the normal waste baskets for broken glass.

25.3 Experimental Procedure

Prepare Hot Water and Ice Baths

- 1. Prepare Hot Water Bath:** One student per bench side should fill a 600 mL beaker about two-thirds full of water and place the beaker on a hot plate. Heat the water in the beaker to near boiling. Continue to add water as needed since you will use this bath for both sections of this experiment. All students along a bench side can use this hot water bath when needed.
- 2. Prepare Ice Bath:** Each student individually can add ice and water to an ice bath pan. Continue to add ice as needed to keep the ice bath cold.

Prepare Equilibrium Systems

- 1. Prepare Iron System:** With two other students, add 5 mL of 0.1 *M* $\text{Fe}(\text{NO}_3)_3$, 5 mL of 0.1 *M* KSCN, and 140 mL of distilled water to a beaker and stir.
- 2. Divide Iron Solution:** Divide the iron solution into three 50 mL portions. Each student in your group can take the 50 mL for use in their own experiments.
- 3. Prepare Cobalt System:** Add 10 mL of 0.05 *M* $\text{Co}(\text{NO}_3)_2$ and 10 mL of concentrated (12 *M*) HCl to a 50 mL beaker and stir.



Be sure to add the acid to the aqueous solution and not the other way around.

Carry Out Changes to Iron System

- 1. Prepare Samples for Iron System:** Line up 8 test tubes in a test tube rack and number them 1 to 8. Add 5 mL of the iron thiocyanate solution to each test tube.
- 2. Record Observations of Control Tube:** Tube 1 is considered the control. You will never make any changes to the system in this tube. Instead, you will always compare other tubes to the control tube. Record the appearance of tube 1 in your laboratory notebook.
- 3. Make Changes to Tube 2:** Add 1 mL of 0.1 *M* $\text{Fe}(\text{NO}_3)_3$.
- 4. Make Changes to Tube 3:** Add 1 mL of 0.1 *M* KSCN.
- 5. Make Changes to Tube 4:** Add 1 mL of 0.1 *M* AgNO_3 . Centrifuge for several minutes.

6. **Make Changes to Tube 5:** Add 1 mL of 0.1 M Na_2CO_3 . Wait several minutes, then shake vigorously.
7. **Make Changes to Tube 6:** Add 1 mL of concentrated HCl.
8. **Make Changes to Tube 7:** Heat the solution in a boiling water bath.
9. **Make Changes to Tube 8:** Cool the solution in an ice bath.

Make Changes to Cobalt System

1. **Prepare Samples for Cobalt System:** Line up 5 test tubes in a test tube rack. Add 4 mL of the prepared cobalt solution to each of these test tubes.
2. **Record Observations of Control Tube:** Tube 1 is considered the control. You will never make any changes to the system in this tube. Instead, you will always compare other tubes to the control tube. Record the appearance of tube 1 in your laboratory notebook.
3. **Make Changes to Tube 2:** add 2 mL of 12 M HCl.
4. **Make Changes to Tube 3:** add 2 mL of 12 M HCl and then 2 mL of 0.1 M AgNO_3 .
5. **Make Changes to Tube 4:** Heat the solution in a boiling water bath.
6. **Make Changes to Tube 5:** Cool the solution in an ice bath.

Dispose of Waste

1. **Place All Waste in Appropriate Waste Container:** Take all waste generated in this lab, including the contents of all test tubes and beakers, to the hood and pour into the designated waste container.

25.4 Before Exiting Lab

- Make sure all waste has been disposed of in the appropriate containers.
- Make sure all hot plates have been unplugged and returned to the shelves if that is where you got them.
- Check your lab notebook for page numbers on all pages.
- Update the table of contents in your notebook.
- Draw a line at the end of your experimental work for the day. Sign your notebook at the line.
- Have your instructor sign your lab notebook before you leave the lab. This helps verify where you stopped lab work for the week.

25.5 Post-Lab Assignments

► Remember, your laboratory notebook should be independent of your laboratory manual. Thus, do not refer to "tube 7." Instead, say "the tube that was heated in boiling water."

► No equation is necessary when describing the results for the heating and cooling changes.

► No equation is necessary when describing the results for the heating and cooling changes.

1. For each change you imposed on the iron thiocyanate equilibrium system
 - a) state the direction the equilibrium shifted after the change and your evidence for believing this,
 - b) indicate which reactant or product caused the change in equilibrium position, and
 - c) write balanced equations showing how the reactant or product concentrations changed.
2. For each change you imposed on the cobalt equilibrium system
 - a) state the direction the equilibrium shifted after the change and your evidence for believing this,
 - b) indicate which reactant or product caused the change in equilibrium position, and
 - c) write balanced equations showing how the reactant or product concentrations changed.
3. Determine whether the iron equilibrium system is an endothermic or an exothermic reaction. State your reasoning for this in very clear and concise language.
4. Determine whether the cobalt equilibrium system is an endothermic or exothermic reaction. State your reasoning for this in very clear and concise language.

Chapter 26

Analysis of Vinegar by Reaction with Sodium Bicarbonate

26.1 Introduction

According to United States Food and Drug Administration (FDA) guidelines, any product labeled vinegar should contain no less than 4 grams of acetic acid per 100. mL of product at 20°C. Any product with less than this amount of acetic acid cannot legally be called vinegar in the United States.

This guideline can be expressed in a more compact form as a percentage. However, there is more than one way to compute this percentage. We could, for instance, divide the required minimum mass of acetic acid by the volume of vinegar to obtain a mass of solute per volume of solution percentage. We could also divide the mass of required acetic acid by the mass of vinegar to obtain a mass of acetic acid per mass of solution percentage. Because there is more than one way to compute the percentage, a label is used to communicate which method was used. When percentages are computed by dividing mass of solute by the volume of solution, the percentage is reported with w/v after it. This stands for weight divided by volume. Otherwise, it is reported as w/w.

Thus, we can say that the FDA guideline for the labeling of vinegar requires vinegar to be at least 4% w/v acetic acid. Reporting the percentage this way, although somewhat out of the ordinary, is convenient because it does not require the density of vinegar that would be needed to obtain the w/w percentage.

As soon as a guideline like this is written, there is a need for a chemist to analyze samples of vinegar to ensure industry complies with the guideline. Without such monitoring, industry might get away with selling a product with less than required quantity of acetic acid. In this laboratory project, we will carry out an analysis of vinegar samples to determine the percent acetic acid (both w/v and w/w) in those samples.

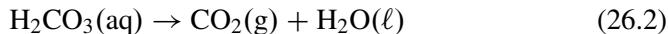
Method of Analysis

In this project we will determine the quantity of acetic acid in vinegar samples by reacting all the acetic acid in the sample with sodium hydrogen carbonate (sodium bicarbonate), a base. This is an acid-base reaction that produces carbonic

acid in solution as shown in Equation 26.1.

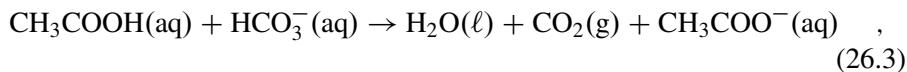


The carbonic acid immediately decomposes in aqueous solution to produce carbon dioxide and water as shown in Equation 26.2.



We will trap the carbon dioxide, determine the volume of $\text{CO}_2(\text{g})$ evolved, and then use that volume, along with its pressure and temperature, to determine the original quantity of acetic acid present in the sample. This quantity can then be converted to the mass of acetic acid present in the sample.

It may be easier to see what is going on if we look at the overall reaction that takes place. Overall, the reaction to be carried out is



which is just the sum of Equations 26.1 and 26.2. You should notice that the stoichiometric relationship between the original quantity of acetic acid and the final quantity of carbon dioxide gas is one to one (1:1). If we are careful to add an excess of hydrogen carbonate to a sample of vinegar such that all of the acetic acid is consumed, the reaction will produce a quantity of carbon dioxide gas equal to the quantity of acetic acid originally present. Because quantity of a gas is related to the volume of gas by the ideal gas law, we can measure the volume of carbon dioxide gas produced and trapped and then relate that to the original quantity of acetic acid present in the sample of vinegar.

26.2 Experimental Design Considerations

From a distance, this experiment appears easy. You will carry out a reaction between vinegar and a base, collect the gas that is released, and then relate the volume of gas to the quantity of acetic acid in the vinegar. This allows you to compute the percent acetic acid in vinegar. There are, however, some details you will need to think about. There are also some decisions we will want you to make on your own. This section provides some insight into the design of the experiment and help with the decisions you will have to make on your own.

Volume of Vinegar to Analyze

Larger samples of vinegar will produce larger volumes of gas. Larger volumes of gas will afford volume measurements with lower percent error because losses and measurement uncertainties will make up a smaller fraction of the total measured volume. However, it is difficult to trap and measure large volumes of gas in a general chemistry lab. Thus, we will want to analyze the largest sample of vinegar that produces a volume of gas that can be collected easily with the equipment we have. Given the equipment you have in your drawer, the appropriate volume of vinegar is 5.00 mL.

Mass of Sodium Hydrogen Carbonate to Add

It is important to add sufficient sodium hydrogen carbonate to the vinegar such that all the acetic acid is consumed. In other words, you must make sure you have added an excess of NaHCO_3 . If you have added an excess, you should be able to see solid NaHCO_3 in the reaction flask after the bubbles of carbon dioxide have stopped forming. If you do not see solid remaining in the flask, you probably need to carry out the reaction again with more NaHCO_3 .

► Decision

You can avoid repeating work by carrying out a simple calculation before doing the experiment. Vinegar is well known to consist of between 4 and 7% w/v acetic acid. If you add enough NaHCO_3 to consume the acetic acid in a sample of vinegar that is as much as 8% w/v acetic acid, you should definitely have an excess of NaHCO_3 for most samples of vinegar. It is left to you to compute the mass of sodium hydrogen carbonate you must add to the reaction flask.

Collecting the Gas

We will collect the gas evolved from this reaction in a 100 mL graduated cylinder that has been filled with water and inverted in a tub of water. The gas will be generated in a reaction vessel composed of a 125 mL Erlenmeyer filter flask sealed with a rubber stopper. The sidearm of the filter flask will be fitted with a rubber hose to direct the gas to the graduated cylinder.

It is important during the experiment to be sure the graduated cylinder used to collect the gas never falls over in the tub of water. This might let out some of the collected gas. It is also important to be sure you place the rubber stopper on the flask immediately after you add the sodium hydrogen carbonate. The reaction will begin the moment the solid enters the vinegar. To avoid losing gas, you must put the stopper on the flask as soon as possible.

► Be sure the stopper fits before you start the reaction.

Volume of Gas Collected

Once the gas is collected, you will have to determine its volume. It is left up to you to devise a procedure for measuring the volume of the gas in the cylinder after the experiment.

► Decision

Pressure of the Collected Gas

The total pressure of the gas mixture collected in the two liter bottle will be the current atmospheric pressure. This means you will need the local and current atmospheric pressure to complete this lab. You may obtain this from a barometer, or your instructor will provide the information to you.

Partial Pressure of the Collected Carbon Dioxide

Once you determine the volume of collected gas, you will need to determine the partial pressure of the carbon dioxide in that volume of gas. This is not the same as the local atmospheric pressure because the gas in the bottle also contains

► Decision

water vapor. You will need to account for this. It is left to you to determine how to do this. The CRC and your text have tables giving water's vapor pressure as a function of temperature.

Density of Vinegar

► Decision

You want to determine the weight/volume (w/v) and the weight/weight (w/w) percent acetic acid in the vinegar. The latter (w/w percent) will require that you know the mass of your original vinegar sample. You could, in principle, mass the reaction flask before and after the addition of the vinegar to obtain the mass of the vinegar sample, but the balances we have in the general chemistry laboratory begin to lose precision at higher masses. Therefore, we need an alternate approach.

When you set up your reaction flask, you will transfer 5.00 mL of vinegar to the flask using a volumetric pipet. If you knew the density of the vinegar, you could determine the mass of the vinegar. It is not possible to just look up the density of your particular vinegar sample. This means you will have to determine the density of your vinegar sample. For this purpose, you will find a weighing bottle at your lab station. It is left up to you to come up with the exact procedure for determining the density based on your past experience.

Although it is good practice to make three measurements of the density, you will only make one measurement in this project. The class data will be pooled to determine an average density for the vinegar. You will then use this average density in all your computations of the w/w percent acetic acid.

26.3 Safety Considerations

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

The chemicals you use today are standard household chemicals (vinegar and sodium bicarbonate). When these two substances are mixed, the solution will contain nothing but the salt sodium acetate and maybe excess sodium bicarbonate. Because of this, it is safe to wash all waste down the sink with plenty of water.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled "broken glass" as shown in Figure 26.1. Do not use the normal waste baskets for broken glass.

Figure 26.1



Broken glass container.

26.4 Experimental Procedure

This section provides the suggested procedure for determining the mass percent of acetic acid in a vinegar sample. Not all steps are provided in detail. In some cases, you will have to provide your own detailed procedures as explained in Section 26.2.

1. **Set Up Gas Collection Cylinder:** Fill a large plastic tub about 75% full with room-temperature tap water. Fill a 100 mL graduated cylinder with water and immerse in the tub of water.
► We set this up first so that the temperature of water can become stable.
2. **Determine Density of Vinegar:** Using a procedure you have already worked out from previous experience, use the provided 5.00 mL volumetric pipet and weighing bottle to determine the density of the vinegar sample. Make only one successful trial.
3. **Place Vinegar in Flask:** Using a 5.00 mL volumetric pipet, add 5.00 mL vinegar to a clean 125 mL Erlenmeyer filter flask.
4. **Mass Sodium Hydrogen Carbonate:** Use the top loading balances to mass out the amount of sodium hydrogen carbonate you have already determined to be appropriate for this experiment. Mass this out in a weighing boat that can be carried back to your bench.
5. **Attach Hose for Gas Collection:** Attach a length of rubber hose to the sidearm of the filter flask.
6. **Find Tight-Fitting Stopper:** Find a tight-fitting stopper or cork for the flask. Test to be sure it fits tightly before going on.
7. **Insert Tubing in Graduate Cylinder:** Insert the tube running from the flask into the opening of the graduated cylinder. Invert the cylinder in the tub of water and hold it in this inverted position. Be sure the tube does not come out of the cylinder, and be sure there is no air in the cylinder.
8. **Carry Out Reaction:** When you are ready, quickly add all the sodium hydrogen carbonate to the reaction flask and immediately stopper the flask. Swirl the flask occasionally until no more bubbles are formed.
9. **Remove Tube from Cylinder:** When you are convinced the reaction has stopped, carefully remove the tubing from the mouth of the graduate cylinder. Do this without letting any of the collected gas out of the cylinder.
10. **Determine Volume of Gas Collected:** Using the procedure you have already developed, determine, to an appropriate number of significant figures, the volume of gas collected.
11. **Repeat Twice More:** Refill the cylinder with water, clean out the reaction flask, and perform steps 3 to 10 again until you have four good measurements of the volume of gas evolved.

26.5 Before Leaving Lab

Before leaving lab for the day, go down this checklist to make sure you have done everything on it.

- Return the volumetric pipets to the front of the room.
- Return the filter flasks to the front of the room.
- Return the weighing bottle to the front of the room.
- Put all of your own glassware back in your drawer.
- Update the table of contents in the front of your notebook.
- Draw a line at the end of your experimental work and sign on the line.
- Have your instructor sign on the line as well.

26.6 Post-Lab Assignments

Calculations

All calculations should appear in your laboratory notebook. If you make an error, just cross through the error with a single line and then move on.

1. Determine the mass of vinegar used in each experimental run.
2. Determine the partial pressure of carbon dioxide collected in each experimental run. Report your answer in units of atm.
3. Determine the moles of carbon dioxide collected in each experimental run.
4. Determine the number of moles of acetic acid present in each experimental run.
5. Determine the mass of acetic acid present in each experimental run.
6. Determine the percent (w/v and w/w) of acetic acid in each vinegar sample for each experimental run.
7. Determine the average percent (w/v and w/w) acetic acid and the standard deviation of the percent.

Chapter 27

Standardization of a Sodium Hydroxide Solution

27.1 Introduction

A standard solution is one for which the concentration of solute is known very well. By “very well” I mean to at least three decimal places. To standardize a solution means to determine the concentration of its solute to this level of precision and accuracy.

Unfortunately, this is not always easy. One might think you could just weigh out the solute and dissolve it in solvent to a known solution volume and determine the concentration by simple division. Due to impurities, this often leads to unacceptable errors. However, there are a few chemical reagents called *primary standards* which can be obtained in a pure enough state that a standard solution can be made by weighing out a known mass of the solid and dissolving it in a known volume of solution.

Is it possible to prepare a standard solution of a solute that is not a primary standard? Yes, it is. In order to do this you have to *standardize* the solution by titration against a known mass of a primary standard. This is the procedure you will carry out in this experiment. You will standardize a solution of sodium hydroxide against a primary standard.

Primary Standards

The requirements which must be met by a primary standard, besides those necessary for any titrimetric analysis, are:

- it must be obtainable in a pure form (usually greater than 99.95% pure) and it should be possible to test for impurities by qualitative tests of known sensitivity,
- it should be easy to dry and should not pick up atmospheric moisture while it is being weighed,
- it should have a high equivalent weight to minimize the consequences of errors in weighing.

► A substance that easily absorbs moisture from the atmosphere is called hygroscopic.

- if it is an acid or a base, it should be highly ionized in solution.

► The abbreviation KHP stands for potassium hydrogen phthalate. It is *not* a chemical formula.

One primary standard which is often employed to standardize base solutions is potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$, abbreviated KHP). This reagent is readily available in at least 99.95% purity, is stable to drying temperatures, is not hygroscopic, and has a high equivalent weight (204.2g/mol). It is a weak, monoprotic acid which can be used with phenolphthalein as indicator to standardize base solutions.

In This Experiment

In this experiment, you will standardize a sodium hydroxide solution with a concentration of approximately 0.15 *M*. You will do this by titrating the sodium hydroxide solution against a known amount of the weak acid potassium hydrogen phthalate, a primary standard. You will thus determine precisely the concentration of the NaOH solution.

The net ionic equation describing the titration you will do in this experiment is given by



If you add a known mass of KHP to a flask with water and place the sodium hydroxide solution in the buret, you can titrate the contents of the flask until the equivalence point. At the equivalence point, the moles of $\text{KHC}_8\text{H}_4\text{O}_4$ used will equal the moles of NaOH added. Since you will also know the volume of NaOH added, you will be able to readily calculate the molarity of the NaOH solution.

It is imperative that the NaOH standardization be done well. Presumably, you will use the results of this experiment in a subsequent experiment. To achieve as much accuracy as possible, you will titrate three samples of KHP with the NaOH solution. The average molarity will be considered the molarity of your NaOH solution.

Titration Notes

It will take some time to become good at titration. Here are some notes on carrying out a titration that may help make mastering this skill less frustrating.

- Before setting up a buret, make sure the stopcock works and that liquid drains easily through the tip. There is no sense in spending time cleaning and setting up a buret that does not work well.
- When cleaning a buret, be sure to drain some of the wash through the tip. You want to be sure every surface along the entire length of the buret is washed.
- Use an appropriate background for the flask so that you can easily see faint color changes. It is usually best to place a white background underneath and behind the flask.

- If you are unsure whether you are at an end point, go ahead and record the current buret level and then add another drop (or fractional drop). If the color change is too much, you were likely at the end point before the added drop. Fortunately, you just recorded that value.
- Be sure there is not a drop of titrant hanging from the tip of the buret when you make a buret reading. That drop has already left the buret, and the buret reading will reflect that. You need to make sure the drop is in the flask.
- Fractional drops can be added during a titration by allowing part of a drop to form at the tip and then washing it into the flask with a squirt of DI water from a water bottle. This assumes the titration is aqueous and that water can be added.

27.2 Safety Considerations

Chemical Hazards

The chemicals used in this lab are not particularly hazardous. If you do spill any chemical on your skin or your clothing, wash it off with plenty of water as soon as possible.

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

All waste in this lab can be put down the drain with plenty of water. Since the product of the titration is just salt and water, this is considered safe.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 27.1. Do not use the normal waste baskets for broken glass.

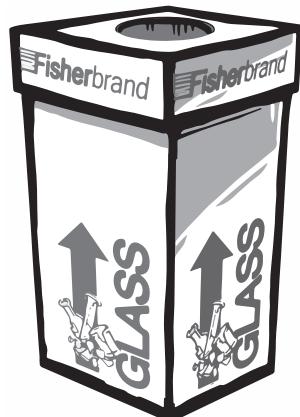


Figure 27.1
Broken glass container.

27.3 Experimental Procedure

Record NaOH Unknown Number

Record the unknown number on your bottle of sodium hydroxide before proceeding with anything else in this project.

Prepare Buret

1. **Obtain Buret:** Obtain a buret and buret clamp from the appropriate laboratory locations. Attach the buret clamp to a ring stand.
2. **Prepare Buret:** Empty the water out of the buret and rinse three times with 5 to 10 mL portions of the sodium hydroxide solution you will use in the titration. Some of the rinse should be drained through the tip to make sure it is clean.
3. **Fill Buret:** Using a clean and dry funnel, fill the buret with the NaOH solution and drain sufficient solution from the tip to bring the meniscus slightly below the top graduation. Remove the funnel from the buret.
4. **Check Buret:** Check for bubbles in the tip, clearing them if they are there by draining more sodium hydroxide from the tip. If you are unsuccessful in clearing any bubbles, see your instructor.
5. **Read Buret:** After allowing about a minute for complete drainage from the walls above the meniscus, read and record the position of the meniscus to the nearest 0.01 mL.

► Burets can be read to two decimal places. Always record buret readings to two decimal places.

Prepare KHP Solution

1. **Weigh Out KHP:** Using the electronic top-loader balance, precisely (to 3 decimal places) weigh out $0.6\text{ g} \pm 0.1\text{ g}$ of the dry potassium hydrogen phthalate (KHP) and place into a clean 125 mL Erlenmeyer flask.
2. **Dissolve KHP in Water:** Add approximately 50 mL of DI water to the flask and gently swirl to dissolve.
3. **Add Indicator:** Add three drops of phenolphthalein indicator to the solution in the flask.

Titrate KHP Sample

► This estimate will help you get to the endpoint more quickly.

► To detect the lightest shade of pink possible, place a sheet of blank white paper under the flask as a background.

1. **Estimate Volume of NaOH Needed:** Assuming that the sodium hydroxide solution is approximately 0.15 M in NaOH, estimate the number of milliliters of NaOH needed to titrate the KHP sample.
2. **Titrate KHP Sample:** Add base to the potassium acid phthalate sample in 1 to 2 mL aliquots. Swirl the flask at the same time to make sure everything is well mixed. Do this until the pink color begins to linger for a longer time. You will know when you are close to the endpoint when you approach the estimate you made in the previous step.
3. **Approach Endpoint Carefully:** As the pink color lingers longer, rinse the sides of the flask with a little distilled water from your wash bottle to wash down any splashed solution. As the end point is approached, add the titrant

one drop at a time with thorough swirling of the flask to obtain complete mixing between additions.

4. **Reach The Endpoint:** Terminate the titration at the first perceptible appearance of a pink coloration throughout the solution that persists for 20-30 seconds. Read and record the position of the meniscus at the end of the titration.
5. **Refill Buret Only If Necessary:** Determine if you have sufficient sodium hydroxide in the buret to carry out another titration. If you do not, refill the buret. Do not refill the buret if you have sufficient solution to carry out another titration.
6. **Titrate Two More Samples:** Prepare two more KHP samples and titrate both of them in the same way. Do not waste time weighing out exactly the same amount of KHP. You may need to adjust the amount of KHP used so you don't use too much or too little NaOH solution (20-30 mL is a good amount).

► The pink coloration will fade as CO₂ from the air is absorbed by the solution. You might want to think about why this is.

► If you screw up one of your titrations, you will have to perform yet another to make sure you walk away from lab with three useable titrations.

Store Remaining NaOH

1. **Store NaOH Solution in Plastic Bottle:** It is presumed that you will use the standardized sodium hydroxide solution in a subsequent experiment. As such, it is important that you store your remaining NaOH. Do not throw it away. Store your unused NaOH in the plastic bottle sealed with parafilm to be used later.

Clean Buret

1. **Drain and Rinse Buret:** When you are finished with the equipment, drain the buret, rinse it once with 1 M HCl and then three times with DI water.
2. **Fill Buret With Water and Store:** Fill it with DI water, place a cork in the top and return it to the drawer from which you obtained it.

Dispose of Waste

1. **Pour All Waste Down Drain:** You can pour all waste down the drain with plenty of water.

27.4 Before Exiting Lab

- Check your lab notebook for page numbers on all pages.
- Update the table of contents in your notebook.
- Draw a line at the end of your experimental work for the day. Sign your notebook at the line.

- Have your instructor sign your lab notebook before you leave the lab. This helps verify where you stopped lab work for the week.

27.5 Post-Lab Assignments

All post-lab assignments should be completed in your laboratory notebook. Show all calculations.

1. Calculate the molarity of the NaOH for each titration from the known weight of potassium acid phthalate and the measured volume of NaOH solution from each titration.
2. Calculate the average molarity of NaOH.
3. Calculate the standard deviation of the molarity of your NaOH solution. You may use a spreadsheet to compute the standard deviation, but make sure all work is shown and all columns are well labeled.

Chapter 28

Analysis of Vinegar by Titration

28.1 Introduction

Chemists are traditionally good at analysis and synthesis. This project is about the former skill: analysis. More specifically, in this project you will determine the mass percent acetic acid in vinegar by titration analysis. Such analyses are common in chemical industry. In many circumstances, commercial products are required by law to have a specific composition. In such cases, accurate analysis is required.

The analysis in this laboratory experiment is analogous to procedures performed in virtually all labs, be they research labs, industrial quality control labs, or hospital labs. The quantitative skills acquired in this type of experiment are invaluable in virtually any type of laboratory.

Acetic Acid

Acetic acid is a weak, organic acid. It is a liquid at room temperature, and it is completely miscible with water. Acetic acid is available commercially in essentially pure form (99.5 to 99.9% acetic acid); this product is called glacial acetic acid. The acetic acid concentration in glacial acetic acid is approximately 17.5 M.

Commercial acetic acid is synthesized almost exclusively from petroleum, and much of the vinegar now used contains this synthetic acetic acid. However, acetic acid is also a product of bacterial oxidation of ethyl alcohol. Cider vinegar is made by fermentation of apple juice (sugars converted to ethyl alcohol) followed by action of acetobacter (bacterial conversion of alcohol to acid). Wine vinegar is similarly made from grape juice. These naturally produced vinegars also contain small quantities of other acids and impurities which give them better flavor than the “purer” synthetic vinegar. Commercial vinegar must, by federal law, contain at least 4% by weight of acetic acid, CH_3COOH .

In This Experiment

In this experiment, you will take on the role of an analytical chemist to determine the mass percent acetic acid in a commercial sample of vinegar. You will do this by titration of a commercial vinegar sample with a standardized solution of sodium hydroxide. Phenolphthalein will be used as the indicator since its endpoint is very near the equivalence point for the reaction of acetic acid and sodium hydroxide.

The titration reaction that is central to this experiment is



You will prepare samples of commercial vinegar with an unknown number of moles of acetic acid. You will then add sodium hydroxide solution of known concentration until the endpoint is reached. At that point you will know that the moles of hydroxide added equals the moles of acetic acid originally present in the sample. From there you should be able to calculate the concentration of acetic acid in the vinegar by dividing the moles acetic acid by the volume of solution originally titrated.

To find the mass percent acetic acid in the vinegar, you will need to convert the molarity unit ($\frac{\text{moles acetic acid}}{\text{liters vinegar}}$) to the unit $\frac{\text{mass acetic acid}}{\text{mass vinegar solution}}$ and multiply by 100. To accomplish this you will need to know the density of vinegar so that you can convert volume of solution to grams of solution. Thus, the first thing you will do in this experiment is determine the density of your commercial vinegar sample.

Titration Notes

It will take some time to become good at titration. Here are some notes on carrying out a titration that may help make mastering this skill less frustrating.

- Before setting up a buret, make sure the stopcock works and that liquid drains easily through the tip. There is no sense in spending time cleaning and setting up a buret that does not work well.
- When cleaning a buret, be sure to drain some of the wash through the tip. You want to be sure every surface along the entire length of the buret is washed.
- Use an appropriate background for the flask so that you can easily see faint color changes. It is usually best to place a white background underneath and behind the flask.
- If you are unsure whether you are at an end point, go ahead and record the current buret level and then add another drop (or fractional drop). If the color change is too much, you were likely at the end point before the added drop. Fortunately, you just recorded that value.
- Be sure there is not a drop of titrant hanging from the tip of the buret when you make a buret reading. That drop has already left the buret, and the buret reading will reflect that. You need to make sure the drop is in the flask.

- Fractional drops can be added during a titration by allowing part of a drop to form at the tip and then washing it into the flask with a squirt of DI water from a water bottle. This assumes the titration is aqueous and that water can be added.

28.2 Safety Considerations

Chemical Hazards

The chemicals used in this lab are not particularly hazardous. If you do spill any chemical on your skin or your clothing, wash it off with plenty of water as soon as possible.

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

All waste in this lab can be put down the drain with plenty of water. Since the product of the titration is just salt and water, this is considered safe. Vinegar is something people at home throw down the drain every day. It is thus safe to throw down the drain here.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 28.1. Do not use the normal waste baskets for broken glass.

28.3 Experimental Procedure

When you come to lab you should find a commercial vinegar sample at your desk. If you do not, see your instructor.

Determine Density of Vinegar

1. **Weigh the Weighing Bottle:** Obtain a clean and dry weighing bottle with lid. Accurately weigh this empty weighing bottle plus stopper using a top loading balance.
2. **Rinse Pipet:** Rinse a clean 5.00 mL pipet with three 2-3 mL portions of the vinegar sample. Take care not to dilute the sample with water from a wet pipet.
3. **Pipet Vinegar Into Weighing Bottle:** With the rinsed pipet, transfer exactly 5.00 mL of the vinegar sample to the weighing bottle and stopper it quickly.

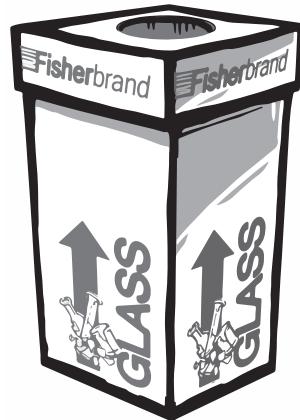


Figure 28.1

Broken glass container.

4. **Weigh the Weighing Bottle Plus Vinegar:** Take the weighing bottle plus vinegar back to the same top loading balance and weigh again.
5. **Calculate Density of Vinegar and Report:** Calculate the density of the sample to the appropriate number of significant figures and report the value to your instructor.

Prepare For Titration

1. **Clean Three Flasks:** Obtain and thoroughly clean five Erlenmeyer flasks. The 125 mL size is probably the best for this titration. Rinse each flask thoroughly three times with DI water. You do not have to dry these flasks.
2. **Obtain Buret:** Obtain a buret and buret clamp from the appropriate laboratory locations. Attach the buret clamp to a ring stand.
3. **Prepare Buret:** Empty the water out of the buret and rinse three times with 5 to 10 milliliter portions of your standardized sodium hydroxide solution you will use in the titration. Be sure to drain some of the rinse through the tip.
4. **Fill Buret:** Using a clean and dry funnel, fill the buret with the standardized NaOH solution and drain sufficient solution from the tip to bring the meniscus slightly below the top graduation. Remove the funnel from the buret.
5. **Check Buret:** Check for bubbles in the tip, clearing them if they are there by draining more sodium hydroxide from the tip. If you are unsuccessful in clearing any bubbles, see your instructor.
6. **Read Buret:** After allowing about a minute for complete drainage from the walls above the meniscus, read and record the position of the meniscus to the nearest 0.01 mL.

Titrate Vinegar Samples

1. **Prepare Vinegar Sample for Titration:** With a 5.00 mL pipet, transfer a 5.00 mL portion of the vinegar sample to a clean Erlenmeyer flask. Add about 50 mL of distilled water and three drops of phenolphthalein indicator to the sample.
2. **Estimate Volume of NaOH Needed:** Assuming that the vinegar is about 5% acetic acid by mass, estimate the number of milliliters of your standardized NaOH needed to titrate the vinegar sample.
3. **Titrate Vinegar Sample:** Add standardized base to the vinegar sample in 1 to 2 mL aliquots. Swirl the flask at the same time to make sure everything is well mixed. Do this until the pink color begins to linger for a longer time. You will know when you are close to the endpoint when you approach the estimate you made in the previous step.

► You can also use 250 mL flasks if you do not have five 125 mL flasks.

► Burets can be read to two decimal places. Always record buret readings to two decimal places.

► This estimate will help you get to the endpoint more quickly and accurately.

► To detect the lightest shade of pink possible, place a sheet of blank white paper under the flask as a background.

4. **Approach Endpoint Carefully:** As the pink color lingers longer, rinse the sides of the flask with a little distilled water from your wash bottle to wash down any splashed solution. As the endpoint is approached, add the titrant one drop at a time with thorough swirling of the flask to obtain complete mixing between additions.
5. **Reach The Endpoint:** Terminate the titration at the first perceptible appearance of a pink coloration throughout the solution that persists for 20-30 seconds. Read and record the position of the meniscus at the end of the titration.
6. **Refill Buret Only If Necessary:** Determine if you have sufficient sodium hydroxide in the buret to carry out another titration. If you do not, refill the buret. Do not refill the buret if you have sufficient solution to carry out another titration.
7. **Titrate Four More Samples:** Prepare four more vinegar samples and titrate each of them in the same way.

► The pink coloration will fade as CO₂ from the air is absorbed by the solution. You might want to think about why this is.

Clean Buret

1. **Drain and Rinse Buret:** When you are finished with the equipment, drain the buret, rinse it once with 1 M HCl and then three times with DI water.
2. **Fill Buret With Water and Store:** Fill it with DI water, place a cork in the top and return it to the drawer from which you obtained it.

► If you screw up one of your titrations, you will have to perform yet another to make sure you walk away from lab with five usable titrations.

Dispose of Waste

1. **Pour All Waste Down Drain:** You can pour all waste down the drain with plenty of water.

28.4 Before Exiting Lab

1. Be sure you have calculated the density of your vinegar sample and submitted the value to your instructor.
2. Check your lab notebook for page numbers on all pages.
3. Update the table of contents in your notebook.
4. Draw a line at the end of your experimental work for the day. Sign your notebook at the line.
5. Have your instructor sign your lab notebook before you leave the lab. This helps verify where you stopped lab work for the week.

28.5 Post-Lab Assignments

All post-lab assignments should be completed in your laboratory notebook. Show all calculations. If you choose to use a spreadsheet for any calculations, these must be printed out and included in your laboratory notebook.

1. Calculate the acetic acid molarity for each of the samples you titrated.
2. Compute the average acetic acid molarity for your samples.
3. Compute the standard deviation of the average acetic acid molarity for your samples.
4. Compute the average vinegar density from all the data obtained by the lab section. You should use a spreadsheet to compute the average.
5. Compute the average vinegar density's standard deviation from all the data obtain by the lab section. You should use a spreadsheet to compute the standard deviation, but do not use any of the program's built-in statistical functions.
6. Using your average acetic acid molarity and the class's average vinegar density, compute the mass percent acetic acid in vinegar.

► You can find the class data for vinegar density on the course web site.

Chapter 29

Semimicro Qualitative Analysis of Known Anions

29.1 Introduction

Qualitative analysis is a type of analysis that seeks to identify whether a particular substance is present, not to quantify the amount present. As long as the substance is present above a certain threshold concentration, qualitative analysis only provides a test that signifies whether the species is present or not. Semimicro qualitative analysis is a type of qualitative analysis that is carried out on relatively small quantities of material.

The detection of anions by semimicro qualitative analysis involves elimination tests to indicate which anions are not present followed by identification tests to verify which of the remaining possibilities are present. These tests rely heavily on acid-base reactions, oxidation-reduction reactions and precipitation reactions.

► In this context, small means a few milligrams of solid or a few drops of solution.

This experiment is concerned with the identification of anions by semimicro qualitative analysis. Small-scale qualitative tests like these are important in many fields such as forensics, medicine, geology, and genetics. After a discussion of the chemistry behind a selected set of elimination and identification tests, the actual laboratory experiment is presented.

In This Experiment

In this experiment you will determine how each of the ions CO_3^{2-} , NO_2^- , NO_3^- , PO_4^{3-} , S^{2-} , SO_4^{2-} , Cl^- , Br^- , and I^- behaves under a series of elimination and identification tests. This experience will give you the needed background for identifying the anion contained in a solution of unknown identity.

Throughout this experiment, test only one ion at a time. The purpose is to determine the elimination and identification test results for each ion individually. Do not mix ion solutions together.

It may be helpful if you record your results in tabular form as shown below. Make one table for elimination tests and a separate (but similar) table for identification tests. Make careful observations since you will need these results to identify the anion in a solution of unknown identity.

29.2 About The Elimination Tests

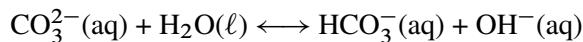
Elimination Test 1 (ET-1)

Description

This is a test for strongly basic anions such as S^{2-} , PO_4^{3-} , and CO_3^{2-} . A positive ET-1 means that a sample contains CO_3^{2-} , S^{2-} , or PO_4^{3-} . A negative ET-1 test eliminates these ions as possible constituents of the sample.

Why It Works

This test works because several anions for which you will test are relatively strong bases in water. For example, the carbonate ion reacts with water to an appreciable degree to form the bicarbonate ion and the hydroxide ion as in



The Procedure

Place a few drops of the solution to be tested in a test tube. Dip a clean stirring rod into the solution, withdraw it, and touch it to a short length of wide-range indicator paper. Determine the pH by comparing the color with the color standards on the indicator paper dispenser.

The Interpretation

A strongly alkaline reaction (pH 10 or more) is given by S^{2-} , PO_4^{3-} , or CO_3^{2-} ions. Only a *strongly* basic reaction is significant; so many ions give weakly alkaline reactions that no help is derived from such an observation.

Elimination Test 2 (ET-2)

Description

This is a test for volatile or unstable acids such as CO_3^{2-} , S^{2-} , and NO_2^- . A positive ET-2 means that a sample contains CO_3^{2-} , S^{2-} , or NO_2^- . A negative ET-2 eliminates these ions as possible constituents of the sample.

Why It Works

Several anions for which you will be testing react relatively vigorously with strong acid to yield compounds which may or may not decompose. The result in each case is a gas.

The Procedure

Put sufficient solid sample containing the anion of interest in a *dry* test tube to make a layer about 1 mm deep (about the thickness of a wooden splint). Add enough 6M H_2SO_4 so that the solid is covered and there is enough solution

above it that you can watch for bubbles. Mix by flicking the bottom of the tube with your forefinger. Watch for the evolution of gas. Note the odor by cautiously wafting some of the gas to your nose. Do this under a hood and use a wafting motion to smell the gases since some of them are obnoxious and toxic.

The Interpretation

If carbonate is present, the gas will be colorless and odorless CO_2 . If nitrite is present, colorless NO gas will be evolved, which will turn into red-brown NO_2 gas in air. This gas has a sharp odor, and it is toxic. If sulfide is present, colorless H_2S gas will be released. This gas has a vile odor.

Elimination Test 3 (ET-3)

Description

This is a test for strong reducing substances such as S^{2-} , NO_2^- , and I^- . A positive ET-3 means that a sample contains S^{2-} , NO_2^- , or I^- . A negative ET-3 eliminates these ions as possible constituents of the sample.

Why It Works

Some of the ions you will test for are strong reducing agents. These ions will reduce the Fe^{3+} , in $\text{Fe}(\text{CN})_6^{3-}$ to Fe^{2+} , producing $\text{Fe}(\text{CN})_6^{4-}$. The Fe^{3+} of FeCl_3 will then combine with $\text{Fe}(\text{CN})_6^{4-}$ to form $\text{FeFe}(\text{CN})_6^-$, in which one ion is Fe^{2+} and one is Fe^{3+} . The combination of this complex ion with K^+ yields $\text{KFeFe}(\text{CN})_{6(s)}$, also known as Prussian blue due to its deep blue color.

The Procedure

Put a few drops of the solution to be tested into a depression in a porcelain spot plate and acidify with HCl. To a separate depression add one small crystal of $\text{K}_3\text{Fe}(\text{CN})_6$ and a few drops of water. Now add a drop of this solution and a drop of FeCl_3 to the anion solution.

The Interpretation

Only strong reducing agents will give a true positive Prussian blue test. Weaker reducing agents, such as Br^- , may yield a color change, to a medium green, but generally will not produce a true positive Prussian blue test.

Elimination Test 4 (ET-4)

Description

This is a test for strong oxidizing agents such as NO_2^- and NO_3^- . A positive ET-4 means that a sample contains NO_2^- or NO_3^- . A negative ET-4 eliminates these ions as possible constituents of the sample.

Why It Works

NO_2^- in the presence of H_2SO_4 , oxidizes Fe^{2+} to Fe^{3+} , being converted to NO in the process. The excess Fe^{2+} reacts with the NO to yield $\text{Fe}(\text{NO})^{2+}$, a brown complex. NO_3^- will undergo a similar reaction at the interface of a solution containing NO_3^- and FeSO_4 and a solution of concentrated H_2SO_4 , forming a brown ring of $\text{Fe}(\text{NO})^{2+}$.

The Procedure

To 5 drops of the anion solution to be tested, add 6 M H_2SO_4 dropwise until the solution is acidic. Now add 5 drops of freshly prepared 0.1 M FeSO_4 . Carefully observe the result, paying particular attention to whether the solution turns brown.

If the solution does not turn brown, hold the test tube in a slanted position and carefully (and slowly) add 5 to 10 drops of 18 M H_2SO_4 , allowing it to run down the inside of the tube. It should form a layer below the other solution. Carefully straighten the tube to an upright position and set it in a test tube rack or a beaker.

► If the two solutions are mixed together by careless addition of the 18 M H_2SO_4 or by shaking, the test will not work.

► The brown ring is due to the formation of $\text{Fe}(\text{NO})^{2+}$.

The Interpretation

If the solution turns brown after addition of FeSO_4 , NO_2^- is present. If the solution does not turn brown after addition of FeSO_4 but a brown ring does form between the layers after addition of the concentrated sulfuric acid, NO_3^- is present.

Elimination Test 5 (ET-5)

Description

This is a test for anions that form insoluble silver salts, such as Cl^- , Br^- , I^- , and S^{2-} . A positive ET-5 means that a sample contains Cl^- , Br^- , I^- , or S^{2-} . A negative ET-5 means that these ions are not in the sample.

Why It Works

Silver forms insoluble compounds with many anions.

The Procedure

Place a few drops of the solution under study into a test tube. Add a drop of silver nitrate solution. If addition of a second drop produces more precipitate, continue the addition of silver nitrate until precipitation appears to be complete. After each addition, mix well by flicking the bottom of the tube with your forefinger.

Now add 6 M HNO_3 to the test tube a drop at a time, mixing well after each drop is added, until the solution is acidic to litmus. Finally, add a few drops of acid in excess.

The Interpretation

If no precipitate forms, S^{2-} , Cl^- , Br^- and I^- ions are absent. A black precipitate indicates S^{2-} . If a white or pale yellow precipitate forms, then one of the halides is present.

Elimination Test 6 (ET-6)

Description

This is a test for anions that form insoluble calcium salts, such as PO_4^{3-} . A positive ET-6 means that a sample contains PO_4^{3-} . A negative ET-6 means that the sample does not contain phosphate.

Why It Works

Many calcium salts are insoluble in water. Since precipitates are easy to identify in solution, this is a simple and straightforward elimination test for ions that form insoluble compounds with calcium.

The Procedure

Place a few drops of the solution to be analyzed into a test tube. Make the solution basic to litmus with 15 M NH_3 to prevent formation of HPO_4^{2-} , $H_2PO_4^-$, or H_3PO_4 . Add a few drops of $Ca(NO_3)_2$ solution.

The Interpretation

If phosphate is present and the solution is basic, calcium phosphate will precipitate when a few drops of $Ca(NO_3)_2$ are added.

Elimination Test 7 (ET-7)

Description

This is a test for anions that form insoluble barium salts, such as SO_4^{2-} . A positive ET-7 test means that a sample contains SO_4^{2-} . A negative ET-7 eliminates this ion as a possible component of the sample.

Why It Works

Many barium salts are insoluble in water. Since precipitates are easy to identify in solution, this is a simple and straightforward elimination test for ions that form insoluble compounds with barium.

The Procedure

Add a few drops of the solution under test to a test tube. Add barium chloride solution drop by drop until precipitation is complete. Centrifuge and draw off the

solution above the precipitate and discard it. Treat the precipitate with several drops of 6 M HCl.

The Interpretation

A white precipitate that is also insoluble in acid indicates the presence of sulfate in the original sample.

29.3 About The Identification Tests

In the absence of interfering ions these tests can be performed independently. A positive result for an identification test confirms the presence of that anion.

Identification Test (IT-1)

Description

This is a test for the identification of chloride ion, Cl^- . A positive IT-1 confirms the presence of chloride ion so long as you have previously confirmed that there are no other halide ions present.

Why It Works

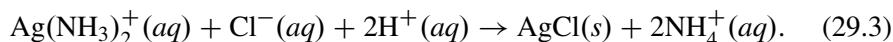
In the absence of interfering ions, chloride can be precipitated as white silver chloride according to the equation



The product, silver chloride, dissolves in ammonia according to the equation



The ammonia-silver complex ion that forms can be converted back to silver chloride precipitate by the addition of acid according to the equation



The Procedure

► A hazy opalescence that does not centrifuge down to a solid is caused by a trace of chloride and should not be reported.

► Do not mistake pale yellow AgBr or yellow AgI for AgCl . The absence of Br^- or I^- must be proved before the test for Cl^- can be conclusive.

Acidify a few drops of the solution under test with 6 M nitric acid and add a drop of AgNO_3 solution. A white precipitate may be AgCl . To confirm, centrifuge and discard the supernatant liquid. Add a few drops of 6 M NH_3 to the precipitate. If it dissolves, acidify the solution with 6 M HNO_3 . The precipitate should re-form if the original precipitate was AgCl . This will confirm the presence of Cl^- .

Identification Test 2 (IT-2)

Description

This is an identification test for bromide ion, Br^- . A positive IT-2 confirms the presence of bromide ion in solution.

How It Works

Bromide ion is oxidized to free bromine by a strong oxidizing agent such as potassium permanganate in nitric acid solution, as shown in the unbalanced equation



Free bromine is more soluble in petroleum ether than in water and gives an orange to brownish red color in that solvent.

The Procedure

Acidify a few drops of the solution under test with 6 M HNO_3 and add 4 drops of nitric acid in excess. Add several drops of petroleum ether. Add just enough to clearly see two layers. Now add 0.02 M KMnO_4 drop by drop, shaking after each addition, until an orange bead is obtained or the water layer remains pink for at least a minute.

► Adding too much petroleum ether will make the color more difficult to see if present.

The Interpretation

The presence of bromide is indicated by the orange upper layer due to the formation of Br_2 .

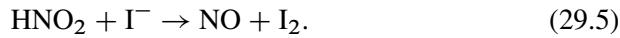
Identification Test 3 (IT-3)

Description

This test is an identification test for iodide ion, I^- . A positive IT-3 indicates the presence of iodide ion in solution.

How It Works

Iodide is an active reducing agent, easily oxidized to iodine or triiodide ion by nitrous acid, as shown in the unbalanced equation



Molecular iodine is much more soluble in petroleum ether than in water and gives a violet solution in this nonpolar solvent.

The Procedure

Acidify a few drops of the solution under test with 6 M H₂SO₄. Add a few crystals of NaNO₂ and several drops of petroleum ether. Shake vigorously to extract the iodine.

The Interpretation

The presence of iodide is indicated by a violet upper layer due to the formation of I₂.

Identification Test 4 (IT-4)**Description**

This test is an identification test for sulfide ion, S²⁻. A positive IT-4 indicates the presence of sulfide ion in solution. This test is the same as ET-2.

How It Works

See ET-2.

The Procedure

See ET-2.

The Interpretation

See ET-2

Identification Test 5 (IT-5)**Description**

This test is an identification test for sulfate ion, SO₄²⁻. A positive IT-5 indicates the presence of sulfate in solution.

How It Works

Of all the anions that form insoluble barium salts, only sulfate ion is too weakly basic to react appreciably with acid, and thus only BaSO₄ will precipitate in strongly acidic solutions. If such a precipitate was obtained in ET-7, no other test for sulfate is required.

The Procedure

See ET-7

The Interpretation

See ET-7

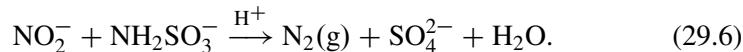
Identification Test 6 (IT-6)

Description

This is an identification test for nitrite ion, NO_2^- . A positive IT-6 indicates the presence of nitrite in solution so long as you know that there is no sulfate in the solution.

How It Works

In acidic solution, nitrates react with sulfamic acid to give bubbles of nitrogen and sulfate ion as described in the equation



The Procedure

First you need to ensure that no sulfate is in the solution before you test for nitrite. To a few drops of the solution under test, add BaCl_2 solution. If a BaSO_4 precipitate forms, add more BaCl_2 until precipitation is complete. Then centrifuge the solution and transfer the solution to a new test tube.

► If you add BaCl_2 and no precipitate results, that just means you have no contaminating sulfate present, so continue with the test.

Since your solution now contains Ba^{2+} , add a few crystals of sulfamic acid to the solution, and flick the bottom of the tube with your forefinger to cause vigorous evolution of gas bubbles.

The Interpretation

The formation of both white precipitate (BaSO_4) and gas bubbles (N_2) indicates the presence of nitrite.

Identification Test 7 (IT-7)

Description

This is an identification test for nitrate ion, NO_3^- . A positive IT-7 indicates the presence of nitrate in solution.

How It Works

Nitrate ion in alkaline solution is reduced to ammonia by active metals, as shown with aluminum in the unbalanced reaction



Ammonia gas may be detected by its action on moist red litmus because the ammonia gas forms hydroxide when exposed to water:



The Procedure

Mix several drops of the solution under test with an equal volume of 6 M NaOH. With a pipet, transfer this mixture to a dry test tube in such a way as not to wet the upper walls of the tube with the basic solution. After withdrawing the pipet, inspect the upper walls of the tube to make sure this critical requirement is satisfied. Have a strip of red litmus ready. Add a piece of aluminum wire to the test tube. Warm briefly in a water bath to induce a vigorous reaction. Withdraw the tube and insert a piece of red litmus, first bending the strip into a V and moistening the fold. The dry upper ends will support the litmus so that it does not fall in. Allow the tube to stand for several minutes.

The Interpretation

The presence of nitrate is indicated if the bottom tip of the litmus turns uniformly blue, indicating NH₃ was formed.

Identification Test 8 (IT-8)

Description

This is an identification test for phosphate ion, PO₄³⁻. A positive IT-8 indicates the presence of phosphate ion in solution.

How It Works

When an excess of ammonium molybdate is added to a solution of a phosphate that is 5-10% HNO₃ by volume, bright yellow ammonium molybdophosphate precipitates. The composition of the precipitate is approximated by (NH₄)₃[PMo₁₂O₄₀]·6 H₂O.

The Procedure

Acidify a few drops of the solution under test with 6 M HNO₃, and add 2 drops of acid in excess. Warm the solution for a minute in a hot water bath; it should reach a temperature of 40-50° (not too hot to hold) for fast reaction in the next step.

Withdraw the tube from the water bath, and add 2 drops of ammonium molybdate reagent [(NH₄)₂MoO₄]. Allow to stand for 5 minutes.

The Interpretation

A bright yellow precipitate of ammonium molybdophosphate indicates the presence of phosphate. White MoO_3 may form if the phosphate is absent or if the solution is too hot.

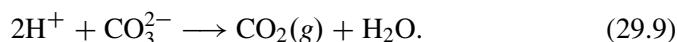
Identification Test 9 (IT-9)

Description

This test is an identification test for carbonate ion, CO_3^{2-} . A positive IT-9 indicates the presence of carbonate ion in solution.

How It Works

The test of carbonates is a modification of ET-2 in which carbon dioxide is evolved when a solution containing carbonate is acidified. The equation describing what happens in ET-2 is



This is where ET-2 ends. However, if the gas is absorbed in barium hydroxide solution, a white precipitate of BaCO_3 is obtained according to the equation



The Procedure

Add 1 or 2 drops of 6 M H_2SO_4 to 20-30 mg of solid sample. Have a medicine dropper (not a Pasteur pipet) ready with a drop of $\text{Ba}(\text{OH})_2$ solution in the tip. After adding the acid, quickly insert the dropper without squeezing the bulb. Look for cloudiness in the drop at the end of the dropper. The drop is *not* to be added to the solution.

The Interpretation

The presence of carbonate is indicated by the formation of a white turbidity, BaCO_3 , in the drop.

29.4 Safety Considerations

Chemical Hazards

During this experiment you will use concentrated acids. Be careful when handling these acids. If you spill any concentrated acid on your skin, wash off immediately with plenty of water.

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.



Figure 29.1

Broken glass container.

Waste Disposal

All waste in this lab must be poured into the appropriate waste containers in the hoods located in the back of the laboratory. No waste can be poured down the drain.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 29.1. Do not use the normal waste baskets for broken glass.

29.5 Experimental Procedure

Some of the tests are carried out directly on solid samples, others on solutions. Solid samples and solutions are available on your lab bench. Use 4 inch test tubes whenever test tubes are called for in the procedure.

Elimination Tests

Elimination Test 1 (ET-1)

1. **Place Solution of S^{2-} in Test Tube:** Place a few drops of a solution containing S^{2-} in a test tube.
2. **Test pH of S^{2-} Solutions:** Dip a clean stirring rod into the solution, withdraw it, and touch it to a piece of wide range indicator paper. Determine the pH by comparing the color of the indicator paper to the color chart.
3. **Repeat for PO_4^{3-} :** Repeat these steps for ET-1 on a solution containing the phosphate anion.
4. **Repeat for CO_3^{2-} :** Repeat these steps for ET-1 on a solution containing the carbonate anion.

Elimination Test 2 (ET-2)

► Carefully record all observations in your laboratory notebook.

► Carefully record all observations in your laboratory notebook.

1. **Put Solid CO_3^{2-} Sample In Test Tube:** Place sufficient solid carbonate sample into a dry test tube to make a layer about 1 mm deep.
2. **Add Sulfuric Acid:** Add enough 6 M H_2SO_4 so that the solid is covered and there is enough solution above it that you can watch for bubbles.
3. **Mix Contents of Test Tube:** Mix the contents of the tube by flicking the bottom of the tube with your forefinger.

4. **Observe Tube and Note Odor:** Watch for the evolution of gas. Note the odor by cautiously wafting some of the gas to your nose. Do this under a hood and use a wafting motion to smell the gases since some of them are obnoxious and toxic.
5. **Repeat for S^{2-} :** Repeat these steps for ET-2 on a solid containing the sulfide ion.
6. **Repeat for NO_2^- :** Repeat these steps for ET-2 on a solid sample containing the nitrite ion.

Elimination Test 3 (ET-3)

1. **Place Solution of S^{2-} on Spot Plate:** Place a few drops of a solution containing S^{2-} into a depression in a porcelain spot plate.
2. **Acidify with HCl:** Add a drop of concentrated HCl to the depression containing the sulfide ion solution.
3. **Prepare $K_3Fe(CN)_6$ Solution on Spot Plate:** To a separate depression add one small crystal of $K_3Fe(CN)_6$ and a few drops of water.
4. **Add $K_3Fe(CN)_6$ Solution to S^{2-} Spot:** Add one drop of the $K_3Fe(CN)_6$ solution to the depression containing the sulfide solution.
5. **Add $FeCl_3$ Solution to S^{2-} Spot:** Add one drop of $FeCl_3$ solution to the depression containing the sulfide ion solution.
6. **Repeat for NO_2^- :** Repeat these steps for ET-3 on a solution containing the nitrite ion.
7. **Repeat for I^- :** Repeat these steps for ET-3 on a solution containing the iodide ion.

► Carefully record all observations in your laboratory notebook.

Elimination Test 4 (ET-4)

1. **Add NO_2^- to Test Tube:** Add 5 drops of a solution containing NO_2^- to a test tube.
2. **Make Acidic with Sulfuric Acid:** Add 6 M H_2SO_4 dropwise to the test tube until the solution is acidic.
3. **Add $FeSO_4$ to the Test Tube:** Add 5 drops of freshly prepared 0.1 M $FeSO_4$. Carefully observe the result, paying particular attention to whether the solution turns brown.
4. **Repeat for NO_3^- :** Repeat the above steps for ET-4 for a solution containing nitrate instead of nitrite. Then continue with the remaining steps for the nitrate solution.

► Carefully record all observations in your laboratory notebook.

► If the two solutions are mixed together by careless addition of the 18 M H₂SO₄ or by shaking, the test will not work.

► Carefully record all observations in your laboratory notebook.

5. **Add 18 M Sulfuric Acid:** Hold the test tube in a slanted position and carefully (and slowly) add 5 to 10 drops of 18 M H₂SO₄, allowing it to run down the inside of the tube. It should form a layer below the other solution.
6. **Observe Tube:** Carefully straighten the tube to an upright position and set it in a test tube rack or a beaker. Observe the region between the two layers.

Elimination Test 5 (ET-5)

1. **Place Cl⁻ Solution In Test Tube:** Place a few drops of a solution containing Cl⁻ into a test tube.
2. **Add Silver Nitrate:** Add a drop of silver nitrate solution to the test tube.
3. **Add Additional Silver Nitrate:** Add an additional drop of silver nitrate to the test tube. If this second drop produces more precipitate, continue the addition of silver nitrate until precipitation appears to be complete. After each addition, mix well by flicking the bottom of the tube with your forefinger.
4. **Add Nitric Acid:** Add 6 M HNO₃ to the test tube a drop at a time, mixing well after each drop is added, until the solution is acidic to litmus. Finally, add a few drops of acid in excess.
5. **Repeat for Br⁻:** Repeat these steps for ET-5 on a sample containing bromide ion.
6. **Repeat for I⁻:** Repeat these steps for ET-5 on a sample containing iodide ion.
7. **Repeat for S²⁻:** Repeat these steps for ET-5 on a sample containing sulfide ion.

Elimination Test 6 (ET-6)

► Carefully record all observations in your laboratory notebook.

► The addition of ammonia prevents the formation of HPO₄²⁻, H₂PO₄⁻, and H₃PO₄.

► Carefully record all observations in your laboratory notebook.

1. **Place PO₄³⁻ Solution In Test Tube:** Place a few drops of the phosphate solution to be analyzed into a test tube.
2. **Add Ammonia:** Make the solution basic to litmus with 15 M NH₃.
3. **Add Calcium Nitrate:** Add a few drops of Ca(NO₃)₂ solution.

Elimination Test 7 (ET-7)

1. **Add Sulfate Solution to Test Tube:** Add a few drops of the sulfate solution under test to a test tube.
2. **Add Barium Chloride:** Add barium chloride solution drop by drop until precipitation is complete.
3. **Centrifuge Test Tube:** Centrifuge and draw off the solution above the precipitate and discard it.

4. **Add HCl to Precipitate:** Treat the precipitate with several drops of 6 M HCl.

Identification Tests

Identification Test 1 (IT-1)

1. **Add Chloride Solution To Test Tube:** Add a few drops of a chloride solution to a test tube.
2. **Add Nitric Acid:** Acidify the contents of the test tube by adding 6 M nitric acid.
3. **Add Silver Nitrate:** Add a drop of AgNO_3 solution to the test tube.
4. **Centrifuge Test Tube:** Centrifuge the test tube and contents. Discard the supernatant liquid.
5. **Add Ammonia to Precipitate:** Add a few drops of 6 M NH_3 to the precipitate. If it dissolves, acidify the solution with 6 M HNO_3 .

► Test for Cl^-

► Carefully record all observations in your laboratory notebook.

► A white precipitate at this stage may be AgCl . The remainder of the steps are to confirm this.

Identification Test 2 (IT-2)

1. **Add Bromide Solution to Test Tube:** Add a few drops of a solution containing bromide ion to a test tube.
2. **Add Nitric Acid:** Acidify the bromide solution with 6 M HNO_3 , and then add 4 drops of nitric acid in excess.
3. **Add Petroleum Ether:** Add several drops of petroleum ether. Add just enough to clearly see two layers.
4. **Add Potassium Permanganate:** Add 0.02 M KMnO_4 drop by drop, shaking after each addition.

► Test for Br^-

► Carefully record all observations in your laboratory notebook.

► Adding too much petroleum ether will make the color more difficult to see if present.

Identification Test 3 (IT-3)

1. **Add Iodide Solution to Test Tube:** Add a few drops of a solution containing iodide ions to a test tube.
2. **Add Sulfuric Acid:** Acidify the iodide solution with 6 M H_2SO_4 .
3. **Add Sodium Nitrite and Petroleum Ether:** Add a few crystals of NaNO_2 and several drops of petroleum ether. Shake vigorously to extract the iodine.

► Test for I^-

► Carefully record all observations in your laboratory notebook.

Identification Test 4 (IT-4)

► Test for S^{2-}

Identification test 4 is a test for sulfide ion. Elimination test 2 is generally considered a sufficient identification test for sulfide ion. If you have already performed ET-2, there is no need to do any additional test for IT-4.

► Test for SO_4^{2-}

Identification Test 5 (IT-5)

Identification test 5 is a test for sulfate ion. Elimination test 7 is generally considered a sufficient identification test for sulfate ion. If you have already performed ET-7, there is no need to do any additional test for IT-5.

► Test for NO_2^-

► Carefully record all observations in your laboratory notebook.

Identification Test 6 (IT-6)

1. **Add Nitrite Solution to Test Tube:** Add a few drops of a solution containing nitrite ion to a test tube.
2. **Add Barium Chloride Solution:** Add a few drops of BaCl_2 solution. If a BaSO_4 precipitate forms, add more BaCl_2 until precipitation is complete. Then centrifuge the solution and transfer the solution to a new test tube.
3. **Add Sulfamic Acid:** Add a few crystals of sulfamic acid to the solution, and flick the bottom of the tube with your forefinger to cause vigorous evolution of gas bubbles.

► Test for NO_3^-

Identification Test 7 (IT-7)

► Carefully record all observations in your laboratory notebook.

1. **Setup Hot Water Bath:** Place a beaker with water on a hot plate and warm to near boiling.
2. **Obtain Red Litmus Paper:** Obtain a piece of red litmus paper from your drawer. Fold it in half end to end to make a V shape.
3. **Obtain Two Test Tubes:** Obtain two clean and dry test tubes.
4. **Add Nitrate Solution to Test Tube:** Add a few drops of a solution containing nitrate ion to one test tube.
5. **Add Sodium Hydroxide:** Add an equal volume of 6 M NaOH to the same test tube.
6. **Transfer Mixture to New Test Tube:** With a pipet, transfer this mixture to the other dry test tube in such a way as not to wet the upper walls of the tube with the basic solution. After withdrawing the pipet, inspect the upper walls of the tube to make sure this critical requirement is satisfied.
7. **Add Aluminum Wire:** Add a piece of aluminum wire to the test tube containing the solution.
8. **Warm Test Tube:** Warm the test tube briefly in a water bath to induce a vigorous reaction.
9. **Add Litmus Paper to Test Tube:** Withdraw the test tube from the water bath. Moisten the bottom of the V in the litmus paper with DI water and then insert the piece of red litmus into the test tube with the bottom of the V pointing down into the tube. The dry upper ends will support the litmus so that it does not fall in. Allow the tube to stand for several minutes.

Identification Test 8 (IT-8)

1. **Add Phosphate Solution to Test Tube:** Add a few drops of a solution containing phosphate to a test tube.
2. **Add Nitric Acid:** Acidify the phosphate solution with 6 M HNO₃. Add 2 drops of acid in excess.
3. **Heat Test Tube in Water Bath:** Warm the solution for a minute in a hot water bath. It should reach a temperature of 40-50° (not too hot to hold) for fast reaction in the next step.
4. **Add Ammonium Molybdophosphate:** Withdraw the tube from the water bath, and add 2 drops of ammonium molybdate reagent [(NH₄)₂MoO₄]. Allow to stand for 5 minutes.

► Test for PO₄³⁻

► Carefully record all observations in your laboratory notebook.

Identification Test 9 (IT-9)

1. **Place Barium Hydroxide Solution in Test Tube:** Place about 10 drops of barium hydroxide solution into a test tube and suck most of it up into a medicine dropper (not a Pasteur pipet). Leave the medicine dropper in the test tube until needed.
2. **Add Carbonate Solid to Test Tube:** Add 20-30 mg of a solid containing the carbonate ion to a different test tube.
3. **Add Sulfuric Acid:** Add 1 or 2 drops of 6 M H₂SO₄ to the test tube containing the carbonate solid.
4. **Bring Medicine Dropper To Test Tube:** After adding the acid, quickly insert the dropper into the mouth of the test tube with carbonate. Do this without squeezing the bulb. The drop is *not* to be added to the solution. Look for cloudiness in the drop at the end of the dropper.

► Test for CO₃²⁻

► Carefully record all observations in your laboratory notebook.

29.6 Before Exiting Lab

- Check your lab notebook for page numbers on all pages.
- Update the table of contents in your notebook.
- Draw a line at the end of your experimental work for the day. Sign your notebook at the line.
- Have your instructor sign your lab notebook before you leave the lab. This helps verify where you stopped lab work for the week.

29.7 Post-Lab Assignments

There are no post-lab assignments to complete. All you have to do this week is record your observations during lab. Once you have done that you are finished.

Chapter 30

Semimicro Qualitative Analysis of Known Cations

30.1 Introduction

In this experiment you will identify the cations present in a solution of known identity. This experiment utilizes the principles of semimicro qualitative analysis.

The Chemistry Involved

Separation of Silver Ion

The separation of Ag^+ from Cu^{2+} , Al^{3+} , and Fe^{3+} is based on the fact that while most chlorides are soluble, AgCl is insoluble, so the formation of AgCl is used to separate the Ag^+ from the remaining cations.

Confirmation of Silver Ion

While AgCl is insoluble, Ag^+ forms the complex ion $\text{Ag}(\text{NH}_3)_2^+$ in the presence of excess NH_3 . This shifts the equilibrium away from the formation of AgCl to the more stable complex ion, thus dissolving the precipitate. Addition of more HCl protonates the NH_3 causing equilibrium to shift away from the complex ion, allowing the AgCl precipitate to reform.

Dissolution of the AgCl precipitate by formation of the $\text{Ag}(\text{NH}_3)_2^+$ complex ion followed by reformation of the AgCl precipitate confirms the presence of Ag^+ .

Separation of Copper(II)

The separation of Cu^{2+} from Al^{3+} and Fe^{3+} is based on the fact that in the presence of NH_3 , Cu^{2+} forms the complex ion $\text{Cu}(\text{NH}_3)_4^{2+}$ while Al^{3+} and Fe^{3+} form insoluble hydroxides. So the formation of $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ is used to separate the Cu^{2+} from the remaining cations.

Confirmation of Copper(II)

The deep blue of the $\text{Cu}(\text{NH}_3)_4^{2+}$ complex ion is strongly indicative of the presence of Cu^{2+} . The addition of HCl causes the protonation of the NH_3 , resulting in the dissociation of the $\text{Cu}(\text{NH}_3)_4^{2+}$ complex ion and the subsequent formation of CuCl_4^{2-} . This complex ion readily dissociates in the presence of $\text{Fe}(\text{CN})_6^{4-}$ as Cu^{2+} reacts to form $\text{Cu}_2\text{Fe}(\text{CN})_6$, a blood red precipitate. This precipitate confirms the presence of Cu^{2+} . Formation of the $\text{Cu}_2\text{Fe}(\text{CN})_6$, a deep red precipitate, confirms the presence of Cu^{2+} .

Separation of Aluminum(III)

The basis for the separation of Al^{3+} from Fe^{3+} is that $\text{Fe}(\text{OH})_3$ is a basic hydroxide (reacts with acid, but not base) while $\text{Al}(\text{OH})_3$ is an amphoteric hydroxide (reacts with acid or base). In the presence of excess hydroxide, $\text{Fe}(\text{OH})_3$ does not react, but $\text{Al}(\text{OH})_3$ reacts to form the complex ion $\text{Al}(\text{OH})_4^-$. So the formation of the complex ion $\text{Al}(\text{OH})_4^-$ puts the Al^{3+} in a soluble form, allowing it to be separated from the $\text{Fe}(\text{OH})_3$ precipitate.

Confirmation of Iron(III)

The orangish-brown of the $\text{Fe}(\text{OH})_3$ precipitate is a strong indicator of the presence of Fe^{3+} . The addition of HCl causes the protonation of the hydroxide, resulting in the dissolution of the $\text{Fe}(\text{OH})_3$ precipitate, thereby freeing the Fe^{3+} , which gives the solution a yellowish appearance. The Fe^{3+} can then react with SCN^- to form the blood red complex ion FeSCN^{2+} . Formation of the FeSCN^{2+} complex ion (blood red solution) confirms the presence of Fe^{3+} .

Confirmation of Aluminum(III)

The addition of HCl to $\text{Al}(\text{OH})_4^-$ will initially cause one hydroxide of the colorless complex ion to react, forming water and the white precipitate $\text{Al}(\text{OH})_3$. The addition of more HCl will cause the remaining hydroxide to react, freeing Al^{3+} from the precipitate. Note that if sufficient HCl is added initially, all the hydroxides can react, allowing the formation of Al^{3+} from $\text{Al}(\text{OH})_4^-$ without the intermediate formation of $\text{Al}(\text{OH})_3$. The free Al^{3+} can then react with PO_4^{3-} to form AlPO_4 , a white precipitate. This confirms the presence of Al^{3+} . Note that if the solution is strongly acidic, the PO_4^{3-} can be protonated (forming HPO_4^{2-} , H_2PO_4^- , and H_3PO_4), thus preventing it from reacting with the Al^{3+} . In such a case, the addition of excess PO_4^{3-} can still result in the formation of AlPO_4 . Formation of a white AlPO_4 precipitate confirms the presence of Al^{3+} .

30.2 Safety Considerations

Chemical Hazards

During this experiment you will use concentrated acids. Be careful when handling these acids. If you spill any concentrated acid on your skin, wash off immediately with plenty of water.

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

All waste in this lab must be poured into the appropriate waste containers in the hoods located in the back of the laboratory. No waste can be poured down the drain.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 30.1. Do not use the normal waste baskets for broken glass.

30.3 Experimental Procedure

The known solution you will be testing contains Ag^+ , Cu^{2+} , Al^{3+} , and Fe^{3+} .

Separation of Silver Ion

1. **Add Solution to Test Tube:** Add 20 drops of solution to be tested to a 4-inch test tube.
2. **Add HCl:** Add 4 drops of 6 M HCl. Mix and allow to stand 3 minutes.
3. **Centrifuge Test Tube:** Centrifuge the test tube for 2 minutes.
4. **Transfer Supernatant:** Using a pasteur pipet, transfer the supernatant to another test tube.
5. **Wash Precipitate:** Wash the precipitate with 10 drops of cold water. Centrifuge and add the wash to the decantate (the decanted solution) from the previous step.
6. **Save Everything:** The precipitate will be used when attempting to confirm the presence of silver ion. The decantate will be used in further separation steps. At this point, you should dispose of nothing.

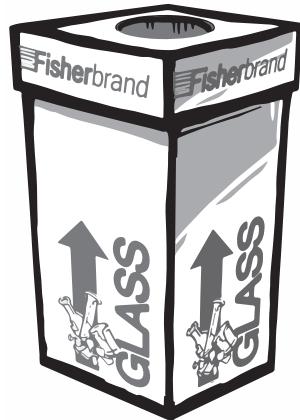


Figure 30.1
Broken glass container.

Confirmation of Silver Ion

1. **Dissolve Silver Precipitate:** Add sufficient 15 M NH₃ (about 10-15 drops) to dissolve the AgCl precipitate from the “Separation of Silver Ion” procedure.
2. **Add HCl:** Add sufficient 6 M HCl to reform the AgCl precipitate.
3. **Discard Mixture:** After you have performed these tests on the silver precipitate, you may discard the mixture.

Separation of Copper(II) Ion

1. **Add Ammonia to Remaining Ions:** Add 10 drops of 15 M NH₃ to the decantate from the procedure “Separation of Silver Ion.” Mix and allow to stand for 3 minutes.
2. **Centrifuge Test Tube:** Centrifuge this test tube for 2 minutes.
3. **Transfer Supernatant:** Using a pasteur pipet, transfer the supernatant to another test tube.
4. **Wash Precipitate:** Wash the precipitate with 10-15 drops of water. Centrifuge the test tube and add the wash to the decantate from the previous step.
5. **Wash Precipitate Again:** Wash the precipitate a second time with 10-15 drops of water. Centrifuge and *discard* this supernatant.
6. **Discard Nothing:** The precipitate you have collected in this procedure will be used in further separation tests. The decantate will be used in confirmation tests for copper(II) ions. Therefore, discard nothing at this stage.

Confirmation of Copper(II) Ion

1. **Add HCl to Decantate:** Add sufficient 12 M HCl (about 4-5 drops) to the decantate from the “Separation of Copper(II) Ion” procedure to cause the loss of most of the blue color.
2. **Add K₄Fe(CN)₆:** Add 3 drops of 0.2 M K₄Fe(CN)₆ solution.
3. **Discard Solution:** After making appropriate notes in your laboratory notebook, discard the mixture into the appropriate waste container.

Separation of Aluminum(III) Ion

1. **Add NaOH to Precipitate:** Add 4 drops of 8 M NaOH to the Al(OH)₃ and Fe(OH)₃ precipitate that remains from the “Separation of Copper(II) Ion” procedure. Mix thoroughly and allow to stand for 3 minutes.
2. **Centrifuge Test Tube:** Centrifuge the test tube for 2 minutes.

► What observation confirms the presence of silver ion?

► What observation confirms the presence of copper(II) ion?

3. **Transfer Supernatant:** Using a pasteur pipet, transfer the supernatant to another test tube.
4. **Discard Nothing:** The precipitate will be used to confirm the presence of iron(III) ion. The decantate will be used to confirm the presence of aluminum(III). Discard nothing at this stage.

Confirmation of Iron(III) Ion

1. **Add HCl to Precipitate:** Add sufficient 6 M HCl (about 15 drops) to the precipitate from the “Separation of Aluminum(III) Ion” procedure to dissolve it.
2. **Add KSCN:** Add 3 drops of 0.2 M KSCN to this solution.
3. **Discard Solution:** After making observation notes in your laboratory notebook, discard the mixture into the appropriate waste container.

► What observation confirms the presence of iron(III)?

Confirmation of Aluminum(III) Ion

1. **Add HCl to Decantate:** Add sufficient 6 M HCl (about 5-10 drops) to the solution remaining from the “Separate Aluminum(III) Ion” procedure to make the solution slightly acidic, as determined with long range indicator paper.
2. **Add Sodium Phosphate:** Add about 20 drops of 0.5 M Na₃PO₄ to this solution. You may need to add more if the solution was strongly acidic.
3. **Discard Solution:** After making observational notes in your laboratory notebook, discard the mixture into the appropriate waste container.

► What observation confirms the presence of aluminum(III) ion?

30.4 Before Exiting Lab

- Check your lab notebook for page numbers on all pages.
- Update the table of contents in your notebook.
- Draw a line at the end of your experimental work for the day. Sign your notebook at the line.
- Have your instructor sign your lab notebook before you leave the lab. This helps verify where you stopped lab work for the week.

30.5 Post-Lab Assignments

During your laboratory work you should have made detailed procedural and observational notes. This is the main purpose of this lab; therefore, there is nothing to do after the lab.

Chapter 31

Semimicro Qualitative Analysis of Unknown Ions

31.1 Introduction

In this experiment you will identify the anion and cation present in a sample of unknown identity. This lab requires that you already be familiar with the techniques of semimicro qualitative analysis for anions and cations.

31.2 Safety Considerations

Chemical Hazards

During this experiment you will use concentrated acids. Be careful when handling these acids. If you spill any concentrated acid on your skin, wash off immediately with plenty of water.

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

All waste in this lab must be poured into the appropriate waste containers in the hoods located in the back of the laboratory. No waste can be poured down the drain.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 31.1. Do not use the normal waste baskets for broken glass.

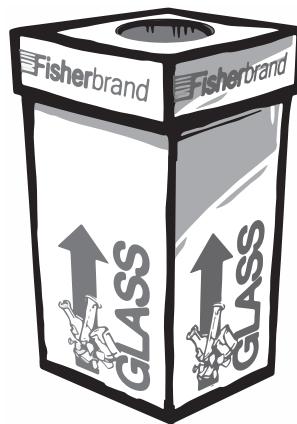


Figure 31.1
Broken glass container.

31.3 Experimental Procedure

Anion Identification

Your unknown anion sample will contain one of the following anions: CO_3^{2-} , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , S^{2-} , Br^- , Cl^- , or I^- . Thus, once you have confirmed the identity of one anion in solution, there is no need to perform other tests as long as you are confident in your results.

1. **Record Anion Unknown Number:** At your desk will be a 4-inch test tube which contains a solid salt sample. Record the number of your anion unknown in your lab notebook.
2. **Prepare Solution of Unknown Salt:** Prepare a solution containing the unknown anion by dissolving about 40 mg of the salt in 2 mL of distilled water. Use aliquots of this solution as needed during the tests.
3. **Perform Elimination Tests on Unknown:** Perform the appropriate elimination tests in order as far as you need to go to narrow down the identity of your unknown anion.
4. **Perform Identification Tests:** After narrowing down the possible anions in solution with the elimination tests, perform the necessary identification test(s) to determine the identity of the anion.

Cation Identification

Your unknown solution contains from one to four of the following cations: Ag^+ , Cu^{2+} , Al^{3+} , Fe^{3+} . Thus, you may not stop testing once you have found one ion in solution. You must continue until you have exhausted all possibilities.

1. **Record Unknown Number:** At your desk will be a 4-inch test tube which contains a solution of unknown cation(s). Record the number of your cation unknown in your lab notebook.
2. **Add Unknown Solution to Test Tube:** Add 20 drops of your unknown solution to a test tube, saving the rest in case you ruin or spill the sample you are testing.
3. **Carry Out Cation Tests:** Carry out the same cation tests that you did while testing the known ions.

31.4 Before Exiting Lab

- Check your lab notebook for page numbers on all pages.
- Update the table of contents in your notebook.
- Draw a line at the end of your experimental work for the day. Sign your notebook at the line.

- Have your instructor sign your lab notebook before you leave the lab. This helps verify where you stopped lab work for the week.

31.5 Post-Lab Assignments

1. Clearly indicate in your lab notebook what you think the identify of your unknown anion is.
2. State, in brief, your reasoning for your identification of the unknown anion.
3. Clearly indicate in your lab notebook what you think the identity of your unknown cation is.
4. State, in brief, your reasoning for your identification of the unknown cation.

Chapter 32

Synthesis of Cobalt(III) Coordination Compounds

Your laboratory section will synthesize two cobalt(III) coordination compounds for spectral analysis in a future project.

32.1 Introduction

The bonding between ligands and the metal in coordination compounds is often discussed in terms of crystal field theory. As ligands approach the metal, the d orbitals are perturbed, causing all of them to go up in energy. Because of the differing spatial orientation of the five d orbitals, some go up in energy more than others. For octahedral complexes, this leads to the energetic splitting pattern illustrated in Figure 32.1.

The difference in energy between the group of orbitals labeled t_{2g} and that labeled e_g in Figure 32.1 is called the crystal field splitting energy. It is given the symbol Δ_0 . The magnitude of Δ_0 depends on the oxidation state and size of the metal as well as the identity of ligand. Some ligands can make Δ_0 small, and these are called weak field ligands. Some ligands can make Δ_0 large, and these are called strong field ligands. The magnitude of Δ_0 can be measured spectroscopically, providing an experimental way to determine the relative crystal field strength of ligands. This, in turn, can sometimes be correlated with reactivity of the ligands, making this a particularly important quantity to determine.

If several coordination compounds are synthesized with the same metal in the same oxidation state and with all ligands the same except one, all changes in spectral properties can be attributed to the one ligand that changed. This makes it possible to spectroscopically distinguish weak field from strong field ligands. In this project your laboratory section will synthesize two coordination compounds that differ only by one ligand. You will spectroscopically analyze these complexes in a future project to determine relative ligand strength.

Coordination compounds of cobalt(III) are relatively stable in water, undergoing ligand exchange with water very slowly. This makes them easier to study than complexes of other metal ions, such as nickel(II). For instance, $\text{Ni}(\text{NH}_3)_6^{2+}$

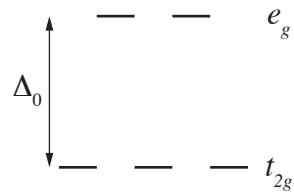


Figure 32.1

Splitting pattern expected for the metal d orbitals in an octahedral complex ion. The three d orbitals lower in energy are called t_{2g} orbitals, and the two d orbitals higher in energy are called e_g orbitals. The energy difference between the t_{2g} and e_g orbitals is given the symbol Δ_0

undergoes nearly instantaneous reaction with water to form $\text{Ni}(\text{H}_2\text{O})_6^{2+}$, making the ammonia complex ion of nickel(II) difficult to study. Thus, in this project we will synthesize two coordination compounds of cobalt(III).

The two complex ions your laboratory section will synthesize are shown in Figure 32.2. For complex ion A, the counter ion is nitrate. For complex ion B, the counter ion is chloride.

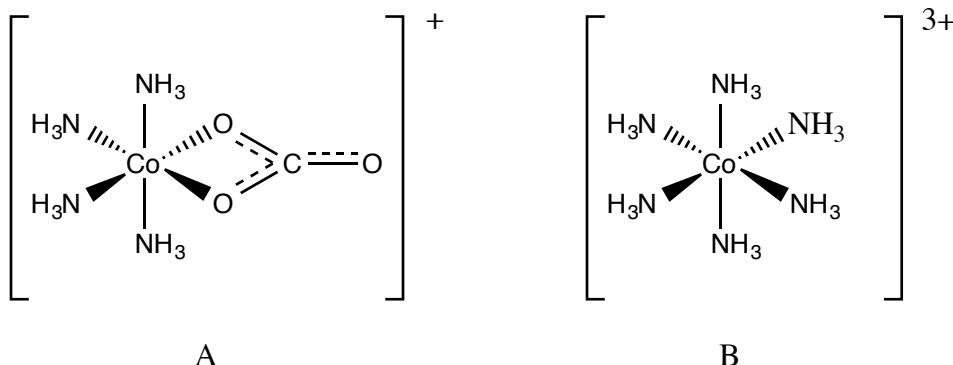
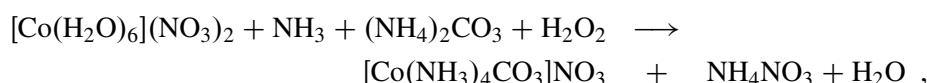


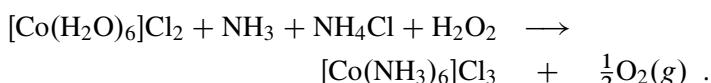
Figure 32.2

Both coordination complexes to be synthesized possess cobalt in the +3 oxidation state. Complex ion A has nitrate as the counter ion. Complex ion B has chloride as the counter ion.

The synthesis of complex ion A will be carried out according to the *unbalanced* equation



and the synthesis of complex ion B will be carried out according to the *unbalanced* equation



Hydrogen peroxide serves as an oxidizing agent in each reaction to oxidize cobalt(II) to cobalt(III).

32.2 Safety Considerations

Chemical Hazards

During this experiment you will work with a solution that is 30% hydrogen peroxide, H₂O₂. This is ten times more concentrated than hydrogen peroxide you can buy in the store. This is a strong oxidizing agent, which means it will cause burns if you get it on your skin or clothing. If you get it in your eyes, it may cause irreparable damage. Use gloves while transferring this chemical. If you get any on your skin or clothing, wash the spill area with lots of cold water immediately. If you spill hydrogen peroxide on your bench, clean it up immediately.

Goggles

You are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

All waste in this lab must be poured into the appropriate waste containers. No waste can be poured down the drain.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 32.3. Do not use the normal waste baskets for broken glass.



Figure 32.3

Broken glass container.

32.3 Experimental Procedure

Synthesize Complex Ion A

- Set Up Hot Plate:** Retrieve a hot plate from the shelves around the lab and set it up under your bench hood.
- Set Up Ice Bath:** Prepare an ice bath.
- Prepare Chilled Water:** Place about 20 mL of DI water into a small beaker. Place the beaker in the ice bath. You will need this chilled water later.
- Prepare Chilled Ethanol:** Place about 20 mL of 95% ethanol into a small beaker. Place the beaker into the ice bath. You will need this chilled ethanol later.
- Prepare Ammonium Carbonate Solution:** Dissolve 4.0 g of ammonium carbonate in 10. mL of DI water in a 50 mL beaker while gently heating on the hot plate.
- Add Ammonia:** Remove the beaker from the hot plate and add 10 mL concentrated aqueous ammonia to the mixture. Be sure to do this under the fume hood.
- Prepare Co(II) Solution:** Mix 2.5 g of $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ with 5 mL DI water in a 250 mL beaker.
- Mix Solutions:** Add all of the ammonium carbonate solution to the Co(II) solution with stirring.
- Add Hydrogen Peroxide:** Slowly add 1.5 mL of a 30% hydrogen peroxide solution to the solution in the 250 mL beaker.

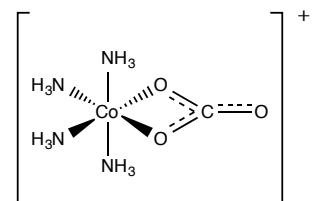


Figure 32.4

Complex ion A.

► Do not allow the bulb of your thermometer to touch the bottom of the beaker. Use your split rubber stopper and a ring stand to suspend your thermometer in the solution.

► Note that it is the filtrate that you keep in this case, not what sticks to the filter paper.

► The more slowly you cool the solution, the nicer the crystals will be.

► It is important that you only wash the product crystals with *chilled* water and *chilled* ethanol.

10. **Evaporate Solution:** Place the 250 mL beaker on the hot plate and set the dial to obtain a solution temperature as close to 75°C as you can without exceeding 75°C. Never let the solution boil. Keep the beaker on the hot plate until the solution volume has been reduced to between 15 mL and 20 mL.
11. **Add Additional Ammonium Carbonate During Evaporation:** While the solution in the 250 mL beaker is evaporating, add a total of 0.8 g of additional ammonium carbonate solid in small portions throughout the evaporation process.
12. **Suction Filter Solution:** When the solution volume has been reduced to between 15 mL and 20 mL, suction filter the contents of the beaker while still warm. Be sure the suction filter flask is clean before you begin to suction filter.
13. **Cool Collected Liquid:** Pour the collected liquid into a 50 mL beaker and then place the beaker into an ice bath. Red needle-like crystals of the product should form.
14. **Suction Filter Crystals:** Suction filter the product crystals onto a piece of *weighed* filter paper. Wash them in the filter funnel with a few milliliters of the chilled DI water you prepared earlier and then with a few milliliters of the chilled ethanol.
15. **Dry Crystals:** Dry the crystals by pulling air through them for about 10 minutes.
16. **Weigh Collected Product:** Weigh the collected product on the filter paper and determine the total mass of product collected.
17. **Store Crystals:** Place the dried crystals and filter paper onto a watch glass and then place the watch glass in a large beaker. Store this in your drawer until needed.

Synthesize Complex Ion B

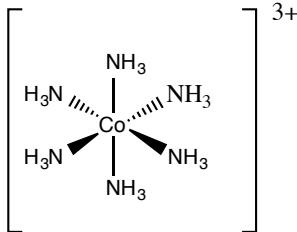


Figure 32.5
Complex ion B.

1. **Set Up Hot Plate:** Retrieve a hot plate from the shelves around the lab and set it up under your bench hood.
2. **Set Up Ice Bath:** Prepare an ice bath.
3. **Prepare Chilled Water:** Place about 20 mL of DI water into a small beaker. Place the beaker in the ice bath. You will need this chilled water later.
4. **Prepare Chilled Ethanol:** Place about 20 mL of 95% ethanol into a small beaker. Place the beaker into the ice bath. You will need this chilled ethanol later.
5. **Prepare Co(II) Solution:** Dissolve 2.5 g of $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ in 15 mL DI water in a 125 mL Erlenmeyer flask.

6. **Add Ammonium Chloride:** Add 1.7 g of ammonium chloride to the reaction mixture and stir to dissolve.
7. **Add Activated Charcoal:** Under a hood, add 0.50 g of activated charcoal to the reaction mixture. This will not dissolve.
8. **Add Ammonia:** Add 25 mL concentrated aqueous ammonia to the reaction mixture. Be sure to do this under a hood.
9. **Cool Mixture in Ice Bath:** Place the flask containing the reaction mixture into an ice bath and cool the mixture to 0°C.
10. **Add Hydrogen Peroxide:** With the flask still in the ice bath, slowly add 2.0 mL of a 30% hydrogen peroxide solution. Be sure to add the hydrogen peroxide drop-by-drop, leaving plenty of time between drops to allow the reaction mixture to cool. Be sure the reaction mixture never goes above 10°C.
11. **Heat Reaction Mixture:** After all hydrogen peroxide has been added, remove the flask from the ice bath, dry the flask, and then place it on a hot plate to heat the mixture to 60°C. Keep the solution on the hot plate at this temperature for 30 minutes.

► This heating step helps facilitate the dissociation of all water molecules from the metal ion.
12. **Cool Mixture in Ice Bath:** Place the flask with the reaction mixture into an ice bath. Look for product precipitating from solution.
13. **Suction Filter Product Mixture:** Suction filter the solid out of the reaction mixture. Note that the solid will contain both the product and charcoal.
14. **Place Solid in Flask:** Transfer the solid collected in the suction filtration to a 125 mL Erlenmeyer flask.
15. **Prepare Hot Water:** Add about 20 mL DI water to a small beaker and heat it on a hot plate until the temperature is about 70°C.
16. **Dissolve Product Crystals:** Add the hot water to the flask containing the collected solid, which contains product crystals and charcoal. Also add 1.0 mL concentrated HCl.
17. **Heat Mixture:** Heat the flask to 70°C on a hot plate. This should dissolve the product, leaving the charcoal as the only solid.
18. **Suction Filter Mixture:** Suction filter the mixture to remove the charcoal. Be sure you carry out the filtration while the solution is still warm. Note that it is the liquid filtrate that you want to save.

► Make sure the filter flask is clean and dry before this filtration since it is the liquid that should be saved.
19. **Chill Filtrate:** Transfer the filtrate to a beaker and place the beaker in an ice bath. Also add 1.0 mL HCl. Crystals should form. If they do not, scratch the bottom of the beaker with a glass stirring rod.

► It is important that you only wash the product crystals with *chilled* water and *chilled* ethanol.

20. **Suction Filter Crystals:** Suction filter the product crystals onto a piece of *weighed* filter paper. Wash them in the filter funnel with a few milliliters of the chilled DI water you prepared earlier and then with a few milliliters of the chilled ethanol.
21. **Dry Crystals:** Dry the crystals by pulling air through them for about 10 minutes.
22. **Weigh Collected Product:** Weigh the collected product on the filter paper and determine the total mass of product collected.
23. **Store Crystals:** Place the dried crystals and filter paper onto a watch glass and then place the watch glass in a large beaker. Store this in your drawer until needed.

32.4 Before Exiting Lab

- Dispose of all cobalt waste in the labeled waste containers.
- Turn off and unplug your hot plate; return it to the location from which you retrieved it.
- Clean up your work area so that it is scrupulously clean.
- Check your lab notebook for page numbers on all pages.
- Update the table of contents in your notebook.
- Draw a line at the end of your experimental work for the day. Sign your name on the line.
- Have your instructor sign your lab notebook before you leave the lab.

32.5 Post-Lab Assignments

1. Compute the theoretical yield of the coordination compound you synthesized.
2. Compute the percent yield of the coordination compound you synthesized.

Chapter 33

Analysis of Synthesized Cobalt(III) Coordination Compounds

33.1 Introduction

As has been emphasized before, chemists are good at two broad categories of things: synthesis and analysis. Synthesis is the making of new molecules or materials. Analysis is the determination of the identity and quantity of substance present in a sample. In this lab you will carry out an analysis of a coordination compound that has already been synthesized. Specifically, you will analyze a coordination compound to determine its wavelength of maximum absorbance, λ_{max} , and its molar absorptivity, ϵ , which is a measure of how strongly a substance absorbs light.

Ultraviolet-Visible Absorption Spectroscopy

An ultraviolet-visible (UV-Vis) spectrophotometer is an instrument designed to measure the ultraviolet and visible light absorbed or transmitted by a sample solution.

Consider a sample container (such as a test tube) which contains a dilute solution of a substance that absorbs visible light. If the solution is placed in a beam of light, some light energy will be absorbed by the solution. That is, the radiant intensity of the light entering the solution, I_o , will be greater than that of the light intensity emerging from the solution, I . The absorbance of the solution, given the symbol A , is related to I_o and I according to

$$A = \log\left(\frac{I_o}{I}\right). \quad (33.1)$$

The absorbance observed for any given solution depends mainly on these three things: the nature of the absorbing molecules, the number of molecules located in the path of the light beam (concentration), and the wavelength of the light being absorbed. Beer's Law expresses this mathematically as

$$A = abc \quad (33.2)$$

► The absorptivity constant is a characteristic of a molecule at a particular wavelength and describes how strongly it absorbs light at that wavelength.

where A is the absorbance of a sample given in absorbance units (A.U.), a is a proportionality constant called the absorptivity constant, b is the length of the path through the sample that light has to travel before exiting, and where c is the concentration of the solution.

If b is given in cm and c is given in M, a is called the molar absorptivity or molar extinction coefficient and is given the symbol ϵ . Thus, we can write Beer's law for absorption as

$$A = \epsilon bc. \quad (33.3)$$

The molar absorptivity is characteristic of a given compound at a given wavelength.

If the path length, b , and wavelength, λ , of the light are kept constant during a UV-Vis absorption experiment, then absorbance, A is directly proportional to concentration, c . This means that a plot of absorbance versus concentration should give a straight line. The slope of this line is ϵb . From this, the molar absorptivity constant can be determined.

Such an experiment will generally begin with the determination of the wavelength at which the solution absorbs the most light. This wavelength is called λ_{max} .

A determination of the molar extinction coefficient (ϵ) begins with preparing a series of solutions of known concentration and determining the absorbance of each at λ_{max} . A plot of absorbance (at λ_{max}) vs concentration gives a straight line with a slope equal to ϵb .

In this experiment, you will determine λ_{max} for each coordination complex (starting material and product) and ϵ for the product.

33.2 Safety Considerations

Chemical Hazards

There are no substantial chemical hazards in this lab. You should treat all solutions with respect and wash them off immediately if you happen to spill any of them on yourself.

Goggles

As with all laboratory experiments, you are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

All waste in this lab must be poured into the appropriate waste containers in the hoods located in the back of the laboratory. No waste can be poured down the drain.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 33.1. Do not use the normal waste baskets for broken glass.

33.3 Experimental Procedure

Determine Mass of Product Collected

1. **Retrieve Product from Storage:** Remove your dried product from its storage location. Do this very carefully since the dried product will easily fall off its watch glass.
2. **Weigh Product:** Weigh your product on an electronic top loading balance and record this value.

Determine λ_{max} of Reactant and Product

1. **Prepare Stock Solution of Product:** Weigh out approximately 50 mg of your product coordination compound and add it to a 50.00 mL volumetric flask. Dilute to the mark.
2. **Collect UV/Vis Spectrum of Product:** Using water as the blank, collect a UV/Vis spectrum of the solution of your product coordination compound to determine the wavelength of maximum absorbance, λ_{max} .
3. **Collect UV/Vis Spectrum of Reactant:** A stock solution of the reactant coordination compound will be provided to you. Collect a UV/Vis absorption spectrum of this solution to determine the wavelength of maximum absorbance, λ_{max} .



Figure 33.1
Broken glass container.

► Be sure to use good quantitative technique. You should be able to determine the concentration of this solution to at least 3 sig figs.

Determine ϵ of Product

1. **Prepare Dilution of Product Solution:** Using a 10.00 mL pipet, dilute 10.00 mL of the product solution you prepared above with 10.00 mL of distilled water. Do this as accurately as you can with the equipment you have.
2. **Prepare Dilution of Diluted Product Solution:** Using a 10.00 mL pipet, dilute 10.00 mL of the diluted product solution you just prepared with an additional 10.00 mL of distilled water. Do this as accurately as you can with the equipment you have.
3. **Determine Absorbance of Solutions:** Using the a UV/Vis spectrometer and water as the blank, determine the absorbance at λ_{max} for the three solutions of your product: the original, the first dilution, and the second dilution.

33.4 Before Exiting Lab

- Dispose of all cobalt product in the appropriate waste container.
- Check your lab notebook for page numbers on all pages.
- Update the table of contents in your notebook.
- Draw a line at the end of your experimental work for the day. Sign your notebook at the line.
- Have your instructor sign your lab notebook before you leave the lab. This helps verify where you stopped lab work for the week.

33.5 Post-Lab Assignments

1. Compute the theoretical yield for your product based on the quantity of reagents you used to synthesize your coordination compound. Note that you should have already balanced the equation for this reaction.
2. Compute the percent yield of your product.
3. Report the wavelength of maximum absorbance, λ_{max} , for the reactant coordination compound and the product coordination compound in water solutions.
4. Rationalize (explain) the color of the two compounds based on their measured λ_{max} values. You should be able to do this based on a simple color wheel argument as you have learned in class.
5. In some computer program such as Excel, plot the absorbance of your product coordination compound solutions as a function of concentration (absorbance on the y axis and concentration on the x axis). Be sure to follow guidelines for plotting graphs electronically.
6. Fit the data in the plot to a straight line using some linear regression tool. Excel's "trendline" functionality will be sufficient. Make sure you show the best fit line on the plot of your data points.
7. Determine the value of the molar absorptivity constant, ϵ , for the product coordination compound in water solution. You can do this from the fit of your data points to a straight line as you did in the previous problem. Be sure to include appropriate units.

Chapter 34

Synthesis of a Cross-Linked Silicone Polymer

In this project you will synthesize a cross-linked polymer that should bounce like the commercial product sold under the trademarked name Silly Putty.

34.1 Introduction

Polymers are molecules constructed from a large number of smaller molecules, called monomers, that are joined together with the same type of linkage. Nature has been making polymers for millions of years. Because they appear in nature without any human intervention, these are called natural polymers. Examples include silk, wool, cotton, DNA, rubber, starch, cellulose, and proteins. Humans learned to make polymers in the late 1830s, and our understanding of how to craft polymers with specific properties has been growing ever since. Polymers that humans synthesize are called synthetic. Some examples of synthetic polymers include vinyl, neoprene, polystyrene, Nylon, Teflon, Kevlar, and Mylar.

One example of a synthetic polymer is Teflon, the trademarked name for polytetrafluoroethylene (PTFE). This polymer is formed by connecting thousands of tetrafluoroethylene monomers end-to-end to form a chain with a molecular weight between 10^6 and 10^7 g/mol. The monomer is shown in Figure 34.1, and a representation of the PTFE polymer chain with n monomers is shown in Figure 34.2. A single Teflon polymer molecule may have a value of n between 10^4 and 10^5 . To be more explicit, a Teflon polymer chain is a long chain of carbon and fluorine atoms, which is better depicted in Figure 34.3.

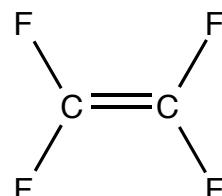


Figure 34.1
Tetrafluoroethylene, the monomer used to synthesize the polymer with the trade name of Teflon.

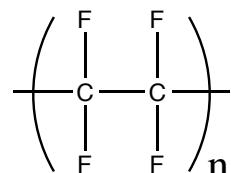


Figure 34.2
Representation of a polymer chain in Teflon indicating the monomer unit repeating n times.

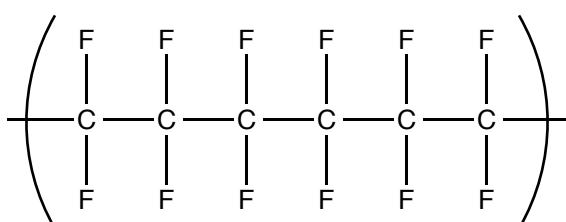
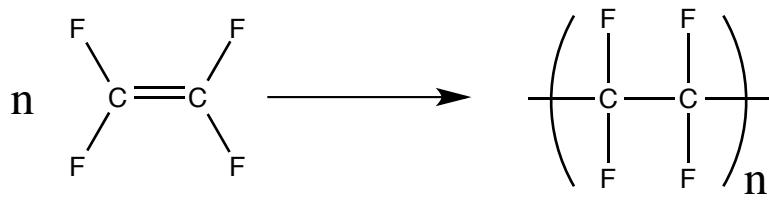


Figure 34.3

A portion of a polymer chain of Teflon. A single polymer chain will be about 10^4 carbon atoms in length. The parentheses indicate that this is just a portion of the full polymer chain, which will extend on both sides of the parentheses for thousands of carbon atoms.

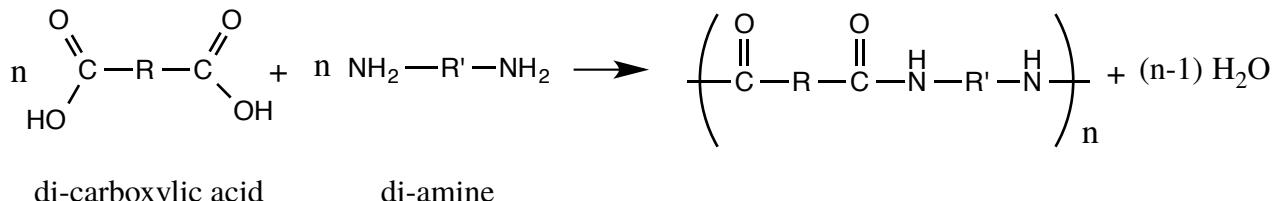
Figure 34.4

The reaction to form the Teflon polymer is depicted as n monomers of tetrafluoroethylene linking end-to-end to form a polytetrafluoroethylene chain that is n monomers long. The value of n is typically 10^4 to 10^5 .



The reaction to form the Teflon polymer is simple to depict and is shown in Figure 34.4. Note that no product other than the polymer is produced. When a polymer is formed in a reaction in which there is no loss of any atoms or molecules, it is referred to as an addition polymer to indicate that the polymer is formed literally by adding monomers together. Other examples of addition polymers include polypropylene, PVC, polystyrene, and Saran wrap.

Another type of polymer is a condensation polymer. This is one that forms with the loss of a small molecule, usually water. One example of a general class of condensation polymerization reactions is shown in Figure 34.5. In this reaction, a di-carboxylic acid reacts with a di-amine to produce the polymer and water. The R and R' can be a wide range of chemical species consisting of carbon and hydrogen. If R is the alkane C₄H₈ and R' is the alkane C₆H₁₂, the polymer is called nylon 6,6. If both R and R' are benzene rings, the polymer is Kevlar. Other examples of condensation polymers include all proteins, which are condensation polymers made from amino acid monomers.

**Figure 34.5**

The formation of a condensation polymer is illustrated by the reaction of a di-carboxylic acid monomer with a di-amine monomer. Note that water is also formed in the reaction. The R and R' can be a wide range of species with carbon and hydrogen.

The properties of polymers can vary widely as the length of the polymer chain is varied. For instance, Teflon is waxy and brittle when the chain length is short, but as the chain length increases it becomes more mechanically hard and viscous. Teflon with a chain length of 10^4 to 10^5 monomers is so viscous that it does not flow when melted.

The properties of polymers can also be altered by interactions between different polymer chains. In some cases, bonds can be formed between different polymer chains. This is known as cross-linking. One of the more famous

examples of cross-linking is the vulcanization of rubber. Natural rubber (a polymer) is sticky, deforms easily when warm, and is brittle when cold. It does not have a high degree of elasticity. If natural rubber is heated in the presence of sulfur, the sulfur will form bonds to two different polymer chains, forming a link between them. This process is called vulcanization. This changes the physical properties of the rubber so that it is more elastic. If too many cross-links are formed, the rubber becomes too hard to be useful.

In this laboratory project you will synthesize a silicone polymer and then cross-link the polymer chains to obtain a material that bounces much like the product sold under the trademarked name Silly Putty. Molecules called silicones are polymers that consist of alternating silicon-oxygen bonds with two organic alkyl groups, such as CH_3 , bonded to each silicon atom. The polymer you will synthesize is called polydimethylsiloxane and is shown in Figure 34.6.

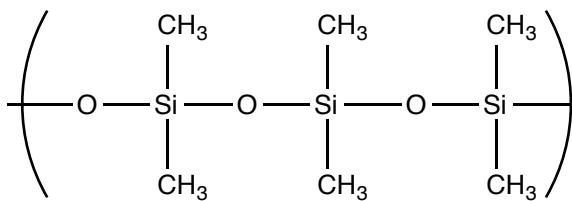
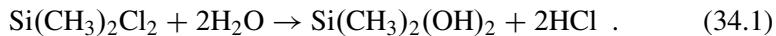


Figure 34.6

Polydimethylsiloxane is the silicone polymer you will synthesize in this project. The parentheses indicate that this is just a portion of the polymer chain. No cross-linking is shown.

To synthesize polydimethylsiloxane, we will start with dichlorodimethylsilane, which has the formula $\text{Si}(\text{CH}_3)_2\text{Cl}_2$. The silicon-chlorine bond can be broken easily by water to produce silanol in the reaction



Silanol molecules then react in a condensation reaction to form the polymer and water. Since silanol has two OH groups, every condensation reaction that adds another monomer to the chain will leave the ends of the chain with an OH group.

Boric acid, H_3BO_3 , can be used to cross link the chains. It is thought that boric acid undergoes a condensation reaction with the ends of the polydimethylsiloxane chains (which have an OH group attached) to cross-link the chains and to release water. This will make the silicone polymer more viscous and elastic.

34.2 Safety Considerations

Chemical Hazards

1. **diethyl ether:** Diethyl ether is extremely flammable. Its vapors can be explosive. You should do all work involving diethyl ether under the hood, and you should be sure to keep it away from open flames.

Equipment Hazards

You will use a separatory funnel in this project. A separatory funnel has a stopcock at one end and a stopper at the other. If you are not attentive, it is easy

► The discovery of vulcanization is attributed to Charles Goodyear in 1839. The production of vulcanized rubber revolutionized industry because it provided a sealing material much better than the oil-soaked leather that had been used previously.

► Diethyl ether has a boiling point below human body temperature. It develops a significant vapor pressure in a closed container just by touching the container.

to close both ends, creating a sealed container. This presents a hazard, especially when the funnel contains a liquid with a low boiling point (like diethyl ether) or when a reaction evolving a gas takes place in the funnel. Only a slight increase in pressure over atmospheric will be sufficient to force open the stopper, allowing the contents of the funnel to be blown all over you, your work area, and your neighbors. Pay attention to your instructor when she describes how to use the separatory funnel.

Goggles

You are expected to wear your goggles at all times while in the lab. Failure to do so may result in expulsion from the lab.

Waste Disposal

You will generate waste in this lab that cannot be thrown down the drains or into the trash can. Please adhere to all disposal policies. When in doubt, ask your lab instructor. All aqueous waste can be poured down the drain with lots of water.

Broken Glass

Do not work with any broken glassware. Dispose of broken glassware in the bins labeled “broken glass” as shown in Figure 34.7. Do not use the normal waste baskets for broken glass.

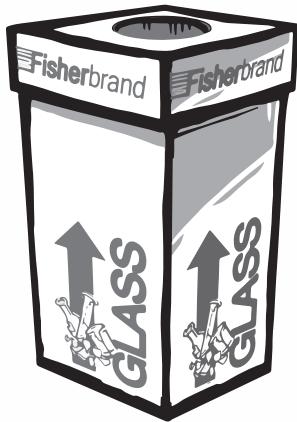


Figure 34.7
Broken glass container.

34.3 Experimental Procedure

Prepare Silicone Oil

1. **Prepare Clean and Dry 250 mL Erlenmeyer Flask:** Obtain a 250 mL Erlenmeyer flask from your drawer and carefully clean it. Dry it completely with paper towels.
2. **Obtain Stopper for Flask:** Obtain a cork stopper for the Erlenmeyer flask.
3. **Obtain Dimethyldichlorosilane:** With the assistance of your laboratory instructor or teaching assistant, place 15 mL of dimethyldichlorosilane in the Erlenmeyer flask and quickly put the stopper back on.
4. **Add Diethyl Ether:** Add 30 mL of diethyl ether to the flask. Swirl the solution in the flask to mix the contents.
5. **Add DI Water:** Obtain 30 mL DI water and add it dropwise to the solution in the flask. Swirl the solution in the flask to mix well after adding every three drops of water.
6. **Swirl Until Reaction Ceases:** There should be some evidence that a reaction is taking place. Gently swirl the contents of the flask until all evidence of reaction has ceased.

► The diethyl ether acts as a solvent for the dimethyldichlorosilane.

7. **Transfer Flask Contents to Separatory Funnel:** Close the stopcock on the separatory funnel and then pour the contents of the flask into the separatory funnel.
 - Make sure the stopcock works before using the separatory funnel. If it is too loose or tight, ask your instructor for help.
8. **Separate Layers:** Separate the two layers, saving the diethyl ether layer and discarding the aqueous layer.
9. **Wash Ether Layer with Sodium Bicarbonate Solution:** Wash the diethyl ether layer twice with 20 mL portions of an aqueous solution that is 10% sodium bicarbonate.
 - This will involve inverting the funnel and swirling the contents while venting through the stopcock. Your instructor will provide guidance on how to do this.
10. **Wash Ether Layer Until Aqueous Layer is Basic:** Continue washing the ether layer with sodium bicarbonate solution until the discarded aqueous layer is no longer acidic. You can test the discarded aqueous layer with long range pH paper.
 - All aqueous washes can be discarded down the drain with plenty of water.
11. **Wash Ether Layer with DI Water:** Wash the ether layer with two 20 mL portions of DI water.
12. **Dry Ether Solution:** Transfer the ether solution to a clean and dry Erlenmeyer flask. Add 2 g of anhydrous magnesium sulfate. Allow this solution to sit for 30 minutes with occasional swirling.
 - Magnesium sulfate is a drying agent that will help remove remaining traces of water.
13. **Weigh Beaker:** Clean and dry a 150 mL beaker and then weigh it.
14. **Filter Ether Solution:** Gravity filter the ether solution using a conical funnel and filter paper. Collect the solution in the clean and dry 150 mL beaker.
 - This removes the magnesium sulfate drying agent.
15. **Evaporate Remaining Ether:** Fill a 400 mL beaker half full with hot water (60°C to 70°C) from the tap. Place the 150 mL beaker with the ether solution into the hot water. Periodically smell the contents of the 150 mL beaker using a wafting motion to test whether any ether remains. When no ether remains, remove the beaker from the hot water.
 - The taps may run out of hot water. If so, you will have to heat water on a hot plate.
 - Silicone oil will have a bitter and biting odor.
16. **Weigh Beaker with Silicone Oil:** Dry the outside of the 150 mL beaker and then weigh it to determine the mass of the silicone oil you have synthesized.
17. **Transfer Silicone Oil to Test Tube:** Transfer the silicone oil to an 8-inch Pyrex test tube. Note that an 8-inch test tube is larger than any test tube you have in your drawer.

Store Silicone Oil or Proceed

Sometimes it is necessary to complete this project over two weeks. In that case, this is a convenient stopping point. To continue this project at a later time, store the silicone oil in the 8-inch test tube by tightly corking the tube and placing it in your drawer without the oil contacting the cork. If you are going to complete this project in one laboratory period, just continue with the next set of instructions.

Cross-Link Silicone Polymer

1. **Obtain Boric Acid:** Mass out a quantity of boric acid with a mass equal to about 5% of the mass of the synthesized silicone oil.
2. **Add Boric Acid to Silicone Oil:** Add the boric acid to the silicone oil in the 8-inch test tube and stir for several minutes.
3. **Heat Test Tube in Oil Bath:** Suspend the 8-inch test tube in an oil bath that is at a temperature between 130°C and 160°C. Be sure the test tube does not touch the bottom of the beaker. Leave the test tube in the oil bath for 15 to 20 minutes or until the mixture becomes gooey.
4. **Remove Test Tube from Oil Bath:** When the silicone oil has reached the desired consistency, remove the test tube from the oil bath and allow it to cool. If the contents of the test tube remain too gooey, put the test tube back in the oil bath.
5. **Remove Polymer from Test Tube:** Remove the cross-linked polymer from the test tube using a spatula. You can add talc to make the polymer less sticky.
6. **Store Polymer in Plastic Egg:** Obtain a polymer egg in which to store your synthesized polymer.

34.4 Before Exiting Lab

- Clean all glassware that came into contact with silicone oil by scrubbing it vigorously with a brush using an abrasive cleaner and warm water.
- Clean your work area with abrasive cleaner and warm water. There should be no trace of silicone oil on your bench.
- Check your lab notebook for page numbers on all pages.
- Update the table of contents in your notebook.
- Draw a line in your notebook where your experimental work ends. Sign on this line.
- Have your instructor sign your notebook on the line at the end of your experimental section.

34.5 Post-Lab Assignments

There are no post-lab assignments for this project.

Periodic Table

1A (1)												8A (18)					
1 H 1.008	2A (2)											2 He 4.003					
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01				
11 Na 22.99	12 Mg 24.31	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8)	8B (9)	8B (10)	1B (11)	2B (12)	13 Al 26.98	14 Si 28.09	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 209	85 At 210	86 Rn 222
87 Fr 223	88 Ra 226	89 Ac 227	104 Rf 261	105 Db 262	106 Sg 266	107 Bh 264	108 Hs 269	109 Mt 268	110 Ds 271	111 Uuu 272	112 Uub 285	114 Uuq 289	116 Uuh 292	116 Uuh 292			
			58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 145	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0	
			90 Th 232.0	91 Pa 231	92 U 238.0	93 Np 237	94 Pu 242	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 260	

Amusement



Elements by xkcd (<http://xkcd.com/965/>)

Colophon

This document was typeset using the L^AT_EX typesetting system created by Leslie Lamport and the memoir class written by Peter Wilson. The text was prepared in Sublime Text 2 running on Apple computer hardware (iMac, Macbook Air, and Macbook Pro). Photographs were taken with a Canon 20D digital SLR and then prepared for inclusion using Adobe Photoshop. Illustrations were prepared using Adobe Illustrator. Illustrations that actually look good were prepared by Kate Ball. All files were version controlled with Git.

1A (1)

8A
(18)



1	H	2A (2)
1	1.008	
2	Li	4 Be 9.012
3	Mg	12 6.941
4	Ca	24.31 22.99
5	Sr	20 39.10
6	Rb	40.08 39.10
7	Fr	38 85.47
8	Cs	87 132.9
9	Ba	137.3 137.3
10	Ra	226 223

Chemical Periodic Table

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	175.0
140.1	144.2	145	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0		
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Esf	Fm	Md	No	Lr
232.0	231	238.0	237	242	243	247	247	251	252	257	258	259	260

1A (1)

8A
(18)



1	H	2A (2)
1	1.008	
2	Li	4 Be 9.012
3	Mg	12 6.941
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Chemical Periodic Table

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	175.0
140.1	144.2	145	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0		
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Esf	Fm	Md	No	Lr
232.0	231	238.0	237	242	243	247	247	251	252	257	258	259	260