

## 1.5: Experimental Techniques

### Filtration

The suction filtration apparatus that you will be using for many of the experiments in this course is illustrated on page 136 of the textbook.

### Cooling Baths

The cooling of flasks can be achieved by putting the flask into a cooling bath, which is a larger container partly filled with a cold liquid or slurry. The choice of coolant is determined by the temperature desired.

#### Caution

Dewar flasks are evacuated glass; if broken they implode and scatter broken glass everywhere - wear goggles.

- a) *Ice/water/salt*. Mix salt (NaCl is cheapest), ice, and a small amount of water in a beaker. The solution will settle around  $-5^{\circ}\text{C}$ .
- b) *Solvent/dry ice*. Place broken pieces of dry ice into a Dewar flask. Slowly pour the solvent onto the dry ice. Choose the solvent that will give you the desired temperature (see Appendix 8 in the textbook). If the dry ice pieces disappear after a while, add more pieces only one or two at a time. Never put solvent in the Dewar flask first and then add dry ice. The mixture will foam up and over the edges of the flask.
- c) *Liquid nitrogen*. The temperature of liquid nitrogen is  $-196^{\circ}\text{C}$ . Evacuate or flush the flask with nitrogen before placing the flask in a liquid nitrogen bath.

#### Caution

Do not place a flask into a liquid nitrogen bath if the flask contains air or argon, because oxygen and argon have boiling points ( $-183^{\circ}\text{C}$  and  $-186^{\circ}\text{C}$ ) higher than that of liquid nitrogen. It is therefore possible to condense liquid oxygen or liquid argon in the flask. When that condensed gas later boils off, it will cause a very rapid increase in pressure and a possible flask explosion. Liquid oxygen could also react with organic materials in the flask.

## Removal of Solvent

When a method calls for the solvent to be removed, or the solution volume to be reduced, this can be achieved in a number of ways.

- a) *Evaporation by heating (not recommended)*: Heating the flask until the solvent is driven off is **NOT** an acceptable method because the residue will get hotter and hotter as the solution volume decreases. Eventually the residue will become dry and will overheat, possibly causing an explosive decomposition. Also, using a hot plate with an organic solvent could easily cause a fire.
- b) *Pump and Trap Method*. Set up a pump, a trap, two stopcock valves, and an adapter, all interconnected with thick-wall flexible tubing, as shown in the diagram below. The adapter to the flask contains a third stopcock valve. With all three valves closed, turn on the pump to evacuate the whole system. After a couple of minutes, place a Dewar flask around the trap and pour liquid nitrogen into the Dewar. Attach the sample flask (with a stir bar in it) to the adapter. Start the stirrer and then slowly open the adapter valve to evacuate the flask. The solution should froth up somewhat. If the solution froths up high enough to approach the adapter, then partially or completely close the adapter valve until the frothing settles down. If the flask becomes cool, warm it up to room temperature with your hands or a beaker of lukewarm water. If the evaporation takes a very long time, use warmer water. Because you are evacuating the flask, the flask may implode, especially if it is large, if it is damaged, or if it has a flat bottom. To decrease the risk, use a roundbottom flask (not an Erlenmeyer), tape up the flask with masking tape (if it is a large flask), and most importantly you must WEAR GOGGLES.

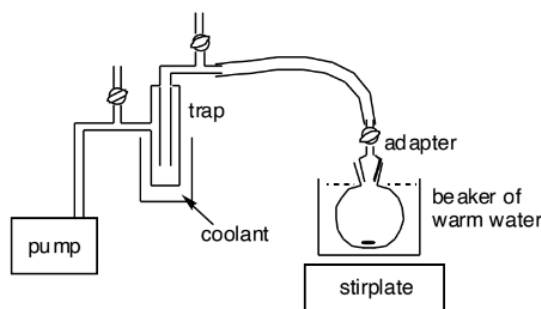


Figure 1. Experimental setup for removing solvent by 'Pump and Trap Method.'

c) *Rotary Evaporator*. You will be given instructions by the TA on the proper use of the rotary evaporator. note that you do not need to have a stir bar in the flask. The warnings about imploding flask\’s are the same for the rotary evaporator as for the Pump and Trap method.

### Manipulation of Air Sensitive Compounds

A compound can be “air-sensitive” for one or more of three reasons:

- it may react with  $O_2$  (e.g. Rh hydride complexes)
- it may react with water (eg. early transition metal alkyls)
- it may react with  $N_2$  (e.g. lithium metal)

In order to protect the compounds from “air”, one must use inert-atmosphere techniques. For most air sensitive compounds,  $N_2$  is not a problem. Because  $N_2$  is cheaper than argon, purified  $N_2$  is usually used as the inert gas under which air-sensitive compound manipulations are performed. For those few compounds which react with  $N_2$ , argon is used. One must also remove water/ $O_2$ / $N_2$  from the solvents and reagents one will use in all preparations and reactions.

The removal of air from a liquid is called degassing. This procedure replaces the air (but not the water) dissolved in the liquid with another gas. This can be achieved by either of two methods: bubbling and freeze-thaw.

- The bubbling method involves bubbling another gas (eg. nitrogen or argon) through the solvent for some time, in order to drive out the dissolved air. This technique is fairly effective, especially if the liquid is in air-free glassware such as a Schlenk tube (to be defined below). If the liquid is in an open container, the degassing effect will only be temporary; air will soon redissolve into the liquid. If the liquid is volatile, some of the liquid will be lost during the procedure.
- Freeze-thaw cycles are somewhat more time-consuming but can be quite effective. The technique (which will NOT be used in this course) involves putting the liquid in a Schlenk tube, closing the flask, freezing the liquid, evacuating the gas phase in the tube, replacing the gas phase with inert gas, and thawing the Schlenk tube again (while it is still open to the inert gas and a bubbler). A blast shield is a recommended precaution when using the freeze-thaw method because pump the liquid may expand as it thaws and this can sometimes cause the flask to burst at the bottom.

Water removal from solvents can be troublesome and time-consuming. Even traces of water in the solvent can destroy some water-sensitive compound. The traditional organic chemistry drying agents such as  $MgSO_4$  are not sufficient. Very strong drying agents such as  $CaH_2$ , elemental sodium/benzophenone ketyl, and Grignard agents are often used. This will not be required in this course.

Experimental manipulations of air-sensitive compounds can be performed in any of three different methods:

- Inert-atmosphere glove box* (otherwise known as “dry-box”). These boxes are very expensive, but can be quite effective and are operationally simple. The oxygen and water content in the gas phase inside such a box are continuously monitored can be kept below 1 ppm level. Experiments involving high or low temperatures inside a glove-box can be problematic, but with extra equipment can be done. Very little training is required.



Figure 2: An inert-atmosphere glove box (reproduced from <https://www.etelux-glovebox.com/prod...x-atmospheres/>)

b) *Gas/vacuum manifolds* and Schlenk-ware: A Schlenk tube is just a test-tube or flask designed for inert-atmosphere work. Often the top of the Schlenk tube is a ground-glass joint, and there is usually a side-arm with a stopcock on it. The gas/vacuum manifold has two long glass tubes (one containing an inert gas and 30 other containing vacuum) connected to several ports; each port has a length of flexible tubing attached to it. One normally attaches the other end of the flexible tubing to the sidearm of a Schlenk tube. By rotating the stopcock inside each port, one can supply either inert gas or vacuum to the Schlenk tube. Manipulation of air sensitive materials by these techniques requires much more training than a glove box, but offer a greater range of options, including high and low temperatures or deliberate addition of degassed water, or even dried oxygen. Filtrations, separations, and other procedures can be performed, but considerable training is required.

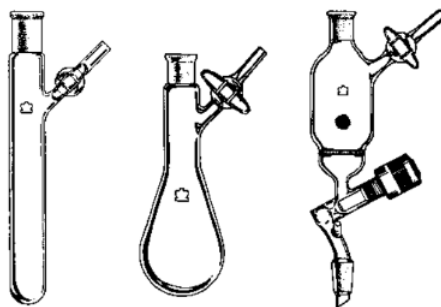


Figure 3: Two types of Schlenk tubes and a Schlenk filter (reproduced with permission from Kontes Glass Company).

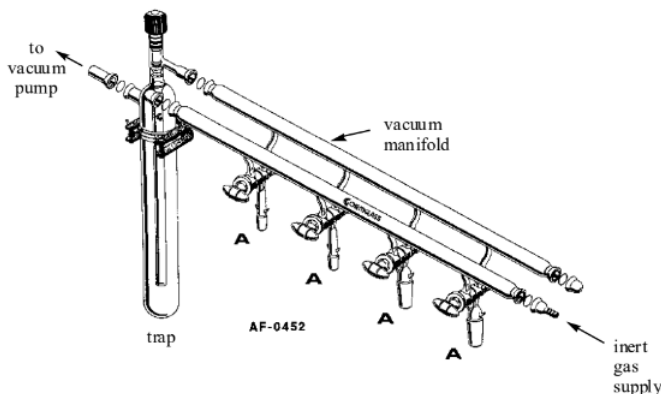


Figure 4: A gas/vacuum manifold. The attachment points for flexible tubing are indicated by the letter "A" (reproduced with permission from the ChemGlass Company).

c) Stand-alone glassware: This is the technique which will be used in this laboratory. It is effective for compounds which are only moderately air-sensitive. The technique is based upon the assumption that compounds in the solid state are much less air sensitive than they are in solution (this is generally true, but some compounds are quite air sensitive even as solids, and so other techniques would be preferable in those cases). In the technique, the solid reagents are placed, along with a stirbar, in standard taper/ground glass join glassware (such as a Schlenk tube) which is then flushed with a gas (either a reagent gas or an inert gas) to remove the air. Solvent is then added to start the reaction.

Alternatively, one can add the solvent and stir bar to an empty flask attached to a condenser and boil the solvent. The vapor of the boiling solvent displaces all of the air. Then the heat is removed briefly and solids are added. The disadvantage of this technique is that it requires the addition of solids to liquids that are close to boiling, and this can lead to bumping (an “eruption” of boiling liquid due to sudden boiling). To avoid being hit by bumping liquids: wear gloves, turn off the heat supply, keep the stirrer going at a high rate, do not place your face over the glassware while you are adding the solids, and never remove the condenser.

### Use and Care of Standard Taper Equipment

1. Standard taper glassware is expensive. The current cost of a single 24/40 outer joint is about \$12.00. A 500-ml three-necked flask with 24/40 joints costs over \$90.00.
2. Bare standard taper joints should not be attached to each other because the seal obtained is often poor, and the joints may freeze together thereby making them worthless. All ground glass surfaces should be greased (Lubriseal is satisfactory for most purposes) before they are connected. To make a good seal, the joints may be pressed firmly but gently together while turning one of them.
3. Assemblages containing standard taper joints are not as flexible as those employing corks and stoppers, so some care must be exercised in clamping the pieces to support bars in order to avoid strain. Pyrex glass will not bend appreciably at room temperature. Three-prong clamps are most convenient for clamping standard taper glassware because they may first be rigidly attached to a bar and finally gripped to the glassware by careful adjustment of the screws on either side of the prongs. The clamp prongs should be covered with rubber or other insulator to prevent contact between metal and glass.
4. Direct heating of a standard taper connection with a free flame should be avoided because it may melt out the grease and cause freezing of the joints.
5. If joints become frozen together, they may usually be separated by cautious warming with a heat gun or a soft flame (not allowed in this laboratory). However, if silicone grease has been used, this treatment may cause permanent freezing. Silicone grease should not be used unless it is specifically required. In cases where the joints are on equipment that has been heated during a reaction or distillation, it is best to separate the joints before the apparatus has cooled completely in order to prevent freezing. If you encounter frozen joints, ask for assistance from a TA.
6. In cleaning standard taper equipment, most of the grease may be wiped away with a cloth. If removal of the last traces is desired, the cloth may be moistened with a solvent such as hexane, toluene, ligroin or ether. **(CAUTION! Avoid free flames and spark sources!)**

### Cleaning Glassware

Laboratory glassware is more easily wetted by water than by the oily and tarry organic matter present in a newly soiled flask. Thus immediate rinsing with water may remove tar which would adhere tightly to the glass if the water were allowed to evaporate. Wash equipment as soon as it is empty.

Soap and detergent in combination with a brush, which may be bent judiciously so that it will reach certain otherwise inaccessible spots, are useful. Abrasive washing powder that will not scratch glass is very often helpful. If the tar is acidic, rinsing with sodium hydroxide solution may serve to loosen the tar. If it is basic, dilute hydrochloric acid may be helpful. Acetone, alcohol, or xylene, in small quantities, may dissolve a tar unaffected by other materials. Never heat a vessel over a flame while cleaning with these solvents. (Removal of seemingly intractable tars is best left to trained laboratory storeroom personnel.)

Glassware, if drained and left in the desk until the next week, will dry spontaneously. If it is needed dry sooner, it may be rinsed with acetone (5-10 ml) two or three times. Blowing nitrogen air into the vessel will then remove most of the acetone. Do not blow

air from the pressurized air supply into clean vessels, as oil droplets contained in the air supply will spray all over the inside of your clean glassware.

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