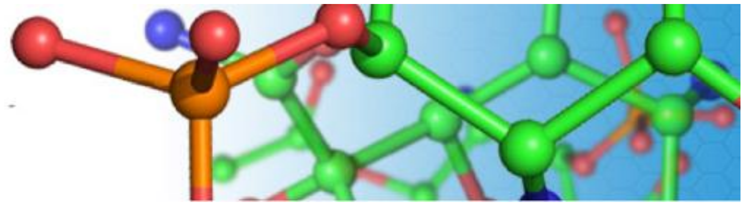
DEPARTMENT OF CHEMISTRY & CHEMICAL BIOLOGY



Schlenk Line

Standard Operating Procedure

A specialized apparatus is needed for performing a variety of common laboratory techniques under air-free conditions and dealing with compounds that are sensitive to the components of normal air (O_2 and water are typically the most problematic).

One disadvantage of working in a glovebox is that organic solvents will attack the plastic seals. As a result, the box will start to leak, and water and oxygen can then enter the box. Another disadvantage of a glovebox is that oxygen and water can diffuse through the plastic gloves. Therefore, an alternative to using a glovebox for air sensitive work is to employ Schlenk methods using a Schlenk line.

A Schlenk line centrally consists of a gas manifold (for delivering either argon or nitrogen), a vacuum manifold (for evacuating glassware), and a vacuum pump (attached to the vacuum manifold). The inert gas is supplied either by a gas cylinder via a regulator or the house nitrogen, which then passes through the gas manifold, and finally bubbles through an oil bubbler or mercury bubbler.

A well-maintained Schlenk line will allow you to do the following: flame dry glassware, vacuum distillation, freeze-pump-thaw degassing, removal of residual solvent, vacuum transfer purification, and run a reaction under an inert or reagent gas. This fact sheet is not a substitute for training on the above procedures.

General Safety and PPE

All lines and systems are different. Everyone, including experienced users, should be trained on a new line.

A Schlenk line must be set up within a working fume hood: it is important to work with the fume hood sash down, particularly with a Schlenk line, because of the reactive nature of common chemicals used and the potential for glassware to break due to non-standard pressure. The hood sash must be pulled down when the Schlenk line is unattended.

Safety goggles are required when a Schlenk line is in use. Face shields are optional. Thermal gloves are required as needed when dispensing or using liquid nitrogen or cold dewars or working with heated glassware. You should also check your gloves for compatibility with the reagents that will be used in the experiment: Some gloves are permeable and can potentially freeze to the skin when handling cold traps.

Lab coat and blast shield are required if using especially reactive chemicals (pyrophorics or explosive mixtures) including potentially reactive/explosive intermediates. Explosion hazard should be evaluated on an experimental case-by-case basis.

Equipment Operations

Traps

Solvent traps are necessary on a vacuum apparatus to prevent organic solvents from ultimately reaching the vacuum pump, where they can mix with and degrade the pump oil. To prevent these situations from occurring, liquid nitrogen traps are placed between the main double manifold where solvents enter the line and the vacuum/diffusion pumps. The traps are designed to be removable and are separated from the main line and pumps through a series of valves. The vacuum trap system collects organic or water vapors exiting Schlenk glassware and these vapors are trapped as liquids or solids. The traps are evacuated during use, and traps with glass defects constitute an implosion hazard.

The typical trap is submerged in a dewar flask containing liquid nitrogen. The liquid nitrogen cools the trap and forces vapors and gases from the Schlenk line to condense. One cold trap is considered the minimum for standard Schlenk line operation. However, if you are intending to use the Schlenk line to evaporate solvent, two traps are recommended. Some lines have space for a second trap in series with the first: If the line you are using does not, a second trap can be included on the flexible tubing between the Schlenk flask and the Schlenk line.

An alternative to liquid nitrogen for the trap is to use an acetone/dry ice combination in the trap. Acetone/dry ice is suitable for many reactions but requires more maintenance because the dry ice needs to be replaced more frequently. Liquid nitrogen cold traps run without much attention and need only infrequent cleaning.

- There might be a low risk of condensing liquid oxygen when using a liquid nitrogen trap but as long as the system is under dynamic vacuum, the oxygen in the trap will pump off eventually. A major hazard from this would be if the inner tube in the trap froze shut so the system wasn’t actually under vacuum. In this case, a dry ice acetone trap would be more appropriate than a liquid nitrogen trap.
- When a sample is left under vacuum overnight or for a long period of time, it is important to make sure there is enough liquid nitrogen in the trap to last the entire time. If there is not, material will be pulled from the trap into the pump. Depending on the solvent removed, it may be appropriate and safer to use a dry ice/acetone trap instead of a liquid nitrogen trap. In this case, it is less likely that a clog will occur, and liquid oxygen won’t condense in the trap.

If you are leaving something on the vacuum line overnight, be sure to use large dewars and fill the traps right before you leave and right when you arrive in the morning. Also, be sure to fill out the Overnight Reactions form, attach it to the fume hood, and make your lab notebook accessible in case of emergencies.

When using the Vacuum line (when possible, label stopcocks: gas or vacuum)

1. Ensure all taps on the line are closed (i.e., the taps are in the off position) and Place/Turn on your Vacuum Monitor piece. Either digital monitors or McLeod Gauges are recommended for use.
2. Turn on the vacuum pump. Starting with the valve closest to the pump, slowly open to fill the line with vacuum. Before opening your reaction to vacuum, place dewars filled with liquid nitrogen on the traps.
3. Open the tap connected to the experiment concerned SLOWLY, paying close attention to bumping and degassing of the experiment. Close the tap if necessary, to prevent contaminants from entering the line.
4. Once tap is fully opened and stable continue to pay careful attention to ensure no leaks are present, using your manometer.
5. To turn the vacuum off, first turn the tap connected to the experiment then the tap connected to the trap. Once both are closed turn the pump off and finally release the vacuum by opening the trap tap slowly, and then the tap connected to the experiment extremely SLOWLY. Finish by closing both taps.

☐ When switching between Vacuum and Inert Gas lines

1. Some Schlenk lines have Teflon screws, and it is possible to have both the vacuum and inert gases (Ar or N2).
2. When turning from vacuum to nitrogen be extra careful to ensure that the bubbler does not get sucked up into the line.
3. Follow the above procedure to shut down the vacuum line.
4. Turn on the nitrogen tap slowly, making sure that it is open to the bubbler. Take careful note of the bubbler’s flow rate and turn the nitrogen on until there is a constant stream from the bubbler.
5. To turn off nitrogen flow, close the tap connected to the experiment first, and then the nitrogen source.

When using the Inert Gas Lines only

1. The first major consideration is that the inert gas inlet must be regulated so that pressure does not build up and explode the glass manifold. A dual-stage regulator attached to the inert gas tank is the primary means of controlling pressure. In addition to the regulator, bubblers can be linked to the line to not only provide a pressure release system but also to provide a means to monitor the general flow of nitrogen in the line.
2. Ensure all taps on the line are closed (i.e., the taps are in the “off” position).
3. Put up the trap and if available, turn on the vacuum monitor/place the vacuum monitor.
4. Turn on the nitrogen tap slowly; making sure that it is open to the bubbler. Take careful note of the bubbler’s flow rate, and turn the nitrogen on until there is a constant stream from the bubbler: use the bubbler attached to the line to adjust the gas flow, typically only need one bubble ever one or two seconds.

5. Turn the appropriate tap connected to the experiment flask requiring nitrogen atmosphere.
6. To turn off nitrogen flow, close the tap connected to the experiment first, and then the nitrogen source.

Cleaning the trap

When the Schlenk line vacuum is quenched and the pump is turned off, the liquid nitrogen dewars used to cool the vacuum traps should be immediately dropped down. Neglecting this step will allow air to condense in the cold traps which is a safety concern because liquid air is a strong oxidant.

Make sure the trap is cleaned on a daily basis when in use. After you've performed your experiment, you should remove the N2 dewar, close the valve to the pump, immediately after isolating the trap, quench the vacuum by opening a stopcock, allow the trap to warm to room temperature, clean it out with acetone or another solvent appropriate to your reaction conditions, blow forced air through it to dry, reassemble the trap, and put the trap and line under vacuum by opening the valve to the left of the trap. Before putting traps back up, be sure that they are completely free of solvent.

Liquid oxygen (when using a cold trap)

If a constant stream of air is pulled through a vacuum trap cooled with liquid nitrogen, liquid oxygen may condense in the trap. Liquid oxygen is exceedingly dangerous and reacts violently with most organic substances, including Teflon tape, vacuum grease, and organic solvents. Even without this consideration, the pressure generated when a small quantity of liquid oxygen vaporizes in a small space such as a vacuum manifold generates enough pressure to shatter the line.

Should you lower the trap on your line and find a pale blue liquid, immediately replace the dewar, close the hood, and back away. Consult your supervisor immediately. Warn others of the danger, posting signs if necessary. To avoid such occurrences, ensure that all experiments done while using a cold trap are only under nitrogen atmosphere only.

Equipment Maintenance

Glassware

Schlenk round bottoms can develop star cracks if directly seated on the floor of the hood during use, or if directly seated on a heating or stirring plate. These star cracks in Schlenk flasks or in other evacuable glassware can produce an implosion on evacuation. All subsidiary and evacuable Schlenk glassware, such as flasks and funnels, should be visually examined for cracks, star cracks, and glass defects prior to every use. Ensure all flasks and manifolds are heavy-walled and designed for vacuum use. Never use thin-walled glassware or flat-bottomed flasks (unless specifically pressure-rated) for vacuum applications.

In use, a Schlenk flask should rest on a cork ring, or be supported using a clamp attached to a trellis rack or a ring-stand. Well-constructed and tempered Schlenk lines are generally robust against cracks, except around over-tightened ptfe vacuum valve seats.

Vacuum and Inert Gas Lines

ended. You should clean it as needed (i.e., if you inadvertently pull a compound into the line, or oil from your bubbler).

Leaks

It is important to check for leaks at the joints of the line to prevent contamination of your reaction, collecting explosive liquid O2 in your traps, or damaging the vacuum pump. This can be done by lightly applying a dilute soap solution to the joints to check for bubble formation. Leaky joints should be greased and tightened.

O-Rings

It is critical to ensure an anaerobic environment when using a Schlenk line. To this end, the valves can have Teflon screws with O-ring seals, or may be constructed from a ground-glass stopcock, and both need to be greased to form an airtight seal. When using Teflon screws in combination with O-rings, make sure that the O-rings are not deformed (i.e., that they do not look crooked or wavy after putting the Teflon screw in place). Inspect o-rings each time before use and replace often.

Tubing

Glassware is attached to the line via flexible rubber or plastic tubing, commonly Tygon or Portex PVC tubing. The tubing needs walls at least 3 mm thick to prevent it from collapsing under vacuum. The tubes should be long enough to reach the bench or floor of the fume hood and have 3–4 cm left over. Any longer and the tubes become unwieldy and can knock pieces of glassware off the bench. If the tubing does not reach the bench or floor of the fume hood, it can be awkward to work with and may require glassware to be positioned in unusual or precarious positions to make the tubing reach.

The line is generally connected with the vacuum pump by a vacuum hose with the help of an adjustable clamp. If the hose is heavy, it requires multiple clamps to support the load.

To connect the tubing to the glassware, gentle pressure should be applied to ease the tubing onto the connector. A wiggling or rocking motion should be used rather than a twisting motion: Twisting can cause the glassware to break as you are attempting to attach the tubing which often results in you stabbing yourself in the hand with broken glassware.

To remove the tubing from the glassware, it should be eased off by applying pressure with the thumb of the hand holding the glassware while the other hand rocks the tubing from side to side. Again, twisting the tubing risks broken glassware and injury so should be avoided. For disconnecting the hoses, it is preferable to use a new razor blade and cut the tubing off the manifold. It is generally a bad idea to try prying the tubing off by force – the glass manifold connectors break off easily.

Vacuum Grease

A fine layer of grease applied evenly is better than a thick layer that seeps out of the top and bottom of the joint. To get a thin layer, apply two stripes of grease, on opposite sides of the male joint of any glassware, insert into the neck or female joint and rotate the two parts gently to evenly distribute the grease. There should be a clear, continuous film between the surfaces of the joint.

Bubblers

The bubbler provides a pressure release system for the line and a visible means of monitoring the general flow of gas. Make sure there is a source of pressure relief in the form of a bubbler and that there is not a closed system when the gas line is open, especially when using pressurized gases or heating a closed system.

Check-valve use is a safety issue because, as noted above, unrestricted backflow will quickly bring air into a Schlenk line, where it will contact the chemicals in use. If a pyrophoric chemical is in use, ignition may occur on exposure to oxygen.

Mercury bubblers work on a similar principle to oil bubblers but provide much higher inert gas pressures within the Schlenk line due to the high density of the liquid metal. Mercury bubblers are often over 76 cm in height (1 atmosphere can support 760 mmHg) which allows the inert gas manifold to be fully evacuated under vacuum, rather than being flushed or purged with inert gas. The major disadvantage with mercury bubblers is the health and safety issues concerned with handling mercury and disposing of waste. Mercury is also incompatible with many chemicals that may be used on the Schlenk line. **Mercury bubblers should only be used in well ventilated fume hoods; furthermore, an additional flask equipped with a gas inlet/outlet adapter must be used to collect any small beads of mercury that exit the bubbler.**

Pumps

If the vacuum pump is an oil pump, the vacuum in an evacuated trap should be quenched immediately after the pump is turned off. If this is neglected, the pump oil will rise through the connecting line and enter the vacuum traps. Therefore, vacuum traps attached to an oil pump should have a separate high-vacuum valve that can be opened to quench the trap vacuum. This valve can be glass-blown onto the trap or placed in any glass manifold to which the trap is attached.

Troubleshooting

The Vacuum Line

A glass flaw on the vacuum side constitutes an implosion hazard. Therefore, Schlenk lines must be visually inspected, especially during and immediately after installation. Cracks can arise in the glass seat of Teflon (ptfe) high-vacuum valves when they are over-tightened. Failure of a valve seat during evacuated operation may cause an implosion. The typical symptom of a cracked valve seat is that the Schlenk line cannot achieve vacuum. Teflon high vacuum valves seal efficiently when only two fingers tight.

Safety Concerns

Explosions

Pressurized gases: High vacuum manifolds are often connected to an inert or reactant gas supply line. One must ensure that the vacuum system is not closed when the gas supply is opened – there must be a source of pressure relief such as a bubbler. The pressure must be monitored with an electronic gauge, manometer or bubbler; make sure the valve to the pressure reading device is open to the manifold! Always check that the manifold and supply line are connected to pressure relief (and the pressure sensor) before opening the gas supply, and always use an appropriate pressure regulator to avoid opening the line to more than 1 atm of pressure at any time.

Condensed gases: Some gases, such as carbon monoxide and ethylene, are easily condensed into a liquid nitrogen-cooled trap. If the coolant level drops or you remove the nitrogen dewar without providing a means of pressure relief, the liquid may convert back to vapor. For example, just 10 mL of liquid CO (b.p. -191.5 °C) corresponds to 6.5 L of gas. In a vacuum line with an internal volume of 500 mL the internal pressure would be 13 atm, more than enough to shatter the manifold with explosive force!

Runaway reactions: Some reactions can occur violently and evolve large quantities of gas. Always provide a source of pressure relief!

Heating a closed system: Never heat a vessel on a vacuum line without being open to a bubbler. Vacuum distillations must always have a pressure relief/regulator such as a manostat (valve).

Explosions of glass vacuum lines have led to death and serious injuries. Always wear your safety goggles to protect your eyes. Consider blast shield if reactions warrant it. Since the Schlenk is kept within the fume hood, always keep the sash down when possible and open only to the maximum height needed to perform your duties in the hood.

Implosion

An unseen star crack or stress in a glass manifold can give rise to a catastrophic failure of the line while under pressure. Likewise, hitting the line with apparatus can cause a failure. While not usually as serious as an explosion, implosions generally involve sharp pieces of flying glass.

Resources

www.chemistry.unm.edu
www.SchlenkLineSurvivalGuide.com
https://www.scribd.com/document/314564344/Shriver-The-Manipulation-of-Air-Sensitive-Compounds-BOOK

All lab personnel who use Schlenk Lines must read and sign this SOP. Basic training to use Schlenk lines will be provided by the PI or assigned postdocs. Viewing other groups' set ups can help with further questions and clarifications. Demonstrations can be provided as requested (cannulas, bubblers, regulators, etc.).

I have read and understood the content of this SOP:

Name	Signature	Date