K15. Vacuum Technology and Evaporation in a Vacuum

I. INTRODUCTION AND OBJECTIVE OF THE EXPERIMENT

Vacuum technology has been widely developed over the past years, due to its numerous applications, ranging from space ships to the manufacturing of microelectronic devices in a vacuum. It has become an industrial discipline, from which researchers benefit greatly.

The techniques for evaporation of chemicals in a vacuum are widely used for thin film deposition on rigid substrates, leading to multiple applications: production of optical interference filters, microelectronic components, solar cells and more. There are a variety of methods and techniques that use evaporative heating sources whether simple or sophisticated, for instance the Joule effect, RF induction, electronic, ionic or photonic (laser) bombardment, etc. We suggest learning about evaporation by Joule effect in this experiment, using some knowledge of vacuum techniques, with the objective of creating a solar cell.

II. PHENOMENOLOGY

II.1. VACUUM TECHNOLOGY

When installing a vacuum pump, two fundamental parameters come into play. The work pressure, which is not to be confused with the limiting pressure, and the time required to reach it. These two parameters depend on the pump, and the vacuum chamber. In the SI unit system, the unit for pressure is the *Pascal* ($1\ \mathrm{Pa} = 1\ \mathrm{N/m^2}$), but we often use the $\mathrm{mbar} = 100\ \mathrm{Pa}$ or the Torr i.e. mm de Hg $= 133.322\ \mathrm{Pa}$.

Limiting pressure

The limiting pressure that can be reached in a vacuum setup is given by the equilibrium between the pumping throughput and the leakage and outgassing of the walls. The equipment must be kept as clean as possible, and most importantly remain dry. Condensable vapor leaves the system through outgassing, after heating the walls by a few hundred degrees. Nitrogen traps can be placed between the gas source and the vacuum chamber as another means of purification.

Pumping speed

The pumping speed (volumetric throughput) through a surface is defined by the volume of gas that crosses it per unit time. The volume is measured according to the pressure of the surface. The pumping rate depends on the type of the pump (vane, diffusion, etc.) on the used liquid (silicone oil) and also the pressure. When designing a vacuum setup, always choose a pumping group with a speed well above that which would maintain the desired limit pressure.

Pump sizing

The effective throughput of a pump *S* can be determined form pumping dynamics. During the pumping process, the pressure inside a chamber of volume *V* evolves according to:

$$\frac{dP}{dt} = -\frac{S(P)}{V}\left(P - P_0\right)$$

where P_0 is the limiting pressure of the pump. In the region where the S can be supposed constant, we can integrate this equation, yielding:

$$\ln\left(\frac{P_2 - P_0}{P_1 - P_0}\right) = -\frac{S}{V}t$$

In this equation, t represents the amount of time required to get from a pressure P_1 to a lower pressure P_2.

II.2. EVAPORATION

Evaporation by Joule Effect

The process takes place in a closed space, where an appropriate vacuum is maintained. The method consists in placing the substance to evaporate in metallic pods (Mo, W Ta, etc.) that will carry a current, and heat the substance by Joule effect. Most materials show no down sides to evaporation, however, some materials, such as Si , Al, Co, Fe and Ni are highly reactive and require special pods. In the event that a chemical reaction could occur with the pod, we can add an intermediate layer of ceramic (e.g. boron nitride). There exist tables that indicate the type of pod that should be used depending on the material to evaporate. Finally, one must verify that non unwanted chemical reaction occurs between the evaporated substance and the surrounding air.

Background Theory

According to the kinetic theory of gases and the Maxwell-Boltzmann velocity distribution (classical theory), the average speed of a molecule of mass m in a gas heated to a temperature T is:

$$\langle v \rangle = \sqrt{8k_B T / \pi m} \qquad (1)$$

and the molecular flux ϕ_M , i.e. the number of molecules that enter or leave the surface per unit time, is given by

$$\phi_M = \frac{P}{\sqrt{2\pi \cdot m \cdot k_B T}} \qquad (2)$$

The molecular flux ϕ_M and the mean free trajectory l, defined as the mean distance that a particle will travel between two impacts, are two very important physical parameters in the thin layer deposition. These two parameters allow us to better understand the contamination problem of surfaces by the residual gases and the energy loss of molecules through multiple collisions.

The pressure of the evaporation space must be low enough for the mean distance l of the atoms or molecules to be greater or equal to the distance h separating the pod from the target. Therefore, pressure control is very important to avoid collisions between atoms and/or molecules of the surrounding environment (N_2, H_2O, CO_2 etc.) and the evaporated atoms. In fact, the fraction of atoms N that are deflected from their original trajectory to a random one is given by $N \approx N_0 \exp\left(-h/l\right)$.

Mean free distance l

Let's define $l = <v> \tau$ where τ is the relaxation time. In order to calculate l, let's suppose that all molecules are at rest, except for one that is moving at a speed $<v_{rel}> = \sqrt{2} <v>$ (Maxwell-Boltzmann velocity distribution law). This molecule only hits the others if their centers are both within a cylinder of surface $\sigma = 4\pi \cdot r^2$ and whose axis is $< v_{rel} >$ where r is the radius of the molecule (Fig. 1).

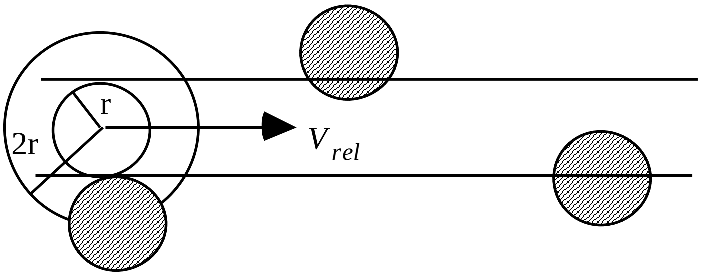


Fig. 1 Effective collision surface σ = 4 πr^2

If n is the number of molecules per unit volume, we can deduce the total number of impacts per second is given by $v = \tau^{-1} = n\sigma < v_{rel} >$, thus $l = 1/\left(\sqrt{2}n\sigma\right)$. An empirical formula gives l for one residual atmosphere of air

$$l = \frac{c}{P} \tag{3}$$

where $c = 6.7 \cdot 10^{-3}$ Pa·m.

Energy loss due to elastic collisions

During an elastic collision, between an incident particle of mass M_i and energy E_i and another particle of mass M_j, the transmitted energy E_t is:

$$E_t = E_i \frac{4M_i M_j}{\left(M_i + M_j\right)^2} \cos^2\theta = E_i K \cos^2\theta \tag{4}$$

where θ is the deflection angle. By integrating over all directions of space, we find that the average value of the transmitted energy is

$$< E_t/E_i >= K \frac{\int \cos^2\theta \cdot d\theta}{\int \cos\theta \cdot d\theta} = \frac{2}{3}K \tag{5}$$

This implies that is the pressure in the container isn't low enough, the evaporated molecules will quickly lose their initial energy through multiple collisions before getting to the target, which will lead to poor adherence.

Deposition speed and geometry effects

The deposition speed of molecules (per unit surface and time) on a substrate depends mainly on the mass and the density of the molecules, and on the geometry of the experimental setup. In the event of a point emission source, , the deposition speed in a direction defined by the angle θ follows **Knudsen's law**, i.e. it goes like $\cos\theta/r^2$.

In a solid angle portion dΩ there evaporates a quantity $\delta m = m\left(d\Omega/4\pi\right)$ of material of mass m and density ρ (see Fig. 2). The thickness corresponding to δm therefore is:

$$e = \delta m/\left(\rho dS\right) = \left(m/4\pi\rho\right)\left(d\Omega/dS\right) = \left(m/4\pi\rho\right)\left(1/r^2\right) \tag{6}$$

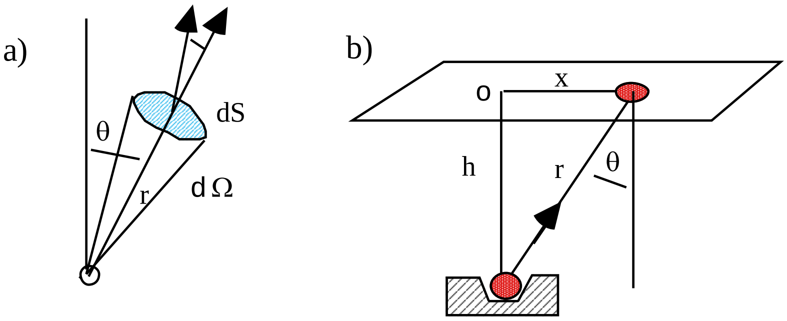


Fig. 2 a) Evaporation solid angle dΩ. b) Evaporation with a target located at a distance h of the source.

If the deposition is made on a planar surface $dS_1 = dS\cos\theta$,inclined by an angle θ with respect to the evaporation direction, then

$$e(\theta) = \left(m/4\pi\rho\right)\left(\cos\theta/r^2\right) \tag{7}$$

We can easily show that the spatial distribution of the evaporation has a large impact on the lateral homogeneity of the deposed layer. Equation (6) can be written as follows (Fig. 2b)

$$e(\mathrm{x}) = \left(m/4\pi\rho\right)\left(h/r^3\right) = \left(m/4\pi\rho\right)\left(h/\left(h^2+x^2\right)^{3/2}\right) \tag{8}$$

Required conditions for a good condensation

Contamination

Table 1 comparatively shows the different physical parameters discussed above. We can see that up to 10^{-5} Torr ϕ_M or its equivalent in number of atomic layers is substantial. This means that even at 10^{-5} Torr the contamination of the surface and rest gases is far from negligible.

Pressure [Torr]	*l* [cm]	Collisions [s^{-1}]	ØM [cm^{-2} s^{-1}]	Nbr of atomic layers
10^{-3}	5.1	$9 \cdot 10^{3}$	$3.8 \cdot 10^{17}$	$4.4 \cdot 10^{2}$
10^{-5}	510	90	$3.8 \cdot 10^{15}$	4.4
10^{-7}	$5.1 \cdot 10^{4}$	0.9	$3.8 \cdot 10^{13}$	$4.4 \cdot 10^{-2}$
10^{-9}	$5.1 \cdot 10^{6}$	$9 \cdot 10^{-3}$	$3.8 \cdot 10^{11}$	$4.4 \cdot 10^{-4}$

Table 1 Estimated values for air at room temperature T_a

Surface to cover

A good adhesion of thin layers requires a faultless surface of the target. This can be acquired as follows.

Using organic solvents

a) manual cleaning
b) ultrasound cleaning

Right before the deposition process:

c) Final impurities are removed by heating in a vacuum
d) eventual layers absorbed by spallation, i.e. ionic bombarding in one atmosphere of (noble or not) gas

III. EXPERIMENTAL SETUP

III.1. SETTING UP OF A VACUUM CHAMBER.

The elements that make up a vacuum setup are, in addition to the pumps and pressure gauges, the junction pieces, joints, valves, separating units, and traps (fig. 3). The most used materials are metal (aluminum or stainless steel), glass, quartz, ceramic, rubber and plastic.

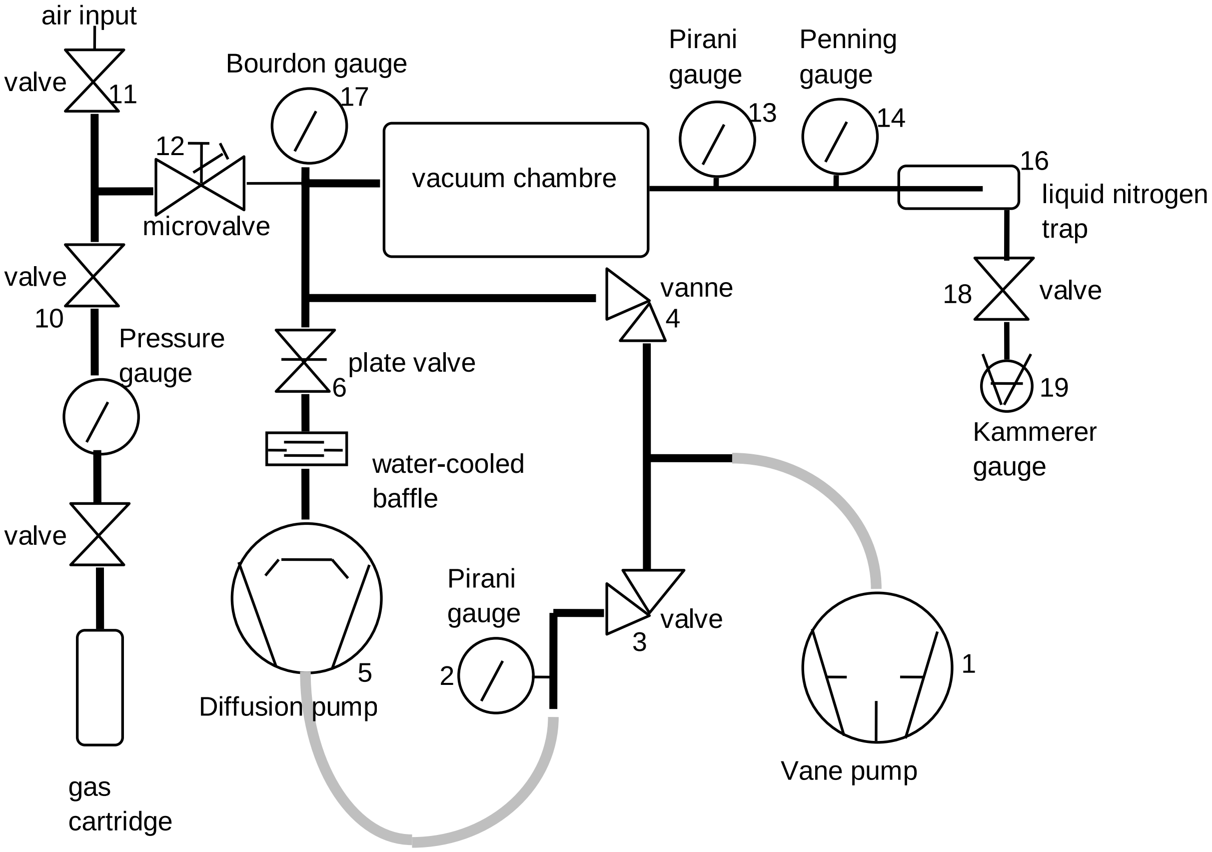


Figure 3: Diagram of the high vacuum setup. The numbering correspond to that on location.

III.2. EVAPORATION INSTALLATION

The equipment of a vacuum evaporation system is mainly made up of:

A vacuum chamber in glass or steel
A pumping mechanism (roughing pump and diffusion pump)
A source of evaporation, masks and substrate holders

Temperature, pressure, and layer thickness measuring devices

In this lab experiment, we will use a BALZERS equipment. The vacuum chamber (cylindrical steel chamber) already contains the pods, substrates, masks and pressure gauges. It also has a few doors and windows that allow it to communicate with the outside through watertight current sources, a junction with the pumping mechanism and a glass front door allowing access to the pods.

Careful: before closing the door with the tightening mechanism, push it in completely with both hands, and keep it pushed while tightening the bolts.

The vacuum, spallation and heating of the pods is achieved by using two control panels, that will be described on location. The procedure is described on location and in appendix 1.

Main precautions:

a) Never get the pods, substrates or the chamber dirty (use gloves if possible)
b) Do not melt the pods

The pods (one for gold and one for silver, don't mix them up) are made of tungsten, and melt at 3650 K, much higher than silver (1234 K) or gold (1336 K). In principle, once, you see fusion of silver or gold (gold evaporates slower than silver) taking place, stop increasing the current going through the pods.

IV. REQUIRED EXPERIMENTS

VACUUM TECHNOLOGY

1. Measure the **primary pumping kinetics** when the vacuum chamber of volume V is emptied. Determine from this the effective throughput S, and the limiting pressure of the vane pump. The vacuum happens very quickly. You may want to film the pressure gauge, and then match the indicated pressure of a given frame to the corresponding time of the video.

2. Calibrate the Pirani gauge using the Kammerer gauge

a) For air
b) For another gas (helium)

Procedure

a) For air

Carefully fill the liquid nitrogen trap. Let air into the system using the microvalve, until the pressure reaches 0.01 Torr. Measure the pressure using the Kammerer gauge.

Repeat this measurement for different pressures ranging from 0.01 Torr to ~ 75 Torr. Compare these values with those indicated by the Pirani gauge.

b) For helium

Open the valve over the gas cartridge. The pressure gauge indicates the pressure in the cartridge. Purge the whole circuit by introducing gas two to three times in the chamber (~ 100 Torr) using the micro valve, and then pumping until reaching the limiting pressure of the vane pump. Then let in a small amount of gas into the chamber, and measure the pressure using the Kammerer gauge. Repeat this process for values ranging from 0.01 to ~ 75 Torr T. Write down the pressures indicated by both gauges. Close the gas cartridge.

3. Measure the **secondary pumping kinetics**, using the diffusion pump. Determine the pumping speed, as well as the limiting pressure of the diffusion pump.

Procedure:

The hot oil of the diffusion pump must never come in contact with that atmosphere at a pressure exceeding 0.01 Torr. Therefore, proceed as follows:

a) Empty out the vacuum chamber until approximately 0.01 Torr using the rotary vane pump.
b) Pump out the diffusion pump until it reaches approximately 0.01 Torr.
c) Start the diffusion pump, while making sure to keep the vane pump running "behind" it. The vane pump serves as an outgassing pump for the oil. After approx. 15 min. The diffusion pump reaches its working pressure.
d) If the pressure inside the chamber is less than 0.01 Torr, then we can open the plate valve, and the pressure quickly drops from 0.01 Torr to $10^{-3}, 10^{-4}$ Torr.

e) Starting at 10^{-2} Torr, turn on the Penning gauge, and write down the pressure as a function of time, until reaching the limiting pressure. Plot the corresponding curve, and determine the corresponding pumping throughput.

Stopping the diffusion pump

Close the plate valve. Turn off the diffusion pump and the Penning gauge.
After MINIMUM 20 minutes, close all the valves leading to the vane pump, before turning it off. Turn off the Pirani gauge, and the main power supply.

Using the microvalve

When the microvalve is correctly closed, the button can turn freely. **NEVER FORCEFULLY TRY TO CLOSE THE VALVE by screwing it passed the free rotation.**

EVAPORATION OF THIN LAYERS

4. Using equations (2) and (3), determine the ideal working conditions while taking into account the geometry of the experimental setup.

5. Estimate the inhomogeneity in percentage (e_x/e_0) due to the effects of the geometry for $x = h/4$.

6. Estimate the thickness of the thin layer. Knowing that the mass m of a material of density ρ evaporates isotropically and that it forms a homogeneous layer of thickness e in the surface S_e of a hemisphere of radius r, show that

$$e = m / \left(2\pi\rho r^2 \right)$$

In reality, the geometry of the pod limits the solid angle to $\Omega \approx \pi$ instead of $\Omega = 2\pi$, which leads to a thinner layer.

$$e \approx m / \left(\pi\rho r^2 \right)$$

Calculate the masses of gold and silver necessary to deposit a layer 200 Å in thickness, knowing the distance d separating the source from the substrate.

7. Make a semi-transparent mirror by deposition of a thin layer of thickness

$e = 2 \cdot 10^{-8}\ \mathrm{m} = 0.02\ \mu\mathrm{m} = 200\ \mathring{\mathrm{A}}$ on a glass substrate (object holder for microscope)

8. Make a basic solar cell. Mount a Si sample on the substrate holder (hold it by a corner).

After an ionic cleaning process (spallation), deposit a thin layer (approx. $200\ \mathring{\mathrm{A}}$) of Ag on one of the faces of the amorphous silicon sample, and an analogous layer of Au on the other side of the sample
Place the solar cell between the contacts of the clamp, illuminate it with a simple light source, and measure the voltage (Fig. 4).

This type of cell can only illustrate a basic principle. Industrially, these cells are produced on large cells of doped amorphous silicon, on which we then deposit layers of materials that will create n and p junctions. Currently, their theoretical efficiency is of 15%. Experimentally, the efficiency doesn't go over 7%.

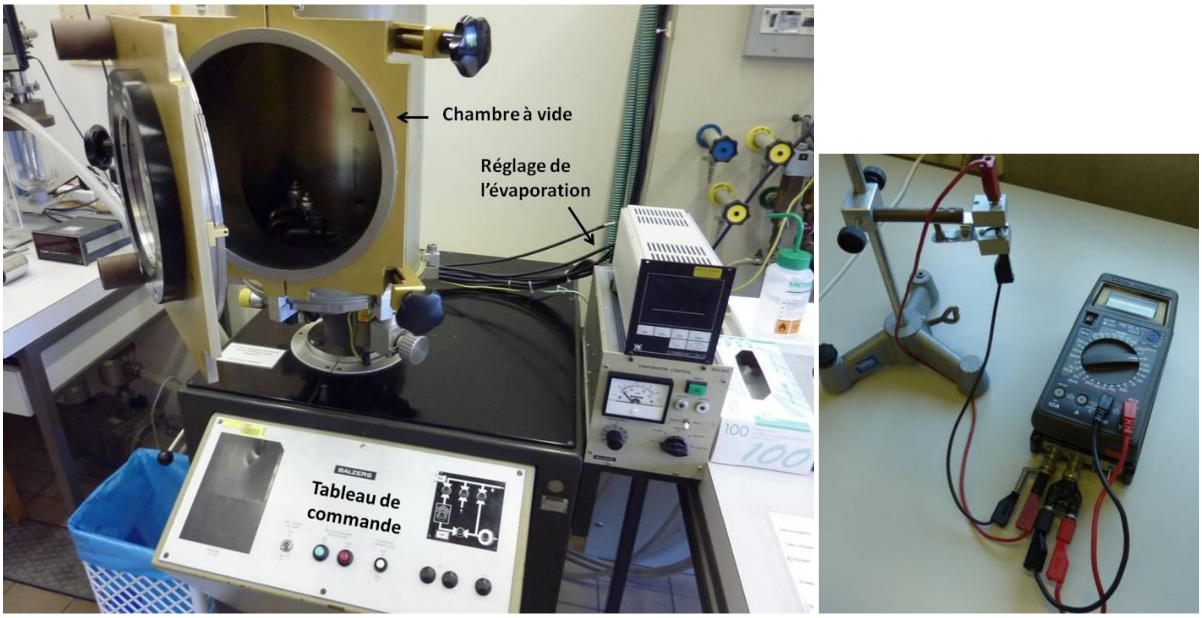


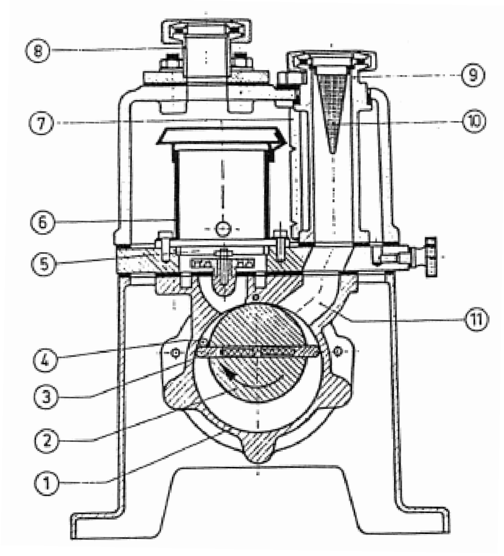
Fig. 4: Images of the experimental setup

ANNEX

VACUUM PUMPS

Rotary vane pumps

A vane pump (fig. 5) consists of a hollow cylinder (1) in which an uncentered rotor (2) containing vanes (3) is rotated. The vanes are constantly pressed against the cylinder walls, thus sucking air from one side of the pump (11) and pushing it through the exhaust valve (5) on the other side. The rotor is off center, so that the volume of gas trapped by two vanes is variable. This allows the air to be compressed when arriving towards valve, which ensures that there will always be enough pressure to lift it. Many parts of the system are covered in oil. The oil simultaneously acts as a lubricant and covers up the remaining gaps.



1. Cylindrical pumping body
2. Uncentered rotor
3. Vanes
4. Gas Ballast entry
5. Oil covered exhaust valve
6. Oil deflectors
7. Oil gauge
8. Exhaust tubing
9. Entrance tubing
10. Impurity trap
11. Suction canal

Figure 5: Sectional view of a rotary vane pump

Fluid pumps

Fluid pumps are all based on the same principle: the gas to be evacuated is transported from a low pressure region to a higher pressure region using a high pressure jet of steam (oil, mercury, water, …). The steam never leaves the pump, since it is condensed as soon as is hits the cooled walls of the pump.

Gaede was the first to notice that a relatively low gas pressure could be sucked into a jet of steam at a much higher pressure, so that the gas molecules were transported from a low pressure area to a higher pressure area. This seemingly paradoxical phenomenon is due to the fact that the steam is first completely gas-free, so that the gases diffuse from an area where there is a gas of high partial pressure (container) to an area where the partial pressure of the gas is lower (the steam). You can consider the steam as a semi-permeable membrane (similar to the osmosis phenomenon), through which the gas can diffuse to enter but not to leave, the partial pressure of the gas is therefore much higher on one side of the jet than on the other.

Diffusion pumps (zone de travail $< 10^3$ Torr)

Diffusion pumps (fig. 6) are made of a pumping body (1), in which the bottom can be heated, and the sides cooled, and an internal body with several stories (generally three) (2). The motor fluid kept in the heating tank (5), is heated and vaporized electrically. The vapor rises in the column (4) and leaves through the nozzle (3) at a supersonic speed. The fluid then condenses on the water cooled walls, and drips back into the heating tank. The pumped gas is absorbed by the oil, and leaves through the exhaust tube.

For oil diffusion pumps, it is necessary to outgas and fractionate the oil before letting it back into the heating tank (5).

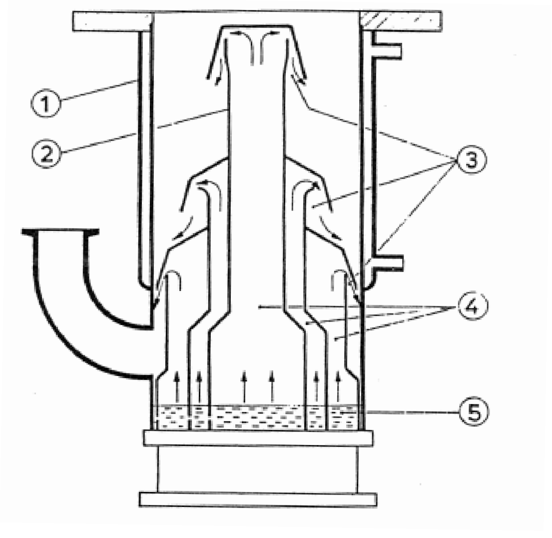


Figure 6: Diffusion pump diagram.(1) Pumping body, (2) Internal body, (3) Nozzles, (4) Steam rising tube, (5) Heating tank.

Outgassing: The condensed motor fluid drips along the walls is brought under the heat tank, at a temperature of approximately $130\ ^\circ\mathrm{C}$, at which point the more volatile molecules are absorbed by the *primary pump*. The less volatile molecules however, remain in the fluid.

Fractionating oil: After being outgassed, the motor fluid is made up of elements varying in weight. The fractionating equipment makes sure the elements easiest to evaporate are brought to the first nozzle, close to the primary vacuum, and the elements hardest to evaporate are brought to the third nozzle, close to the molecular vacuum.

Stopping oil molecules: Most of the time, we place a cold trap between the diffusion pump and the vacuum chamber, to stop the oil molecules from leaving the pump.

PRESSURE GAUGES: MEASURING PRESSURE

To this day, the region of measurable pressures ranges from 760 Torr to 10^{-13} Torr, over 16 decimal points. In order to measure pressures in such a large region, we use instruments called pressure gauges. Since no physical object is capable of measuring pressures over this whole range, we resorted to designing a whole family of pressure gauges that are used for measuring pressures in different ranges, each of which spreads over a few decimal points.

Mechanical pressure gauges: the mechanical energy is either supplied by the gas whose pressure we wish to determine (e.g. membrane gauge, U-pressure gauge) or by and external source of work (compression gauges, e.g. Kammerer gauge).

Electrical pressure gauges: The electrical energy is either transformed into heat, on which we then base our measure (e.g. thermal conductivity gauge, Pirani gauge) or used to ionize the gas (e.g. ionization gauge, Penning Gauge)

Bourdon gauge

The pressure gauge is mainly made of a curved tube, closed off at one end, whose other end is connected chamber whose pressure we would like to determine (fig. 7).

As the pressure P reduces with respect to the atmospheric pressure P_{atm}, the radius of the tube decreases (easy to prove). This motion is then amplified and calibrated by connecting the tube to a needle. Since the tube deforms elastically, the scale is linear.

The measured pressure varies with the atmospheric pressure, but does not depend on the type of gas contained in the chamber.

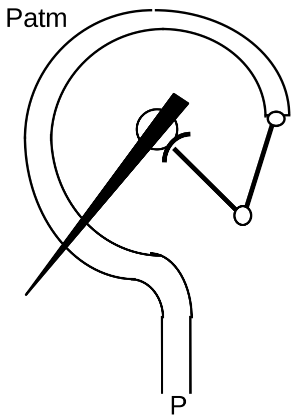


Figure 7: Bourdon gauge

Pirani gauge

This gauge uses the thermal exchange between a hot wire and the gas (fig. 8). The heat exchange depends on the pressure, but also on the type of gas. The temperature of the wire is determined according to its resistance. The wire is connected to a compensating voltage via a Wheatstone bridge. This is a simple and solid gauge when the required precision isn't too high. The main disadvantages of the Pirani gauge are that it must be recalibrated for each gas, and is only useful for a limited range of pressure ($10^1 - 10^{-3}$ Torr).

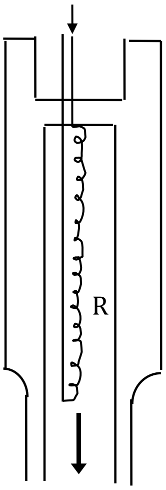


Figure 8 : Pirani gauge

Penning gauge

This gauge uses the ionization of the gas between two electrode (fig. 9) to determine the pressure. The current that travels through the discharge gauge varies as a function of the pressure. In this gauge, the path of the electrons is increased using a permanent magnetic field, which extends the range of measureable pressure

The usable pressure range of the Penning gauge is $10^{-2} - 10^{-7}$ Torr. These instruments are robust, insensitive to air and vibrations, but is pretty imprecise when the cathode is cold. The precision doesn't exceed 20 %. This gauge needs to be recalibrated for each gas.

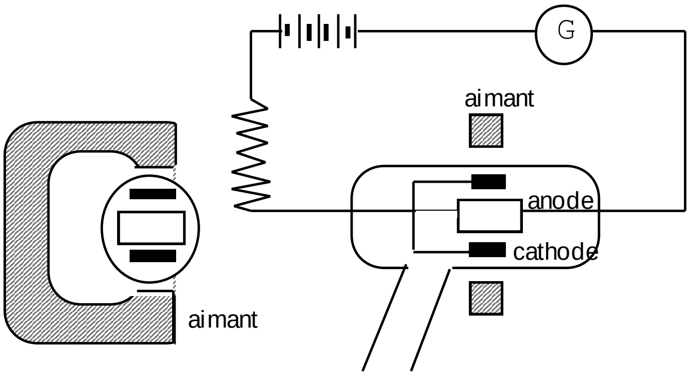


Figure 9 : Penning gauge

Kammerer gauge

After filling a volume V of a few cubic centimeters, the gas is compressed in a capillary tube, and its pressure is measured according to a mercury height difference h (fig. 10). A wheel moves the membrane in or out, forcing the mercury up. The pressure is then determined from the height difference, according to a simple calculation given by Mariotte's law

$PV = (P+h)V_C$ if $V_C \ll V$, then $P = h\frac{V_c}{V}$

and since $V_c = \frac{pd^2}{4}h$ ($d =$ capillary diameter)

$$P = \frac{pd^2}{4V}h^2$$

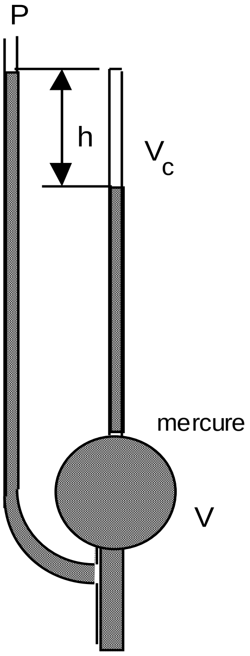


Figure 10: Kammerer gauge

The tube has been previously calibrated, and allows a direct reading of the pressure.

The Kammerer gauge is sensitive to two types of error: The surface tension, which forces the two tube to be of equal diameter, and the presence of mercury vapor in the capillary tube. This systematic error can be eliminated by knowing the temperature and pressure of the mercury vapor. To avoid the mercury penetrating in the chamber, we use a valve and a liquid nitrogen trap. Before measuring the pressure, the valve must be opened very slowly, to avoid mercury sputtering.