The intent of this manual is to inform you, the chemist, of the potential hazards that exist in the laboratory. This is by no means a manual to memorize or a manual of instruction. These procedures are not intended to be exhaustive or to serve as a single method of training. The procedures outlined here are meant as a refresher for those who have already received training by senior lab members. If in doubt of any procedure, please ask someone before carrying out said procedure. Asking for help when in doubt is the responsibility of every lab member. The first time you use all equipment and perform new experimental procedures, you should have someone work with you to teach you and to inform you of potential hazards, and to help prevent accidents. The purpose of this manual is to supplement personal one-on-one training with safety information that will protect you personally, as well as other lab members. It is important to make sure that you minimize your exposure to chemicals and decrease the chances of any accidents. By reviewing (and later referring to) this manual, you can be aware of the potential hazards in the lab and learn careful techniques. It is your responsibility to learn about safety and proper handling of chemicals from the resources available, including your laboratory members, other persons in the department, and the Chemical Hygiene Plan, which can be accessed via the web, from the Safety link on the Chemistry Webpage www.chem.umn.edu, or http://www.chem.umn.edu/services/safety/. This manual contains helpful links to safety procedures, Material Safety Data Sheets (MSDS), waste disposal, and much more.

The general rule in our lab is that most glassware is shared, so please clean up after yourself. Make sure all glassware is clean using the appropriate solvents and procedures to clean it. Also, syringes should be washed after use, using a 5 solvent wash (usually tetrahydrofuran (THF), methanol, acid water, distilled water, and finally acetone). We generally store the syringes in the oven. Sign up for equipment (using the shared group Google Calendar)
# TABLE OF CONTENTS

I. Guidelines for Good Lab Citizenship in the Tolman Lab ................................................. 3  
   a. Office Etiquette .......................................................... 3  
   b. Replace what you use .................................................. 3  
   c. Glass and Equipment Repair ....................................... 4  
   d. Balance Etiquette ....................................................... 4  
   e. Cleaning Procedures: Base/Acid Baths .......................... 4  
   f. Glassware Drawers ..................................................... 5  
   g. Fume Hoods ............................................................. 5  
   h. Oil Baths .................................................................. 5  
   i. Notebook Page Format .............................................. 5  
   j. Exit Checklist ................................................................ 7  

II. Tolman Group Responsibilities/Group Member Contact Information ......................... 8  

III. Standard Operating Procedures (SOPs) for the Tolman Lab ..................................... 8  

IV. Chemical Storage, Use, and Disposal .................................................................... 8  
   a. Using the Chemical Inventory ........................................ 8  
   b. Storing and Labeling Chemicals .................................... 9  
   c. Purchasing Chemicals .................................................. 9  
   d. Standard Operating Cards (SOCs) ................................. 10  
   e. Diamines .................................................................. 11  
   f. Chemical hazards: Toxicity and peroxide forming chemicals ........... 12  
   g. Techniques for handling pyrophoric liquids ................. 13  
   h. Techniques for handling fuming/concentrated acids ........ 16  
   i. Techniques for handling elemental halides .................... 17  
   j. Solvent health hazards ............................................... 22  
   i. Choosing gloves ....................................................... 23  
   k. Scaling-up Reactions .................................................. 24  
   l. Manifesting Chemical Waste ...................................... 30  
   m. Materials Safety Data Sheets (MSDS) ........................... 32  

V. General Procedures .................................................................................. 32  
   a. Syringes and needles .................................................. 32  
   b. Safety and sharps ....................................................... 32  
   c. Proper use of chemical fume hoods ......................... 33  
   d. Gas tanks ................................................................ 33  
   e. Dispensing liquid N₂ tank ......................................... 34  
   f. Elemental Analysis .................................................... 34  

VI. Airfree Procedures .................................................................................. 34  
   a. Oil Baths ................................................................. 34  
   b. Safety and high pressure reaction flasks .................... 35  
   c. Vacuum Oven and Vacuum line procedures .......... 35  
   d. Vacuum Pump Maintenance ..................................... 37  
   e. General Schlenk line manipulation review .............. 38  
   f. Vacuum transfer of solvents using Schlenk line ......... 40  
   g. Solvent purification system (SPS) .............................. 41  

VII. Equipment ......................................................................................... 41  
   a. Comments that apply to all equipment .................... 41  

I. Guidelines for Good Lab Citizenship in the Tolman Lab

a. Office Etiquette

First and foremost, under no circumstances should laboratory samples be brought into the office. Use of the group office is a privilege that all group members are entitled to during their stay in the Tolman lab. Each member is responsible for his/her personal and work-related items stored in the office. Personal items should be stored within the space of the member’s individual desk/shelf space whenever possible. The group office is a shared space, and all members are responsible for general cleanliness and maintenance of the office space (don’t make a mess, and if you do clean it up as soon as possible).

The refrigerator, microwave, toaster oven, and coffee maker are all shared items of the group. Courteous use and up-keep is expected of all group members. All appliances should be restored to a clean, working order after your personal use. Space in the refrigerator is limited, therefore group members must be sure to not monopolize space by “forgetting” to remove items. In the case of spoiled, moldy, smelly random items being found in the group fridge the item in question will be disposed of without question.

b. Replace what you use

If you use the last of something, properly dispose of the empty container and buy a new one. Some common examples are emptying reagent chemicals, bottles of solvent, vials, syringes, pipettes, printer paper, or toner. Laboratory chemicals and supplies should be replaced for the side of the lab that the bottle originated from. Taking supplies from the other side of the lab is an acceptable temporary solution for running out of something, however the item should be replaced from the stockroom, or ordered for your side of the lab as soon as possible. In the case of office supplies, be sure to use the Office Supply purchasing card in the stockroom (the
stockroom employees and our purchasing representative can advise you on what items should be purchased with the Office Supply purchasing card).

c. Glass and Equipment Repair

If you break something, make arrangements to fix or replace it in a timely manner. If a particular piece of equipment or an instrument is not working properly, promptly notify the person in charge (group job list is posted on the group website). If a piece of customized glassware, such as a UV-vis cuvette is broken or damaged accidentally the pieces should be saved and taken to the glass-repair shop for repair by the group member responsible.

d. Balance Etiquette

Any materials spilled on the balance must be thoroughly cleaned/removed. While most chemicals can be removed by simply sweeping off the balance with the provided brushes, sticky polymers, liquids, or corrosive materials pose a far greater hazard to the balance housing, weighing mechanism, and group members. Corrosive or liquid chemicals may require solvent to clean. Try water first, followed by a mild organic solvent such as acetone. Only try stronger solvents such as THF, or dichloromethane as a last resort. *Never* use corrosives such as acids or bases to clean off the balances. In the case of excessive or uncommon reagents being spilled on a common balance, the group member in charge of the balances should be consulted.

e. Cleaning Procedures: Base/Acid Baths

Anytime you use common glassware/syringes, they must be thoroughly cleaned and put away after use. Clean appropriate glassware (see below for exceptions) by dissolving excess material in an appropriate solvent, and discarding it in a waste container; followed by soaking in a Base bath, and subsequently soaking in an Acid bath for an appropriate amount of time. Several important guidelines for the use and preparation of Base and Acid baths are listed below. Base and Acid baths should always be stored in secondary containers; over time Base and Acid baths have been known to dissolve the buckets used (see below). This can be prevented from getting a new bucket after changing your Base or Acid bath a few times.

It is important that the gas-tight syringes and reusable metal needles are cleaned promptly after use to prevent corrosion and (in the case of water and air-sensitive initiators) the formation of difficult-to-remove salts. This is generally done by using a five solvent wash (often THF, methanol, acid water, DI water, and acetone, however other solvents like methylene chloride may be substituted when appropriate).

**Base Bath**

Do not use anyone else’s base bath without their explicit consent. They may have placed chemicals in the base bath that could be detrimental to your reactions or glassware. Likewise, your glassware may contain contaminants that will compromise others’ reactions. The most reasonable approach is to prepare your own base bath. This is most conveniently done in a 5 Gallon white bucket, which can be purchased from the stockroom. Base baths are most commonly prepared by dissolving 300 grams of KOH in approximately 8 L of Isopropyl Alcohol. When preparing a new base bath, stirring overnight is required to thoroughly dissolve the KOH. Alternative recipes for Base baths can be found online or from an experienced lab
mate. There are several items that should NEVER be placed in a base bath. The base etches the glass, leaving a clean glass surface for the next reaction. Therefore, glass frits, volumetric glassware, and syringes should never be placed in Base Baths.

**Acid Bath**

As with Base baths, do not use anyone’s Acid bath without explicit permission. Acid baths are commonly prepared in the same type of buckets with no more than 200 mL conc. HCl/8 L Isopropyl Alcohol. Alternative recipes can be used when appropriate.

*f. Glassware Drawers*

Laboratory drawers should be clearly labeled indicating the glassware or other lab materials that they contain, either with permanent marker or magnetic signs. Upon reorganization the drawer should be immediately re-labeled to reflect the changes by the person responsible. Only properly cleaned glassware that is fit for safe use should ever be stored in drawers (free from vacuum grease, chemical residue and permanent marker labeling). Glassware should never be hoarded on drying racks or ovens, unless it is intended for specific use.

*g. Fume Hoods*

Fume hoods must be kept in a safe and orderly state in accordance with the chemical hygiene plan. Regular inspections will be conducted by the Group’s safety officers and violations must be addressed immediately. Keep the sash fully closed as much as possible, and at all times when the hood is unattended.

*h. Oil Baths*

Unless otherwise labeled all of the oil baths in the lab contain either mineral or silicone oil and are appropriate for heating reactions under 200 °C. A different type of oil, that won’t catch on fire is required for higher temperature reactions; high temperature oil baths should be prepared and used only as needed by the specific group member when needed to avoid confusion.

*i. Notebook Page Format*

Checklist for keeping a proper lab notebook

1. Full chemical equation(s)
2. All calculations, amounts (g, mL, etc.)
3. Sources of chemicals, purity, methods of purification (e.g. distillation, recrystallizations, etc.)
4. Literature references
5. Detailed, reproducible procedure
6. References to spectra, other data (where is it?)
7. Signed and dated at the bottom of every lab notebook page, IN PEN
8. Be sure to write down your own hypotheses and/or thoughts with appropriate reactions
9. Take photos of apparatus when possible
10. Be sure that all entries are written in legible English
11. Lab notebook and page number should be indicated on group meeting slides when displaying specific syntheses and/or techniques (e.g. slide with $^1$H NMR should have label, WT123-01H, to relate it to notebook and page number); see Exit Checklist section for appropriate labeling procedure.

**PRIOR TO PERFORMING A NEW EXPERIMENT AND/OR REACTION YOU MUST DETERMINE ALL POSSIBLE HAZARDS...** check the MSDS of all chemicals and communicate with senior members who may have done similar experiments and/or reactions to ensure you do not endanger your own safety.**

**SAMPLE LAB NOTEBOOK PAGE:**

![Sample Lab Notebook Page](image-url)
j. Exit Checklist

All students and post-doctoral associates must complete the exit checklist form prior to leaving their respective positions. The exit checklist, seen below, must be signed and reviewed by both the group member and/or post-doc and Bill. Only when both parties agree that all parts of the checklist have been accounted for may the student and/or post-doc leave the group. The exit checklist may be found online in the “Tolman Lab Documents” Google Drive folder.

EXIT CHECKLIST
Tolman Group Laboratory

Member Name:_________________________________________________________

Please ensure that you have completed all of the following prior to officially checking out of the laboratory. You must return this form once complete to your PI to finalize the lab check out process.

☐ Chemicals no longer useful for current research aims have been properly disposed of

☐ After narrowing down which chemicals to keep, all corresponding data/spectra have been named properly:

\( (\text{your initials})(\text{lab notebook number})(\text{page number})(\text{file number/descriptor}) \)

\[ \text{[e.g. WBT1234-01H]} \]

and saved in a file (titled "LAST NAME, FI.") to the terabyte drive

☐ All data files have been cross-referenced in appropriate notebook pages

☐ All waste has been properly manifested

☐ All acid and base bath glassware has been removed, rinsed and put away

☐ Glassware in hood and/or on benchtop has been fully cleaned and stored in appropriate location

☐ Synthesized chemicals have been properly labeled and stored in no more than one secondary container (titled "LAST NAME, FI.") in the appropriate place

• Freezer? ☐
• Glove box? ☐
• Benchtop/shelves? ☐

☐ Pump oil has been changed within personal vacuum line

☐ All materials and/or chemicals have been removed from hood and the hood wiped clean (with the exception of stir plates, hot plates, clamps, cork rings, or appropriate Schlenk line materials)

☐ Laboratory notebooks are fully indexed and finalized

Member Signature:_________________________________________________________________

Date: ____________________________________________________________________________

PI Signature:_______________________________________________________________________

Date: ____________________________________________________________________________
II. **Tolman Group Responsibilities/Group Member Contact Information**

For up-to-date Tolman Group responsibilities refer to the group website (see link below) or posted list in the group office. Group member contact information can also be found on the list posted in the office or on the individual’s fume hood. An up-to-date emergency phone tree/calling plan is always posted inside the group office as well. Bill’s phone number and an emergency contact group member’s information is also posted for each of the laboratories outside the main doors.

http://www.chem.umn.edu/groups/tolman/Group%20Responsibilities.html

III. **Standard Operating Procedures (SOPs) for the Tolman Lab**

**See SOP resources page for more information at http://www.jst.umn.edu/**

General SOPs for techniques/equipment used regularly in the Tolman lab will be discussed in the specific sections of this document. More specific SOPs can also be obtained from the group member with the group job pertaining to the SOP desired. *A JST “template for writing SOP’s” can be found in the “Tolman Lab Documents” folder on Google Drive.*

IV. **Chemical Storage, Use, and Disposal**

*a. Using the Chemical Inventory*

The chemical inventory is online at [www.quartzy.com](http://www.quartzy.com). New group members need to create an account and then search for “Tolman Lab” under the University of Minnesota and request to be added to the group. Once added to the group, members can view the inventory and add/remove chemicals along with place orders (see Purchasing Chemicals) and view the Tolman Lab calendar for important dates. Documents can also be uploaded to the group in order to more efficiently share procedures and/or important articles (See General Quartzy information).

The inventory should always be checked before purchasing a new chemical. All cabinets, shelves and refrigerators along with the specialty solvents, acids and bases are in the inventory and should be kept up to date. Chemicals can be searched for using names, CAS number or product number. CAS number and product number are probably the easiest way since many chemicals have more than one name. Solvents are not in the inventory (unless in the specialty solvent cabinet) but are easily found by the labels under the hoods.

After placing an order through Quartzy, there will be an option to directly add it to the inventory after it has been received. It is the responsibility of the person requesting the chemical to add it to the inventory after it has been received. If placing an order through Sigma, most of the information will be directly imported. For Sigma, the only information needing to be added is the CAS number, the DDC code and the location. Other vendors need more chemical information added when adding to the inventory. **ALL CHEMICALS MUST BE ADDED TO THE INVENTORY REGARDLESS OF LOCATION (including personal shelves)!** When a chemical is completely used, the chemical needs to be removed from the inventory immediately.
This can be done by finding the chemical in the inventory, selecting it and pressing delete under the “more” tab.

b. Storing and Labeling Chemicals

After a chemical has been received, it must be added to the inventory and correctly stored according to hazard class. To add a chemical to the inventory, find the order under the Order Requests tab on Quartzy and click “mark as received”. There will be a box that pops up and “add to inventory” should be selected. Double check the name, quantity, vendor, etc is correct and then select a location and sublocation (if necessary).

To determine the proper location, the DDC code needs to be known by looking it up by going to [www.dehs.umn.edu/hazwaste_chemwastereg.htm](http://www.dehs.umn.edu/hazwaste_chemwastereg.htm) and searching for the CAS number. The number correlates to the proper bin within the cabinets. Example, if the DDC code is 08SW, the chemical should be placed in a 08 bin. There are many bins associated with each number and the letters on the bins are only to distinguish between bins so a 08 chemical can be placed in any 08 bin. If the chemical does not have a DDC code, the hazards of the chemical need to be determined and a DDC code needs to be assigned to the chemical based on hazards. The safety officer can be consulted to confirm the correct assignment. Salts, filter/drying agents, and commonly used chemicals that have very low hazard and that are solid can be placed on the shelves in the labs. The chemical still needs to be inventoried, however, and a location should be assigned to it. Specialty solvents, acids and bases are kept in the cabinets under hoods in each lab. As always, check the chemical for special storage designations (heat sensitive, light sensitive, moisture sensitive, acid, base, etc) and store appropriately. If you still aren’t sure where to store a chemical, consult the safety officer. It is very important chemicals are stored properly to avoid incompatible chemicals stored together and potential hazardous situations.

When a chemical is finished, the inventory must be updated and the bottle must be properly cleaned for disposal. To remove from the inventory, find the chemical, select it and click delete under the “more” tab. Make sure you are deleting the correct entry as some chemicals have duplicates. The empty bottle should be rinsed out with an appropriate solvent and then disposed of in the glass waste or trash.

c. Purchasing Chemicals

The purchasing of chemicals is done on Quartzy by placing an order request. **It is up to the chemical requestor to find the lowest price, not the person doing the purchasing.** When ordering chemicals, the inventory should be checked before placing a new order. The chemical requester should check UMarket for the chemical by going to umarket.umn.edu. We get a special discount through Sigma so if the Sigma price is close to other vendors, we probably get it cheaper. If you aren’t sure, you can have the purchaser check the Sigma website (in general, most chemicals are cheaper through Sigma than with other vendors). For some chemicals, they must be ordered through UMarket no matter what the price (due to shipping restrictions). This list of chemicals should be consulted and can be found at [www.dehs.umn.edu/PDFs/chemical_poster.pdf](http://www.dehs.umn.edu/PDFs/chemical_poster.pdf).

After consulting the inventory and UMarket list, the order request can be placed on Quartzy. Click on the order request tab and then search for the chemical based on product
number, CAS number or name. If ordering through Sigma or TCI, the information will be automatically populated. Other vendors need to have the information added. Make sure the name, amount, product number and vendor are noted. Also, please include the account number to charge it to. Once the chemical is ordered, you will receive an email from Quartzy. After the order is received, it is up to the order requester to put the chemical in the inventory on Quartzy by marking the chemical as received under the order request tab.

\textit{d. Standard Operating Cards (SOCs)}

When doing potentially hazardous reactions, SOC’s must be filled out to inform other coworkers. Reactions that require an SOC include:

- Extreme temperature/pressure (low and/or high)
- Pyrophorics (see Section IV: Chemical storage, use and disposal, part f for more info on pyrophorics)
  - E.g. organolithium, Grignard, alkylaluminum, alkylzinc, and borane reagents
- Mixing strong oxidants with organics
  - E.g. nitric acid, sulfuric acid, or aqua regia [H$_2$SO$_4$/$\text{HCl}$] with any small amount of organic material like acetone
- Featuring liquid nitrogen (for the risk of condensing liquid oxygen)
- Potential explosives
  - E.g. perchlorate salts, azides, diazoalkanes, hydrazines
- Extremely toxic compounds
  - E.g. alkyl mercury salts, alkyl tin compounds, cyanide salts, hydrazines

\textbf{Sample SOC to be kept on outside of fume hood:}
e. Diamines

Many of the diamines used in our lab for ligand synthesis are extremely corrosive (especially to skin). Before using diamines, and any other chemical, the MSDS should be consulted and proper PPE should be worn. Lab coat, high collared shirt, goggles (not glasses) and gloves should be worn especially when working with liquid diamines. When removing excess diamine from a reaction, a secondary trap should be used to avoid diamine from condensing in the schlenk line tube and creating a possible hazard (see incident report below). Concentrated diamine should be disposed of properly after removing with a trap to ensure no contact is made with skin or other tissue.

Tolman Lab incident: In 2014, a graduate student in the Tolman lab was working with 2,2’-dimethyl-1,3-propanediamine. An excess was required for the reaction and the excess was removed with a schlenk line after completion. A secondary trap was not used (only the two traps on the line) and some diamine condensed in the tubing. After the line had been vented and the graduate student was cleaning up, the glass above the tubing (but below the stopcock) broke causing the tubing to fall and bounce in the hood. The hood sashes were open and some of the diamine splashed on the student’s face and chest. The student was wearing a lab coat and safety glasses but with a v-neck sweater causing some of the chest to be exposed. The student suffered minor burns and immediately went to the urgent care. The burns were cleaned but no medical procedures were needed. It was concluded that the line likely broke from a previous crack but
since a secondary trap was not used, the glass breakage turned into a more serious incident. Researchers must always be prepared for freak accidents!

**f. Chemical hazards: Toxicity and peroxide forming chemicals**

**Organic Peroxides and Peroxide-Forming Chemicals**

(Information from the UMN Hazardous Waste Disposal Guidebook available online) [http://www.dehs.umn.edu/hazwaste_chemwaste_umn_cwmgbk_sec2.htm](http://www.dehs.umn.edu/hazwaste_chemwaste_umn_cwmgbk_sec2.htm).

Organic peroxides are hazardous chemicals to handle due to their low stability. If you need to work with this class of materials (identified by the digits “12” as the first two numbers in the DDC code), you should consult available resources to learn how to handle these chemicals safely. Far more common in our laboratory are peroxide-forming chemicals—those which can form peroxides upon exposure to air. As a result, these chemicals must be tested with some regularity to assure that peroxide concentrations remains at safe levels. Take special note of the monomers and solvents commonly used in our laboratory in the categories below:

**Table 1. Common Peroxide-Forming Chemicals**

<table>
<thead>
<tr>
<th>Peroxide Hazard with Storage after Air Exposure</th>
<th>Peroxide Hazard with Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Discard within 3 months</strong></td>
<td><strong>Test for peroxides prior to distillation or evaporation, otherwise after 6 months of storage</strong></td>
</tr>
<tr>
<td>Disopropyl ether (isopropyl ether)</td>
<td>Acetaldehyde diethyl acetal (acetal)</td>
</tr>
<tr>
<td>Divinylacetylene (DVA)</td>
<td>Ethylene glycol dimethyl ether (glyme)</td>
</tr>
<tr>
<td>Potassium amide</td>
<td>Cumene (isopropylbenzene)</td>
</tr>
<tr>
<td></td>
<td>Cyclohexene</td>
</tr>
<tr>
<td></td>
<td>Cyclopentene</td>
</tr>
<tr>
<td></td>
<td>Decalin (decaldehydephthalene)</td>
</tr>
<tr>
<td></td>
<td>Diacetyl (butadiene)</td>
</tr>
<tr>
<td></td>
<td>Dicyclopentadiene</td>
</tr>
<tr>
<td></td>
<td>Diethyl ether (ether)</td>
</tr>
<tr>
<td></td>
<td>Diethylene glycol dimethyl ether (diglyme)</td>
</tr>
<tr>
<td></td>
<td>Dioxane</td>
</tr>
<tr>
<td></td>
<td>Rapid Polymerization Hazard by Internal Peroxide Formation</td>
</tr>
<tr>
<td></td>
<td><strong>Discard or test for peroxides after 6 months</strong></td>
</tr>
<tr>
<td></td>
<td>Chloroprene (2-chloro-1,3-butadiene)</td>
</tr>
<tr>
<td></td>
<td>Styrene</td>
</tr>
<tr>
<td></td>
<td>Butadiene</td>
</tr>
<tr>
<td></td>
<td>Tetrafluoroethylene</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Discard after 12 months</strong></td>
</tr>
<tr>
<td></td>
<td>Vinyl acetate</td>
</tr>
<tr>
<td></td>
<td>Vinylpyridine</td>
</tr>
<tr>
<td></td>
<td>Vinylacteylene (MVA)</td>
</tr>
<tr>
<td></td>
<td>Vinyl chloride</td>
</tr>
</tbody>
</table>

**Labeling and Storing Peroxide-Forming Chemicals:**

All potential peroxide hazards must be labeled with the following information:

**Date received**
Date opened

Time period for testing/disposal (1, 3, or 6 months)

These materials should be stored away from heat and light and protected from ignition and shock sources.

What if I find an old/expired bottle?

If you are holding it, place it gently on a secure surface away from heat or ignition sources. Protect yourself thoroughly and notify others around you. Examine the bottle without moving it. If any of the following conditions exist, call Chemical Waste Program immediately:

- Look for crystals around the cap, on the container, or in solution (these may resemble finely-spun glass-wool).
- The container has a metal screw cap.
- The container has been stored for more than two years.

Testing for Peroxides

Commercial peroxide testing kits are available for purchase from the University stockroom. The kit should be stored in a refrigerator to ensure the quality of the test strips. The test strips do expire, so make sure to check the condition of the strips prior to use. Follow the directions for testing either aqueous or organic solutions, as appropriate. If a chemical contains a peroxide concentration less than 80 ppm it is fine for use. If the chemical exhibits a concentration between 80-400 ppm contact Chemical Waste Program for removal. Peroxide concentrations of over 400 ppm are extremely dangerous; rope off the area, leave, and contact Chemical Waste, who will contact the Bomb Squad.

**g. Techniques for handling pyrophoric liquids**

The handling of pyrophoric liquids is extremely dangerous and requires specific training in order to ensure your personal safety and that of your fellow lab members. For new group members the following guide should be used as a starting point, in addition to hands-on training and supervision from an experienced group member. This written guide and the Pyrophoric Liquid Safety Video produced by UCLA will also serve as a point of reference for all group members.

https://www.youtube.com/watch?v=21iC4YEkOAs

Pyrophoric chemicals are highly reactive with oxygen and moisture, so exposing these chemicals to open air can cause spontaneous and violent exothermic reactions (triggering intense fires). The reactivity of these chemicals with open air is compounded by the fact that most pyrophoric chemicals are stored in flammable organic solvents. Due to the high degree of risk involved in transferring pyrophoric liquids proper technique must be followed at all times when handling these types of chemicals. Common examples of pyrophoric liquids include, but are not limited to, organolithium, Grignard, alkylaluminum, alkylzinc, and borane reagents. It is important to always review the MSDS of the reagent before using any of the above compounds; or if you are
unsure whether the reagent you are about to use is pyrophoric. When handling pyrophoric liquids
the following safety precautions must always be met:

1. Either work in an inert atmosphere glove box, or a clean laboratory fume hood free of
exogenous ignition sources.
2. Proper personal protective equipment must be worn, minimally including a fire resistant lab
coat, gloves, and safety glasses. When working with large quantities of pyrophoric reagents a
chemical apron, face shield, portable shield, and non-combustable gloves (not nitrile gloves,
which are combustable) should be used as protection.
3. Familiarize yourself with the location of the emergency eye wash and shower locations. 
   Optimally these should be located within 10 seconds of travel time from your work station, in 
   case of emergency.
4. A class C dry fire extinguisher must be available within 75 feet of the work station when
pyrophoric reagents are in use. Know where the fire extinguisher is and how to use it.

There are two methods for appropriately transferring pyrophoric reagents, the Syringe method
and the Double-Tipped Needle/Cannula method. Standard operating procedures for both
methods can be found below:

**Syringe Method**

1. Choose an appropriate syringe! When transferring pyrophoric liquids it is unsafe to fill the
syringe more than 60% full with pyrophoric reagent, so make sure your syringe of choice can
hold an appropriate volume. There are also several different types of syringe bodies
available, including plastic syringes and glass syringes with ground glass or teflon plungers.
Syringes with glass bodies and plungers are more prone to malfunctions due to defects in the
glass, plastic disposable syringes have a good seal around the plunger and work well, but
glass syringes with teflon plungers provide the best seal and are recommended. It is also
important that you used a needle that is clean, unclogged, and of appropriate bore and length
for the type of transfer that you are performing.
2. Clamp the reagent bottle and reaction vessel to prevent them from moving during the
transfer.
3. Insert a needle tip from an inert gas source, with a bubbler outlet, into the reagent bottle.
Make sure the needle tip is inserted above the liquid level inside the reagent bottle. The goal
of this technique is to equalize the pressure in the reagent bottle. **DO NOT OVER
PRESSURIZE THE REAGENT BOTTLE TO FORCE PYROPHORIC LIQUID UP
THROUGH A SYRINGE TIP.** Using this potential method of transfer is more difficult to
control and runs a much greater risk of accidentally exposing an uncontrolled amount of
pyrophoric liquid to open air.
4. After placing your inert gas source into the reagent bottle, you should flush your gas-tight
syringe with inert gas. To do so, fully depress the plunger and insert the needle tip into the
headspace of the reagent bottle and draw up inert gas into the body of the syringe (be careful
not to draw up any reagent while doing so). Then remove the needle from the reagent bottle
and expel the inert gas, and quickly re-insert the needle back into the headspace of the
reagent flask.
5. Now you are ready to draw reagent into your syringe. Position the needle tip into the reagent
liquid and slowly pull the plunger to the desired volume. Drawing the plunger back too
quickly can result in air bubbles, effecting your total volume.
6. Once the desired volume is drawn into the body of the syringe, the needle tip should be drawn above the liquid level inside the reagent bottle without removing the needle from the bottle. Then a plug of inert gas should be drawn into the syringe to ensure that there is no excess reagent in the needle volume and to protect the reagent from open air while transferring the needle from the reagent bottle to the reaction flask.

7. Remove the needle tip from the reagent bottle and quickly transfer the tip needle tip to the reaction flask by piercing its rubber septum. After doing so you may begin dispensing your reagent by depressing the syringe plunger.

8. Ensure that all of the pyrophoric reagent has been evacuated from the syringe body and needle volume prior to removing the needle from the reaction flask. Then quench the syringe body and needle with an appropriate solvent to ensure that all trace reactant has been safely transferred.

9. Don’t forget the reagent bottle! Remember to remove the inert gas source from the clamped reagent bottle, replace the lid and return the bottle to its appropriate storage location.

**Double-Tipped Needle/Cannula Method**

1. The Cannula method is recommended when using large volumes of pyrophoric liquids (10 mL or more).

2. Make sure the reagent bottle and reaction flask are securely clamped to ensure that they do not move during the transfer. Also make sure that you are using an appropriately sized additional funnel that is also securely fastened to your reaction flask. Also ensure that the entire set-up is under inert gas.

3. First insert a gas line into the reagent bottle from an inert gas source. Then insert one end of the double tipped needle into the headspace (above the liquid volume) of the reagent bottle. Insert the other end of the double-tipped needle through the rubber septum of the calibrated additional funnel that should be attached to your reaction flask.

4. Submerge the end of the needle in the reagent bottle below the liquid level, allowing liquid to transfer through the needle into the addition funnel.

5. When the desired amount of liquid has been transferred pull the needle tip in the reagent bottle above the liquid level. Allow gas to flush through the needle, and when you are sure there is no more liquid dispensing from the cannula, remove the needle tip from the reaction vessel, and then the reagent bottle.

6. Immediately clean your cannula to ensure that any trace reagent is quenched, and to prevent your needle from clogging.

7. Remember to remove the gas needle from the reagent bottle, replace the cap, and return to its proper storage location.

**Summary of how to transfer pyrophoric liquids**

1. Review MSDS Sheets before using any reagent.

2. Choose a handling procedure that suits the volume of reagent that your are transferring and appropriate glassware for the entire reaction.

3. Work in a clean fume hood or glove box.

4. Wear APPROPRIATE Personal Protective Equipment at all times.

5. Know how to locate and operate the relevant safety equipment.

6. Appropriately clean all needles/syringes used, and store reagent bottles under inert gas in an appropriate location.
h. Techniques for handling fuming/concentrated acids

When diluting acids, always add acid very slowly to cold water—not water to acid! When working with concentrated acids, make sure all incompatible material is removed from the hood and the hood is cleared of objects that may cause a spill. Incompatible materials include, but are not limited to, metals, oxidizing agents, reducing agents, bases, chlorates, nitrates, perchlorates, permanganates, aniline, organic materials, flammable liquids. Do not use metal spatulas around acids. Use only the amount necessary for experiment. Avoid large quantities if possible. After use, wash hood down with copious amounts of water to prevent any side reactions. When transporting from one side of the lab to another, use a secondary container.

- **Concentrated sulfuric and hydrochloric acid**

  When using concentrated acids, make sure to wear proper PPE including nitrile gloves, goggles and a lab coat. The biggest hazard with concentrated acids is skin burns so make sure all skin is covered. If a spill does occur, neutralize with sodium bicarb and rinse with water before cleaning.

- **Concentrated nitric acid-strong oxidizer of organic molecules CAUTION!!!!!!**

  Nitric acid is considerably more dangerous than sulfuric or hydrochloric acid due to its high reactivity with acetone and other organic molecules. When using nitric acid, make sure all glassware is free of acetone before adding nitric acid. Also, when wasting any nitric/aqueous waste put waste in a separate waste container than typical aqueous waste. There could be some acetone in aqueous waste that will slowly react with nitric acid potentially causing an explosion due to over pressurization.

  When using nitric acid, make sure to only use neoprene gloves. Nitric acid can react with nitrile gloves. Also make sure to wear a lab coat, goggles and cover all exposed skin in case of splashes.

- **Fuming sulfuric acid (also called oleum)**

  Fuming acids are especially dangerous due to the extremely corrosive fumes produced. When using fuming sulfuric acid, thick gloves should be worn (or multiple pairs of nitrile gloves) and goggles and a face shield should be worn. Make sure to do everything in the middle to back of a hood to avoid fume inhalation. If spilled, neutralize before cleaning and use large amounts of water to rinse glassware.

- **Fuming nitric acid- strong oxidizer of organic molecules CAUTION!!!!!!**

  When using fuming nitric acid for nitration reactions, many steps need to be taken to avoid safety hazards. Always wear neoprene gloves when using fuming nitric acid and wear goggles and face shield if not using hood sashes in front of body. Remove all chemicals from hood that may react with acid and make sure all glassware is free of acetone. Fumes are highly dangerous so do all reactions in hood with hood sash down to avoid fumes getting into the lab. Incompatible materials include acids, reducing agents, alcohols, acetic anhydride, acrylonitrile, acetonitrile, organic materials, alkali metals.
When doing nitration/oxidation reactions, toxic, brown, NO$_2$ gas is released from the reaction and must be quenched. To do this, attach a reflux condenser to reaction vessel and attach an adapter with a rubber tube to the reflux condenser. Tubing should be connected to filter flask half filled with concentrated NaOH solution. A watch glass should be placed on top of flask to avoid gas from escaping but prevent pressure buildup (see diagram).

- **Aqua Regia Solution for cleaning**

  Aqua regia may be made in small quantities (less than 200 mL) for cleaning of frits or other glassware when no other cleaning method is successful. Aqua regia is a 3:1 volume ratio of concentrated hydrochloric acid (30%) and concentrated nitric acid (70%). Preparation must be done in a hood with full PPE. Neoprene gloves should be worn as the nitric acid can react with nitrile gloves. Solution will decompose over time so solutions should be prepped fresh before use. ALWAYS add nitric acid to hydrochloric acid slowly and use only glass containers. Solution will get hot so take caution to add nitric acid very slowly! NEVER PUT AQUA REGIA IN A CLOSED CONTAINER!!!!! It will oxidize over time and form toxic gases (i.e. nitrosyl chloride, nitrogen dioxide, chlorine). Do not mix or add to container where there could be acetone as nitric acid can react explosively. Before disposing, let cool overnight in open container in hood and then neutralize with sodium bicarbonate before manifesting in nitric acid/aqueous waste. Do not tighten waste bottle do allow for any remaining gasses to escape.

  i. **Techniques for handling elemental halides**

**Bromine**

**Purpose**

Bromine can be a strong oxidizing agent, corrosive, and toxic. It’s used in organic chemistry as a general oxidant and as an electrophilic source of bromine (“Br”). It’s reactive with a wide range of functional groups, especially olefins.

**Physical & Chemical Properties/Definition of Chemical Group**

CAS#: 7726-95-6  
Class: Oxidizing Agent  
Molecular Formula: Br$_2$
Form (physical state): liquid
Color: dark red-brown
Boiling point: 59 ºC
Cal OSHA: 0.1 ppm; 0.7 mg/M³ (Both Ceiling)

**Potential Hazards/Toxicity**

Strong oxidizer. Contact with other material may cause a fire. Corrosive. Toxic. Causes eye and skin burns. May cause severe respiratory tract irritation with possible burns. May cause severe digestive tract irritation with possible burns. Lachrymator (substance which increases the flow of tears). May cause central nervous system effects. May cause cardiac disturbances. May cause liver and kidney damage.

**Engineering Controls**

NOTE: Lab-specific information on engineering controls may be included in the Protocol/Procedure section.

Work with liquid bromine should be conducted in a fume hood unless other controls are designated in the Protocol/Procedure section. Sash height should be kept low to minimize escaping fumes and provide a physical barrier. A face shield should also be worn when handling liquid bromine.

**Personal Protective Equipment (PPE)**

NOTE: Lab-specific information on PPE selection may be included in the Protocol/Procedure

**Respirator Protection**
Respirators should be used only under any of the following circumstances:

- As a last line of defense (i.e., after engineering and administrative controls have been exhausted).
- When Permissible Exposure Limit (PEL) has exceeded or when there is a possibility that PEL will be exceeded.
- Regulations require the use of a respirator.
- An employer requires the use of a respirator.
- There is potential for harmful exposure due to an atmospheric contaminant (in the absence of PEL)
- As PPE in the event of a chemical spill clean-up process

**Hand Protection**
Fluorinated rubber gloves should be worn when handling liquid bromine. When working with aqueous solutions of bromine (bromine water), nitrile and neoprene are the recommended gloves.

Consult with your preferred glove manufacturer to ensure that the gloves you plan on using are compatible with bromine.

**Eye Protection**
Wear chemical splash goggles and a face shield when working with liquid bromine to protect from splash hazards and bromine vapors. This work must take place in a chemical fume hood. The sash should be as low as possible and still allow safe work.

**Skin and Body Protection**
Long pants, closed-toed and closed-heel shoes, cotton-based clothing/attire, and apron/lab coat offering known bromine protection must be worn for protection against bromine hazards.

**Hygiene Measures**
Avoid contact with skin, eyes and clothing. Wash hands before breaks and immediately after handling.
First Aid Procedures

If inhaled
Get medical aid immediately. Remove from exposure to fresh air immediately. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Do NOT use mouth-to-mouth resuscitation. If breathing has ceased apply artificial respiration using oxygen and a suitable mechanical device such as a bag and a mask.

In case of skin contact
Get medical aid immediately. Immediately flush skin with plenty of soap and water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. Destroy contaminated shoes.

In case of eye contact
Get medical aid immediately. Do NOT allow victim to rub or keep eyes closed. Extensive irrigation with water is required using an emergency eyewash station (at least 30 minutes).

If swallowed
Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Get medical aid immediately.

Special Handling and Storage Requirements

Handling: Wash thoroughly after handling. Use only in a well-ventilated area. Do not breathe dust, vapor, mist, or gas. Do not get in eyes, on skin, or on clothing. Keep container tightly closed. Avoid contact with clothing and other combustible materials. Avoid ingestion and inhalation. Discard contaminated shoes.


Protocol/Procedure:

1. When dealing with Br₂, it’s imperative to be working in a hood. If possible, close the sash of the hood partially when the reagent bottle is opened or if you are adding the Br₂ to another piece of glassware (i.e., an addition funnel).
2. It’s imperative to have a Br₂ trap set up so that any gas that may escape is quenched immediately. The best way to do this is to attach tubing which is connected to a funnel immersed in a beaker of sodium bisulfite to the piece of glassware that the Br₂ is in. This is especially important if the system that’s holding the Br₂ is not completely closed.
3. When adding Br₂ to another reagent, add it slowly (dropwise) over a period of at least 15 minutes. Stay close to the hood in which you are working until completion of addition to make sure it goes smoothly.
4. When done using the glassware that held the unreacted Br₂, it’s important to first quench the glassware with sodium bisulfite in the hood before cleaning it as per usual protocol.

Spill and Accident Procedure

Chemical Spill Dial 911 from campus phone / DEHS

Spill – Assess the extent of danger. Help contaminated or injured persons. Evacuate the spill area. Avoid breathing vapors. If possible, confine the spill to a small area using a spill kit or absorbent material. Keep others from entering contaminated area (e.g., use caution tape, barriers, etc.).
Small (<1 L) – If you have training, you may assist in the clean-up effort. Use appropriate personal protective equipment and clean-up material for chemical spilled. Double bag spill waste in clear plastic bags, label and take to the next chemical waste pick-up.

Large (>1 L) – Dial 911 from campus phone / DEHS

Chemical Spill on Body or Clothes – Remove clothing and rinse body thoroughly in emergency shower for at least 15 minutes. Seek medical attention.

Chemical Splash Into Eyes – Immediately rinse eyeball and inner surface of eyelid with water from the emergency eyewash station for 15 minutes by forcibly holding the eye open. Seek medical attention.

Medical Emergency Dial 911 from campus phone / DEHS

Life Threatening Emergency, After Hours, Weekends and Holidays - Dial 911 from campus phone or go to the nearest emergency room.

Needle stick/puncture exposure (as applicable to chemical handling procedure) – Wash the affected area with antiseptic soap and warm water for 15 minutes. For mucous membrane exposure, flush the affected area for 15 minutes using an eyewash station. After hours, go to the nearest emergency room.

Decontamination/Waste Disposal Procedure

Lab-specific information on decontamination/waste disposal may be included in the Protocol/Procedure section.

Wearing proper PPE, please decontaminate equipment and bench tops using soap and water. Quench any remaining Br₂ with sodium bisulfite.

Iodine

Purpose
Iodine and iodides are expensive, therefore many industrial processes that once used iodine have been superseded by other reagents. Sodium and potassium iodides are produced for use in the chemical industry, in the production of silver iodide for photographic film, and potassium iodide as an additive to ‘iodized salt’ which contains 0.023% potassium iodide to prevent iodine deficiency in humans and animals.

Physical & Chemical Properties/Definition of Chemical Group
CAS#: 7553-56-2
Class: Corrosive
Molecular Formula: I₂
Form (physical state): solid
Color: black, violet
Boiling point: 184 ºC

Potential Hazards / Toxicity
Target Organs: Thyroid, Kidney, Endocrine system, Skin, Eyes, Reproductive system, Central nervous system
Inhalation: Toxic if inhaled. Material is extremely destructive to the tissue of the mucous membranes and upper respiratory tract.

Skin: Causes skin burns.

Eyes: Causes eye burns.

Ingestion: May be harmful if swallowed.

**Personal Protective Equipment (PPE)**

**Respiratory Protection**
Where risk assessment shows air-purifying respirators are appropriate use a full-face particle respirator type N100 (US) or type P3 (EN 143) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Respirators should be used only under any of the following circumstances:
As a last line of defense (i.e., after engineering and administrative controls have been exhausted).
When Permissible Exposure Limit (PEL) has exceeded or when there is a possibility that PEL will be exceeded.
Regulations require the use of a respirator.
An employer requires the use of a respirator.
There is potential for harmful exposure due to an atmospheric contaminant (in the absence of PEL)
As PPE in the event of a chemical spill clean-up process
Lab personnel intending to use/wear a respirator mask.

**Hand Protection**
Handle with gloves. Use proper glove removal technique to avoid skin contact with this product. Nitrile gloves are recommended.

**Eye Protection**
Wear chemical splash goggles and a face shield to protect from splash hazards and chemical vapors.

**Skin & Body Protection**
Lab coat
Full-length pants
Closed-toe rubber or leather shoes

**Hygiene Measures**
Avoid contact with skin, eyes, and clothing. Wash hands before breaks and immediately after handling the product.

**First Aid Procedures**

**If inhaled**
Move to fresh air. If the person is not breathing, give artificial respiration. Avoid mouth to mouth contact. If breathing is difficult, give oxygen. Call 911 from a campus phone / DEHS.

**In case of skin contact**
Remove all contaminated clothing. Immediately (within seconds) flush affected area for FIFTEEN (15) minutes. Call 911 from a campus phone / DEHS.

**In case of eye contact**
Remove any contact lenses. Use nearest emergency eyewash immediately for at least FIFTEEN (15) minutes. Cover the eye with a dry eye pad. Seek medical attention immediately. Call 911 from a campus phone.

**If swallowed**
DO NOT INDUCE VOMITING. Rinse mouth with water and give large quantities of milk (preferable) or water. Never give anything by mouth to an unconscious person. Call 911 from a campus phone / DEHS.
Special Storage & Handling Requirements

Storage
Ensure the container is tightly closed at all times.
Keep in a dry and well-ventilated area away from incompatible materials and conditions.
Store and handle under inert gas- hygroscopic.

Handling
The lab where the material is being handled has an approved / certified emergency eyewash and safety shower.
Ensure you are wearing the following minimum PPE: tightly fitting safety goggles and face shield, lab coat, full length pants, close-toe rubber or leather shoes, nitrile gloves.
Lab emergency contact information must be readily posted. Easy access to a cellular phone or land line is readily available.
Avoid contact with skin, eyes, and clothing.
Avoid inhalation of vapor and mist.
Avoid formation of dust and aerosols.
Provide appropriate exhaust ventilation at places where dust is formed.

Spill and Accident Procedure

Personal precautions
Avoid dust formation. Avoid breathing vapors, dust, mist or gas. Ensure adequate ventilation. Evacuate personnel to safe areas. Do not attempt clean-up without minimum PPE.

Environmental precautions
Prevent further leakage or spillage – if safe to do so. Do not allow product to enter drains. Discharge into the environment must be avoided.

Methods and materials for containment and clean-up
Consider material compatibility prior to clean-up. Verify spill kit is available. Pick up and arrange disposal without creating dust. Sweep up and shovel. Keep in suitable, closed containers for disposal.

Decontamination / Waste Disposal Procedure

Label waste

Store waste
Store hazardous waste in closed containers, in secondary containment and in a designated storage location.
Double-bag dry waste using sealable transparent bags.
Waste must be under the control of the person generating and disposing of it.

Dispose of waste
Dispose of regularly generated chemical waste within 90 days.

j. Solvent health hazards

All organic solvents have the potential to damage bodily systems, so care should be taken to minimize exposure. Consulting the Glove Guide to determine the correct equipment can help lessen solvent exposure by skin absorption. Using solvents inside the fume hood helps minimize solvent vapor inhalation. The list below details specific health hazards associated with common laboratory solvents.
Skin-Penetrating Solvents

Dimethylformamide (DMF), Glycol ethers, Methanol, Toluene, Xylene

Central Nervous System Damage

Aliphatic hydrocarbons (hexanes, pentane, cyclohexene, etc.), Aromatic hydrocarbons (toluene, xylenes, etc.), Chlorinated hydrocarbons (methylene chloride, chloroform, etc.)

Carcinogens

Benzene, Chlorinated Solvents (known for lab animals, suspected for humans), Dimethylformamide (suspected), Dioxane (suspected)

Fire Hazards (Flashpoints below room temperature)

Acetone, Cyclohexane, Diethyl ether, Hexanes, Pentane, Tetrahydrofuran, Toluene

i. Choosing gloves

Gloves should be worn in a laboratory environment to protect your hands from chemical, temperature, or impact exposure. (Although you wear gloves in the lab, do NOT wear your gloves in public areas, such as the hallway, to use the phone or computer, or in the office areas. This transmits chemicals to our “safe” area!!! This will NOT be tolerated!). Many different kinds of gloves exist, so choosing the appropriate type for the job is important. Some tips for glove use follow, as well as an extensive section detailing proper glove selection. Gloves made of different materials can be purchased in the research stockroom.

Do NOT wear your gloves in office areas or when touching phones or computers that other people use without glove protection. Wearing your gloves in these areas serves only to spread chemicals from contaminated gloves onto common-use items.

Avoid powdered gloves. Powder can absorb microorganisms and aerosolized chemicals.

Glove specifications can vary from brand to brand, so check the manufacturers specifications when in doubt, a general guide can be found below:
k. Scaling-up Reactions

**Reaction Risk Assessment**

If the reaction is being conducted for the first time, or the scale-up reaction has potentially dangerous reagents/products present, follow the steps below until you are confident the reaction can be performed safely:

- Review the scientific literature, web sources, SDS’s, *Bretherick’s Handbook of Reactive Chemical Hazards*, and consult resident experts to identify hazards.
- Are these reactions known to be dangerous and what controls can be utilized to mitigate the dangers?
Scale-up Reactions

Every reaction must be assessed before scale-up to determine if there is any potential for uncontrolled events. Start hazardous reactions small and increase the scale by a maximum of five-fold for each scale-up. Diligently watch for warning signs and reaction rates each time. More mundane reactions can be scaled up by more than five-fold (e.g., EDC couplings, base hydrolysis, Fischer esterification). If any reaction conditions or reagents change, restart the reaction over again at a small scale to test its safety. Avoid changing reaction conditions and reagents in the middle of an experiment.

Scale

- Small: Reactant and solvent amounts: <1 gram of substrate, solvent < 25 mL.
- Moderate: Reactant and solvent amounts: 1-15 grams of substrate, solvent 25 – 500 mL.
- Large: Reactant and solvent amounts: >15 grams of substrate, solvent > 500 mL.

Communication

Good communication is essential when performing reaction scale-ups. Talk with others who have done the experiment before – they may have forgotten to record some critical detail(s) about the experiment. Inform anyone working nearby who might be affected if the reaction gets out of control.

- Notebooks must be sufficiently clear and legible (with detailed information) to allow someone else to perform the experiment.
- Include details on the solvents and reagents used, such as purity and manufacturer.
- Record any concerning adverse events, observations, dangers, and other important facts such as induction periods and runaway reactions.
- Provide an explanation for why a certain technique is critical. An example is the use of a magnetic stir bar as a heat sink during drop-wise additions and how it affects the formation of side products. Always alert others in the area when your reaction emits substances that could react with other substances; e.g., emission of hydrogen gas when others are working with pyrophorics; emission of NH$_3$ gas as others are emitting HCl in chemical fume hoods that could lead to NH$_4$Cl build-up in duct work.
- Alert others when you are working with or creating compounds that contain hazardous bonds (e.g., large scale nitration reactions, cyanohydrin reactions, diazomethane generation). These reaction scale-ups can affect others in the area if they are not contained by the fume hood.

Time

The bigger the reaction, the longer the setup, run, and workup of the reaction will take. Allot extra time for the experiment, and do not try to rush the reaction.

Temperature

Temperature control is critical for safely performing scale-up reactions. Remember basic reaction kinetics. As the temperature increases, so will the reaction rate and therefore produce more heat. This additional heat then feeds into a positive feedback loop and can cause a reaction
to spiral out of control. Loss of temperature control can have devastating results and cause side-products to form.

- Use a thermocouple probe or thermometer to monitor the *internal* reaction temperature, which can differ significantly from the temperature of the oil bath outside of reaction vessel.
- If heat generated from reaction is not controllable using standard methods, do not scale up further.
- Determine if the cooling method you have chosen is sufficient for the scale you will be working with. Have a backup plan in case it fails.

**Stirring**

Use overhead stirrers for consistent stirring of larger reactions to prevent hot spots. Magnetic stir bars do not mix large, thick mixtures well, and overhead stirring is more consistent when scaling up from one level to the next.

**Monitoring Reaction**

Monitor the reaction frequently for warning signs. Be alert to equipment failures (e.g., condensers not working, leaks in glassware joints, obstructed stirring), gas evolution, color change, viscosity differences, and temperature spikes.

**Equipment**

Choosing the right equipment for reaction scale-up can make a major impact on the efficiency and safety of the reaction to be performed.

- Use Teflon sleeves to prevent leaks and facilitate glassware disassembly.
- Use wide mouth glassware to facilitate entry and removal of materials along with good venting if emergency arises (massive gas evolution).
- Use lab jacks to elevate vessel heat sources so that they can be removed quickly if thermal runaway occurs.
- The volume of the vessel should be *at least* twice the volume of all added substances (including quenching material). Leave enough headspace in the event the reaction gets out of control.
- Avoid oil baths for large scale reactions – use heating mantles with probes. Oil baths have limited capacity and can create oil spills from equipment movement (sloshing).
- Avoid needle use for gas in-letting/out-letting on scale up reactions. This leads to excessive pressure increases. Rather, utilize gas inlet (or vacuum) adapters for gas lines. Adapters allow for better gas flow and venting if gas evolution increases rapidly.
- Make sure the fume hood ventilation system is sufficient for the scale you are working with. Larger equipment takes up more volume in the hood and can affect air flow. Be sure large equipment will not interfere with the chemical fume hood’s ability to operate properly.

**Solvent and Reagent Selection**

Solvent and reagent selection can have a critical effect upon reaction scale-up safety, especially if things go wrong. Here are a few general things to consider:
• Pay attention to the age of reagents and solvents—is the concentration of that old HCl bottle really 12M?
• Do not use materials from unlabeled containers.
• Be careful using materials from different lots (e.g., 5 grams from lot #A, 2 grams from lot #B, and 5 grams from lot #C).
• Be careful using materials from different manufacturers (e.g., previous reactions were done using vendor A materials but you intend to use vendor Z this time). Purity levels vary amongst manufacturers.
• If changing reagents or solvents is unavoidable, perform a front-run first. That means first performing the reaction on a small scale and comparing the results with past reactions.

Solvents

Be aware of the flammability of solvents around the equipment you choose, and take the appropriate precautions.

• If possible, choose solvents that will boil before the product decomposes. This helps to prevent the formation of tar, impurities, and other side products.
• Be aware of the dangers (explosions) from concentrating peroxide-forming solvents. When working with >1000 ml of peroxide-forming solvent, check peroxide levels when the volume of solvent has been reduced to 10-20% of the original volume.
• Use freshly distilled or purchased solvents, especially if anhydrous conditions are needed.
• Avoid highly volatile solvents with low boiling points and peroxide-forming issues. Use of these solvents poses fire and explosion hazards, especially during operations involving transfers, heating, and concentrating. Highly volatile solvents are also prone to concentration changes (e.g., running the reaction vessel dry).
  o Avoid THF and use 2-MeTHF (less peroxide issues, slightly higher b.p., and more environmentally friendly);
  o Avoid Et₂O and use t-BuOMe (less volatile, higher b.p., less peroxide issues);
  o Avoid hexanes and use heptanes (higher b.p., less toxic, less volatile)
  o Avoid CH₂Cl₂ & CHCl₃ and use 1,2-dichloroethane (higher b.p., ALL halogenated solvents have toxicity issues).
• When performing air-sensitive reactions (e.g., Suzuki, Buchwald) sparge the solvents (run a steady stream of bubbling inert gas through the solvent via a 12-18” needle while in the reaction vessel). This is safer and works better than degassing with vacuum (freeze-pump-thaw method). Sparg solvent mixture for 30 minutes with stirring before adding sensitive reagents, then sparg for another 5-10 minutes after addition but before heating.

Reagents

Reagent quality can vary greatly from one manufacturer to another.

• Impurity profiles vary from lot to lot and from manufacturer to manufacturer. Perform front-runs first to verify results before proceeding.
• If using large equivalent excesses of a reagent, try running a more concentrated reaction with less equivalents.
• Use reagents that allow for better stoichiometric control and safer chemical handling and storage. Examples:
  o Use NH₄Cl and base rather than NH₃ dissolved in Dioxane.
  o Use NH₄NO₃ and H₂SO₄ rather than HNO₃ and H₂SO₄
o Use dimethylamine hydrochloride and base rather than dimethylamine dissolved in water, THF, or methanol.

o Use TMS diazomethane or generate diazomethane in diethyl ether rather than distilling diazomethane.

o Use Oxalyl chloride/DMF (cat.) to create acid chlorides rather than using thionyl chloride.

- Avoid sensitive intermediates. Carefully determine how you will drive a reaction to completion. For example, with amide formation, it is easier to add more EDC, HOBT, and carboxylic acid than make more acid chloride if the reaction does not go to completion. Use reactions that will allow you to easily add more reagents (to drive reactions forward) rather than having to create more of an intermediate.

- If possible, use reagents that can make workups and purifications cleaner and easier. This can lead to cleaner reactions, less intensive purifications, lower flammable solvent usage, lower fire hazard, and less expenditure of time. Ultimately, efficiency and safety are increased. Examples:
  o For Mitsunobu or Wittig reactions, use Me₃P (1M solution) rather than Ph₃P; Me₃P=O is water-soluble and can be washed away; Ph₃P=O is sometimes difficult to remove during purification.
  o Use N,N-Dimethylethylenediamine (CAS# 108-00-9) to scavenge excess acid chlorides, acrylates, mixed anhydrides. Then wash away with a simple acid wash during workup.

**Figure 1.** N,N-Dimethylethylenediamine

![N,N-Dimethylethylenediamine](image)

* A Note Concerning Air- and Water-Sensitive Materials

- When using air- and water-sensitive materials, always be sure to properly inert your reaction vessel. It also helps to reduce the chance of fires with flammable solvents. Insufficient inerting is a recipe for disaster!

- Consider using a less hazardous reagent (substitution) or in a less hazardous form (attenuation). Examples:
  o Hydrogen transfer agent rather than Raney nickel;
  o Use n-BuLi rather than t-BuLi, if possible;
  o Use NaH 60% dispersion in mineral oil rather than NaH, dry, 95%;
  o Use 10% Pd on carbon (wet) rather than 10% Pd on carbon (dry);
  o To prevent explosions and fires from chemical dusts (especially air and water sensitive dusts), use them in the form of slurries.

**Runaway Reactions (Thermal Runaway)**

Definition (Wikipedia): “A situation where an increase in temperature changes the conditions in a way that causes a further increase in temperature, often leading to a destructive result.”

- Determine if a reaction can generate significant heat.
• If possible, replace highly reactive reagents with less reactive ones.
• Use proper volume of solvent for sufficient heat transfer.
• Do not use large equivalent excesses of reagents.
• Watch reaction concentrations (on average should be between 1M–0.1M).
• Use heat sinks if possible.
• Avoid “neat” reactions on large scale.
• Ideally choose a temperature that allows the reaction to proceed efficiently (good rate with minimal side product formation) and is easily controllable below the solvent’s boiling point or is easily cooled (e.g., 0°C–55°C).
• Assure constant reactant supply by choosing solvents that will not freeze (e.g., HOAc at 0 °C) at reaction temperatures, and be sure all reactants are soluble in the solvent. Be careful of heterogeneous mixtures that may dissolve unevenly in solvent.
• Monitor internal reaction temperature (via probes) during additions. Ensure constant mixing to prevent reaction hot spots.
• Ensure that the addition rate does not exceed the reaction vessel’s ability to dissipate heat or relieve pressure.
• Never add additional reagents if the optimal reaction temperature is not being maintained.
• If refluxing, do not rely on a condenser as the only means to remove heat from the reaction. Use Lab Jacks to remove the heat source quickly from the reactor vessel.
• Cooling is mandatory if heat generated by the reaction exceeds the vessel’s heat transfer ability.
• Always have a means to cool the reaction vessel if the reaction gets out of control, e.g., pull the heat source and cool in a water bath.

Good temperature control (albeit addition rates or cooling) is key to preventing thermal runaways!

Induction Periods

Definition (IUPAC compendium of Chemical Terminology): “The initial slow phase of a chemical reaction which later accelerates.”

Many reactions that have induction periods quickly turn into runaway reactions.

• Is there evidence of an induction period from previous reactions? Nitinations, free radical reactions, and Grignard formations all have been known to have induction periods.
• If there is evidence of an induction period:
  o Develop a strategy to control it (e.g., addition rates, cooling);
  o Have a cooling method ready before initiating the reaction;
  o Monitor the reaction closely, watching for signs of pressure, heat, color, gas evolution, solvent viscosity, and do not get complacent, regardless of the time involved.

To control induction periods via addition rates, add 5-10% of the reactant and watch for reaction initiation. If initiation is observed, carefully add the rest in a controlled manner. If it does not initiate, add another 5-10% of reactant and monitor. Remember the more reactant that is added, the greater the chance a runaway reaction will occur once the reaction initiates! Be patient and have a cooling system ready.

Workups
Scale-up reaction workups can pose many safety issues not normally encountered during smaller scale work. A few issues to consider:

- Be sure you have the right sized equipment for the scale, especially the use of separatory funnels and the number of extractions needed. Remember basic extraction rules—it is better to use more extractions with less solvent than fewer extractions with larger solvent amounts.
- Large equipment also poses physical constraints due to larger amounts of solvents, washes, and materials. Multiple extractions of dichloromethane on a large scale can not only pose physical difficulties on personnel but also on equipment, e.g., ring stands, clamps, monkey bars.
- Cleaning large glassware after workup in sinks designed for smaller glassware can easily lead to broken glassware, which may cause lacerations.
- Workups on scale take longer to accomplish due to the scales involved. Quenches, extractions, and rotovaping of highly flammable materials on scale all pose major hazards that must be approached carefully and methodically.
- Quenching reactions (especially with reactive reagents) on scale must always be approached with special care. Allow the reaction to fully cool before quenching. Take your time and be thorough.
- Take the time to analyze each layer to be certain where your desired product is. Don’t dispose of any waste until you are satisfied with your yield and purity.
- When using peroxide-forming solvents on scale, be certain to check peroxide levels when solvent levels are reduced to ~10-20% of the starting volume.

1. Manifesting Chemical Waste

Samples demonstrating how to properly fill out a Hazardous Waste Packing Form are located in 264 Kolthoff; you should consult the group safety officer with any questions prior to starting a hazardous waste container, or boxing up a full container. Substances packed in the same container should have the same first two digits in the DDC# if possible (see below). If percentages are used to indicate the relative contents of the container, the total volume must be labeled. If the container contains acidic or basic media the pH of the solution must also be recorded. Full chemical names must be used on all University Waste forms and containers; do not use abbreviations or chemical formulae like THF or CH₂Cl₂. If you are manifesting solid waste use units of kg for the contents of the container; for liquid waste, units of L must be used. Pack especially hazardous waste or aqueous waste separately. Typically organic waste should be collected in a separate waste container than aqueous especially if the aqueous waste is not neutral. Consult the group safety officer with questions prior to manifesting your waste if you have any questions!!! Waste is removed every Wednesday between 1:00-3:00 pm by the safety officer.
Drum Designator Code (DDC)

The DDC is an internal system developed by the Chemical Waste Program for classifying hazardous substances through the use of a two-part designation code. The first two digits of the DDC relate to the Department of Transportation (DOT) code and designate the chemical's primary hazard. The second part of the DDC consists of two letters which further describe the chemical/physical characteristics of the substance or defines the type of disposal or treatment methodology required.

Hazard Class Codes (first two digits of DDC)

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>Corrosive bases</td>
</tr>
<tr>
<td>02</td>
<td>Corrosive acids</td>
</tr>
<tr>
<td>03</td>
<td>ORM-A (Other Regulated Materials-A)</td>
</tr>
<tr>
<td>05</td>
<td>ORM-E (Other Regulated Materials-E)</td>
</tr>
<tr>
<td>06</td>
<td>Combustible materials</td>
</tr>
<tr>
<td>07</td>
<td>Flammable gases</td>
</tr>
<tr>
<td>08</td>
<td>Flammable liquids</td>
</tr>
<tr>
<td>09</td>
<td>Flammable solids</td>
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<tr>
<td>11</td>
<td>Non-flammable gases</td>
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<tr>
<td>12</td>
<td>Organic peroxides</td>
</tr>
<tr>
<td>14</td>
<td>Explosives</td>
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<tr>
<td>16</td>
<td>Oxidizers</td>
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<td>18</td>
<td>Poisons</td>
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</table>

Disposal Type Codes (second two digits of DDC)

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
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<tr>
<td>BS</td>
<td>Bulkable solvent</td>
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<tr>
<td>CG</td>
<td>Compressed gas</td>
</tr>
<tr>
<td>CL</td>
<td>Chlorinated organic liquid</td>
</tr>
<tr>
<td>CN</td>
<td>Cyanide</td>
</tr>
<tr>
<td>CS</td>
<td>Chlorinated organic solid</td>
</tr>
<tr>
<td>DX</td>
<td>Dioxin containing</td>
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<tr>
<td>EX</td>
<td>Explosive</td>
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<tr>
<td>FB</td>
<td>Fuel blending</td>
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<tr>
<td>HM</td>
<td>Heavy metal</td>
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<tr>
<td>HP</td>
<td>Pesticide</td>
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<tr>
<td>LI</td>
<td>Liquid inorganic</td>
</tr>
<tr>
<td>LO</td>
<td>Liquid organic</td>
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<tr>
<td>NA</td>
<td>Nitric acid</td>
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<tr>
<td>NH</td>
<td>Nonhazardous</td>
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<tr>
<td>PA</td>
<td>Poison A</td>
</tr>
<tr>
<td>PB</td>
<td>Poison B</td>
</tr>
<tr>
<td>PI</td>
<td>Poisonous inorganic</td>
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<tr>
<td>PO</td>
<td>Pourable oil</td>
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<tr>
<td>PX</td>
<td>PCB contaminated</td>
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<tr>
<td>RX</td>
<td>Radioactive material</td>
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<tr>
<td>SC</td>
<td>Sulfuric/chromerge</td>
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<tr>
<td>SI</td>
<td>Solid inorganic</td>
</tr>
<tr>
<td>SO</td>
<td>Solid organic</td>
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<tr>
<td>SS</td>
<td>Shock sensitive</td>
</tr>
<tr>
<td>TW</td>
<td>Trade Waste Incinerator</td>
</tr>
<tr>
<td>WS</td>
<td>Water sensitive</td>
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<tr>
<td>BP</td>
<td>Boiling point</td>
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<tr>
<td>CAR</td>
<td>Carcinogenic</td>
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<tr>
<td>CL</td>
<td>Chlorinated liquid</td>
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<td>COM</td>
<td>Combustible</td>
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<tr>
<td>COR</td>
<td>Corrosive</td>
</tr>
<tr>
<td>CSA</td>
<td>Cancer suspect agent</td>
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<tr>
<td>DRUG</td>
<td>Drug</td>
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<tr>
<td>EXP</td>
<td>Explosive</td>
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<tr>
<td>F</td>
<td>Flash point</td>
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<tr>
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<td>Irritant</td>
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<td>Lachrymator</td>
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<td>Mutagen</td>
</tr>
<tr>
<td>OX</td>
<td>Oxidizer</td>
</tr>
<tr>
<td>P</td>
<td>pH</td>
</tr>
<tr>
<td>PIH</td>
<td>Poison inhalation hazard</td>
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<tr>
<td>PLY</td>
<td>Polymerizes</td>
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<tr>
<td>PRX</td>
<td>Peroxide former</td>
</tr>
<tr>
<td>PYR</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td>SKC</td>
<td>Skin corrosive</td>
</tr>
<tr>
<td>SOL</td>
<td>Solid at room temperature</td>
</tr>
<tr>
<td>SS</td>
<td>Shock sensitive</td>
</tr>
<tr>
<td>STENCH</td>
<td>Stench</td>
</tr>
<tr>
<td>TER</td>
<td>Teratogen</td>
</tr>
<tr>
<td>TOX</td>
<td>Toxic</td>
</tr>
</tbody>
</table>
m. Materials Safety Data Sheets (MSDS)

Materials safety data sheets are important sources of information for the properties of many compounds with respect to safe handling and storage. A chemical’s MSDS contains physical properties as reported in the literature. The MSDS often contains information about toxicity levels including LD50 values for certain animals. The MSDS should always be consulted prior to handling any chemicals in the lab, especially those with which the user is unfamiliar! They can be found on the website for the chemical supplier. Sigma-Aldrich is an excellent source of MSDS’s for thousands of chemicals. Additionally, the department of health and safety at the University of Minnesota has a website dedicated to MSDS’s.

http://www.dehs.umn.edu/msds_sheets.htm

http://www.ilpi.com/msds/index.html

V. General Procedures

a. Syringes and needles

1. Be careful not to stick yourself with any needles! Remember that other people may have previously stuck themselves with that needle, and it is a hazard not only from chemicals, but also potentially from blood-borne pathogens.
2. Check out the syringes and needles before you use it to make sure that they are not leaking or clogged. Use the proper size of syringe and needle. The research stockroom keeps a large variety of syringes of different sizes and materials.
3. After you finish using the glass syringes and non-disposable needles, use THF, MeOH, acid water, DI water, and acetone to wash them and store them in the oven or return them to their appropriate lab drawer. Only syringes that don't have any Teflon seals should be stored in high temperature ovens. Gas-tight syringes with Teflon seals become damaged from intense and prolonged exposure to heat.
4. Be mindful when using needles and syringes in the glove box so as not to puncture the gloves.
5. Disposable needles must be placed in a sharps container after use.
6. Pasteur pipettes do not belong in sharps container. They should be disposed in special broken glass container. The disposable containers designated for broken glass can be purchased from the research stockroom. Full containers should be well sealed and labeled as trash so that the custodians will remove them. Only broken glass can be thrown into the broken glass bin. Gloves, Kimwipes, caps, etc must be thrown in the trash.

b. Safety and sharps

There are three main things to keep in mind when working with sharps:

1. The sharps are SHARP and could cut or puncture you.
2. The sharps could potentially spread blood born diseases if two people are pricked by the same sharp object.
3. Sharps must be disposed of in strong walled containers that cannot be punctured.

There are several types of sharps used in our lab including:

Razors: if you are going to reuse them be sure they are stored in a place where nobody will accidentally cut themselves. They should be placed in a petri dish or other hard container for storage, not directly on the bench top. Also, if a razor starts to get rusty it should be disposed of to avoid contracting tetanus. Razors must be placed in the red or white plastic sharps bins for disposal.

Pipettes: the tips can break easily and leave jagged glass. Dispose of these in the special blue cardboard boxes for glass disposal.

Capillaries: just be careful with them and be sure to get them thrown away as they are small and hard to see.

Syringe Needles: handle carefully to avoid pricking yourself and injecting something foreign into your body. When disposing of needles do NOT recap them because there is a high chance of getting pricked.

c. Proper use of chemical fume hoods

1. Fume hoods should always have a flow indicator of some type. Our hoods have an electronic flow indicator. Do not shut off that flow indicator unless absolutely necessary.
2. You should always work with chemicals six (6) inches behind the sash. Usually this means behind the lip in the surface. The lip keeps spills contained within the hood. The farther back in the hood you work, your exposure to chemical fumes is minimized.
3. Sashes or shields should always be left in place and not removed from their runners. In hoods with sashes, the sash should never be up higher than 18 inches. There are guards on the hoods to prevent you from sliding the sash up too high. Do not raise the sash higher than this unless it is necessary for experiment set-up or safety. In any regard, the sash should be brought back to its proper height immediately.

d. Gas tanks

Most of the large gas tanks we use contain inert gases, but still possess several dangers associated with uncontrolled decompression of the gas. If the pressure is released too quickly (if dropped or opened without a regulator), the cylinder can become a rocket – the 200 lb. tank can travel up to 66 mph, straight through concrete walls (Mythbusters did a whole show on the power inside a gas cylinder)! The large volume of gas can also cause asphyxiation as it quickly replaces the oxygen in the room. Extreme caution should be used at all times!

To avoid these hazards, follow these precautions, especially when transporting tanks:

1. Always restrain gas cylinders to a fixed object (i.e. the wall). Never leave a cylinder unrestrained, even temporarily while it’s being moved.
2. Never move a gas tank without its cap. The cap helps protect the valve from breaking open should the tank fall over.
3. Use a cart, with the strap secured, to move gas tanks. Tanks should not be rolled on
their bottom edges more than 1-2 ft. Never roll a tank on its side – the sides are not strong enough to support the weight of the tank. Gas tanks are heavy; don’t be afraid to ask for help if you need it.

4. Never ever open a tank without a regulator. The extreme force of the gas in contact with your body can cause cuts, abrasions, asphyxiation, and even hearing loss. Besides, opening the tank without a regulator doesn’t even show you how much gas is in the tank.

For smaller cylinders containing chemical reagents, follow the same rules. Always use a regulator. Always securely restrain the tank to keep it from tipping over. Be aware of the health hazards of the chemical, its reactivity and flammability, and work in a hood whenever possible. The chemicals are often extremely flammable and/or poisonous. Two excellent articles about gas cylinder safety (and reasons behind the rules): Hinshaw, J. V. LCGC North America 2002, 20, 532-536. Hinshaw, J. V. LCGC North America 2002, 20, 600-604. (www.chromatographyonline.com)

e. Dispensing liquid N₂ tank

1. Always wear wool gloves and goggles when you are handling liquid N₂.
2. Never tighten liquid N₂ hose with a wrench (hand tight is OK).
3. When you hear the sharp noise from the hose, liquid N₂ is used up. Inform the person in charge of acquiring new liquid N₂ tanks that the tank is empty.

f. Elemental Analysis

We send our elemental analysis samples away for analysis. Because it is an expensive and time-consuming experiment, please be sure that your material is extremely pure, and free of residual solvent. It is good practice to place a sample under vacuum for 8-24 hours (depending on solvent and compound) to remove any residual solvent. Samples can be sent in either screw-cap vials or flame-sealed ampoules. Air-sensitive compounds should be sent in flame-sealed ampoules if you want to get reliable results from the EA test. If you have a compound to send for elemental analysis, please speak with a senior member of the lab to obtain the proper forms and procedure for preparing and sending samples. Please do this a few days in advance of when you actually want to send your samples. It is not recommended to send samples Thursday or Friday (they might sit over the weekend), and highly recommended to send samples Monday or Tuesday.

VI. Airfree Procedures

a. Oil Baths

1. Always use a stir bar or paper clip to help to distribute the heat evenly. Increase the temperature of oil step by step to the target temperature to avoid overheating.
2. Use the proper oil bath according the temperature that you need. The upper use temperature of the clear silicone oil is 230 °C (Sigma Aldrich brand). The clear paraffin (mineral) oil has a maximum temperature of about 150 °C. Do not mix different types of oil. Always label an oil bath with the oil type it contains to avoid mixing.
3. When moving the oil baths, check whether they are still hot.
b. Safety and high pressure reaction flasks

1. Make sure the screw top is fitted with a good o-ring (no cracks) before use.
2. Think carefully about the solvent level in the flask. It should be based on the volatility of the solvent and the temperature you are working at. If you are heating the system over the boiling point of the solvent, never fill the flask over half full.
3. The flask will be hot when you remove it from an oil bath. If you must open it right away be careful about the pressure build up – work in a hood and wear gloves. Also, watch out because the solution may bump if you open the reactor when it’s hot. It is best to allow it to come to room temperature before opening the pressure flask.

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c. Vacuum Oven and Vacuum line procedures

Vacuum oven setup and takedown procedure:

Components: vacuum, oven, trap/dewar, vacuum pump, vent, **inlet Pump remains “off” when not in use**

**ALL VISIBLE SOLVENT MUST BE REMOVED BY ROTARY EVAPORATION PRIOR TO USING VAC OVEN**

**New people should observe vac oven use at least FIVE TIMES prior to using vac oven alone**

Procedure:

1. To place samples in the oven:
   i. Samples should be labeled and covered with a Kimwipe secured with a rubber band.
   ii. Place sample(s) in the oven and close the oven door.
   iii. If using heat, place a thermometer in the oven to monitor the temperature.

2. To evacuate the oven:
   a) Check the trap:
      a. Make sure the trap is clean, dry, and greased.
      b. Trap should be at room temperature and not immersed in the dewar with liquid N2. Empty the dewar if there is LN2 remaining from the last use.
   b) Close both the vent and inlet valves on the vacuum oven.
   c) Turn the pump on by turning the on/off switch to “on.”
   d) Let the pump run for a few minutes to remove any air remaining in the oven.

   **DECIDE WHETHER TO USE LN2 OR DRY ICE:**
   
   **LN2:** For solvents with melting points < -79 °C (e.g. between -80 °C to -196 °C)
   
   **DRY ICE:** For solvents with melting points > -79 °C (e.g. between -78°C to 100°C)

   e) Get LN2 from tank or obtain dry ice/acetone mixture
      **NOTE: DO NOT FILL TRAPS YET! (Just fill 4L transfer container)**
   f) Place the trap over the empty dewar.
   g) While opening the inlet valve a ¼ turn, begin pouring LN2 or dry ice into the dewar until full. Cover and wrap the top of the dewar with towels.
   h) When the gauge has reached -20 to -25 mm Hg, open the inlet valve fully.
i) Set the temperature, if desired.
   a. The heating light will glow when the oven is heating.
   b. Adjust the temperature control knob as necessary.
   c. Temperature key:
      i. \( 2 = 45^\circ C \)
      ii. \( 2.5 = 55^\circ C \)
      iii. \( 3 = 65^\circ C \)

3. Record sample information in the logbook.

4. To add samples when vacuum oven is already running:
   a) Fully close inlet valve.
   b) Open vent valve slowly.
   c) Add your new samples to the oven and close the oven door.
   d) Fully close vent valve.
   e) Slowly open inlet valve. When gauge has reached -20 to -25 mm Hg, open inlet valve fully.
   f) Record your new sample information in the logbook.

5. To remove dried samples from the oven:
   a. **Turn off heat, if applicable.**
   b. Close inlet valve on vacuum oven tightly.
   c. Open vent valve on vacuum oven slowly to avoid vials falling over.
   d. Remove sample.
   e. If finished, go to step 6 for shut down procedure
   f. If not finished and there are still samples in the oven:
      i. Fully close vent valve
      ii. Slowly open vent valve. When gauge has reached -20 to -25 mm Hg, open inlet valve fully.
      iii. Top of LN2 or dry ice/acetone as necessary.

6. Shut down procedure:
   Do the following 3 steps in rapid succession:
   i. Remove dewar from under the trap.
   ii. Shut off vacuum pump by turning the on/off switch to “off.”
   iii. Open inlet valve on vacuum oven.

7. When finished:
   a. Thoroughly clean trap after it reaches room temperature.
   b. Thoroughly dry the trap before reattaching.

**Important Issues**

- Always have the trap immersed in liquid N2 when drying (dewar lasts approximately 14-16 hours when filled with LN2).
- Never condense air in the trap (e.g. leave inlet valve on oven open to the trap while it is immersed in LN2 and closed to the manifold). **Condensed air/oxygen is blue.** If you see this color when you remove the dewar from the trap, make sure the inlet valve on the vacuum oven is
open or that the trap is open to the manifold. **Close your horizontal panels on your hood sash or place a blast shield in front of the trap if the trap is located outside of the hood and vacate the area!!!** Alert others working in the area to move out of the lab and close the connecting door to other lab as liquid oxygen is an explosion hazard. Allow the trap to warm up slowly in order to reduce the chances of explosion and empty the trap when it has warmed to room temperature.

• If the pump seizes for any reason, turn it off and inform the person(s) in charge.

For vacuum (Schlenk) line procedures, follow the same set up (a vacuum line just isn’t attached to a vacuum oven). In this case you need to worry about condensing argon gas, as it is also attached to the manifold. You never want to condense any gas (except volatile solvents). You should have someone else work with you the first time you use the vacuum ovens and the vacuum line.

d. Vacuum Pump Maintenance

Vacuum pumps eventually suck up moisture and solvent vapors over time, even if liquid nitrogen traps are rigorously used. Additionally, the heating of the pump oil from the pump itself will breakdown the oil overtime. As such, pump oil NEEDS to changed at least every 6 months for Schlenk Lines and every 3 months for Glove Boxes. If the pump is being heavily used, more frequent oil changes are REQUIRED. It is a good idea during an oil change to check belts for any tears or fraying (if applicable) and tighten down nuts and bolts.

If using a belt driven pump, after the oil is drained, run a Force Oil Flushing procedure (see below). The pump can then be refilled and tested.

If using a direct drive (rotary) pump, drain the oil first, add in ‘Flushing oil’ or regular pump oil to the oil level line and let pump run with intake port covered with a large rubber stopper for 20 minutes. After which time, drain the oil away. If the drained oil contains lots of black chunks or is emulsified and cloudy, rerun this procedure with clean ‘Flushing Oil’. If the drained oil appears a similar color as when you started, then refill with clean, regular pump oil to the oil level line.

For any type of pump, after the oil has been changed and flushed, be sure to turn on the vacuum for a minute (with the intake port covered) and ensure that the oil level is appropriate. The oil level will go down slightly after turning the pump back on. It is ALWAYS necessary to check the vacuum with a CALIBRATED vacuum gauge. The pump alone should be pulling between 10 to 50 millitorr. If not, something may be wrong with the pump (check oil level to start). Once the pump is operational, reattach it to the Schlenk Line or Glove Box, and ensure that the vacuum is pulling an acceptable amount with the vacuum gauge. Treat your pump right, and it will treat you right.

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**Forced Oil Flushing (taken from the Welch Vacuum Pump Manual)**

When you drain oil through the drain valve, you are not removing the oil and contaminants that are inside the pumping mechanism. You are removing oil only from the oil case. Welch recommends a forced oil flush of DUOSEAL pumps be performed at the regular maintenance oil
change. The procedure for the forced oil flush is given below.

1. **Check the oil level.** If the oil level is well above the fill mark, (This may indicate either the pump has been overfilled with oil or has ingested a liquid or a large amount of vapor water or organic solvents.) Please go to step 2. If the oil level is even with the fill mark and you do NOT suspect corrosive gases or particulates (hence forth called contaminants) ingested have damaged the mechanism, run the pump for 15 minutes to allow the pump oil to warm up before going to step 2.

2. **Turn off motor for the vacuum pump.** Drain the oil into a waste container (may need pliers to open drain valve). Look for contaminations settling to the bottom of container. If you see contaminants, you will need to repeat step 3 through 5 several times until the oil comes out clear. The oil you drained from the pump came from the oil case only. There may be contaminants in the pumping mechanism. To be sure all contaminants have been removed, the pump mechanism needs to be flushed.

3. **Make sure the belt guard is installed before proceeding further.** Attach a short hose to the drain valve which runs into a clear plastic container.

4. **Flushing the pump is carried out by adding a cup of DUOSEAL vacuum pump oil through the intake port (IN) while the pump is turned on for 15 to 20 seconds.** While adding the pump oil, a rubber stopper is placed lightly over the exhaust port (OUT). Look for water coming out of the drain. **Turn off the pump.**

5. **Repeat step 4 until clean oil comes out of the drain hose.**

6. **Fill the pump with the amount of DUOSEAL vacuum pump oil your pump needs.**

7. **Plug the intake (IN) port with a rubber stopper.** Turn the pump on and run the pump for 10 minutes.

8. **Check the vacuum reading of the pump by connecting a thermocouple gauge tube to the pump’s intake.** If the pump is running nearly as good as when it was new, the total pressure you will read will be at least 10 micron.

A simple way to connect the gauge tube to the pump is to run the threaded tip of tube through a hole in a rubber stopper. Use pump oil as a lubricant for inserting the tube. The stopper chosen should be bigger than the outer diameter of the intake flange.

**e. General Schlenk line manipulation review**

A Schlenk line is an indispensable part of any synthetic organic and inorganic laboratory particularly for performing air and moisture-free manipulations. A laboratory Schlenk line features a twin manifold with typically about 4-5 ports for using nitrogen/vacuum. One manifold is connected to a source of purified inert gas such as nitrogen or argon, while the other is connected to a high-vacuum pump. The inert gas line is vented through an oil bubbler, while solvent vapors and gaseous reaction products are prevented from contaminating the vacuum.
pump through a liquid nitrogen or dry ice/acetone cold trap. Three-way stopcocks or Teflon taps allow for vacuum or inert gas to be selected without the need for placing the sample on a separate line.

**Pumping down the line.**

a) Wear appropriate PPE while working in the hood.

b) Ensure that the schlenk line is ready to be evacuated,
   - all the joints are well-greased, use appropriate grease (Apiezon M) and do not over apply.
   - all the stopcocks are in the horizontal position,
   - liquid traps are in installed and secured.
   - check the mercury bubbler for the inert gas flow rate.

c) Turn on the vacuum pump, the gurgling noise should fade and the pump should be running smooth. If pump is not quiet with in a few minutes, stop the pump and identify potential sources of leak. If bringing up the line after oil change, re-greasing joints etc, use a vacuum gauge to measure how well the pump is doing. Most of the belt-driven Welch pumps would pull down to ~ 50 mTorr without the liquid N2 traps on and to ~20-25 mTorr with traps. If your pump cannot get down to these values in about 1 h at max, it points to a leak in the system.

d) Place the liquid N2 Dewar under the vacuum trap and carefully fill with liquid N2 using a secondary Dewar. Make sure to add the liquid N2 in small batches giving enough time for the traps to cool down or the liquid N2 may splash over as it boils off. *Liquid N2 is a cryogenic liquid and can cause severe burns if on skin.*

e) The vacuum line is now ready for use.

**Safety concerns**

a) Always check for glassware for cracks before evacuating as an implosion may occur. Secure the glassware while you use it to avoid accidents.

b) If argon is used as the inert gas, beware of condensing argon in the reaction flask while using a liquid N2 bath for cooling. The boiling point if Ar (-185.7 °C) is lower than that of N2 (-195.8 °C).

c) A high pressure of the inert gas can also lead to explosion of the line/reaction flask.

d) Care should be taken to avoid the condensation of oxygen (blue liquid) in the liquid traps. For this reason, a Schleck line using liquid N2 as the coolant should never be opened to the atmosphere without bringing down the Dewars. The boiling point if oxygen (-183 °C) is lower than that of N2 (-195.8 °C). If liquid oxygen is accidently condensed in the trap, leave the liquid
N2 Dewar on, and the vacuum pump running and clear the lab area. Inform other people sharing the lab area.

**Vent procedure**

1. Close all the taps so that they are aligned horizontal.
2. Either stop the vacuum pump or close the tap connecting the vacuum hose to the Schlenk manifold.
3. Immediately remove the liquid N2 Dewar, taking precaution not to spill any on you. Use cryo-gloves if available.
4. Open air vent, take down the liquid traps and let them thaw. Manifest any condensate (waste) appropriately. The trap may be left in the hood (closed sash) to dry overnight.
5. The fume hood with a Schlenk line must be kept uncluttered before and after manipulations.

*f. Vacuum transfer of solvents using Schlenk line*

Please do not vacuum transfer any liquid without being shown the proper procedure by another knowledgeable member of the lab. This procedure is meant as a reminder for those who have already been trained.

1. Get ready with a solvent flask (SF) containing the dried solvent (usually containing sodium metal and benzophenone, or calcium hydride or molecular sieves). Apply standard freeze-pump-thaw procedure at least three times. Attach to an adjacent port on the Schlenk line to be purified.
2. Have a receiving Straus or Kontes flask (RSF) ready from oven; attach it to the Schlenk line, set on vacuum, allow to cool under vacuum. Connect the SF and RSF with a suitable transfer adapter bridge that has been oven dried. You may also attach the SF, RSF and bridge together, set bridge and RSF under vacuum and flame dry the bridge and SF under vacuum.
3. Set the whole system under vacuum except the SF.
4. Raise a cooling bath (liquid nitrogen or acetone / dry ice) to cool/freeze the RSF; if liquid nitrogen is used, during the solvent transfer it will need to be continuously replenished (*the flask should not be left under static vacuum for more than 15 minutes*).
5. Open vacuum valve **SLOWLY** on SF and start transferring solvent to RSF. During this, the solvent in the flask should begin to boil vigorously. Be careful not to bump the drying agent (CaH$_2$ or Na/benzophenone) into the RSF. If you do this, you may have to start all over again.
6. Once the solvent is has finished transferring, seal off the RSF from the Schlenk line and the vacuum. Close the vacuum valve on SF to be used for next time.
7. The RSF filled with solvent should be put through three freeze-pump-thaw cycles before being taken to glovebox.

**Caution:**

a) Keep an eye on the transfer process.
b) If the transfer is very slow, check and make sure there is no leakage, which could cause oxygen condensation, especially when using liquid nitrogen as cooling bath.

c) Do not transfer more than 50-60% of the capacity of the RSF as certain polar solvents like water, methanol and acetonitrile expand upon thawing and may break the RSF.

**Large Scale processes using metal hydrides (NaH, KH and CaH2)**

*a. NaH and KH are used as strong bases in synthesis. Both are usually supplied and acquired as dispersions in oil (60%). CaH2 is supplied pure.*

*b. NaH and KH can ignite in air, especially upon contact with water (even with moisture in air) to release H2 which is highly flammable. KH is highly reactive even in air and should be handled under a blanket of inert gas.*

*c. CaH2 is relatively stable in air and may be handled outside, however, contact with water should be provided.*

*d. Reactions involving NaH or KH should be worked up with extreme caution as there may be unreacted metal hydride in the mixture. Quenching of the reaction mixture should be performed under an inert atmosphere.*

*e. Excess hydrides can be quenched by adding iPrOH in an ice bath.*

*f. CaH2 is frequently used for drying acetonitrile, dichloromethane, toluene-d8, benzene-d6 etc. Excess hydride can be quenched by adding a iPrOH/hexane mixture and stirring under inert atmosphere.*

*g. Solvent purification system (SPS)*

There is an SPS in 264 Kolthoff. We have tetrahydrofuran, diethyl ether, methylene chloride, pentane and toluene. Training by the group member in charge is required before using solvent columns for the first time!

1. Make sure the vacuum and nitrogen lines are correctly connected.
2. Connect a flame-dried flask to the line and secure it with the metal clamp.
3. Purge and evacuate the flask at least 3 times with argon (at least 10 minute evacuate cycles).
4. Close the valve from the nitrogen and vacuum line.
5. Open the valve of solvent purifying column.
6. After transferring solvent, close and disconnect the flask and flow argon gas to remove solvent trapped inside the tube.
7. Leave the SPS as you found it.

If the solvent level is low or the argon tank is empty, tell the person in charge of the SPS.

**VII. Equipment**

*a. Comments that apply to all equipment*
1. Leave equipment cleaner than you found it.
2. Do not use equipment without being trained by the person in charge of the instrument. No one else may train you on an instrument other than the person in charge.
3. Follow rules and procedures for that instrument. No rules or procedures are optional.
4. **IF YOU NOTICE SOMETHING WRONG WITH THE INSTRUMENT, INFORM THE PERSON IN CHARGE IMMEDIATELY.**
5. If you have a question about an instrument, please ask the person in charge. Do not try and fix an instrument without consulting the person in charge of the instrument.
6. You must sign the logbook associated with the instrument. This is also not optional.

**b. Dryboxes**

There are a few personal safety issues associated with the actual drybox. Important points to remember:

1. Before using any of the dryboxes for the first time (even if you have previous drybox experience), you must be trained by the person in charge of the box. If you do not follow the procedures outlined by the person in charge, you may lose access to the glove box.
2. Pump items into the box properly, and use caution when removing glassware and syringes that may have residual air/water sensitive chemicals. To avoid fires or violent reactions, be sure to cap syringe needles with a rubber septum until they can be quenched and cleaned in the hood.
3. Keep the drybox clean! Remove everything you bring in, immediately after you finish using it. Clean up spills. Store chemicals away from working area. This helps prevent breakage and chemical spills.
4. Protect your hands and the drybox gloves by removing sharp jewelry (rings, watches, etc.), being careful when working with syringes and scissors, and by wearing regular nitrile gloves over (if using chemicals that may harm butyl rubber) and cotton or nitrile gloves underneath the drybox gloves.

Each drybox has its own set of operating procedures. Please refer those for specific details on a particular box.

**What kind of objects can be brought through the antechambers into the glove box:**

Objects have to be dried overnight in the drying oven, except reagent bottles that cannot be heated.

8. Solid objects such as glassware, metal implements, etc. may be brought in as long as they are not capable of trapping air and need to be oven dried overnight. They also must enter the antechamber hot.
9. Reagents that are in their original unopened bottles and were packaged under argon may be brought into the glove box without further preparation. The unopened bottle is all the containment that is required.
10. Liquids should be dried over an appropriate drying agent and kept in a Straus or Kontes flask and put through three freeze-pump-thaw cycles. The liquids should be at room temperature when they go through the antechamber.
11. Bottles or jars of air-stable, but dry, solids should be opened, and a folded Kimwipe should be placed over the jar and held down with rubber bands to protect powders from spilling out into antechamber and vacuum pump. The original cap should go into the glove box along with the Kimwipe-covered jar.

**Dry box names:**
- Left box (Vac)
- Right box (Vac)
- Polymer box (Mbraun)

**Polymer Glovebox (Mbraun) Standard Operating Procedure (SOP)**

Current glovebox managers: Hanna Macaranas and Dr. Megan Fieser

**WARNINGS**

1. Failure to follow this SOP can result in damage to the equipment and exposure to chemicals. Failure to follow the guidelines, etiquette, and procedures as outlined in this SOP may result in loss of access to the glovebox.

2. New users must be trained by the above managers before using the box, regardless of prior glovebox experience. If you have not been trained by a current manager, DO NOT use the box until training is obtained.

3. Prior to reading this SOP, you should have already read, signed, and dated the most recent Tolman Lab SOP.

**Equipment**

*a. Comments that apply to all equipment*

1. Leave equipment cleaner than you found it.
2. Do not use equipment without being trained by the person in charge of the instrument. No one else may train you on an instrument other than the person in charge.
3. Follow rules and procedures for that instrument. No rules or procedures are optional.
4. **IF YOU NOTICE SOMETHING WRONG WITH THE INSTRUMENT, INFORM THE PERSON IN CHARGE IMMEDIATELY.**
5. If you have a question about an instrument, please ask the person in charge. Do not try and fix an instrument without consulting the person in charge of the instrument.
6. You must sign the logbook associated with the instrument. This is also not optional.

**Excerpt from the Tolman Lab SOP** (for more detail, consult the full SOP or contact the LSO):

**1. GENERAL GUIDELINES AND GLOVEBOX ETIQUETTE**

1.1 Always use clean gloves over your hands before placing in the glovebox gloves and using the box (linen gloves can be purchased from the stockroom). If using a labcoat, make sure it is a
dedicated glovebox labcoat so that no chemicals from lab are transferred from the coat to the shared glovebox gloves. Additionally, there are disposable gloves in the box to use over the glovebox gloves. If you spill anything on the glovebox gloves while working in the box, make sure to clean them with kimwipes.

1.2 Fill out the logbook. This includes initials, date, contents, antechamber evacuate/fill times, length of time purging after solvent/volatile compounds use, turning circulation on, and vacuum trap setup/cleanup. Use the comments line, as necessary (if the N\textsubscript{2} tank is low, if a small N\textsubscript{2} tank is being used, etc).

1.3 Clean up any spills. No exceptions. Use the duster brush and dustpan to sweep up any spilled solids or broken glass generated while working in the box. Every user is accountable for messes made in the box and must make sure the box is clean for the next user. If the box was left dirty before a user begins their work in the box, it is that user’s responsibility to either have the previous user clean it immediately or to clean it up themselves. Common areas to clean: inside the balance, under the balance (without moving the balance), under the ring stand, under the vacuum tubing, and under the freezer.

1.4 All users are responsible for restocking commonly shared supplies. If supplies are low at any point during the day, restock asap and inform the other users (especially if vials, vial caps, needles, and disposable syringes are low). If you use the last of a shared supply, you MUST restock immediately or coordinate with other users to have the item restocked. This includes commonly shared supplies such as vials, vial caps, pipets, pipet bulbs, septa, disposable syringes, needles, weigh boats, and electrical tape. This also includes less common supplies, if used: NMR tubes, volumetric flasks, 4 mL brown bottles, vacuum adapters, frits, vacuum flasks, and microliter syringes. If running low on any supplies, mark it in on the whiteboard and make sure it is added to the overnight tray so that the box stays fully stocked.

1.5 Coordinate with all other users when bringing items into and out of the box. The antechamber evacuate/refill procedure MUST be followed as outlined in section 2.3.

1.6 Common bulk solvents must be dried as outlined in section 2.6, as well as degassed using freeze-pump-thaw procedures and transferred to oven-dried Kontes sealed flasks via vacuum transfer (see the Tolman Lab SOP for more detail) before being brought into the box. No exceptions.

1.7 The glovebox must be purged after solvent use for at least 5 min and must be purged for at least 15 min after working with large amounts of solvent/volatile compounds or if working with open containers of solvent/volatile compounds (see section 2.5 for purging procedure).

1.8 If the vacuum line needs to be setup in the box, notify a manager to receive additional training. It is the responsibility of the user to make sure that the vacuum trap is taken down and cleaned after use. Make sure to write in the comments section of the logbook when the vacuum line was used and when the trap was taken down and cleaned. DO NOT leave the trap dirty overnight. An isopropanol bath can be used to speed up thawing so that the trap can be cleaned after use.

1.9 Be extremely careful when working with or around any sharp materials such as needles, syringes, and scissors in the box. Be extremely careful when scoring and breaking open ampules. Use tweezers whenever possible to avoid puncturing the gloves and any potential injuries while handling sharp objects (such as removing needles from syringes). For proper syringe and needle
use, see the current Tolman Lab SOP. DO NOT leave broken pipets or uncapped needles on the glovebox floor, as these items can damage the gloves.

1.10 If the gloves are ripped or punctured in any way, seal with electrical tape and notify a manager. If any electrical tape that is currently on the gloves begins to peel, replace and reseal with new tape.

1.11 DO NOT move the balance. The balance has been calibrated to its current position (marked with red electrical tape). Keep the balance clean and use the long tweezers whenever possible. This includes pressing on any buttons or sliding the doors open.

1.12 If the large N\textsubscript{2} tank is running low, order a new tank from whomever is in charge of purchasing and switch to a small N\textsubscript{2} tank (these are located to the right of the solvent system and will not have a ring of pipe cleaners around the top of the tank). Notify a manager if necessary. Make a note in the logbook to inform other users that a small N\textsubscript{2} tank is being used so that purging is kept to a minimum.

1.13 All large N\textsubscript{2} tanks delivered by Airgas must be cleared before being accepted. Check the whiteboard near the gcms to make sure that the N\textsubscript{2} tank is not a “banished tank.” Record the serial number (S.N.) of the tank on the clipboard with the date received and your initials. If you notice an issue with the N\textsubscript{2} after it has been accepted, describe the problem on the clipboard and update the “banished tank” list.

2. GENERAL PROCEDURES

2.1 First user in the box

a. *Turn the lights ON and turn circulation OFF:*
   - Touch Panel $\rightarrow$ Press “light.” The green light above the button should turn on. The lights in the glovebox should turn on.
   - Touch Panel $\rightarrow$ Press “circulation.” The green light above this button should turn off.

b. Circulation should always be OFF during normal operation.

c. Check the large N\textsubscript{2} tank to ensure that there is enough N\textsubscript{2} to work in the glovebox. If low, inform the person in charge of purchasing. If empty, switch to a small N\textsubscript{2} tank and make a note in the logbook to let other users know.

d. Check the atmosphere by opening the bottle of ZnEt\textsubscript{2}. If the bottle smokes, the glovebox atmosphere is at $> 50$ ppm O\textsubscript{2} or H\textsubscript{2}O. Purge the box as described in section 2.5 until the bottle no longer smokes.

e. Bring in the overnight tray following the antechamber evacuate/refill procedure outlined in section 2.3. Update the logbook to indicate that the tray was brought in.

f. Put away any common use supplies from the overnight tray and place them in their designated bins/containers. Any user specific items can be left in the tray or put off to the side.

g. Make note of any supplies that are low and record on the whiteboard.
2.2 Last user in the box

a. Make sure to sweep and clean so that the box is not dirty at the beginning of the next day.

b. Place the overnight tray in the small antechamber and leave under dynamic vacuum overnight following the antechamber evacuate/refill procedure outlined in section 2.3. Fill out the logbook to indicate that the tray is in the antechamber.

c. Check the logbook to see if the trap was used and if so, make sure that it was taken down properly and the associated pump was turned off.

d. Purge the box for at least 5 min. Purge for at least 15 min if a large amount of solvent/volatile liquid was used or if containers for solvent/volatile compounds were left open while working in the box. Follow the purging procedure outlined in section 2.5. Use the timer at the top of the box, if desired.

e. **Turn the lights OFF and turn circulation ON:**
   - Touch Panel ➔ Press “light.” The green light above the button should turn off. The lights in the glovebox should turn off.
   - Touch Panel ➔ Press “circulation.” The green light above this button should turn on.

f. Double check that the small antechamber is left under dynamic vacuum and that the large antechamber is left under static vacuum (see section 2.3.2 for information on antechamber valve positions).

g. After 4 pm: unless you have verbally confirmed that another user will use the box after you, assume you are the last person and shut it down for the day.

2.3 Antechamber Operation

2.3.1 General Information

a. The small antechamber should always be kept under dynamic vacuum and the large antechamber should always be kept under static vacuum when not in use.

b. Always check the logbook for status of the antechamber:
   - If another user is in the middle of transferring material into/out of the box, you must wait until they are done cycling.
   - Every time the antechamber has been exposed to air, you must follow the antechamber evacuate/refill procedure below to avoid contaminating the atmosphere in the box. This includes bringing something out immediately after a previous user came out.

c. Each antechamber must be pumped down to -30 in. Hg three times (three cycles of evacuating and refilling with N₂) before its contents can enter the glovebox. This must also be done if the antechamber is empty and you need to bring something out immediately after a previous user came out.

d. Each cycle requires that the antechamber be under dynamic vacuum for at least 5 min for the small chamber and at least 10 min for the large chamber. A minimum of 3 cycles ensures that materials can be transferred into or out of the glovebox without contaminating the internal box atmosphere or the room atmosphere.
   - One exception for the small chamber applies if and only if you are coming out of the box and a previous user came out MORE THAN AN HOUR earlier. Assuming the chamber has been under dynamic vacuum this entire time, the
small chamber can be cycled within 5 min (1-2 quick cycles) instead of the full 15 min (3 cycles) to bring the contents out.

e. DO NOT leave the antechamber doors open for extended periods of time. Never open the inner and outer antechamber simultaneously. Never open the inner door if the antechamber has been exposed to air from room atmosphere.

f. DO NOT use the antechamber evacuate/refill procedure to remove solvent. All materials should be dried as outlined in section 2.4 prior to being placed in the antechamber and being brought into the box.

### 2.3.2 Antechamber Valves

**Small Chamber Valve:**

<table>
<thead>
<tr>
<th>Evacuate</th>
<th>Closed</th>
<th>Refill</th>
</tr>
</thead>
</table>

**Large Chamber Yellow Valve:**

Turn counterclockwise to Refill

**Large Chamber Round-tipped Valve:**

Horizontal Position (Closed)  Vertical Position (Evacuate)

### 2.3.3 Evacuate/Refill Procedure

a. *To place materials in the antechamber or remove from the antechamber:*
Check the pressure gauge on the top of the antechamber and make sure the pressure is at -30 in Hg (the needle may not reach -30 in Hg exactly).

Ensure that the inner antechamber door is closed.

Bring the antechamber to atmospheric pressure with $N_2$:
  i. Small chamber: turn the valve to the “Refill” position.
  ii. Large chamber: turn the yellow valve counterclockwise very slowly and do not open the valve all the way unless almost at atmospheric pressure. Make sure that the black, round-tipped valve under the large chamber is clicked into the horizontal position. If this valve is slightly open, the chamber will not fully fill with $N_2$.

Close the valve after filling with $N_2$:
  i. Small chamber: turn the valve to the vertical “Closed” position.
  ii. Large chamber: turn the yellow valve clockwise all the way.

Open the antechamber door.

Place contents into the antechamber and close the antechamber door. Ensure that the chamber door is secure by running your fingers along the seal.

If bringing materials into the box: you must complete 3 evacuate/refill cycles (see section 2.3.2.b) and record the time for each cycle in the logbook.

If taking materials out of the box and the previous user has NOT come out, then open the outer chamber door to come out. Record the time in the logbook. Then make sure that the small chamber is placed under dynamic vacuum or that the large chamber is placed under static vacuum
  i. Small chamber: turn the valve to the “Evacuate” position.
  ii. Large chamber: slowly turn the black round-tipped valve to the vertical position. Wait for the chamber to be fully evacuated and check that the pressure is at -30 in Hg. Turn the valve to the horizontal position and make sure that it is fully closed (you should feel it click into place).

b. To cycle in contents of the antechamber and bring into the box (or to come out of the box after the chamber has been exposed to air and is empty):

If under vacuum, bring the antechamber to atmospheric pressure with $N_2$:
  i. Small chamber: turn the valve to the “Refill” position.
  ii. Large chamber: turn the yellow valve counterclockwise very slowly and do not open the valve all the way unless almost at atmospheric pressure. Make sure that the black, round-tipped valve under the large chamber is clicked into the horizontal position. Sometimes this valve is not fully closed and the chamber will not fully fill with $N_2$ if it is slightly open.

Close the valve after filling with $N_2$:
  i. Small chamber: turn the valve to the vertical “Closed” position.
  ii. Large chamber: turn the yellow valve clockwise all the way.

Evacuate the antechamber and place under dynamic vacuum:
  i. Small chamber: turn the valve to the “Evacuate” position and leave for at least 5 min before starting the next cycle.
  ii. Large chamber: slowly turn the black round-tipped valve to the vertical position. Wait for the chamber to be fully evacuated and check that the pressure is at -30 in Hg. Leave the chamber under dynamic vacuum for at least 10 min. Then make sure to turn the valve to the horizontal position and that it is fully closed (you should feel it click into place) before starting the next cycle.

Record the time in the logbook.

Repeat 2 more times.
2.4 Materials that can enter the glovebox

- ALWAYS follow the above antechamber evacuate/refill procedure (section 2.3) when bringing anything into the box. Material transferred into the box must be able to withstand the pressure difference during the purging process.
- Glassware must be clean and dried in the oven overnight or dried in the vacuum oven for at least an hour before pumping in the box. Check for star cracks, as outlined in the Tolman Lab SOP. Pipets and vials must also be dried overnight in the oven before entering the glovebox.
- Kimwipes, tape, and septa must be pumped down overnight before entering the glovebox.
- Any compounds brought into the box and stored in the box must be labeled and sealed with electrical tape when not in use.
  - New, unopened, reagent bottles can be brought in as is. Once open in the box, keep sealed with electrical tape when not in use.
  - Non-powdery solids that have been dried in the vacuum oven for at least an hour can be brought into the box in a labeled vial with a loosely screwed on cap. Once in the box, secure the cap and store sealed with electrical tape.
  - Powdery solids that have been dried in the vacuum oven for at least an hour must be brought into the box in a labeled evacuated flask or in a vial sealed firmly with a Kimwipe and rubber-band. Once in the box, either seal the flask or cap the vial and seal with electrical tape.
- All solvents/volatile compounds must be brought into the box in a labeled Kontes-sealed flasks with a headspace of N₂ or Ar and dried as outlined in section 2.7. Solvents/volatile compounds can be stored in labeled Kontes-sealed flasks, in oven-dried brown bottles with Teflon-lined caps sealed with electrical tape, or in clear, colorless bottles with lined yellow caps.

2.5 Purging the box

- The box is a closed system and any solvent/volatile compounds that enters the atmosphere of the box will contaminate solvent that you open subsequently.
- The glovebox must be purged if the atmosphere of the box is contaminated with solvents, volatile liquids, O₂, H₂O, etc. Use the bottle of ZnEt₂ to check the glovebox atmosphere for O₂ or H₂O. The box must be purged until the bottle no longer smokes.
- When working with large amounts of solvent/volatile liquids or open containers of solvents/volatile liquids, the box must be purged for at least 15 min.
- Before purging, make sure that all containers containing solvents/volatile compounds are tightly sealed with Teflon lined caps and taped with electrical tape.
- To start purging: Touch Panel  ACK then F3. The digital screen will read “Box is Purging.”
- To stop purging: Touch Panel  ACK then F3.
- Record the purging time in the logbook.

2.6 Waste

- Use the waste container for small amounts of waste generated.
- If you generate large amounts of trash, remove it when you exit the box or put it in your tray. Make sure the workspace is clean for others to use.
c. If you are the last one to use the waste container and it is full, you must replace it with an empty waste container (when pumping in the empty waste container, make sure to unscrew the cap) and dispose of the contents of the old waste container appropriately outside the box.
d. When placing used pipets into the waste container, do not force them into the waste container with your hands. Instead, use the cap to push on the pipets, as this may help prevent broken glass from exiting the container in any way.

2.7 Solvents

a. Bulk solvents must be dried as outlined below prior to entering the box. Further detail of the freeze-pump-thaw and vacuum transfer procedure can be found in the current Tolman Lab SOP.
   - Benzene, toluene, tetrahydrofuran: stir over Na/benzophenone overnight, freeze-pump-thaw 3x, and vacuum transfer to a clean, oven-dried, Kontes-sealed flask.
   - Chloroform: stir over calcium chloride overnight, freeze-pump-thaw 3x, and vacuum transfer to a clean, oven-dried, Kontes-sealed flask.
   - Dichloromethane: stir over calcium hydride overnight, freeze-pump-thaw 3x, and vacuum transfer to a clean oven-dried, Kontes-sealed flask.
   - Pentane: acquire from the solvent system in a clean, oven-dried, Kontes-sealed flask.

C. UV-vis and cryostat

As with all instruments, please contact the person in charge of the instrument before using the instrument. These are meant to be reminders for those who have already been trained on the UV-vis and cryostat. Do not use the UV-vis and cryostat if you have not been trained.

General UV-vis guidelines:

1. Handle UV cells carefully! They are expensive and can easily scratch. Handle the cell either by the Schlenk neck or by the frosted sides of the cell. DO NOT HANDLE BY THE CLEAR SIDES OF THE CELL.
2. UV cells are stored in the oven in 263 Kolthoff and are for everyone to use. No hoarding of cells is allowed. Clean them after you use them.
3. Reserve the UV instruments and UV cells before using them at least a day in advance. There is a sign up on the Tolman group Google Calendar. List which UV-Vis instrument(s), number of cells, and the approximate timeframe you will require on the Google Calendar schedule. If you need multiple days, please speak to ALL the UV users before booking.
4. Filling out the logbook is mandatory for all users.

UV-Vis Instructions

1. Turn on UV-Vis lamps
   b. Hit “cancel” when asked for login information.
   c. Under the “instrument” tab go to “lamps.”
d. A window will appear with “on” and “off” buttons for both the deuterium and tungsten lamps. Click “ON” for both lamps.

e. Allow lamps to warm up for approximately 45 min. before recording experimental data and be sure to record the time of lamp ignition in the logbook.

f. When all UV-Vis experiments are complete for the day, repeat this process but click “OFF” for both lamps. Record the time the lamps were turned off in the logbook. (NOTE: failing to turn off lamps will result in reduced lamp lifetime and create the need to order and replace these expensive lamps more frequently)

2. Running a sample

a. Please consult the Agilent UV-Vis Chemstation manual at the end of this SOP document for information on setting up standard sample runs as well as kinetics mode runs.

3. Cleaning UV-Vis cells

a. Empty sample solution and rinse the cell thoroughly with the same solvent used for collection

b. Rinse cell thoroughly with DI water.

c. Rinse cell thoroughly with a dilute aqueous solution of HCl

d. Rinse cell thoroughly with DI water once again

e. Rinse cell thoroughly with acetone

f. Place cell in designated oven to dry

(NOTE: small stir bars should be kept in UV-Vis cells while in the oven. Be sure to replace them if they were removed during cleaning process.)

Cryostat instructions:

1. Set-up Cryostat on UV-vis:

a. Open the argon needle valve for the UV-vis purge line and open the bubbler.

b. Purge cell holder with argon, enough to hear a whistle when you place your thumb over the hole. Close the bubbler.

c. Attach hose from the dewar to the UV-vis console. Make sure there are no kinks in the hose.

d. Turn on the cryostat and set to the desired temperature.

e. Fill the dewar with liquid nitrogen.

f. Add sample cuvette and immediately seal with clay.

g. Open the UV-vis purge bubbler.

2. To turn off the cryostat:

a. Take the cuvette out and place the cap back on the sample holder. Close the bubbler.

b. Set cryostat to 25 °C and turn the heater switch on.

c. Begin massaging the transfer line to warm it up.

d. At ~10 °C pinch the transfer line and pull the line off and empty the dewar. NEVER remove the dewar at low temperature.

e. Turn off the cryostat.

f. Turn off the UV-vis argon purge.

Turn on the house nitrogen line (located above the polymer glove box) and open the valve behind the UV-Vis manifold to allow nitrogen to flow through the tygon tubing. Place the tygon
tubing in the UV sample cell holder. This prevents condensation from forming in the cell. Allow nitrogen to flow for at least 30 minutes or until the sample holder is at room temperature. You may leave the nitrogen flow overnight but remember to turn it off early the next morning.

d. FT-IR

These are meant as a reminder to those who have already been trained. Do not use the FT-IR if you have not been trained.

General rules:

12. Keeping a clean bench is everyone’s responsibility.
13. **Filling out the log is mandatory for all users!**
14. Before your work, check that the desired IR accessory (ATR or Transmission cell) is in place and clean prior to use.
15. After your work, clean the bench top and take the sample/solvent with you. Clean the IR plates or ATR accessory. Replace the salt plates in the de
dissicator immediately after use and cleaning.

**Liquid samples:**

1. Salt plates are located above the IR computer in a dessicator. Do not touch them with bare hands or use solvents that will dissolve the plates.
2. We have two cell holders: a tray and a clamp-like holder. Both are in the tray above the IR computer labeled “IR Stuff”.
3. Use the Transmission E.S.P setup for liquid plates. Remove the ATR accessory if the Transmission E.S.P setup is not in place. The OMNIC software will indicate that the experiment has changed from Smart Performer to Transmission E.S.P. Allow the software to perform the diagnostic tests and proceed after the instrument passes them. If the accessory does not pass the tests, please inform someone who is in charge of the instrument.
4. Clean the salt plates in the appropriate solvent and return to dessicator immediately to prevent fouling.
5. If you want to use the solution cells (**ONLY FOR USE WITH AIR SENSITIVE COMPOUNDS**) do not use without training. Contact the person in charge of the solution cells for training.

**ATR accessory guidelines:**

6. Take a background spectrum **WITH THE FOOT UP**. Taking a background with the foot down can damage the Ge crystal.
7. Place only enough sample to form a thin layer on the crystal face. **Be very careful not to touch the crystal face with spatulas.**
8. When lowering the foot, do not over tighten the foot. If the foot is too tight, the Ge crystal can crack and be damaged.
9. Clean the Ge crystal with the provided isopropanol and cotton balls very gently. Do not use Kimwipes, chlorinated solvents or acetone to clean the crystal (they may scratch or dissolve glues within the Ge crystal).
e. GC-MS

These are meant as a reminder to those who have already been trained. Do not use the GC-MS if you have not been trained.

General rules:

1. Keeping a clean bench is everyone’s responsibility.
2. **Filling out the log is mandatory for all users.**
3. Before your work, check the helium cylinder. If the pressure is less than 1000KPa, report it to the person who is in charge of the GC-MS.
4. After your work, clean the bench top and take the sample/solvent with you.
5. **MAKE SURE YOUR GC-MS SAMPLE HAS NO METAL OR H₂O.**

Sample preparation guidelines:

1. Sample components to avoid completely
   a. The following should never be injected: metals or metal complexes, strong acids or bases and salts, water. These classes of compounds are unsuitable for gas chromatography, and can damage the GC column.
2. Overview
   a. Volatile analyte (boiling point < 300°C)
   b. 0.5 – 2 mL in volume
   c. << 100 ppm
   d. Volatile, organic solvent
   e. **FILTER TO REMOVE PARTICULATE MATTER.**
3. Concentration
   a. Mass spectrometry is several orders of magnitude more sensitive than NMR, so please do not use the same samples you have prepared for NMR analysis for MS analysis. The upper limit of concentration needed is 100 ppm. If you introduce a more concentrated sample, you will damage the EI filament. **WHEN IN DOUBT, DILUTE!**
4. Acceptable solvents
   a. Hexane, acetone, and methanol are the recommended solvents for sample preparation. Other acceptable options are benzene and ethers. If in doubt, ask.

f. React-IR

Before Running a Reaction:

**At least three hours in advance:**
(a) Make sure the instrument is on (switch on side).
(b) Test to make sure the purge is on (pinching the tubing running from the instrument to the Y-joint should cause nitrogen to flow through the bubbler).
(c) Cool the probe with liquid nitrogen using the inlet with the black cap on the top of the instrument. (A funnel can be found in the box beside the instrument.) The probe usually requires about one Dewar of liquid nitrogen, and will remain cool for about twelve hours once filled.
Additionally, if you are using the oil bath, turn it on and adjust the temperature as necessary.

**Immediately before beginning your reaction:**
(a) Using the software, set up a new experiment (see below).
(b) Carefully adjust the Teflon joint on the probe so that it is at an appropriate height for your reaction vessel (the tip of the probe should sit in your solvent mixture; if you are using a stirbar, there should be sufficient room to stir). Be gentle with both the probe and the fibre optics cable, and protect the probe tip in your fist when you adjust the Teflon joint.
(c) Remove the black plastic cap from the tip of the probe.

**Setting up a Reaction:**
1.) Open the ReactIR software by clicking on “iC IR 4.1.”
2.) (Optional) Adjust instrument settings by clicking on “Configure Instrument” (located under “Instrument Maintenance” on the start page of the program). Standard settings are acceptable for most uses, but for fast reactions, you may want a narrower spectral width and reduced instrument resolution. The settings you can adjust are listed under “Probe Acquisition Settings” on the first page of the instrument configuration panel. **Do not adjust the other settings.** (By clicking “next”, you will test the probe alignment – see below – and can collect a background spectrum and a water vapor spectrum. A new background spectrum may be desirable if one has not been collected recently; you can ignore the water vapor spectrum.)
3.) Set up a new experiment by clicking on “New Experiment” (on the start page, under “Experiments”).
   (a) Name your experiment and select the appropriate file location for storage. (Note that the instrument parameters are listed on this page – check to make sure they are appropriate.) Click “next”.
   (b) Establish your experiment duration. Click on either the number of scans per hour or the duration of time to adjust the values; click “Add” or “Delete” to add another set of scans. Check the “Manual Selection” box to manually collect spectra (for, e.g., a set of calibrations). Click “next”.
   (c) Collect reference spectra.
      (i) Align the probe. The probe should be aligned already (both boxes should be green); if not, ask Beth for assistance. Note that a dirty or wet probe may appear to be misaligned, so it may be worth trying briefly to clean the probe if you obtain strange results. Click “next” once done.
      (ii) Clean the probe. Boxes will be blue if the probe is clean and dry. The spectrum should give you a flat line, possibly with a slight dip at higher frequencies. This panel essentially subtracts the background spectrum from the current probe reading. If the probe is dirty, positive peaks will be present (see the section on cleaning the probe to correct this problem). Negative peaks indicate the absence of impurities that were present when the background spectrum was collected. In this case, you may want to collect a new background before proceeding (see above under instrument configuration). Alternately, collect a background spectrum on the next panel.
      (iii) Collect a background spectrum. This will be subtracted from subsequent spectra that you collect.
(iv) (Optional.) Collect reference spectra (e.g. of substrate, solvent, etc.). This may be useful during analysis but is not required.
(v) Clean the probe. This should only be necessary if you have just collected reference spectra.
(vi) Collect a background spectrum. This should not be necessary if you’ve already collected on during step (iii). Click “next”.
(d) You should now be at an open experiment window.

To Run a Reaction:
1.) **Attach your reaction vessel to the probe:**
   (a) If your reaction is air-sensitive, turn on the argon tank (located beside the instrument) and purge the vessel with argon.
   (b) Carefully remove the stopper from your reaction vessel and fit the probe into your reaction vessel. The Teflon joint should already be at the appropriate height for your vessel! **Do not try to adjust the joint while your vessel is attached to the probe.** The vessel should fit snugly onto the Teflon joint.
   (c) If you are going to purge your reaction continuously with argon, then wire your septem down (copper wire and wire cutters should be in the blue-lidded box) and insert a needle for purging to prevent excessive pressurization.
2.) **Initialize the reaction by pressing the “Start Experiment” button** on the yellow strip at the top of your experiment page.

When Your Reaction is Completed:
1.) Finish acquiring data by pressing the “Stop” button on the instrument panel.
2.) Remove the probe from your reaction vessel (heating may help if your polymer is very viscous).
3.) **Clean the probe** (see below).
4.) Shut down the instrument and computer:
   (a) Once the probe is clean, place the black cap on the probe tip. The probe sensors are sensitive to light – doing this prolongs the lifetime of the probe!
   (b) Turn off the oil bath and the stirplate.
   (c) Exit the ReactIR program and close the lid of the laptop.

To Clean the Probe:
1.) **Probe cleanliness.** In order for subsequent users to obtain reliable data, the probe must be clean – both free of visible material and free of material in the IR spectrum. **If you are uncertain about whether the probe is clean enough,** start a new experiment and see if residual material is visible, either in the raw spectrum observed during probe alignment or in the background-subtracted spectrum seen during probe cleaning.
2.) **Initial cleaning procedure:**
   (a) First, make sure the majority of the material is gone from the probe. If you are doing a polymerization, it is sometimes easier to warm the polymer up before removing the probe from your sample. There is a provided oil bath for your convenience.
   (b) If there is material on the probe or probe tip, it can often be removed effectively (if slowly) by submerging the probe in an appropriate solvent for several hours or overnight. (Small
stir bars and vials are available in the blue box.) So long as the instrument is not needed immediately, this is an effective way to remove material.

3.) **Follow-up procedures:**

   (a) Wipe the probe tip with acetone. Cotton swabs are provided in the blue box. Alternately, you can dip the probe tip in acetone for the same effect. Let the acetone dry and then examine the ReactIR spectrum to see if residual compound still remains.

   (b) If acetone fails, try another solvent such as THF.

   (c) Finish with acetone – it evaporates quickly. 4.) **Steps of Last Resort:** If the IR spectrum indicates that the probe is still dirty, even after following the steps listed in (2), the following methods should help to finish cleaning the probe:

   (a) Wash the probe tip with warm soapy water.

   (b) Sonicate the probe tip in acetone or another solvent.

**Data Processing:**

1.) Open your experiment, either by finding it in your folder (a shortcut to the experiments folder is on the Desktop) or through the ReactIR program.

2.) Display desired spectra in the spectra window. Under the “Events” window, click the “Events” tab to display a list of all collected spectra. Right click on a spectrum and select “Pin Sample” for it to be displayed in the “Spectra” window. **Do not pin all spectra** if you have a large number of spectra – this may be difficult for the computer to process. Instead, pick a few representative spectra (e.g. at the beginning, middle, and end). The “Surface” window in the lower right shows a 3D representation of all spectra. If you are interested, you can zoom into a narrower window in the “Surface” display by selecting the region in the “Spectra” window.

3.) Measure desired peaks. Under the “Spectra” window, the “Peaks” tab will allow you to quantify the evolution of one or more peaks as a function of time. To specify what to examine:

   (a) **do what to open to that peak?**

   (b) Select your stop and start wavelength.

   (c) For a typical analysis, you will want to look at the evolution of peak height. To do this, under “Group”, select “Height.”

   (d) Baselines often shift over the reaction timecourse. You can compensate by selecting “Height to Two Point Baseline” under the “Type” menu. Then select two points in the baseline around the peak you are examining.

4.) To export quantitative results, go to the “Trends” window and right click on the graph. (If you have multiple peaks, you may need to select all of them in the check-boxes listed underneath the graph before right clicking.) Scroll to “Copy Chart to Clipboard” and select “As Text (Data Only)”. This will allow you to paste a list of peak heights as a function of time into a text file. Note that this does not export any additional information, so you may want to annotate the file to include what each peak measures, what its ranges are, etc.

**Experiment Completion Checklist:**

When your experiment is complete:

[] the benchtop should be clean and free of litter.

[] the probe should be clean (see above).

[] the probe tip should be capped.

[] the ReactIR program should be exited and the laptop closed.

[] your name and experimental information should be recorded in the logbook.
the stirplate should be turned off.

g. **Electrochemistry**

These are meant as a reminder to those who have already been trained. Do not use the electrochemistry setup if you have not been trained.

**General Considerations:**

Remember to sign up on the Tolman lab equipment Google Calendar online prior to use.

Prior to doing electrochemistry, decide the appropriate solvent you want to run your experiments in. Choice of solvent is determined by multiple factors ranging depending on solubility and reactivity of your compound of interest. Also, different solvents have varying solvent windows depending on the oxidative/reductive stability of the solvent. These are discussed in details elsewhere and worth keeping in mind when trying to run experiments or drawing conclusions from them.

It is highly recommended that you use **pure and anhydrous solvents** and **pure compound** for your experiments as electrochemistry is highly sensitive to small amounts of impurities. (If you are using water as the solvent, it is recommended that you use HPLC grade water unless there are some other specific requirements that you have). Also, for electrochemistry in non-aqueous solvents, you will need tetra-$n$-butylammonium hexafluorophosphate as the supporting electrolyte (in some cases you might need more specialized supporting electrolyte like TBA[BArF$_4$] or something else depending your analyte or experiments). For aqueous electrochemistry some recommended supporting electrolytes are sodium perchlorate or hexafluorophosphate. Sometimes you will need to use phosphate or other buffers as the electrolyte. For specific details consult proper resources available elsewhere. **Remember to always use extremely pure supporting electrolyte** (generally recommended that it is recrystallized three times).

**Setting up the equipment and Running Experiments:**

1. Before your work, check that the cells are clean and the working electrodes (Platinum/Glassy Carbon) are polished prior to use. The detailed procedure of polishing the electrodes are described in the booklet kept with the electrochemistry equipment. **Do not polish the electrodes if you have not been shown the proper procedure.**

Note: You could use either the Glassy Carbon working electrode or the Platinum electrode depending upon your preference. The Platinum electrode has a lower surface area than the Glassy Carbon so generally slightly higher concentration of analyte is required for a good signal to noise ratio. However, in some cases the analyte might interact with Glassy Carbon electrode, so you have to use a Platinum electrode in such circumstances. It is worth noting that some types of compounds will interact differently with different working electrode surfaces and you might have to adjust your working conditions accordingly. It is always a good practice to check a new compound first with both working electrodes to check for such cases before you run your experiments in details.

The recommended analyte concentration is generally around 1-2 millimolar, but you might have to adjust this according to your current response. The current response is a function of the nature of the analyte and the solvent. Also, the supporting electrolyte concentration
should generally be kept at least 100 times more than the analyte concentration. This might again need to be adjusted, particularly when using non-polar solvents like tetrahydrofuran and methylene chloride. A discussion of this is available in the booklet by the electrochemistry equipment.

If you are using the Ag wire as the reference electrode remember to clean it first in boiling aqueous hydrochloric acid (3-6 M) and then thoroughly in distilled water and acetone prior to use.

2. Switch on the computer and potentiostat using the power button at the back. Connect the appropriate leads to the electrode (depicted in the diagram below).

3. Open the BASi Epsilon program and open a new experiment. Select the appropriate experiment that you want to run. For more details regarding available experiments and software usage refer to EC Epsilon software manual available online at [www.basinc.com](http://www.basinc.com).

4. It is always advised to run a blank (with solvent and supporting electrolyte) before you run your experiments with the analyte sample. The blank should have no current response within the solvent window. If so, there is some possible contamination in the supporting electrolyte/solvent/cell/electrodes. Re-polish the electrodes thoroughly, use a clean cell again and re-check your blank. If all looks good progress with your experiments with the analyte. If not you might have to re-purify your solvent and supporting electrolyte. Electrochemistry experiments run with contaminants/residual responses from the background are often misleading and erroneous.

5. Depending on your experiment choice, particularly when running electrochemistry outside the glove-box, you might need to degas your solvent in the cell. This is primarily done in order to get rid of any dissolved oxygen in the solvents as oxygen has an intense reductive response which corresponds to its one/two electron reduction event (the position and nature of this feature is a function of the solvent of choice). This intense reductive feature will in most cases suppress any reductive features for your analyte. 

   *Note:* It is always strongly recommended to degas your solvents before your experiments. The only exception to this would be if you are trying to utilize the dissolved oxygen in the solvent for some studies.

6. After your work, clean the cells using a similar procedure as any other used glassware. Then rinse thoroughly with Acetone and store the cells in the designated oven in the CV cell tray.

7. After you are done using the setup, remember to **thoroughly wash the electrodes with your solvent and then acetone.** Any solid deposited on the working electrode will **damage the electrode permanently if not cleaned immediately.** When in doubt about the electrode, always polish it.

8. After you are done using the setup, remember to **switch off the potentiostat and unplug the**
setup and return the cart and all other equipment to the appropriate place.
9. If you need to use the electrochemistry setup in the glove box, you must speak with the users of the glove box that holds the electrochemistry setup (Bioinorganic Glove-box 2) before using the electrochemistry setup inside the glove box. Users are responsible for bringing in their own solvent, syringes, and needles when performing experiments inside the box. Any items brought in for such experiments must be clean and dry. Also, after you are done running, be courteous enough to clean up the mess. Generally a lot of waste is generated when running electrochemistry inside the box, so it is advised to bring in extra vials/trays to bring the waste out at the end of the experiments. Also it is advisable to purge the box before running any new experiment. Running electrochemistry inside the glove-box requires time and patience to assemble the setup, so please remember to plan accordingly. Also, if possible coordinate with other potential users so that time required for the setup is minimized.
10. Additionally, the reference electrode used inside the glove-box is the standard non-aqueous reference electrode that needs to be assembled every time prior to use. The procedure to assemble this is described in the manual kept alongside the electrochemistry equipment. Again, do not try to do this unless you have been previously trained at doing it. Also remember to dis-assemble it after usage.
11. Also, when running electrochemistry inside the glove-box remember to bring in extra pair of X-Large gloves. These must always be worn inside on top of the gloves to prevent any sort of cross-contamination of the electrochemistry equipment.

Note: These instructions are meant to be a refresher for someone who is already trained to use it. Please do not use the equipment unless you have been trained by the person in-charge of the electrochemistry set-up in the group. Also, when in doubt please ask other users who have been trained and consult the online resources at www.basinc.com. Additionally there are also a lot of extremely helpful resources available elsewhere.

h. Rotary Evaporators

There are three rotovaps (one in 265, and two in 263), and all function in the same basic way. Inspect your glassware prior to using the rotovap for star cracks and defects. Placing cracked glass items under vacuum presents an implosion/explosion hazard.
1. Plug in and turn on the power strip associated with the rotovap.
2. Turn on water for aspiration and fill the water bucket with ice so that the water in the condenser is cold. If you do not cool your water, you will have problems removing solvent from your flask. Refill the ice in the bucket as needed.
3. Turn on power of rotovap (usually on the rotovap itself). Be sure a bump trap and solvent trap are attached to the rotovap.
4. Make sure solvent trap is empty (if not, contact the previous person who used the rotovap, punch them in the arm and ask them what was in the trap. Dispose of the waste in an appropriate waste container).
5. Attach your flask to the bump trap, turn on rotation and close the valve so vacuum is attained.
6. After solvent removal is finished, MAKE SURE THE ROTOVAP IS CLEANER THAN YOU FOUND IT. If you dirty the rotovap and don’t clean it up, you are a horrible person. Rinse the bump trap in the appropriate solvent to remove residues and prevent contamination for future users.
7. Dismantle the rotovap (turn off rotovap itself, shut off water, shut off power strip).
i. Fisher-Porter Bottle

**General Use and Guidelines**

The Fisher-Porter Bottle is a high pressure reactor made out of heavy walled borosilicate glass which is coated with polymer for added safety. The mouth of the opening fits an O-ring lined metal coupling, which is clamped in place with a two piece screw cap (Figure 1).

**Figure 1.** Diagram showing the Fisher-Porter bottle along with the correct orientation of the necessary connector pieces.
The coupling is connected via Swagelok fittings to the gas plumbing (Figure 2), which also includes a pressure gauge and a pressure release valve (safety valve) which will vent if the pressure in the bottle exceeds the set pressure of the valve. Currently this valve is set to 100 psig. The bottle can withstand a maximum pressure of 225 psig at room temperature. At higher temperatures, the maximum pressure decreases at a rate of 0.25 psig/°C.

In general, the bottle can be used for a variety of high-pressure reactions. The reaction volume should never exceed 75% of the total volume of the bottle (), and should be kept at a minimum whenever possible. It is crucial to remember that the pressure in the bottle at room temperature will increase when heated, and this is especially important if you are heating your reaction above the boiling point of your solvent.

**Specific Safety Precautions**

THE OBVIOUS DANGER OF USING ANY HIGH PRESSURE REACTOR IS THE RISK OF EXPLOSION. THIS VESSEL MUST ALWAYS BE USED IN A CLOSED FUME HOOD WITH A BLAST SHIELD FOR ADDED SAFETY. ALWAYS NOTIFY YOUR LABMATES WHEN YOU’LL BE RUNNING A HIGH PRESSURE REACTION.

THE BOTTLE MUST NEVER BE PLACED IN A BASE BATH AND SHOULD NOT BE STORED IN THE OVEN. DRYING OF THE VESSEL IS BEST DONE WITH A HEAT GUN AND MUST NEVER BE FLAMED DRIED.
Setting Up and Taking Down a Reaction in the Fisher Porter Bottle

1. CONNECT THE VALVE HEAD TO THE APPROPRIATE GAS CYLINDER USING THE BRAIDED HOsing.

Note: Depending on the reaction, you may need to purge the bottle with inert gas prior to introducing your gaseous reagent (e.g. H₂ gas for hydrogenations), which will mean that at some point you will have to switch gases during the reaction.

2. CONNECT THE BOTTLE TO THE METAL COUPLING FULLY SEATING THE O-RING IN THE MOUTH OF THE BOTTLE FOLLOWED BY SECURING THE COUPLING WITH THE SCREW CAP.

Note: Ensure that the cap is screwed as tight as you can possibly get it (get some help if you need it) as this will prevent leaking over time. Teflon tape can also be used to help ensure a good seal, which can be checked using SNOOP once the bottle is pressurized. It is normal for the screw cap to be able to rotate around the bottle. Also, depending on your reaction, you may want to load your DRY reagents in the bottle prior to connecting the bottle to the valve head. Alternatively, these can be added as solutions using a syringe through the top valve (V2 in Figure 2).

3. CLOSE V2 AND OPEN V1 AND V3. ENSURE THAT THE BLAST SHIELD IS PROPERLY IN PLACE. (PERFORM AFTER STEP 4 IF VESSEL CONTAINS AIR-SENSITIVE COMPOUNDS).


Note: Adjustment of the output pressure on a gas cylinder must ALWAYS be done under conditions of active gas flow (i.e. with the system open to atmosphere). This is why V1 is left open in the previous step. However, if the bottle is pre-loaded with air-sensitive compound, then V1 can be opened after the gas cylinder has been opened in order to protect the atmosphere in the bottle.

5. CLOSE V1; THE BOTTLE SHOULD BECOME PRESSURIZED. CHECK FOR LEAKS AROUND THE SEAL BETWEEN THE BOTTLE AND THE VALVE HEAD USING SNOOP.
6. CRACK OPEN V1, SUCH THAT THE BOTTLE IS VENTED AT A HIGH PRESSURE (e.g. IF PRESSURE IS SET TO 100 PSI, OPEN VALVE SO THAT THE PRESSURE GAUGE ON THE BOTTLE READS 70 PSI). DO THIS FOR 10-15 MIN TO FULLY PURGE THE BOTTLE OF ANY GAS WITHIN THE BOTTLE.

Note: Depending on the reaction conditions, this step may be omitted. If for example, the bottle was loaded in the glovebox, this step may not need to be performed. Also, if there are solid reagents already present in the bottle, the venting pressure may need to be adjusted so that these are not blown out of the bottle.
7. CLOSE V3; ALLOW THE BOTTLE TO STAND FOR 15-30 MIN IN ORDER TO CHECK FOR SIGNIFICANT LOSS OF PRESSURE DURING THIS TIME.

Note: It is in general better to do this over a longer period of time (overnight), and these longer term pressure checks should be performed periodically. In general, as long as the coupling is screwed tight and the O-rings are still in good shape this shouldn’t be a major problem.

8. AT THIS POINT SOLVENT/REAGENT SOLUTIONS CAN BE ADDED TO THE VESSEL THOROUGH V2 USING A SYRINGE. VENT THE SYSTEM BY OPENING V1 UNTIL THE PRESSURE IN THE BOTTLE IS CLOSE TO 0 PSIG, AND THEN CLOSE V1 (THIS IS DONE TO ENSURE THAT THE SEPTUM ATOP V2 DOES NOT SHOOT OFF). OPEN V2 AND QUICKLY ADD YOUR SOLVENT/REAGENT SOLUTION(S) AND CLOSE V2. OPEN V3 AND ALLOW THE BOTTLE TO PRESSURIZE.

Note: If the system is especially air sensitive, the addition of reagents can be done under an active gas flow. In this case, the input pressure (controlled by the regulator) will need to be reduced, such that the rubber septum placed atop V2 (see Figure 2) will not shoot off. This can be further controlled by adjusting the flow rate of the gas using the needle.

**Figure 4.** Diagram showing Fisher-Porter pressurized to 100 psig. Note all three valves are closed.
valve. The above steps can then be performed as described, only with V3 open the whole time.

9. THE REACTION IS NOW READY TO PROCEED. AT THIS POINT HEATING CAN ALSO BE DONE.

10. WHEN THE REACTION IS COMPLETE, ALLOW TO COOL TO ROOM TEMPERATURE (IF HOT) AND VENT THE VESSEL COMPLETELY BY OPENING V1.

Note: Again, if the reaction is still air-sensitive at this point, the contents of the vessel can be transferred via canula to a Schlenk flask using the septum on V2 by reducing the input gas pressure as described above in step 8. Alternatively, the bottle, connected to the valve head assembly, can be disconnected from the gas cylinder (AFTER THE TANK AND REGULATOR HAVE BEEN CLOSED) and pumped into the glovebox for further disassembly.

11. WHEN FINISHED WITH THE BOTTLE, RINSE WITH ORGANIC SOLVENTS, FOLLOWED BY WASHING WITH SOAP AND WATER. AIR DRY, OR DRY USING THE HEAT GUN AND STORE AT ROOM TEMPERATURE.

j. Laboratory ovens

Each person has one glass tray in an oven near his or her hood. Please do not change the temperature of the ovens. Only glass or metal materials should be placed in these ovens. Stir bars and frits are fine as well. NMR tubes should not be stored in the oven – if you want to bring them in the glove boxes, heat them for only 1 hr to prevent warping of the tube. Gas tight syringes should NEVER be placed in the oven. There is a high temperature oven in 263 for UV cuvettes and other common glove box materials – do not use this oven for personal glass storage. Do not hoard large amounts of glassware in your tray.

k. Other Resources

- “Safe Chemical Manipulations Using a Schlenk Line” – Tilak Chandra and Jeffrey Zebrowski, U. W. Madison (posted on in the “Tolman Lab Documents” Google Drive folder)

VIII. Emergency Response

The proper response to an emergency situation is essential. An inappropriate response can lead to a situation far more hazardous than the original emergency. Some, though not all, chemical spills and fires will require outside assistance. The following sections are intended to provide guidance in emergency response. For smaller, lab fixture related emergencies (hoods, sinks, electricity, etc), please contact the Director of Operations for the Chemistry department. Currently, this
person is Chuck Tomlinson (612-624-2321, chuck1@umn.edu).

a. Evacuation

The building emergency alarm system can be activated in the event of an emergency requiring building evacuations such as a fire or major chemical spill. Any time the building alarm sounds, evacuation of the building is mandatory. If there is no alarm sounding but a police, fire or haz-mat official tells you to evacuate you are required to leave the building. Failure to evacuate when requested by authorities can result in arrest. Evacuate by the nearest exit and stay off of the elevator. Move away from the building. Do not return to the building until the police, fire official, or a member of the haz-mat team gives the all clear.

b. Fires

Fires in areas where there are chemicals are potentially very dangerous. Besides the rapid spread of fires in areas where there is a large quantity of stored chemicals and the potential for explosions, there is always the possibility of producing highly toxic unknown vapors during chemical fires. Approaching chemical fires must always be done with extreme caution. While it is University Policy that personnel are not required to extinguish fires, appropriately trained personnel may attempt to extinguish fires under certain conditions. All Chemistry Department laboratories are equipped with dry chemical extinguishers and most laboratories are also equipped with carbon dioxide extinguishers. Personnel should only attempt to extinguish fires under the following conditions:
1. if it is safe to do so.
2. if the person know how to use a fire extinguisher.
3. if the appropriate fire extinguisher is available.
4. if the fire is small and isolated.
5. if the person is familiar with the hazards in the area.
6. if there is no possibility of being exposed to toxic fumes.
7. if there is no potential for explosions to occur.

Use and Types of Fire Extinguishers

There are different types of fire extinguishers available. Not all fire extinguishers are suitable for all types of fire. Be sure you are using the proper extinguisher for the type of fire. In attempting to extinguish a fire make sure that it is safe to do so and remember that an extinguisher is only a first aid tool and should not be used to control large fires. Fire extinguishers are intended for small isolated fires only. The extinguisher only has about 10 to 30 seconds of spray and is only effective over a short distance of about 5 to 10 feet. In using a fire extinguisher, make sure that the exit is always within reach. Be careful not to trap any persons on the other side of a fire. It is best to have more than one individual present when attempting to extinguish a fire. Do not take any chances. It is helpful to remember the acronym "P.A.S.S." when using an extinguisher.

P Pull the Pin
A Aim at the base of the flames
S Squeeze the trigger while holding the extinguisher upright
Sweep from side to side

Whenever a fire extinguisher is discharged it should be inspected and recharged. Discharged fire extinguishers must be taken to the Departmental Stockroom for replacement. Facilities Management inspects and tags fire extinguishers annually. Individuals are not required to fight chemical fires and have the right to call 911 and activate the building alarm.

**Emergency Response to Fires**

If there is a fire in an individual's laboratory or work area, the first concern should be for the safety of all individuals in the area. The area should be evacuated immediately regardless of who attempts to extinguish the fire. In the event of a fire:

- Remove all personnel from the area of immediate danger.
- Attend to any victims only if it is safe to do so.
- Confine the fire by closing all doors and windows to the area.
- From a safe area DIAL 911. Inform the emergency operator where the fire is and whether there is smoke odor, visible smoke or visible flames. Inform the operator of other hazards in the area.
- Active the building alarm at the nearest manual alarm station.
- Only attempt to fight the fire if it can be done safely.
- Report all fires to the main office, 139 Smith, 4-6000.
- Evacuate the building by the nearest exit.

**c. Chemical Spills**

It is always possible for a chemical spill to occur in a laboratory even when following all the chemical hygiene rules and working safely. Most of the time, spills in the laboratory involve relatively small quantities of materials. However, even small amounts of highly toxic or highly reactive materials can be life threatening and dangerous. Some spills can be cleaned up by laboratory personnel. However, there are a number of circumstances which indicate that outside assistance should be requested. If there is a chemical spill in the work area or if a spill is discovered in another area, the first concern should be for the safety of all individuals. Regardless of the size of the spill, all persons in the vicinity of the spill should evacuate the area. Notify any neighbors that there has been a chemical spill. If any one has been injured, remove them from the spill area if it can be done safely. Do not enter an area where there are toxic gases or vapors. If a person cannot evacuate an area where there has been a spill call 911 immediately. Confine the spill as best as possible without exposing any persons to fumes. As the area is evacuated, shut off any electrical equipment if it is safe to do so. If possible establish exhaust ventilation and open windows. Be sure to vent fumes only to the outside of the building. Close the fire doors as this will help to confine the spill. After individuals have been evacuated and the spill confined, it will be necessary to assess the situation and decide if outside assistance should be requested or if it is safe for laboratory personnel to cleanup the spill. Caution should be used in making this judgment.

**Assessing the Spill**

Laboratory personnel can cleanup low hazard level spills. Low hazard level spills are those spills
that do not spread rapidly, do not endanger people and do not endanger the environment. All other spills are high hazard level spills and require outside assistance. The existence of a number of conditions indicate that outside assistance should be requested as suggested below:

- spills involving medical treatment – CALL 911
- spills involving fire or explosion hazards
- spills that are potentially life threatening
- spills occurring after hours CALL EHS(626-6002)
- all spills larger than one pint (half liter)
- spills involving any amount of highly reactive or toxic material
- all metallic mercury spills
- spills involving unknown materials
- spills for which you do not have the proper training or protective equipment
- spills for which you have any questions or doubts

If none of the above conditions exist, the spill can be cleaned up by laboratory personnel. Otherwise call either 911, or EHS as outlined above. In either case, inform the main office (4-6000). An incident form must be filled out for all spills regardless of who cleans it up.

**Reporting the Spill**

When reporting a spill to 911 or EHS, information about the situation will be requested. This information is necessary so that a proper assessment of the spill can be made and includes:

- name, telephone number and location
- location, time and type of incident
- name and quantity of material involved
- extent of any injuries
- possible health and environmental hazards
- other hazards in the area such as large quantities of stored chemicals, radioactives, biohazards etc.
- safest route of approach to the incident

While waiting for emergency responders, the spill area will have to be secured. Block off entrances to the area by both locking doors and posting signs, taping or roping off stairwells and elevators or posting staff by commonly used entrances. Any persons securing the area must remain at a safe distance from the spill.

**Release of Toxic or Explosive Material**

In the event of a release of toxic or explosive materials, it is best to evacuate the entire building. For example, if an individual is working with any of the inhalation hazards given on the prior approval list and there is a release the building should be evacuated. These materials are highly acute toxins and can be life threatening. Any spills of volatile highly acute toxins which cannot be confined (for example, in a hood) also require building evacuation. For releases of toxic or explosive materials or for any situation that in one's professional judgment requires total evacuation, the immediate area should be evacuated and from a safe area call 911 and activate the building alarm. The emergency should be reported to the main office, 4-6000.
Chemical Spill Cleanup

For high hazard spills either EHS or the fire department will clean up or stabilize the spill. High hazard spills are those which present fire, health or reactivity hazards. If assistance has been requested from EHS, and it has been determined that the spill can be safely cleaned up by laboratory personnel, they will provide advice on how to safely clean up the spill. When cleaning up a low hazard spill the proper clean up procedure must be known. If experimental work has been properly planned, this information should be readily available. The appropriate personal protective equipment should be worn and any hazardous waste should be disposed of appropriately. The following guidelines are intended to aid in chemical spill cleanup:

1. The spread of dusts or vapors can be prevented by closing the laboratory door and increasing the ventilation (for example, through the fume hood).
2. The spread of a liquid spill can be controlled by making a dike around the edges of the spill using absorbent materials such as vermiculite or spill pillows.
3. Special absorbents are required for some chemicals such as hydrofluoric acid and concentrated sulfuric acid.
4. If flammable liquids are spilled, remove all potential sources of ignition if it can be done safely.
5. In cleaning spills involving direct contact hazards, select personal protective equipment resistant to the chemical. It is a good idea to wear two sets of gloves.
6. Acid spills can be neutralized with soda ash or sodium bicarbonate.
7. Base spills can be neutralized with citric acid or ascorbic acid.
8. Cleanup residues should be placed in a plastic bucket or other suitable container and disposed of through the Chemical Waste Program.

\textit{d. Power Outage}

While a power outage is generally not thought of as being an emergency, hazardous situations can develop if there is a loss of power. When there is a power loss, fume hoods and the ventilation system will not necessarily function properly. If one is in the process of an experimental procedure and there is a power outage, there is the risk of toxic vapors accumulating. The situation can easily become hazardous. In the event of a power outage:

1. Place gloveboxes on emergency power.
2. Close fume hood sashes. No work is allowed in fume hoods.
3. Be certain that the caps are on all bottles of chemicals.
4. All non-essential electrical devices should be turned off.
5. Explosion proof refrigerators and freezers should be left on.
6. The doors of refrigerators and freezers should be kept closed.
7. Turn off all gas cylinders at the tank valves.
8. Check all cryogenic vacuum work, distillations and glove boxes used for airless/moistureless reactions and all reactions in progress.
9. All non-essential staff and students must leave the building.

\textit{e. Injury}

In the event of an injury:
1. If the injury is minor, students should go to the Boynton Health Service and employees should go to the Hospital Emergency Receiving Room, ACCOMPANIED BY ANOTHER PERSON.

2. In case of serious injury, DIAL 911 and describe the injury and your location. Report injuries to the Front Office, 139 Smith 4-6000 and to Professor Tolman 5-4061.

_f. Emergency Calling Tree_

In the event of an emergency (power outage) during off-peak hours (later in the evening or on weekends) the calling tree will be used. It is everyone’s responsibility to utilize the calling tree if an emergency occurs in the lab that will affect gloveboxes and instrumentation.

_g. Emergency Lab Map_

- A = Eye-wash station
- B = First Aid Kit
- C = Safety Shower
- D = Fire Extinguisher
- E = Emergency Gas Shut Off
- F = Water Shut Off (on the ceiling)
- G = Emergency Phone Numbers