Vacuum technology
Preparative vacuum-systems

István Csonka

Dávid Frigyes

Uses of fore vacuum

Discussed areas:

- Distillation, evaporation, drying (laboratory, chemical industry, food industry)
- CVD (Chemical Vapor Deposition)
- Inert atmospheric techniques (vacuum-line, glove box)

Most of the industrial systems use rough vacuum down to 1 mbar, but there are lot of fine vacuum systems too, even down to below 10^{-3} mbar.

Fore vacuum system

Usually pretty simple systems:

- Fore vacuum-pump (water jet, stem jet, liquid ring, membrane, rotary vane, rotary piston, scroll, Roots (with it own fore vacuum pump))
- Piping, valves etc.
- Traps
- Fore vacuum gauge (capacitive, piezo, Pirani, thermocouple, McLeod)
- Vacuum control, if possible
- All the aboves can be on a mobile working station
- Working chamber/equipment

Distillation, evaporation, drying

- Gentler and uses less energy (~1/3) than thermal operations
- Vacuum distillation, vacuum drying, sublimation, lyophilization (sublimation of frozen solvent)
- In laboratory: water jet pump, membrane pump, rotary vane pump with trap (can work with a small water and solvent), scroll pump
- In industry: as above, plus water ring, steam jet, rotary piston, screw and Roots pump; nescafe, dried fruit/vegetable, milk powder, paper, sugar, wood drying, vacuum melting, foundry and so on

CVD (Chemical Vapor Deposition)

For comparison: PVD (Physical Vapor Deposition) in high vacuum (10^{-6} mbar). Evaporation and precipitation. Disadvantage: does not adhere well, limited choice of material (mainly metals, Al, Cu, Ag, Au, Ge, Ti, even NiCr resistive material), only in optical sight. Actually, the titan sublimation pump works on the same principle.

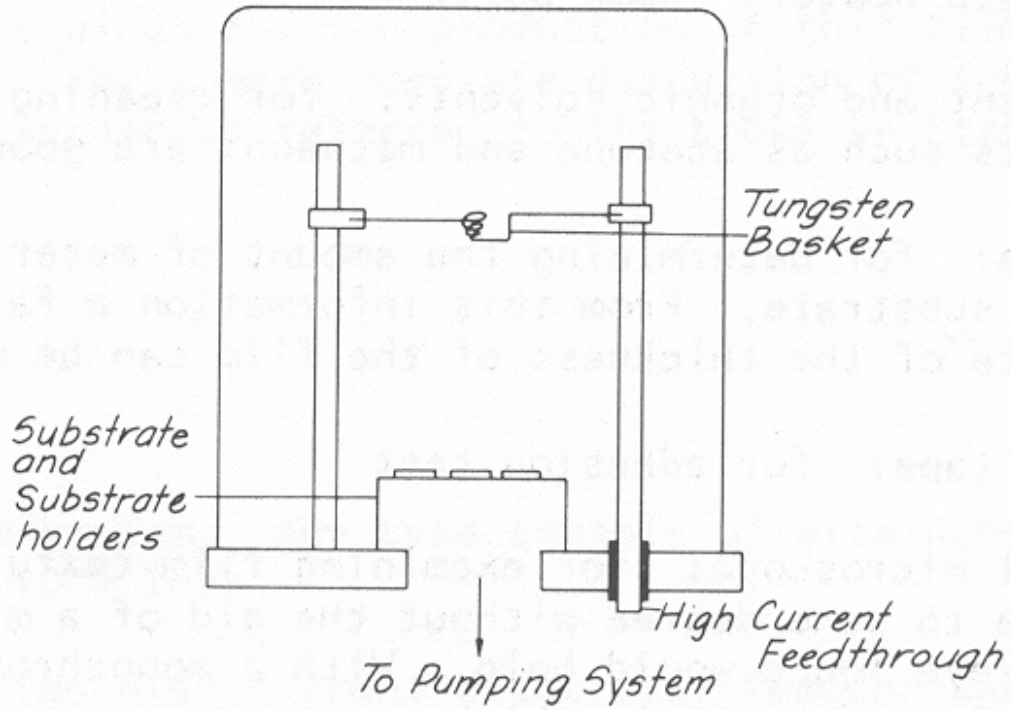


FIG. 1. Bell jar evaporation system.

CVD (Chemical Vapour Deposition)

For comparison: ion sputtering. Ion bombardment sputters the material. For example Ar-plasma. Actual work in fine vacuum (glow discharge) needs HV-system.

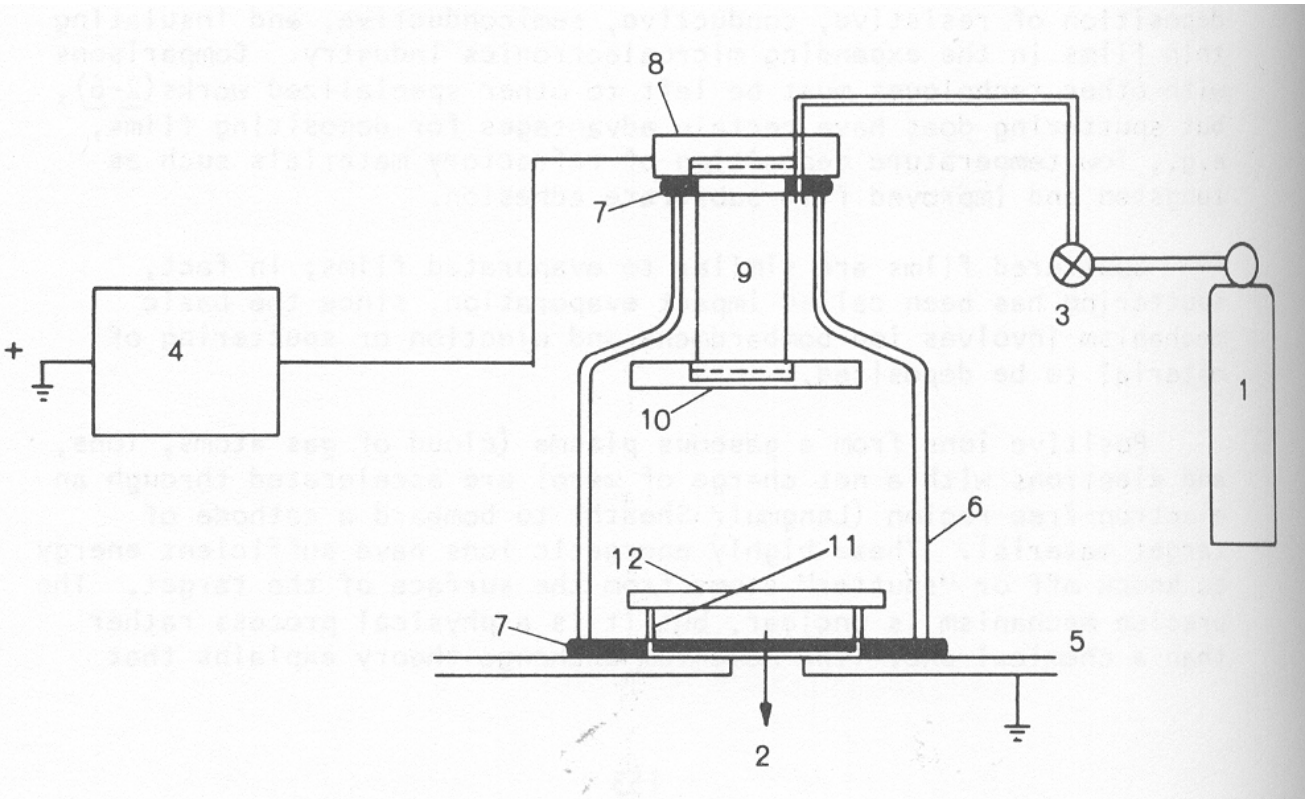
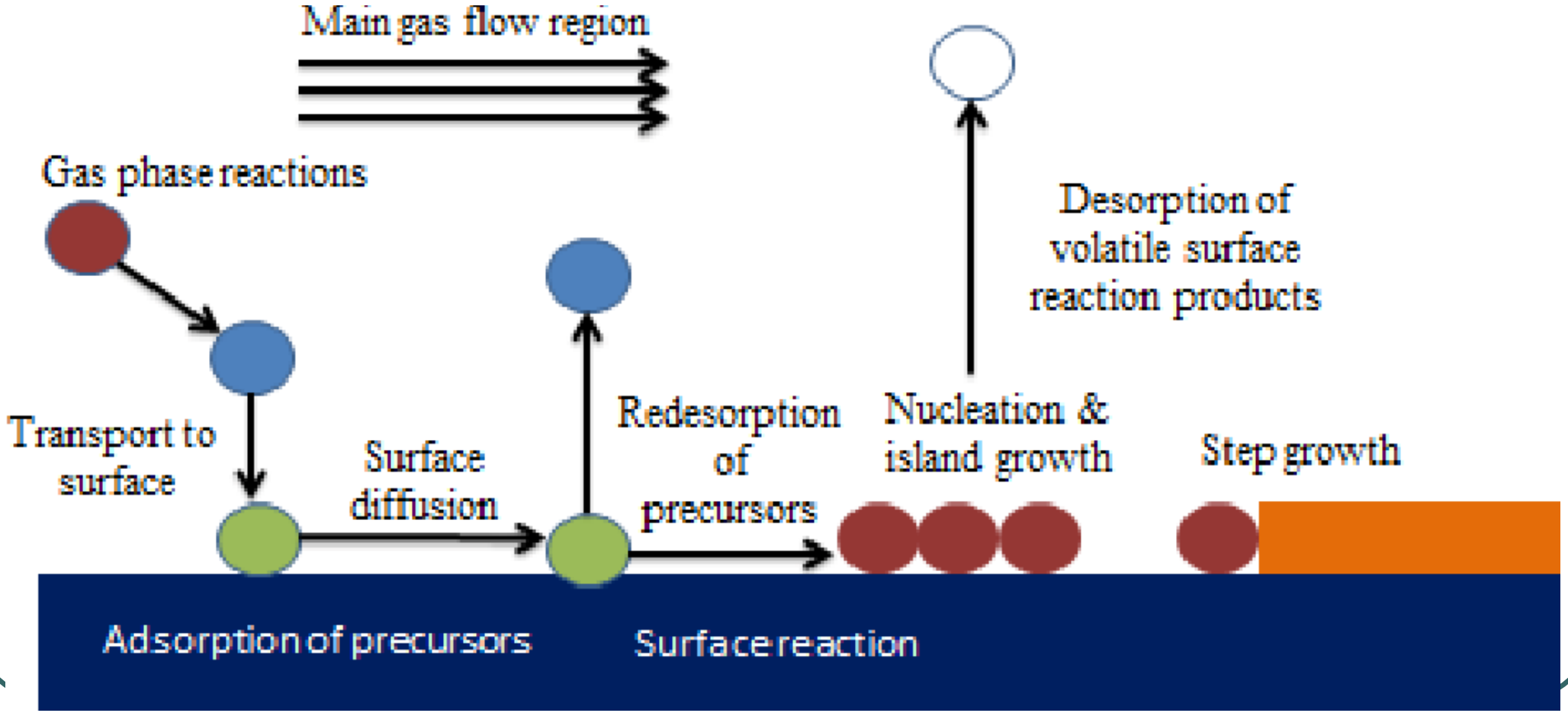


FIG. 1. Diode sputtering system. 1. argon cylinder, 2. vacuum system, 3. needle valve, 4. H.V. supply, 5. metal base plate, 6. chamber walls, 7. seal, 8. metal plate, 9. holder, 10. target, 11. support, 12. substrate.

CVD (Chemical Vapor Deposition)

Chemical way: the layer prepared on site in chemical reaction :-)



CVD (Chemical Vapor Deposition)

Advantages:

- Wide range of possible coatings (metals, ceramics)
- Good adherence of coatings
- Coats evenly from each direction (even fills up holes)

Disadvantages:

- Reactive reagents (metal halogenides, organometallics)
- More wear on substrate, than with PVD (temperature, reactions, plasma)
- More wear on pumps (traps, chemically compatible pumps)

CVD (Chemical Vapor Deposition)

- Some examples:

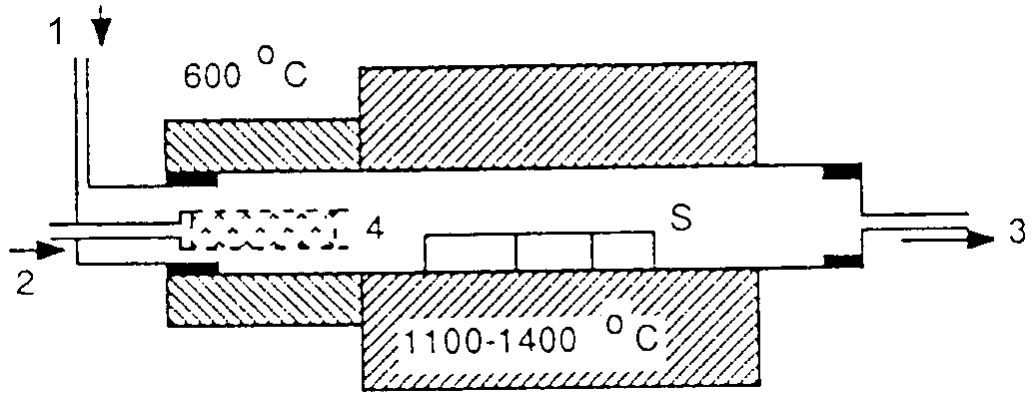
$TiCl_4 + N_2 + H_2$	$\xrightarrow{950\text{-}1200^\circ C}$	TiN
$SiH_4 + N_2H_4 + H_2$	$\xrightarrow{550\text{-}1150^\circ C}$	Si_3N_4
$TiCl_4 + SiCl_4 + CCl_4 + H_2$	$\xrightarrow{1000^\circ C}$	Ti-Si-C (several phases)
$Zr/Hf(BH_4)_4$	$\xrightarrow{400^\circ C}$	Zr/Hf-boride
$Zr/Hf(BH_4)_2Cp_2$	$\xrightarrow{400^\circ C}$	Zr/Hf-carbide
$Cr(Ar)_2$	$\xrightarrow{400^\circ C}$	Cr_7C_3 ($Ar=PhEt_{1\text{-}4}$)

It happens for example in hot cathode gauges too…

CVD (Chemical Vapor Deposition)

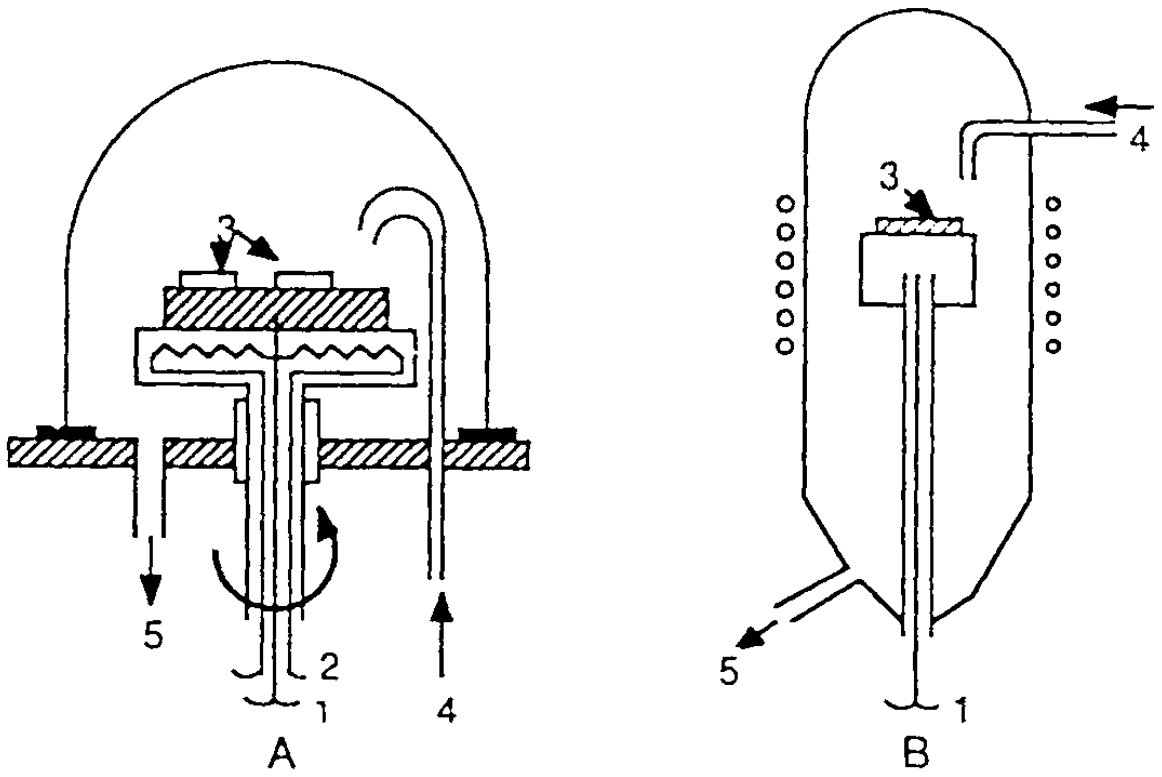
Variations:

- Atmospheric (APCVD; viscous flow)
- Low pressure (LPCVD; molecular flow)
- Hot walled furnace, as a tube furnace. Coating on the oven wall



CVD (Chemical Vapour Deposition)

- Cold wall furnace. The substrate is heated specificaly. Contact, inductive.



CVD (Chemical Vapor Deposition)

- Plasma CVD (PACVD, PECVD). Cold plasma
- Photo-CVD (PCVD). Precursors excited directly or through Hg-atoms.
- Laser-CVD (LACVD). Heating the substrate with laser beam.
- Metal Organic CVD :-) (MOCVD). Lower temperatures. The composition of the coating can be set by tailored molecules. Halogen-free coatings.

CVD (Chemical Vapor Deposition)

Related: metal atom reactor.

$$Pd + RX + 2\,PR_3 \rightarrow PdR(X)(PR_3)_2$$

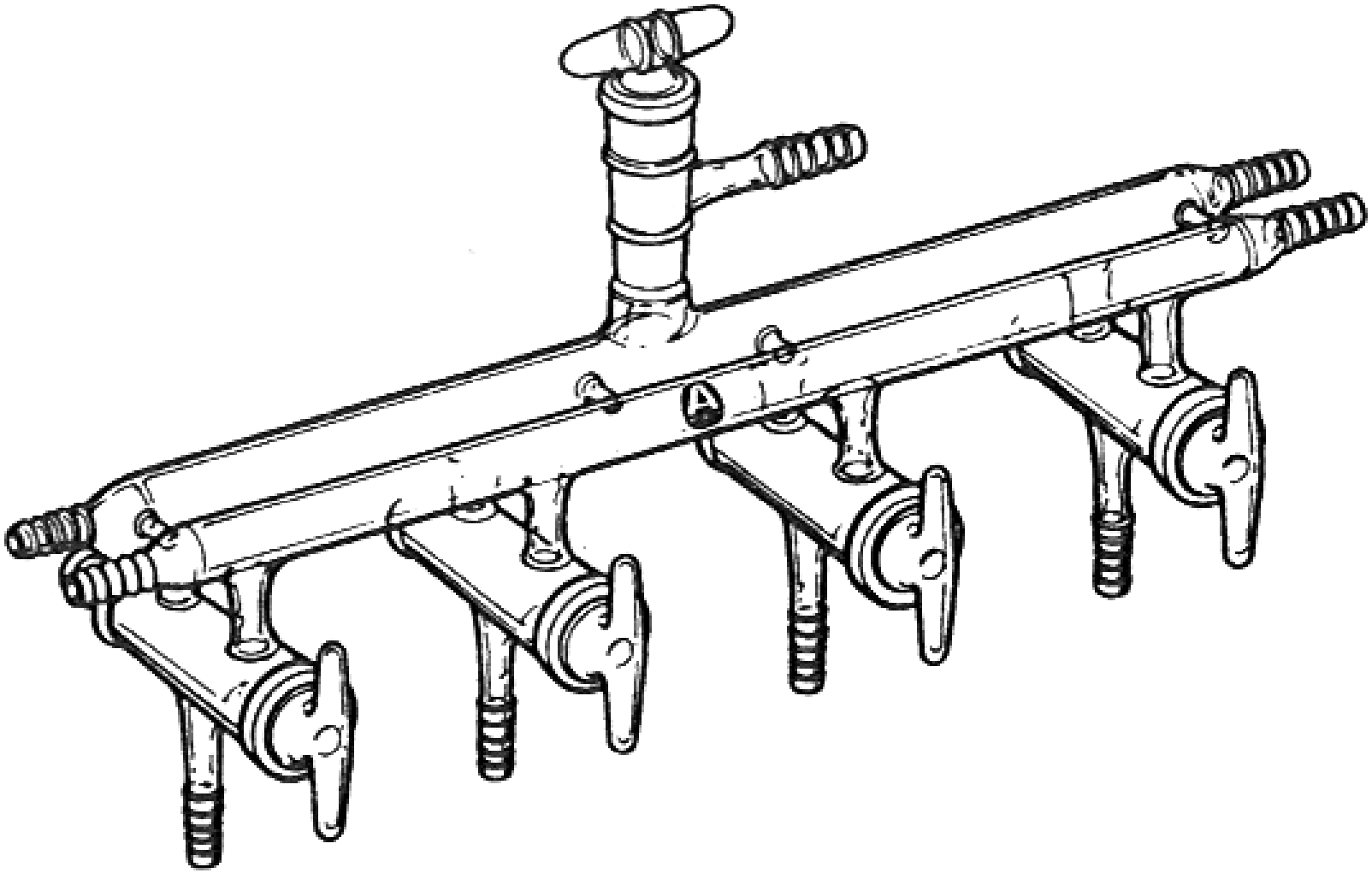
$$Ni + C_6F_5Br + C_6H_5Me \rightarrow NiBr_2 + (C_6F_5)Ni(\eta\text{-}C_6H_5Me)$$

$$Cr + 2\,C_6H_6 \rightarrow Cr(C_6H_6)_2$$

Vacuum-line (inert atmosphere)

- Purpose: inert environment for sensitive materials. In most cases one wants to exclude air and/or water, but up to taste.
- A typical configuration is vacuum and inert gas on double piping: one for vacuum, other for inert gas, one can choose by bidirectional valves.
- Enchancments: gas and liquid storing vessels, gas burette with Toepler pumpfor dosing gases (pV=nRT accurate enough)

Vacuum-line (inert atmosphere)



Vacuum-line

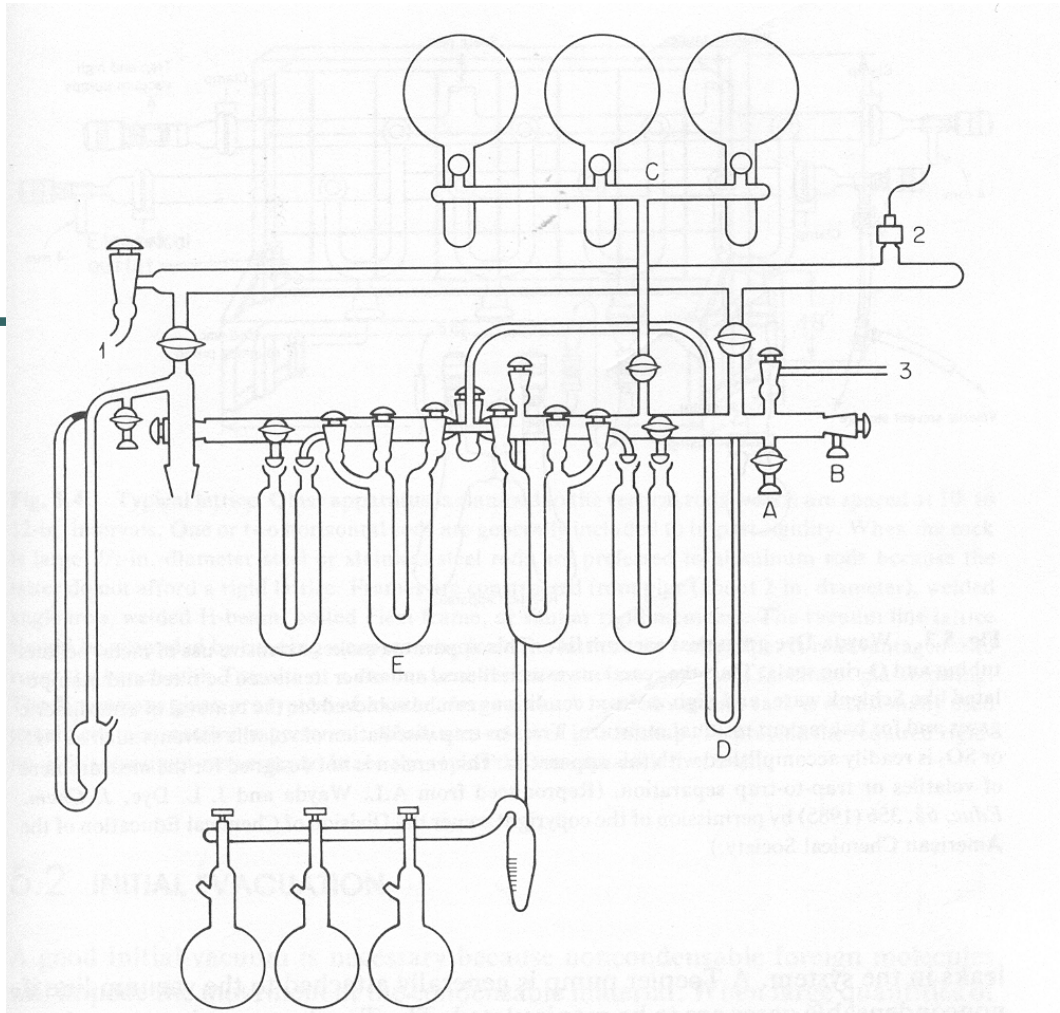


Fig. 5.2. Multipurpose high-vacuum system. Bulbs for gas storage are at the top of the figure. Directly below these is the high-vacuum manifold, which is attached to a trap and pumps at site 1 and connected to a high-vacuum gauge at 2. The working manifold in the center of the figure is attached to a train of U-traps and to various inlets. It is also connected to a Toepler pump at 3. Gases and volatile liquids are introduced through the inlets attached to this manifold, and large reaction vessels or special apparatus are frequently attached to the large joint. At the bottom of the figure is a manifold with solvent storage vessels attached; it is also connected to a graduated trap which allows measurement of the volume of solvent before it is transferred to the main working manifold. Standard high-vacuum stopcocks are employed except on the solvent and gas storage bulbs, where greaseless needle valves are used.

Vacuum-line

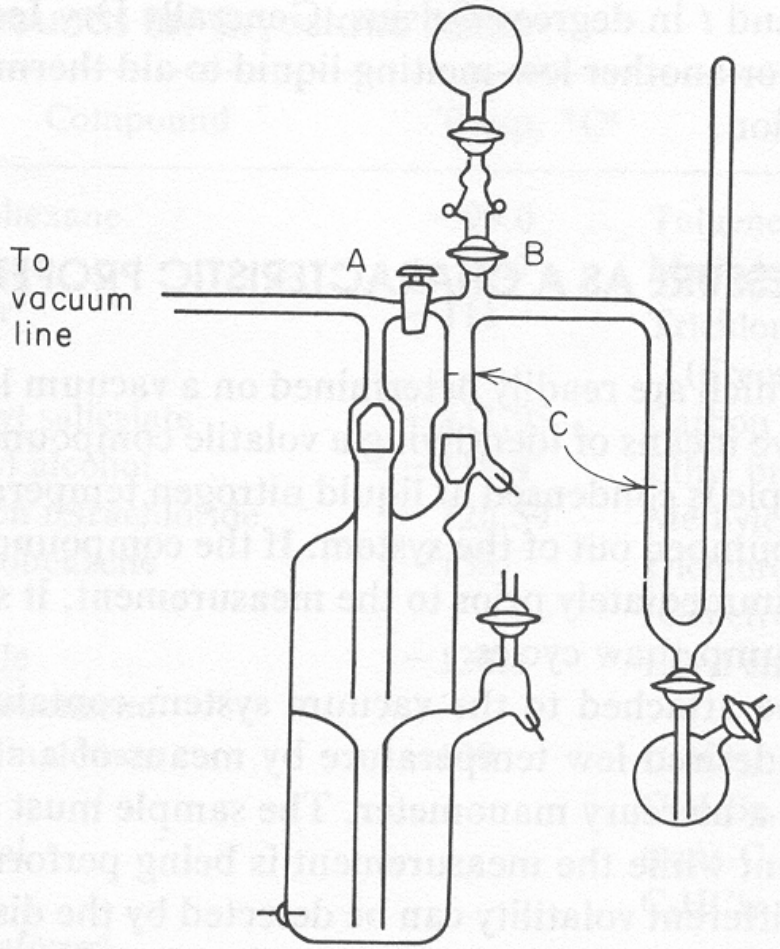


Fig. 5.9. Toepler pump and gas buret. In this installation a "constant-volume" manometer is used for measuring the pressure. Stopcock B allows the attachment of a sampling bulb or a large expansion bulb for use with large volumes of gas. Stopcock A is used for initial evacuation of the calibrated volume and sample bulbs. It is closed during the operation of the pump. When a gas is to be measured, the mercury levels in the right arm of the Toepler pump and in the left arm of the manometer are adjusted to levels (C) for which the gas volume has been calibrated. An excellent version of this pump is manufactured by the Rodder Instrument Co., Los Altos, Calif.

Vacuum-line (inert atmosphere)

- Vacuum: rotary vane pump with trap, membrane pump
- For higher vacuum: turbo or diffusion pump
- Gauge: Toricelli, McLeod, diaphragm (capacitive/piezo), thermal conductance (Pirani, thermocouple), Penning ionisation
- Flexible tubing: silicone (water permeable!), Tygon. For higher demands spherical glass joint, or even welded glass
- Trap: material to be frozen onto the cold wall. For more dangerous materials, which require safe disassembling: U-trap with spherical joints.

Vacuum-line

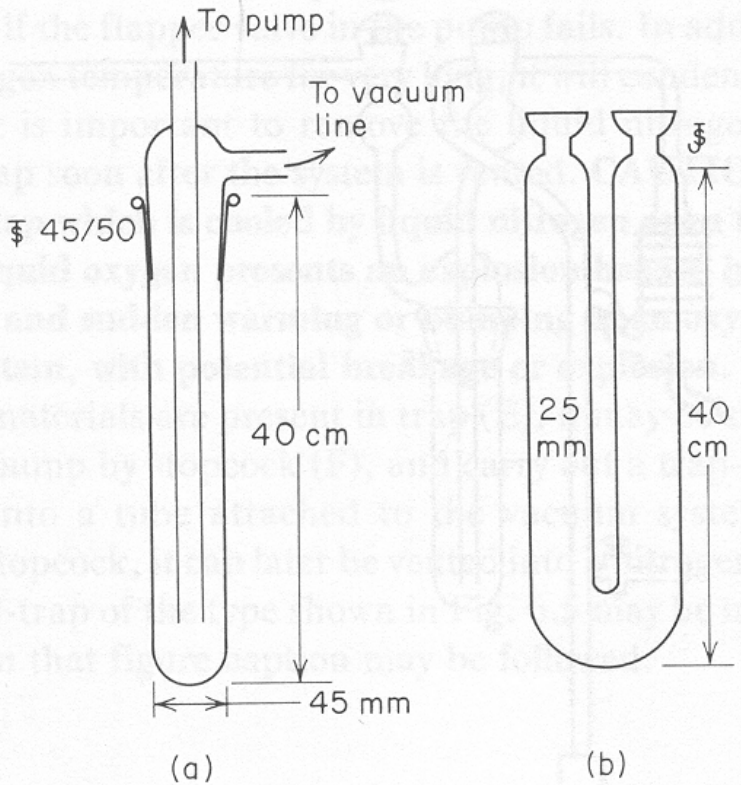


Fig. 6.5. Main traps. (*a*) This trap is long enough to extend to the bottom of a 1-L Dewar and sufficiently small in diameter to avoid excessive displacement of liquid nitrogen. These features allow the trap to remain partially immersed in liquid nitrogen after standing overnight. The arrangement of inlet and outlet shown here minimizes clogging of the trap because most of the condensate is deposited on the large outer tube rather than the smaller inner tube. (*b*) A U-trap is advantageous if there is a likelihood of condensing significant quantities of pyrophoric or highly toxic compounds, because a finite amount of material is always condensed on the center tube of trap (*a*). To remove a trap such as (*b*) from the line, one should fill it with nitrogen and quickly take it to a hood, where a slow stream of nitrogen may be passed through it to moderate the reaction which will occur when the contents of the trap warm up and volatilize. Ball joints facilitate the removal of a U-trap.

Vacuum-line (inert atmosphere)

- Inert gas: usually N_2 (Ar can freeze in lN_2 trap)
- 4.6 quality is OK, more practical to clean than to buy higher purity
- Oxygene-scavenging: BTS-catalyst (BASF). Supported Cu_2O, captures oxygen as CuO. Regeneration with 5% H_2/N_2 max. 200 °C. Black→green colorchange indicates oxidation.
- Drying: silicagel, molecular sieve, supported P_2O_5 / Sicapent(beware of possible PH_3)

Vacuum-line (inert atmosphere)

- Inertisation of equipment: (vacuum-heating-inertgas)*3
- Complicated equipment: drying oven 105 °C overnight, cooling in inert gas stream
- Ultrasound bath
- Solvents: see for example Purification of Laboratory Chemicals

Vacuum-line (inert atmosphere)

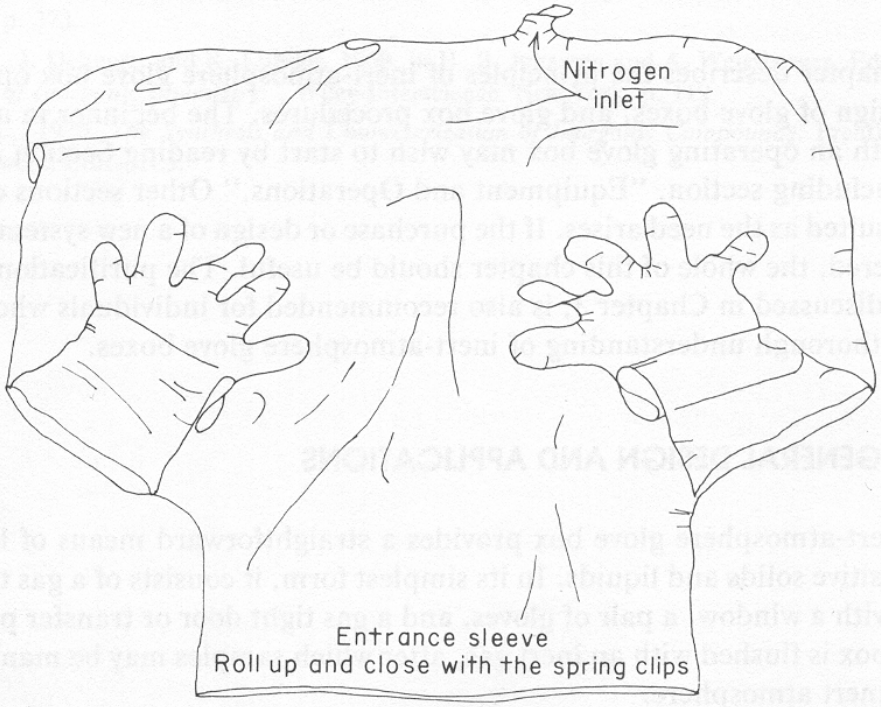


Fig. 2.1. Polyethylene glove bag. Several sizes are available, including glove bags with two pairs o gloves. (Adapted from Instruments for Research and Industry, Cheltenham, PA, Glove Bag bro chure.)

Fig. 2.13. Commercial metal glove box. An aluminum glove box with a recirculating gas-purification system. (Reproduced by permission of the copyright owner Vacuum Atmospheres Corp., North Hollywood, Calif.)

Glove bag can be home-made with (modified) PE-welder (vacuum bags into the freezer), PE-bag and PE-glove

Glove bag, glove box, dry box

Vacuum-line (inert atmoshere)

- Gas should be circulated through purifiers (or plenty inert gas flow thorugh the boksz).
- Chemical tests for gas purity: $TiCl_4$ should not produce smoke (water), $ZnEt_2$ should not smoke/ignite (O_2). Naked incadescent lamp should not burn out (O_2).
- Measurement: for example Rapidox (Cambridge Sensotec)

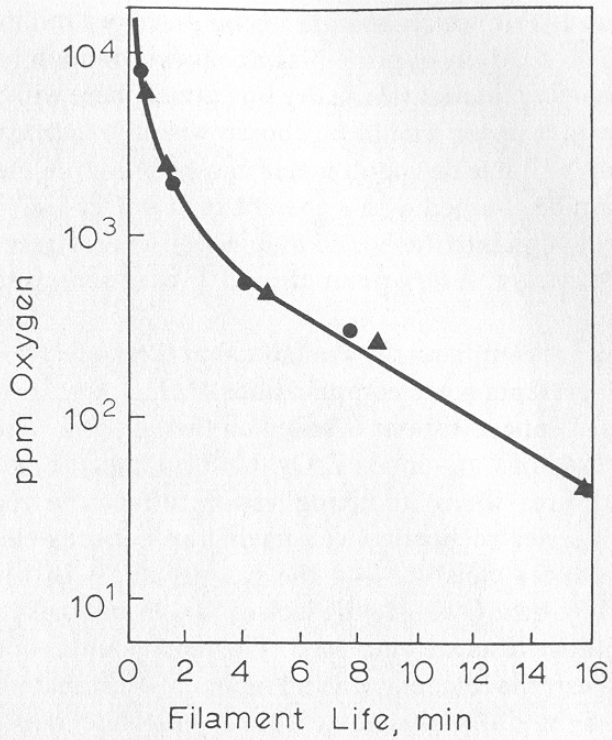


Fig. 2.8. Oxygen concentration versus filament lifetime for an exposed light bulb filament burning in an inert atmosphere. By noting how long the light bulb stays lit, a reasonable estimate of the oxygen plus moisture impurity level can be obtained. These data correspond to an A/C No. 63 bulb filament run with 10 V potential and a gas flow rate of 1.1 L/min.

Vacuum-line (inert atmosphere)

- Gas purification system of a glove box

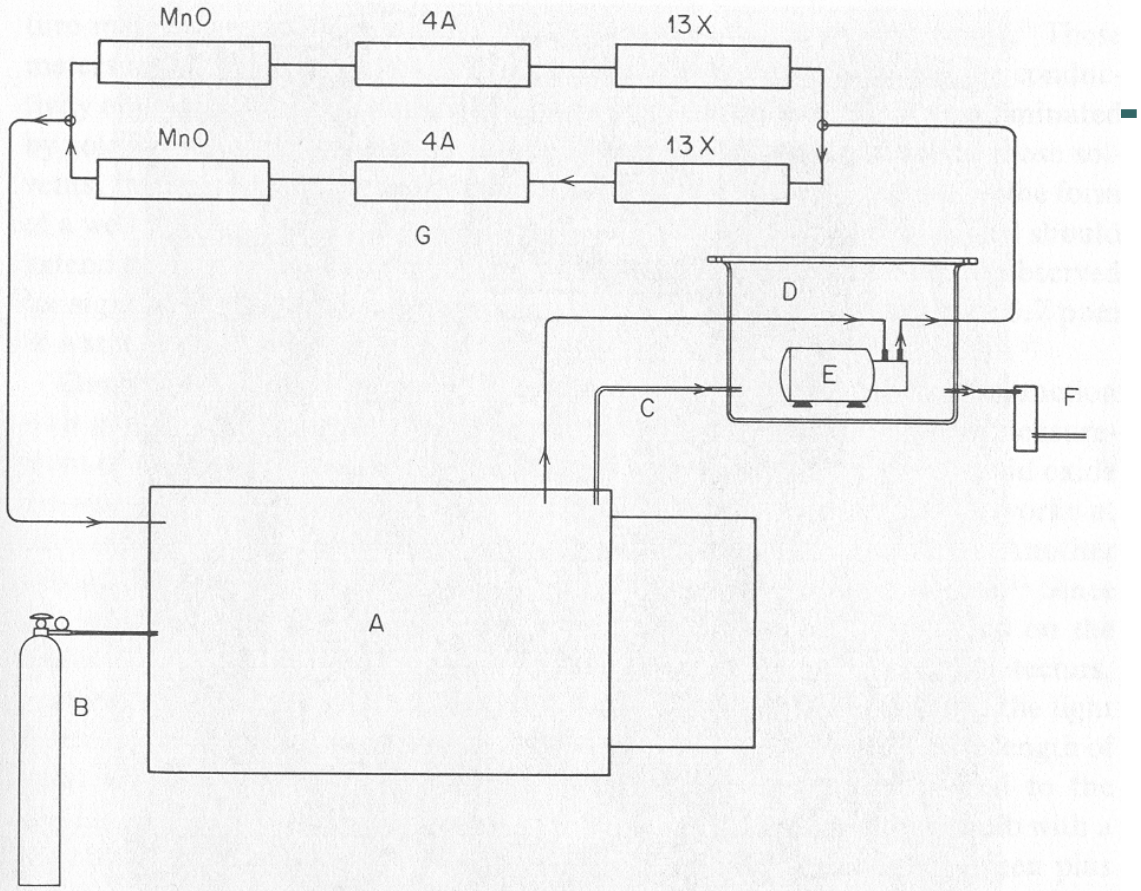


Fig. 2.6. Schematic representation of a dry-box purification scheme. (A) Glove box; (B) tank argon; (C) purge line for pump container; (D) gastight pump container; (E), 2.7 ft^3/min graphite ring pump; (F) bubbler; (G) purification train consisting of Linde 13X and 4A Molecular Sieves, and Vermiculite-supported MnO at room temperature (see Chapter 3). In some installations an additional drying column follows the MnO column. Approximate column dimensions are 3-in. diameter by 4-ft length. (Unpublished design of T. L. Brown.)