Shaughnessy Group Procedures--Drybox, vacuum lines, and stills

Drybox:

The drybox is critical to the success of your and all of your labmates research. It is crucial that you follow the procedures below to ensure that you do not harm the box. Before using the drybox for the first time you must be trained by Dr. Shaughnessy or the group member in charge of drybox maintenance.

1. Entering the Drybox

- The resting state for the box is as follows: Both antechambers should be under vacuum (active or static), the circulator should be on, the purge valve should be closed, and the auxiliary vacuum valve should be closed. The main vacuum pump should never be turned off except for service. When you arrive at the box you should ensure that this is the case unless someone is using the box. When you are finished using the box you must ensure that you leave it in its resting state condition.
- All items taken into the box should be dried if possible. Glassware should be left in an oven for a minimum of 30 minutes and then taken directly to the antechamber. Porous items, such as wood and paper, should be dried overnight if possible. These should be pumped down overnight before taking into the box. Plasticware should also be dried if possible, but be sure that the item is autoclavable before placing in the oven.
- Any closed flask that is to be taken into the box must be sealed under vacuum before taking into the box. This is particularly necessary if the flask has any ground glass joints, which tend to fail under vacuum in the antechamber. Solvent bombs are designed for this purpose and do not need to be evacuated. NMR tubes general are OK, although it is best to secure the plastic cap with parafilm to ensure it does not pop off. Ampoules and bottles of chemicals which are to be taken into the box directly after receiving from the distributor do not require special precautions if it is already under a nitrogen or argon atmosphere. If the bottle has been opened in air, or if you are unsure if it was sealed under nitrogen, take off the cap and cover the mouth with aluminum foil or a kimwipe held on by a rubber band to prevent the material from spilling.
- Use of the large antechamber: Since the large antechamber is rarely used, it should be left under static vacuum. To bring an item into the box with the large antechamber, first close the valve to the small antechamber. Next evacuate the large antechamber to remove any residual air due to leaks (using the ante evac button on the control panel). When the antechamber has been completely evacuated, refill the antechamber using the ante refill button on the PLC panel. Open the exterior door and place your item(s) in the antechamber. Evacuate and refill the antechamber 3 times using the buttons on the console. The antechamber should be left under vacuum for a minimum of 5 minutes in each cycle. After 3 evacuate/refill cycles, you may open the interior door and bring your items into the box. To bring an item out of the box through the large antechamber, repeat the above process. When finished with the antechamber be sure to evacuate it. When the evacuation is done, turn off the active vacuum to the large antechamber (ante evac button) and reopen the small antechamber to active vacuum.
- Use of the small antechamber: Before using the small antechamber, ensure that the large antechamber is not open to vacuum. The small antechamber should be under active vacuum when you start. To bring an item into the box, refill the antechamber and insert your items. Evacuate and refill the antechamber 3 times. Make sure your evacuation cycle is long enough to achieve full vacuum--you should wait 30 sec after the gauge has stopped moving before refilling. After 3 cycles you may open the interior door and bring your items into the box. To remove something from the box, make sure the antechamber is under active vacuum. If it is not, evacuate and refill 3 times. Open the interior door and insert your items. Close the interior door, open the exterior door, and remove your items. Close the antechamber and evacuate it. Leave the antechamber under active vacuum.

2. Use of chemicals in the box.

- **Volatile chemicals will degrade our analyzers and catalyst likely resulting in expensive repairs and poor box performance. If possible, please avoid the use of volatile chemicals, particularly ethers, amines, and chlorinated solvents in the box. Except on the most sensitive of compounds, most solvent manipulation can be accomplished using schlenk line techniques. It is vital that proper precautions be taken when using any volatile chemical (bp < 180 ˚C)**. Before using volatile chemicals, the circulator should be shut off (button on PLC panel). When finished using volatile chemicals purge the box for 30 minutes to allow the vapors to be fully removed. To purge the box, partially open the valve on top of the box near the antechamber until the box pressure is ca 0.5 mbar. After 30 minutes or more, close the purge valve and restart the circulator. **While purging the box should not be used. If you must use the box, close the purge valve until you are finished. If the box pressure drops below zero while the purge valve is open (i.e. when removing your hands), air will be drawn into the box.**
- Storage of volatile chemicals in the box. Storage of volatile chemicals, particularly ethers, amines, and chlorocarbons should be avoided if possible. Any vessel used to store volatile solvents (including hydrocarbons) must have a tight seal. A Teflon to glass seal is preferred (i.e. a bomb). For larger volumes of solvent, a glass jar with a poly-seal cone lid should be used. **Evaporation of solvents while the circulator is running will damage the oxygen analyzers and the catalyst bed**.
- Before taking any liquids into the box, they should be degassed. Volatile solvents (see above) must be freeze-pump-thawed before taken into the box unless they are taken directly off the still using the solvent bomb. Nonvolatile liquids should be placed in a flask which is then evacuated and refilled several times. On the final cycle leave the flask under vacuum and take it into the box. Purchased reagents in small bottles can be taken directly into the box.

3. Working in the Box

- Gloves**:** The gloves on the drybox are the area of the dry box most prone to failure. Extreme caution must be taken to ensure that the gloves are not compromised. Before inserting your hands into the gloves, take off any jewelry with sharp edges (rings, watches, bracelets, etc.). For ease of entry, powder your arms and hands with corn starch or baby powder. Slowly insert your hands. Rapid movements should be avoided as they can over- or underpressurize the box, or in extreme cases tear the gloves. When working in the box, be careful to not cut or puncture the gloves on sharp edges (i.e. needles, knives, glassware). Also be careful when using clamps or opening and closing the antechamber doors, as the gloves can be pinched and cut in these cases. **If you feel you may have cut or punctured the gloves, carefully examine them. If there are any holes, the gloves must be replaced or patched (see below).**
- While working in the box, keep the interior antechamber doors closed, unless you will be going out immediately after entering. This will ensure that the outer door is not accidentally opened while the interior door is open.
- Internal vacuum system. Our box is equipped with an internal vacuum source. This must be treated just as your vacuum line (see below). If you are the first person to use the vacuum that day, use the following procedure. First clean out the cold trap and then reattach it to the trap assembly. Start the vacuum pump and turn the stopcock so the vacuum is open to the box and not to vent. Fill the Dewar with liquid nitrogen. Use the foot pedal to open vacuum valve to the drybox. Use the vacuum as needed. If you are the last one to use the vacuum that day (or the last one to leave at night) you must turn off the vacuum using the following procedure. Make sure the foot pedal-controlled valve is closed (the foot pedal clicks upon opening the valve, there is no sound when the valve is closed. There is a light on the valve

which indicates if it is open). Lift the cold trap out of the liquid nitrogen. Turn the stopcock so the pump is open to the atmosphere and turn off the pump. Allow the cold trap to warm to room temperature and then pour out any collected solvent in an appropriate waste container.

- When finished working in the box, clean up the work area. Return all chemical vials, tools, etc to their proper place. All dirty glassware should be removed from the box for disposal or cleaning. All trash can be deposited in the trash can in the box, **unless it is contaminated with even moderately volatile chemicals**. Contaminated trash should be removed from the box. Use the dustbuster to vacuum up any powders that have been spilled.
- After removing your arms from the box, wipe down the gloves to remove sweat and corn starch.
- Remove your items from the antechamber and leave the antechamber under vacuum.

4. Emergency procedures.

- Over/Underpressure: The drybox is equipped with sensors to shut down the box in the case of a dangerous over or underpressure situation. If these fail do the following:
  - Overpressure: Open the purge valve slowly to release pressure. Determine why the overpresurization is occurring. Most likely this will be due to failure of the solenoid controlling box pressurization and/or the regulator on the house nitrogen line.
  - Underpressure: Make sure that both antechambers are closed to vacuum. If underpressurization is still occuring, the high pressure solenoid is likely stuck in the open position. Gently tap on this to get it to close. If you cannot achieve this, turn off the vacuum pump and repair the solenoid.
- Power failure: If the building loses power, the drybox should be shut down to prevent power surges from damaging the box. Turn off the vacuum pump and release the vacuum by refilling the small antechamber and then turning the valve to evacuate with the pump off. Repeat until the vacuum is released. Turn off the circulator and freezer. Pressurize the box as much as possible. Turn off the main power switch located on the back of the box under the antechamber. Unplug the main box power cord and the cords to the internal power strips. Finally close the needle valve on the nitrogen line.
- In case of fire or tornado, turn off the box using the above procedure is this can be accomplished safely. Do not endanger yourself to protect the box.

Vacuum/Nitrogen lines:

Next to the drybox, your most important piece of equipment is your line. This is a sensitive piece of equipment and must be treated accordingly.

2. Stopcocks: Proper care of your stopcock's is the key to achieving a good vacuum. Stopcocks should be cleaned and regreased on a regular basis. If they become stiff and hard to turn, you are more likely to turn too hard and snap off the stopcock. Note that the stopcocks are numbered. You must be careful to put the correct plug in each stopcock whenever cleaning them. They are custom made to fit in a specific stopcock and will leak if interchanged. Your stopcock's should always be kept turned so that the bulb at the back of the stopcock is under active vacuum. Each stopcock plug has a small hole in the back which when placed in line with the vacuum line will evacuate this bulb helping to hold the plug in tightly.
3. Dewar Flasks: You must always be careful when using Dewar flasks. They are under internal vacuum and can implode unexpectedly. **Therefore always handle Dewar flasks gently.** Always wear safety glasses when adjusting them or adding liquid nitrogen to the dears. All Dewars used in the lab must be shielded either by a metal casing, plastic matting, or electrical tape. See below for cautions about handling liquid nitrogen.
4. Vacuum pump: Vacuum pumps are expensive somewhat delicate pieces of equipment. You must never allow solvents to pumped into the vacuum pump. If this does happen, immediately shut off the pump and change the oil. Always have sufficient liquid nitrogen in the cold traps before exposing any flask containing volatile materials to the vacuum system.

The oil in your vacuum pump should be changed every 3 months or when exposed directly to solvents. Reaction flasks which may contain corrosive gases, such as HX, halogens, or volatile metal chlorides, should not be pumped on unless a suitable trap is placed in line to protect the pump.

5. Nitrogen line and mercury bubbler. Adjust your nitrogen flow to give slow, gentle bubbling in the mercury bubbler for general use. Be sure to shut off the flow when you are not using your line. While we do not pay directly for house nitrogen, yet, it costs the department money if you leave your line bubbling nitrogen all night. Be careful when opening evacuated flasks to the nitrogen line, particularly very large flasks (> 500 mL). Open the stopcock slowly so the mercury does not rise too fast. While we have float valves to prevent Hg from overflowing, it is still best to be careful.

Solvent Stills.

The group has 6 continuously operating solvent stills with the common solvents toluene, THF, ether, benzene, pentanes, and methylene chloride. The THF, benzene, and pentane stills are over sodium/benzophenone, while the methylene chloride is dried over calcium hydride. Toluene is reluxed over sodium alone. Small stills for other solvents will be set up as necessary. A still containing large amounts of drying/deoxygenating agents and flammable liquids is a potentially dangerous situation if not treated properly. Carefully follow the procedures described below when using the stills.

- Before using the stills for the first time get trained by Dr. Shaughnessy or the group member in charge of the stills.
- Stills will be maintained by one group member. That person will be in charge of ensuring the stills are in good condition and regenerating stills as necessary. If you think a still needs more sodium or benzophenone consult with the person in charge of the stills.
- In general, stills are kept at a temperature below reflux when not in use. The water flow should never be turned off. If there is interruption in the water flow, all the stills should be shut off and allowed to cool to room temperature.
- To collect solvent. Assuming the still is not at reflux.
    1) Ensure that there is enough solvent for the amount you need to collect. If there is any doubt add more solvent (see below).
    2) Increase the flow rate through the bubbler to give a moderate stream of bubbles.
    3) Turn the variac to the appropriate voltage.
    4) Allow the solvent to reflux for the necessary amount of time. For sodium/benzophenone stills the solvent should be refluxed until the color is dark purple. If the still is purple when you start, allow it reflux for an hour or so. For calcium hydride stills a couple hours is sufficient if new solvent has not been added. After adding new solvent, the still should be refluxed for several hours or overnight.
    5) After the solvent is ready, close the drainage valve and collect the necessary amount of solvent.
    6) Once the solvent has collected, turn off the variac. You may remove the solvent in three ways. If you are taking the solvent into the box, use the solvent bomb after allowing it purge with nitrogen for at least 20 minutes (increase the nitrogen flow rate if purging). To remove small amounts of solvent use a syringe. A cannula can be used to transfer larger amounts to a flask. Use the extra nitrogen line to purge your flask before adding the solvent (depending on the sensitivity of your reaction).
    7) Once you are done collecting solvent, drain the remainder back into the pot (if there is a significant amount still collected, ask if anyone else will need that solvent). Be sure to increase the nitrogen flow before draining the solvent. Since the collected solvent is cool, it will rapidly cool the pot temperature, resulting in a sudden decrease in pressure. If the nitrogen flow is not high enough, the bubbler oil will be sucked into the nitrogen line. Slowly drain the solvent while watching the bubbler. If the oil starts to rise in the bubbler, increase the nitrogen flow (or slow the drainage rate).
    8) When you are done, turn the variac to the low setting.

- **You must never allow a still to run dry**. When the still level is low, you must refill it before collecting more solvent. Be a good lab-mate. If you distill off most of the solvent, refill the still allow to reflux for several hours.
- To refill the still: Always use a fresh bottle of solvent to refill the still. Turn the nitrogen flow up and remove the flask stopper. In general you should add all of a 4L bottle of solvent when refilling the still. Do not overfill the still however. The solvent level should remain below the base of the lower ground glass joint. Allow the still to reflux for an extended period after refilling.
- Before adding drying/deoxygenating agents to the stills consult the person in charge of the stills. Since the performance of calcium hydride stills cannot be monitored, they should be cleaned on a regular basis (every 6 months). Particularly for sodium/benzophenone stills adding more sodium or benzophenone should not be the first option and can actually worsen still performance. If after a long period of reflux (> 8 hours) the color does not turn to purple you may need to add fresh sodium or benzophenone. If the still appears black or brown, first try adding small amounts of benzophenone. The color should turn blue or purple. Adding too much benzophenone will just result in tar formation from its decomposition. If the still is green or blue, but will not turn purple (or benzophenone addition had no effect), add fresh sodium. Wipe off excess oil from the sodium and cut small pieces of sodium at the mouth of the flask under strong nitrogen flow to give a fresh sodium surface. Add a few grams of sodium and allow to reflux for several hours before adding more. If two additions do not result in any change, and its been several months since the still was last regenerated, it is time to regenerate the still.
- Still regeneration (sodium benzophenone).
    1) Distill off most of the solvent (save this for refilling the next still) until only 500 mL or so are left. Lift the solvent head off and cap it with a small flask under nitrogen flow. If the still head is dirty this is a good time to clean it in the base bath.
    2) Take the flask to another hood and use hexanes to transfer the material in the flask to a large beaker or bucket (4 L preferably plastic). Transfer as much of the residue at the bottom of the still as possible. Place 200 mL of hexanes in the flask and add isopropanol to destroy any remaining sodium.
    3) Slowly add small amounts of isopropanol to the beaker. You should observe gas evolution. Add isopropanol at such rate that only slow bubbling is observed. This may take several hours.
    4) When no more sodium is observed add small amounts of water until no bubbling is observed. This solution can then be transferred to an excess chemical container for disposal.
    5) Clean the still pot in a base bath and then wash repeatedly with water. Rinse with acetone to speed drying. Allow the flask to stand until the acetone has evaporated. When the still is completely dry, assemble the still under a flow of nitrogen. Attach the heating mantle and heat under nitrogen flow at a variac setting of 45 for 1 hour.
    6) Allow the flask to cool to room temperature and then add fresh solvent. To this add several grams of freshly cut and cleaned sodium. Heat the solution to reflux for 1 hour. Allow the still to cool and add several grams of fresh benzophenone.
    7) For hexane, ether, and benzene stills add 100 mL of tetraglyme to the still to improve the solubility of the ketyl. THF and toluene do not need tetraglyme.
- Still regeneration (calcium hydride).
    1) Follow sections 1-3 above. Calcium hydride is less reactive with alcohols, but will give a large amount of hydrogen and tends to foam. When isopropanol produces no more gas evolution, use water. Be careful as there will still be a lot of unquenched calcium hydride.
    2) When finished clean the pot as described above and assemble the still.
    3) Fill the still with methylene chloride and then add ca. 20 g of calcium hydride. Be careful when adding to the still with nitrogen flowing as the calcium hydride will blow around if the nitrogen flow is too high.

4) Allow the still to reflux overnight before collecting any methylene chloride.