Chem 1140; Techniques for Handling Air-Sensitive Compounds

- *Introduction*
- *The Glove Box*
- *Schlenk Techniques*
- *Drying and Degassing Solvents*

What are Air-Sensitive Compounds?

Materials which oxidize, decompose or even explode under the influence of oxygen or moisture.

- Pyrophoric Compounds

Metal alkyls and aryls	e.g. RMgX, RLi, RNa,R_3Al, R_2Zn
Metal carbonyls	e.g. $Ni(CO)_4$, $Fe(CO)_5$, $Co_2(CO)_8$
Alkali metals	e.g. Na, K, Cs
Metal powders	e.g. Al, Co, Fe, Mg, Pd, Pt, Zn
Metal hydrides	e.g. NaH, KH, $LiAlH_4$
Hydrides	e.g. B_2H_6, PH_3, AsH_3
Boranes, phosphines, arsenes, etc.	e.g. Et_3B, R_3P, R_3As

- Chemicals which react violently with water

  Metal hydrides, metal amides ($NaNH_2$), metal alkyls and aryls, metals, metal powders, hydrides, many main group halides (BCl_3, BF_3, $AlCl_3$, PCl_3, $SiCl_4$), inorganic acid halides ($POCl_3$, $SOCl_2$), low molecular weight organic acid halides and anhydrides.

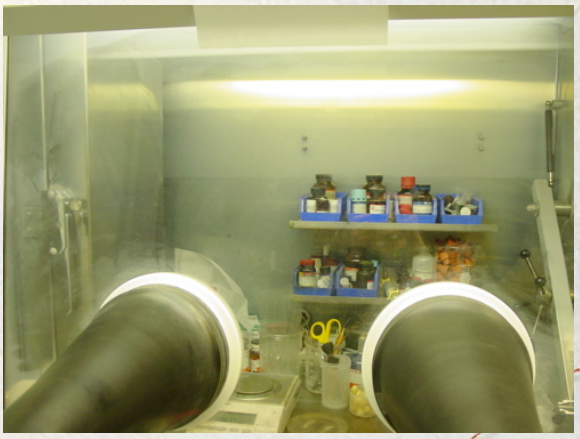
Glove boxes and Schlenk techniques do NOT protect from explosive or shock sensitive materials or mixtures!!! Also, they only provide limited protection from toxic compounds.

The Glove Box

- The best way to keep things away from atmospheric oxygen and water is to work in a fully enclosed “bench top,” containing an “inert atmosphere,” which one could reach into with gloves. Such a device is called a “glove box” or a “dry box”. There are also cheap “glove bags”, bags you can fill with inert gas and reach into with attached gloves.

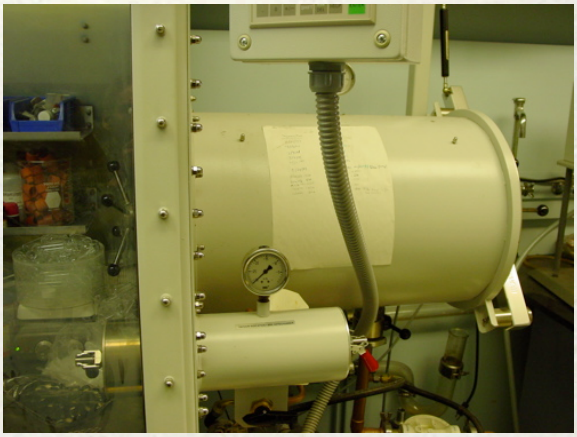
The Glove Box

- A glove box has four important components:
1. The actual “box” is a large aluminum chamber with a plastic front window and two impressive looking gloves. This is the working area. Organic solvents will spoil the plastic, and fancy fingerware, opulent wedding trophies, or pointy fingernails will puncture the rubber gloves and deflate the system.



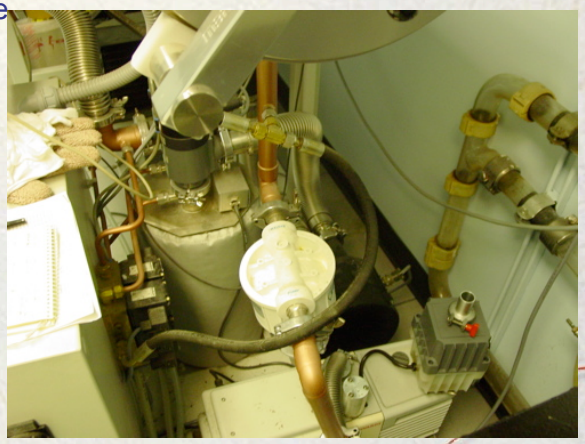
The Glove Box

2) There is an antichamber (like a submarine or spaceship airlock) which is how things get in and out without letting in air.



The Glove Box

3) The gas in the box is constantly circulated over a scrubber (often called the "catalyst") which removes any air or water that has made its way into the enclosure. Since the catalyst is damaged by many kinds of reactive chemicals (chlorinated solvents, sulfur compounds, etc.), we must be careful what we allow to evaporate into the box atmosphere. A fan inside the box circulates the box atmosphere through the canister.

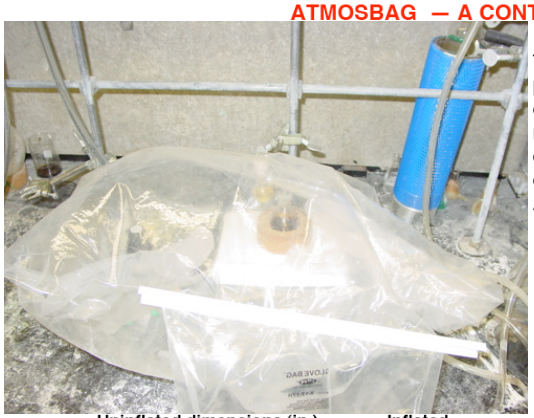


The Glove Box

4) The glove box must be able to regulate pressure inside. The device that regulates the pressure is set to tolerate only a few millibar of positive and negative pressure and automatically pumps nitrogen out if the pressure gets too high or draws fresh nitrogen in from a tank/dewar if the pressure gets too low. One can also regulate pressure manually with a foot pedal.

The Glove Bag

ATMOSBAG — A CONTROLLED - ATMOSPHERE CHAMBER



The Aldrich AtmosBag is a 0.003-in. gauge PE bag that can be sealed purged, and inflated with an appropriate inert gas, creating a portable convenient, and inexpensive two handed "glove box" for handling air- and moisture-sensitive as well as toxic materials. Other applications include dust-free operations, controlled-atmosphere habitat, and, for the ethylene oxide-treated AtmosBag, immunological and microbiological studies. Small AtmosBags have one inlet per side. Includes instructions.

CAUTION: *When handling toxic materials use only in a hood or other controlled system to prevent and protect against exposure in case of leakage. All products made of PE may tear, break, or puncture. To assure that air-sensitive materials do not become exposed to air, follow instructions on package; also test and monitor AtmosBag for leaks before and during use*

Size	Uninflated dimensions (in.) Opening	Width	Length	Inflated volume (in.3)	Cat. No.	Ethylene oxide treated Cat. No.
S	12	27	30	3,000 (50L)	**Z11,283-6**	**Z11,837-0**
M	24	39	48	17,000 (280L)	**Z11,282-8**	**Z11,836-2**
L	36	51	58	32,000 (520L)	**Z10,608-9**	**Z11,835-4**

Teflon sealing tape
In 520-in. roll.

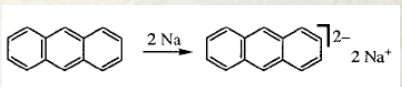
Width (in.)	Cat. No.
¼	**Z14,881-4**
½	**Z10,438-8**
1	**Z22,188-0**

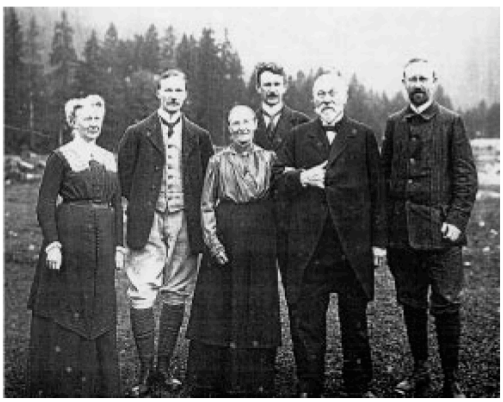
The Dry Box

Schlenk Techniques

Wilhelm Schlenk: The Man Behind the Flask**

Thomas T. Tidwell*





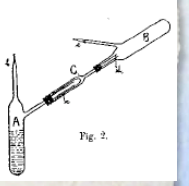
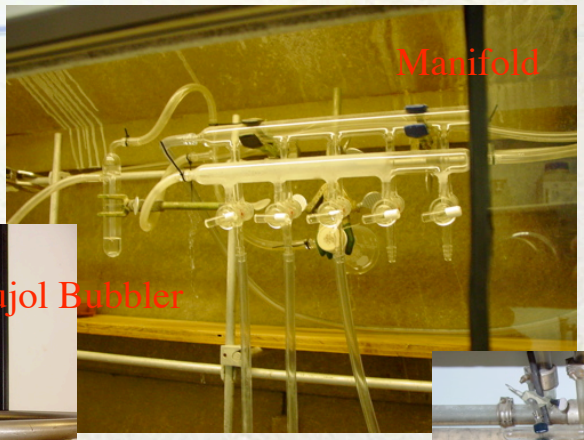


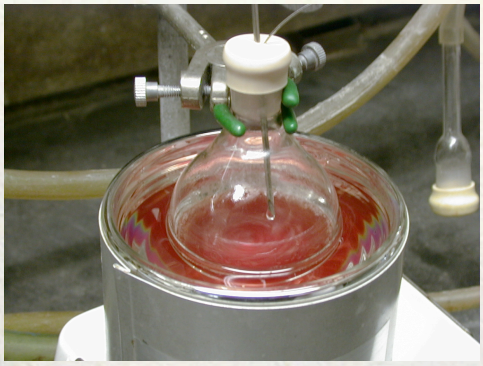
Figure 2. Left: Wilhelm Schlenk (about 1905); right: Schlenk family (1915): sister Augusta, Hermann, Emile, Wilhelm, Georg, Oskar, (courtesy of Edward Schlenk).

Schlenk Techniques

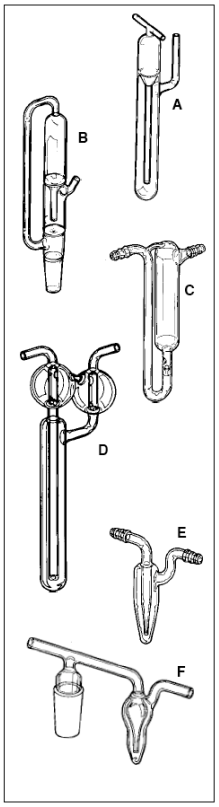
4) The centerpiece of the defense against atmospheric intrusion is the double manifold, or the Schlenk line.



Schlenk Techniques



Bubblers



Standard
Mineral oil or mercury, 5-7ml. For monitoring gas evolution or rate of flow, or closing off a reaction vessel from the atmosphere. Model (b) has a ⅀24/40 joint.
A Z10,121-4
B Z10,432-9

Check-valve bubblers
Permits gas flow under positive pressure. Check-valve ball seats on ground surface under negative pressure preventing oil from being drawn into the purged system. Single inlet tube, top outlet
C Z22,501-0
T inlet tube, side outlet
Z22,502-9

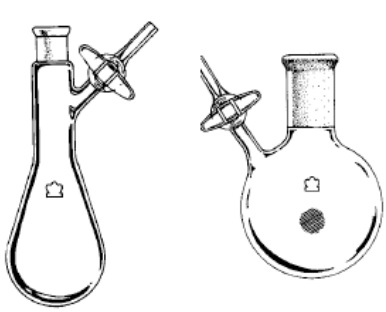
Safety bubbler
The built-in flash arrester bulbs prevents the backflow of mercury and mineral oil to pumps and prevents reactions due to overflow or violent bubbling. 15ml maximum fill mark prevents over-filling.
D Z22,372-7

Mini gas bubbler
For bubble counting. Maximum volume is 4ml.
E Z22,371-9

In-line oil bubblers
For precise N_2 pressure control during inert atmosphere reactions. Connect reaction vessel to in-line ⅀ joint or use with a ballast bulb to keep pressure constant.
⅀14/20 joint **F Z22,322-0**
⅀19/38 joint **Z22,334-4**
⅀24/40 joint **Z22,335-2**

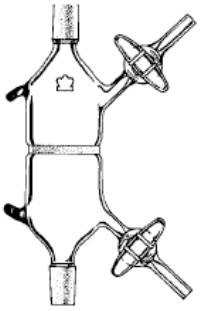
Schlenk Techniques

The Schlenk flask is an ordinary round-bottom flask with a sidearm with a stopcock (greased!). You can connect this sidearm to the Schlenk line with thick rubber tubing and use it to admit nitrogen to the flask or to evacuate it. The tubing needs to be thick so that it won't collapse under vacuum. Put something in the neck of the flask, such as a septa or glass stopper (greased) or another piece of apparatus such as a Schlenk addition funnel or a Schlenk filter .



flasks

addition funnel

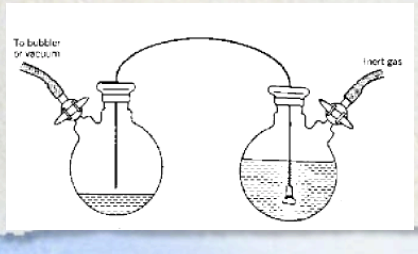


Schlenk filter

Schlenk Techniques

Convenient ways to transfer solutions into and from Schlenk flasks is via septa and syringes or cannula.

A cannula is a hollow steel needle with two sharp ends. It can serve fortransferring liquids when set up as shown. If the pressure in the flask at the right is greater than that in the other flask, the liquid will be pushed from the right to the left flask. This pressure difference can be achieved by placing one flask under nitrogen and partially evacuating the other.



Choose the right needle gauge! http://en.wikipedia.org/wiki/Needle_gauge

Schlenk Techniques

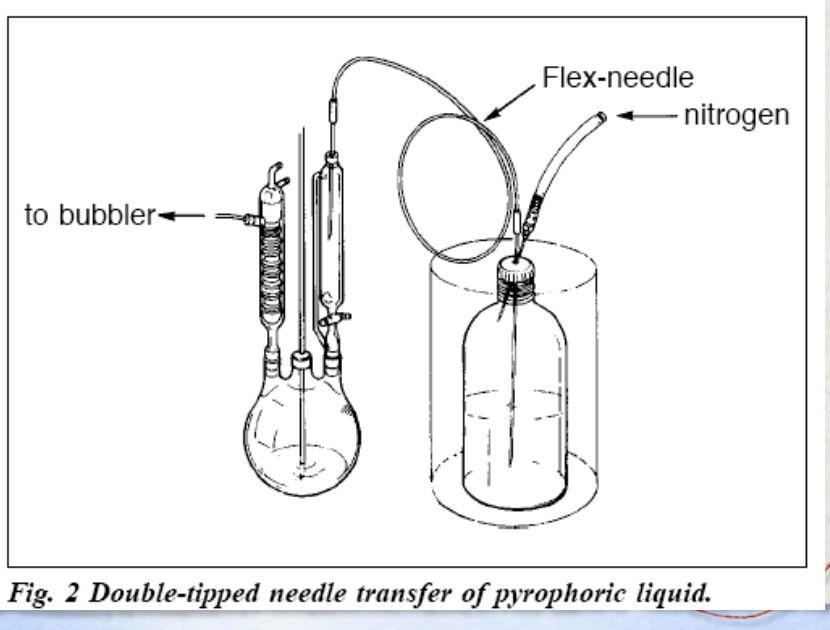
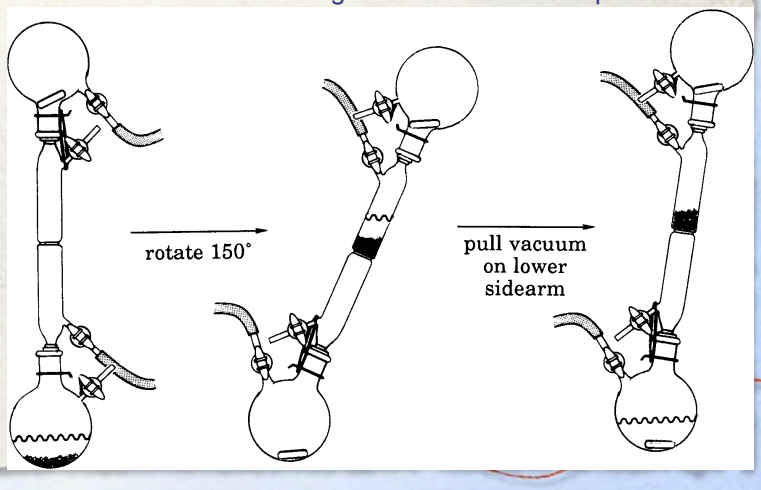


Fig. 2 Double-tipped needle transfer of pyrophoric liquid.

Schlenk Techniques

To address the difficult task of no-air filtrations, the Schlenk filter (illustrated below) can be used. Its effective use requires some practice and "good hands". The filter is placed on top of the flask with the material to be filtered, and on top of it is placed a flask in which to catch the filtrate. The whole assemblage is then inverted, and you try to get as much of the solid as possible to run down on to the fritted glass disk. You can help the solid down with the stir bar, which you can move around with a hand-held magnet on the outside of the flask. Applying a touch of vacuum to the underside of the frit while the top is under nitrogen will move the filtrate through just like in a ordinary suction filtration.



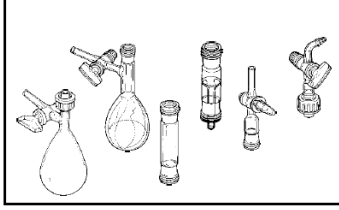
Schlenk Techniques

Aldrich Schlenk-type Glassware

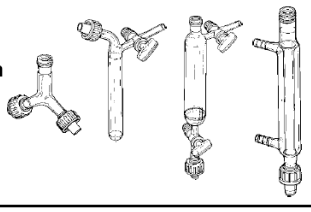
- Request Technical Bulletin AL-166

Aldrich Schlenk-type glassware features threaded ground glass joints. They require no grease, thus eliminating it as a potential contaminant, and need no cumbersome clamps. The joints consist of a ground glass male joint (**M**) and a ground glass interior female joint (**F**) with exterior threads that allow the male portion to be secured by a septum-type plastic cap using an "O"-ring compression seal. (Cap and "O"-ring are included with all threaded male joints.) Most pieces have stopcock side arms which permit the evacuation of air and the introduction of an inert gas. A high vacuum is not necessary since the purge cycle is repeated a number of times. The versatility of Aldrich Schlenk-type glassware makes the manipulation of air- and moisture-sensitive reagents easier and safer.

Designed for small-scale manipulation of air- and moisture-sensitive reagents

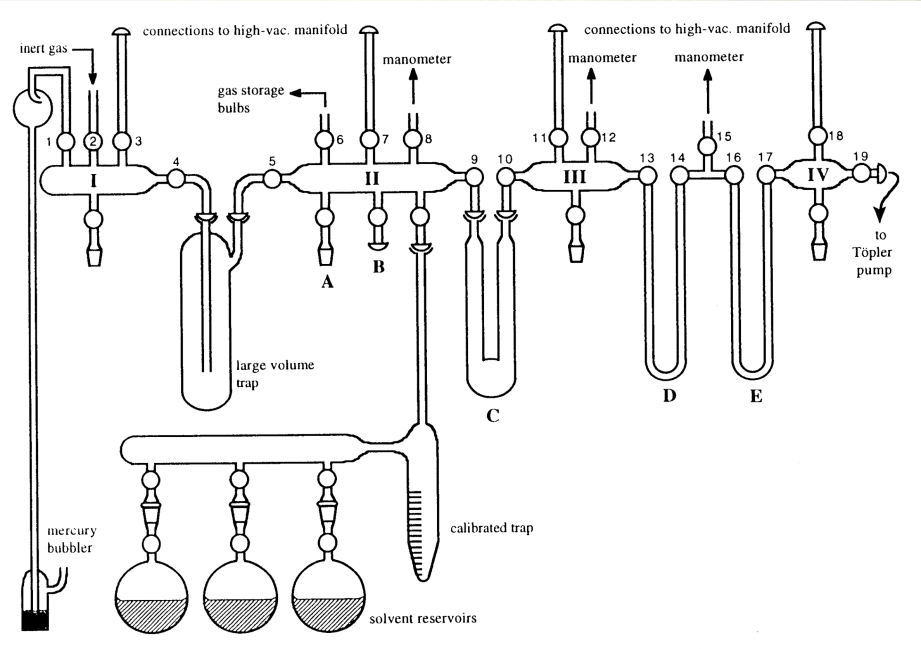


Addition of Liquids · Chemical Reaction
Distillation · Drying · Extraction
Filtration · Recrystallization
Degassing · Transfer of Solids

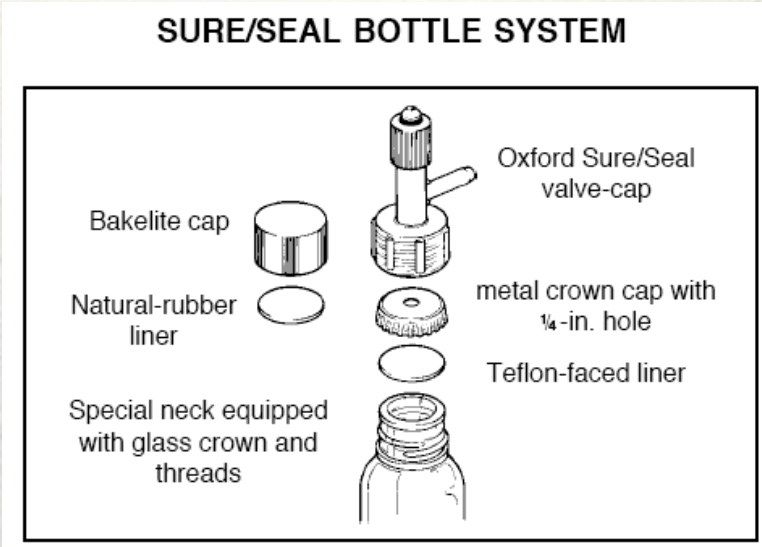


For instructional videos on Schlenk-line techniques and dry box manipulations, see:
http://www.chem.cuhk.edu.hk/lab_technique_6handling.htm

The Crown Jewel of Schlenk Techniques - The High Vacuum Line



Storage



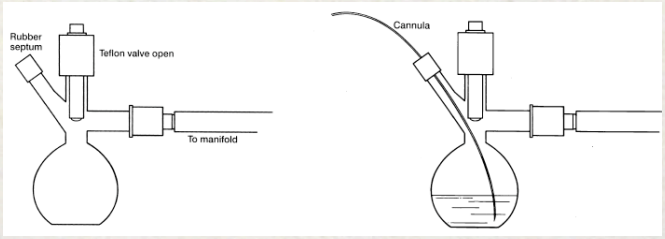
Storage

SURE/STOR FLASKS

Designed for safe, reliable storage and dispensing of air-sensitive and odoriferous chemicals, pyrophorics, alkyl lithiums, Grignards, corrosives, and purified or deuterated solvents.

Features:

- High-vacuum Teflon valve-to-glass seal eliminates air contamination in storage and septum leakage after initial needle penetration
- Heavy-wall borosilicate glass
- Removable sidearm hose connector for easy attachment of vacuum and inert gas lines. For long-term storage, replace hose connector with a rubber septum for secondary protection. Flasks supplied with 2 septa. Order replacement septa, Z10,649-6, below
- Plastic-coated* flasks reduce chance of breakage and contain spills
- Amber flasks protect light-sensitive products



Gas Handling

You must be very careful not to let pressure build up in any piece of apparatus. Schlenk techniques can tolerate pressures only slightly greater 1 atm. If you have a pressure of 2 atm in a flask (twice the external pressure) that's 15 pounds on every square inch (psi) of your apparatus. So a stopper with a one square inch opening will have 14.7 pounds pushing it open. This is equivalent to hanging a bowling ball off of it! Be sure—whenever you work with gases—that you know what will happen anytime you open a valve, where the gas is supposed to be going, and where the gas will go if the pressure by accident gets too high.

Gas Handling

For lecture bottles

Note: you will be expected to know—perhaps on the exam—
all the various pressure units used in this class:
1 atm = 1.01 bar = 14.7 psi = 760 mm Hg = ~33 ft or ~400 in of water

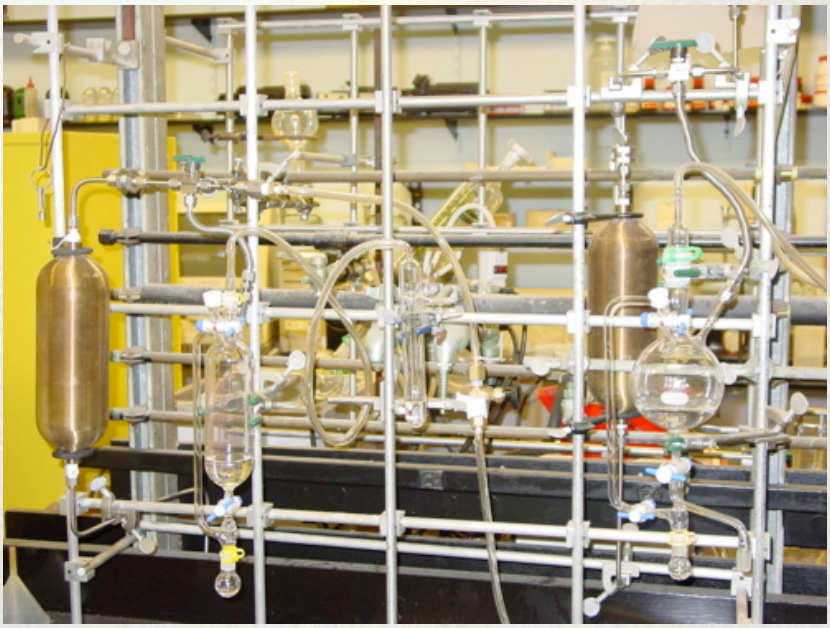
Safe Handling of Diazomethane

Diazald kit

The Diazald kit is a set of distillation glassware designed for the safe preparation of diazomethane (~100mmol). Glassware without sharp edges or ground-glass joints is recommended by de Boer and Backer (Org. Syn., Coll. Vol. 4 1963, 250). The Diazald kit features ₹19/22 Clear Seal joints; these joints do not require grease even for vacuum applications, thus avoiding that source of contamination. The glassware in the kit should be washed with care and without the use of wire brushes which will scratch the inner surface. For further information, request Technical Information Bulletin No. AL-180 and for a review on the preparation and reactions of diazomethane, see Aldrichim. Acta 1983, 16 (1), 3.

Cat.No.	Each
Z10,025-0	

Solvent Purification and Degassing



Solvent Purification and Degassing

Solvent Purification and Degassing

Methods of Degassing

• ***Freeze-Pump-Thaw***

This is the most effective methods for solvent degassing. A solvent in a sealed Schlenk or heavy wall sealed tube is frozen by immersion of the flask in liquid N_2. When the solvent is completely frozen, the flask is opened to the vacuum (high vacuum) and pumped 2-3 minutes, with the flask still immersed in liquid N_2. The flask is then closed and warmed until the solvent has completely melted. This process is repeated (usually three times) and after the last cycle the flask is backfilled with an inert gas. Degassed solvent in a sealed Schlenk flask can usually be kept for 1-2 days.

• ***Atmosphere Exchange Under Sonication***

Solvents can be roughly degassed by repeated sonication under light vacuum (i.e. house vacuum) for 0.5-1 min and replenishing the atmosphere with an inert solvent. By using 5-10 cycles, degassed solvents for HPLC and some reactions can be obtained quickly.

• ***Purging***

Of the methods listed here, purging is the least effective way of degassing solvent, however it is acceptable for some applications, particularly when large amounts of solvent need to be roughly degassed. Purging consists of bubbling an inert gas (usually N_2 or Ar) through the solvent for 30 min - 1 hour. Care should be taken to prevent solvent evaporation and especially the condensation of water in the solvent by using an appropriate setup.

Further Reading

- Good references for the handling of air-sensitive compounds are the books
- The Manipulation of Air-Sensitive Compounds (2nd Ed.) by D. F. Shriver and M. A. Drezdzon, Wiley-Interscience, New York, 1986.
- Advanced Practical Inorganic and Metalorganic Chemistry by R. J. Errington, Blackie, London, 1997.