

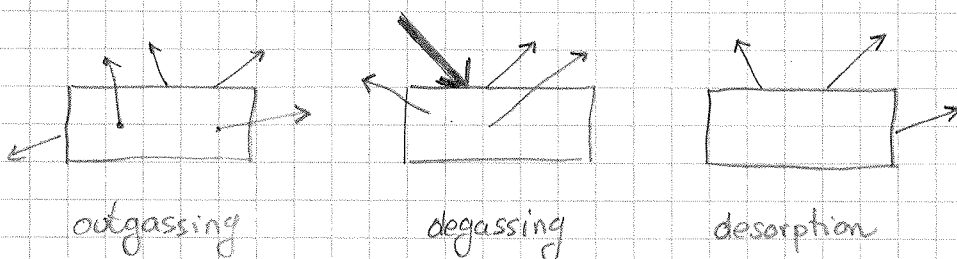
THE GAS SOURCES IN BEAM VACUUM

① SOME DEFINITIONS

Outgassing: is the spontaneous evolution of gas from solid or liquid

Degassing: is the deliberate removal of gas from a solid or liquid

Desorption: is the release of adsorbed chemical species from the surface of a solid or liquid



Intrinsic outgassing rate: is the quantity of gas leaving a material per unit of time and unit of exposed geometric surface (or unit of mass) at a specific time after the start of the evacuation.

Geometric surface: is the visible surface without correction for roughness or open porosity.

Measured outgassing rate: is the difference between the intrinsic outgassing and the rate of readsorption in the test chamber.

② UNITS OF MEASUREMENT

The rate of gas release is expressed in term of number of molecules or pressure-volume units at a specific temperature T :

$$N \Leftrightarrow P \cdot V$$

The two values are correlated by the ideal gas equation :

$$P \cdot V = n R T = N \cdot K_B \cdot T$$

↑ pressure ↑ Boltzmann constant
↑ volume ↑ nr of moles ↑ gas constant ↑ number of molecules

$$K_B = 1,38 \times 10^{-23} \frac{\text{Pa} \cdot \text{m}^3}{\text{K}} = 1,04 \times 10^{-22} \frac{\text{Torr} \cdot \text{l}}{\text{K}} = 1,38 \times 10^{-22} \frac{\text{mbar} \cdot \text{l}}{\text{K}}$$

To convert PV quantities in number of molecules, we have to divide by $K_B T$.

WARNING : a quantity of gas expressed in PV units consists of a different number of molecules at different temperatures.

CONVERSION TABLE AT 20°C

↶	Pa m	Torr l s cm ²	mbar l s cm ²	molec s cm ²	mol s cm ²
Pa m s		7.5x10 ⁻⁴	10 ⁻³	2.5x10 ¹⁶	4.1x10 ⁻⁸
Torr l s cm ²	1330		1.33	3.3x10 ¹⁹	5.5x10 ⁻⁵
mbar l s cm ²	10 ⁻³	0.75		2.5x10 ¹⁹	4.1x10 ⁻⁵
molec s cm ²	4x10 ⁻¹⁷	3x10 ⁻²⁰	4x10 ⁻²⁰		1.7x10 ⁻²⁴
mol s cm ²	2.4x10 ⁷	1.8x10 ⁴	2.4x10 ⁴	6.02x10 ²³	

③ ORDER OF MAGNITUDE FOR OUTGASSING RATES

MATERIAL	$\frac{\text{ Torr } \cdot \text{ l}}{\text{ s} \cdot \text{ cm}^2} (20^\circ\text{C})$	$\frac{\text{ molecules}}{\text{ s} \cdot \text{ cm}^2}$	main gas
<u>NEOPRENE</u> , NOT BAKED AFTER 10h PUMPING	10^{-5}	$3,3 \times 10^{14}$	H ₂ O
<u>VITON</u> , NOT BAKED AFTER 10 h PUMPING	10^{-7}	$3,3 \times 10^{12}$	H ₂ O
<u>AUSTENITIC ST. STEEL</u> NOT BAKED, 10h PUMPING	2×10^{-10}	$6,6 \times 10^9$	H ₂ O
<u>AUSTENITIC ST. STEEL</u> BAKED IN SITU $150^\circ\text{C} \times 24\text{h}$	2×10^{-12}	$6,6 \times 10^7$	H ₂
OFS COPPER BAKED IN SITU $200^\circ\text{C} \times 24\text{h}$	$\approx 10^{-14}$	$6,6 \times 10^5$	H ₂
Ti, Zr, V NEG coating activated at $180^\circ\text{C} \times 24\text{h}$	$< 10^{-16}$ $\approx 10^{-18}$	$< 3,3 \times 10^3$ ≈ 30	CH ₄ Kr

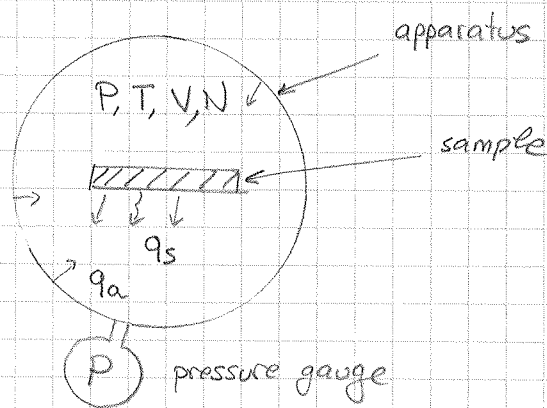
⇒ The outgassing rates can span more than 10 orders of magnitude. The choice of materials and their treatments is crucial. A small piece of bad material can spoil the performance of the vacuum system as a whole.

It is important to underline that even the vacuum instruments are source of gas. They can release molecules in the range $10^{+9} \div 10^{11}$ molecules/s. Vacuum instruments will be considered in unit 4.

④ MEASUREMENT OF OUTGASSING RATE.

The aim of the measurement is to evaluate the number of molecules leaving a piece of material. In general the procedure implies the installation of the sample in a dedicate vacuum system and the recording of the gas density or pressure ($P = nRT$).

a) Pressure rise measurement



The sample is installed in a vacuum system which is pumped, treated as for specification and then isolated.

In the gas phase the number N of gas molecules increases. The variation is equal to number of

molecules released from the sample ($q_s \cdot A_s$) and the system itself ($q_a \cdot A_a$):

$$\frac{dN}{dt} = q_s A_s + q_a A_a$$

$$PV = NK_B T \Rightarrow \frac{dP}{dt} = \frac{K_B T}{V} \cdot \frac{dN}{dt} = \frac{K_B T}{V} \cdot (q_s A_s + q_a A_a)$$

$$\Rightarrow \Delta P = \frac{K_B T}{V} \cdot (q_s A_s + q_a A_a) \Delta t$$

$$L = \frac{q_s A_s + q_a A_a}{V} \cdot \Delta t$$

in PV units
(Torr · e / (s · cm³))

the pressure increases linearly if there is no repumping in the system.

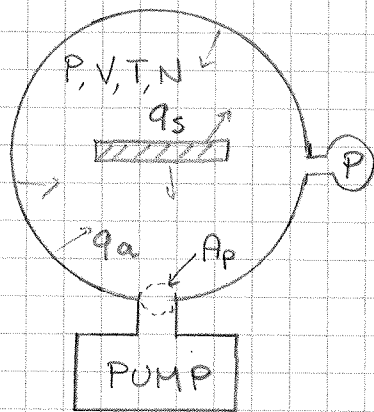
⇒ The sensitivity of the system is limited by the outgassing rate of the system: $q_s A_s$ versus $q_a A_a$.

The pressure rise method is used only:

- for the measurement of upper limit
- when the sample is the system itself
- when the sample surface area is very large ($A_s \gg A_a$)

Another major inconvenient is the interference between the pressure gauge and the gas.

b) The throughput method



In this case a continuous pumping is applied to the test system. In a stationary regime, the outgassing rate of the system is equal to the flux of gas definitely removed from the volume by the pump.

$$Q = q_a A_a + q_s A_s$$

$$\frac{dN}{dt} = Q - \sigma_c \cdot A_p \cdot \Gamma$$

σ_c = probability of pumping for a molecule entering A_p

$$\rightarrow \frac{dP}{dt} = \frac{k_B T}{V} Q - \frac{k_B T}{V} \cdot \left(\frac{1}{4} \frac{N}{V} \bar{v}_{th} \right) \cdot \sigma_c A_p$$

since $PV = Nk_B T$:

$$V \frac{dP}{dt} = (k_B T) Q - (k_B T) \cdot \sigma_c \cdot P \cdot \left(A_p \cdot \frac{\bar{v}_{th}}{4} \right)$$

conversion factor

conductance of the pump aperture C_a

$$\Rightarrow V \frac{dP}{dt} = Q - \sigma_c P C_a \rightarrow \left[\frac{\text{volume}}{\text{time}} \right]$$

$$\Rightarrow \Delta P = \frac{Q}{\sigma_c \cdot C_a} \left(1 - e^{-\frac{t}{\tau_p}} \right) \quad \tau_p = \frac{V}{S_{eff}}$$

$\sigma_c \cdot C_a$ = effective pumping speed of a given pump = S_{eff}

τ_p is in general much smaller than the time of measurement:

Remember:

For a maxwellian gas, the rate of impingement Γ onto a surface is

$\Gamma = \frac{1}{4} n \bar{v}_{th}$

gas density n average speed \bar{v}_{th}

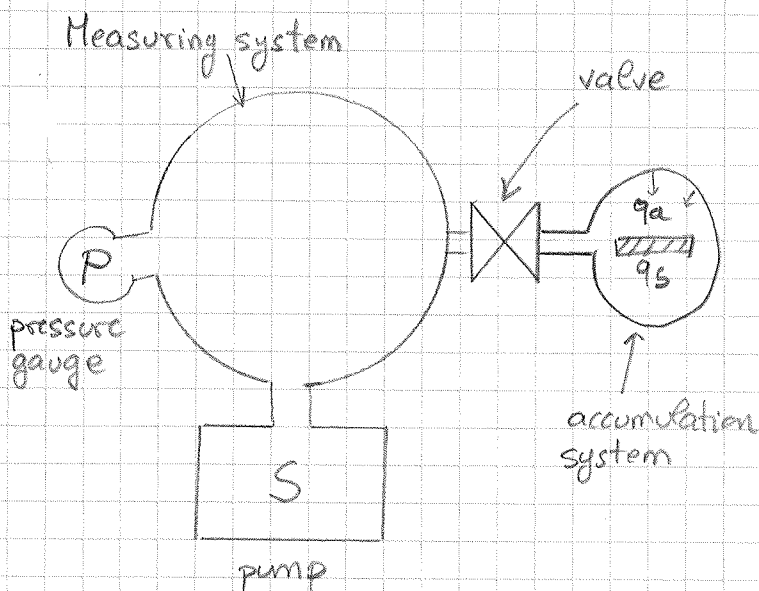
$\bar{v}_{th}^2 = \frac{\sum_i v_i^2}{N}$

$\frac{1}{2} m \bar{v}_{th}^2 = \frac{3}{2} kT$

$$\Delta P = \frac{Q}{S_{eff}} = \frac{A_a q_a + A_s q_s}{S_{eff}}$$

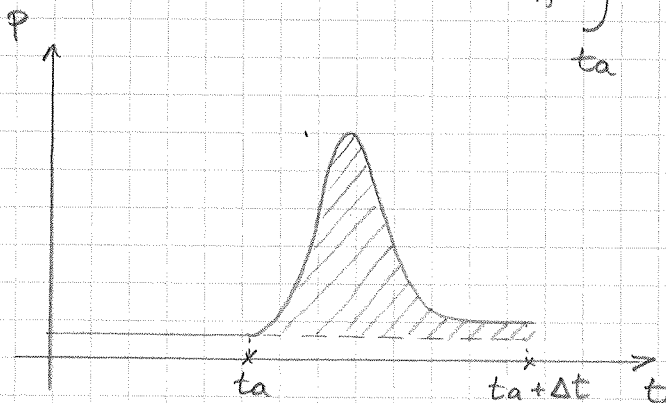
Here again the main limitation is the outgassing of the test system. The gauge interference is not so important as for the pressure rise method.

c) Coupled method



The sample can be separated from the rest of the system by a valve. The gas evolving from the sample is accumulated for a time t_a . Then the valve is opened slowly and the accumulated gas expands toward the test system where it can be quantified.

$$Q = S_{eff} \int_{t_a}^{t_a + \Delta t} \Delta P(t) dt$$



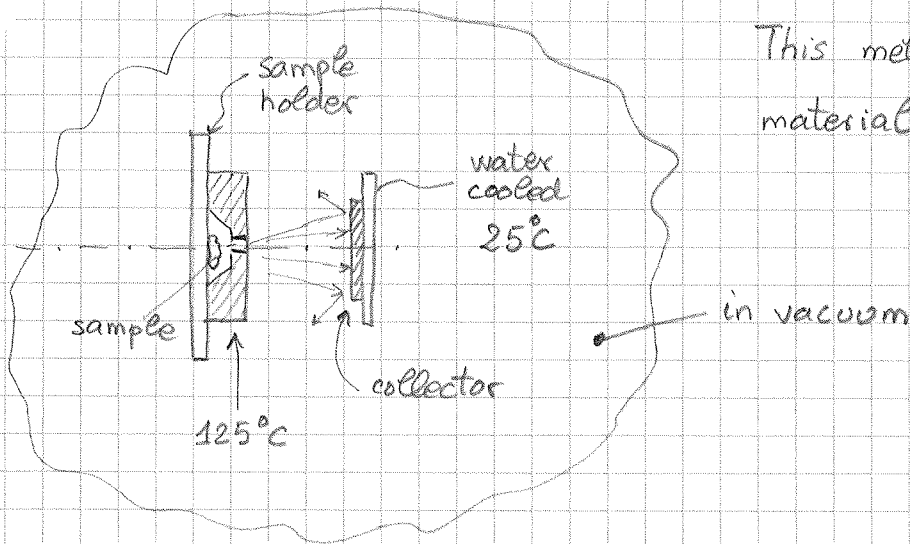
→ The limitation of this system is given by the outgassing rate of the accumulation vessel, however this can be minimized.

→ There is no more effect of the pressure gauge on the accumulated gas.

→ This method works only for gas molecules that are not repumped by the system.

d) Weight loss

This method is used only for organic materials.



The material (a few grams) is stored for one day in a room where humidity and temperature are controlled. Then it is quickly weighted and installed in a sample holder made of copper. The gas can escape from the sample through a small aperture placed in front of a Cr plated collector of known weight.

The system is evacuated to at least 10^{-6} mbar; the sample holder is heated at 125°C while the collector is kept at 25°C.

24 h later, the system is cooled down to room temperature; sample holder and collector are weighted again.

Two important quantities are obtained:

- the total mass loss (TML)
- the collected volatile condensable material (CVCM)

This method is largely used in the space research and industry. A very useful database is available in the NASA website:

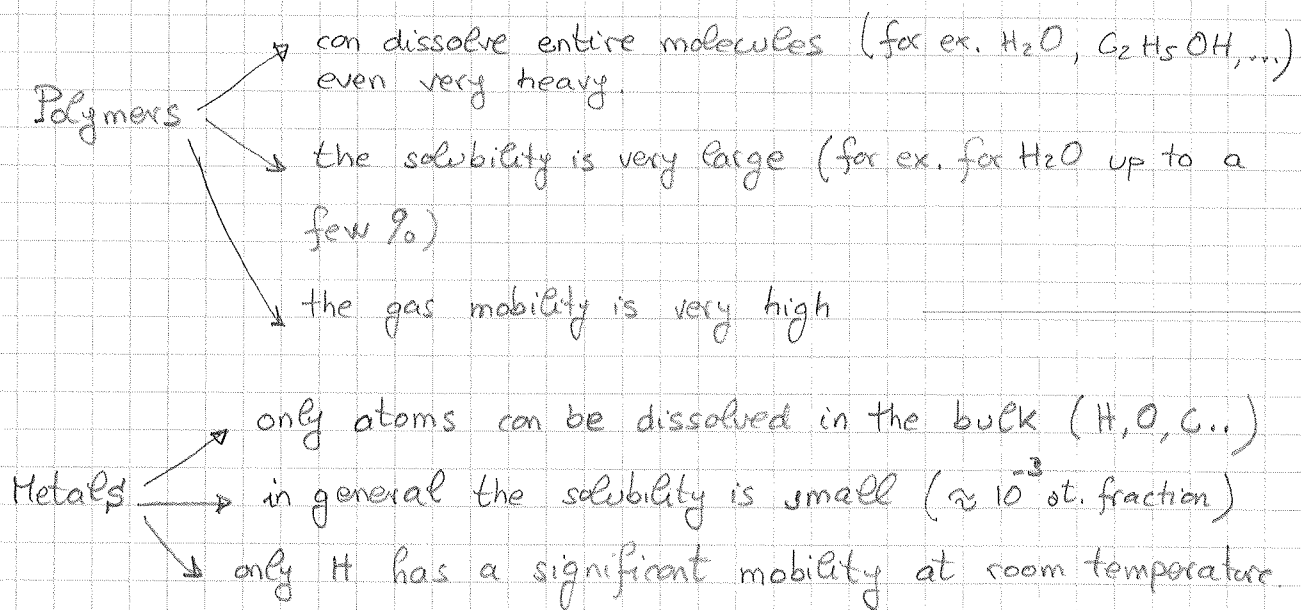
outgassing.nasa.gov

⑤ THE OUTGASSING RATE OF METALS

In general, both surface and bulk of materials are source of gas. The gas molecules can be chemisorbed onto the surfaces or dissolved in the bulk.

The molecules bound to the surface can be released if enough energy is given to the molecule to break the chemical bonding with the surface. In addition the gas atoms dissolved in the material have to diffuse toward the surface, where they can be released.

Organic materials and metals behaves differently in term of outgassing:
(polymers)



⇒ In one day, H atoms travel in average $4 \mu\text{m}$ in austenitic stainless steels. O atoms travel the same distance in about 1000 years!

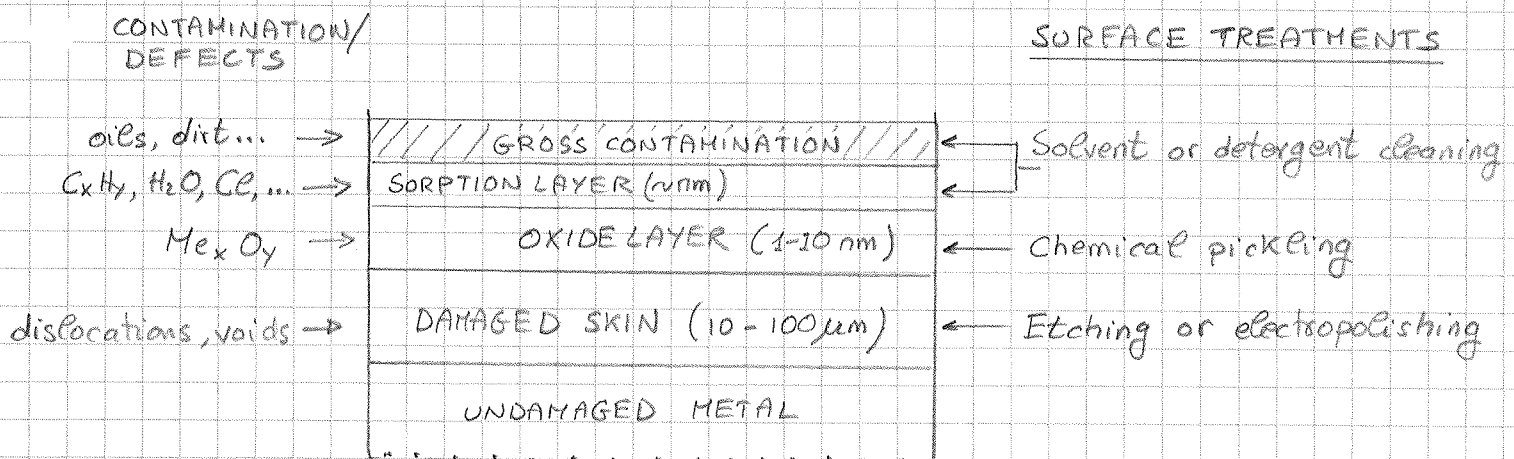
In the same time, H_2O moves about $20 \mu\text{m}$ away in PEEK, a high-tech polymer.

⇒ IN METALS, among the gas dissolved in the bulk, only hydrogen can be released and participate to the outgassing phenomena at room temperature. As a consequence, the reduction of H content in metals is a crucial step in the preliminary treatments for vacuum applications.

When a material is not in vacuum, its surface is in direct contact with atmospheric gas and its contaminants.

In addition metals are machined, welded, extruded, laminated and manipulated. The result is a surface covered by hydrocarbons, moisture, hydroxides and oxides over thicknesses in the range between a few to hundreds of nanometers.

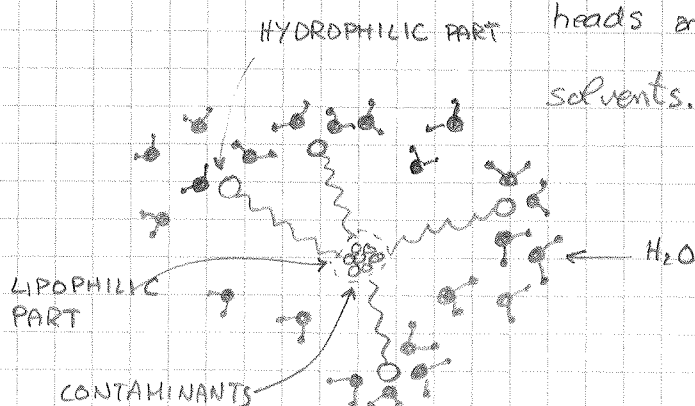
These contaminations are incompatible with the vacuum system of accelerators: surface treatments are mandatory.



SOLVENTS: their molecules interact and transport away contaminants by diffusion in the liquid (dilution) → quite selective!

DETERGENTS IN WATER: allows organic molecules and water to combine by forming micelle (surfactants: surface acting agents)

They are based on molecules with hydrophilic heads and lipophilic tail ⇒ less selective than solvents.



After surface treatment, in general a metallic surface is covered by a thin oxide layer with, on top, water vapour in equilibrium with atmospheric moisture (about 10 Torr in air).

Water vapour dominates the outgassing process of metals unless the whole vacuum system is heated in situ (bake-out).

Heating the vacuum chambers to reduce the outgassing rate of water vapour has a strong impact on cost, design and operation of vacuum systems for particle accelerators.

5.1 OUTGASSING OF WATER VAPOUR FROM METALLIC SURFACES.

This is one of the most puzzling subjects still open in vacuum technology:

"After evacuation, the outgassing rate of water molecules for typical metals (st. steel, copper, Al alloys, Ti, Be, ...) varies approximately inversely as the first power of pumping time"

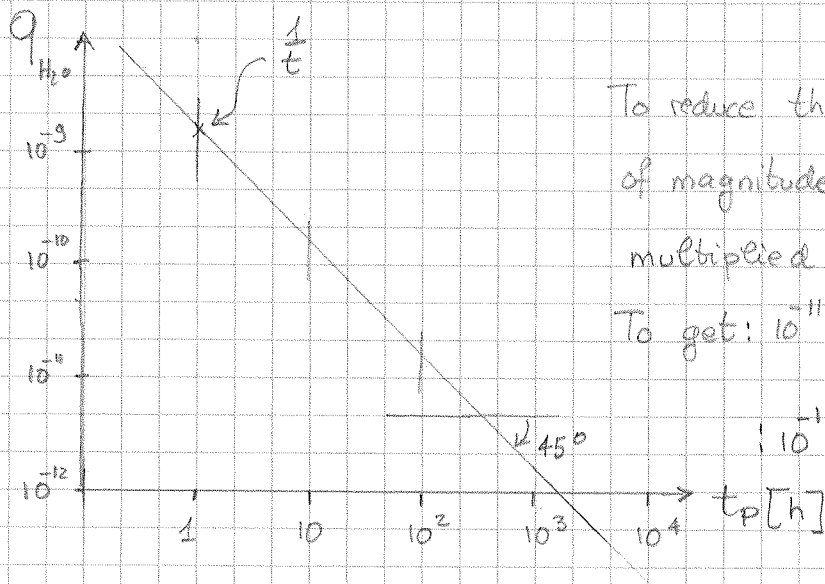
$$q_{\text{H}_2\text{O}} \propto \frac{1}{t_p^\alpha} \quad \leftarrow \text{FOR METALS } \alpha \approx 1$$

"For technically smooth surfaces" after 1 h of pumping:

$$q_{\text{H}_2\text{O}} \approx 2 \times 10^{-9} \frac{\text{Torr} \cdot \text{L}}{\text{s} \cdot \text{cm}^2} \quad \text{FOR ANY METAL USED IN VACUUM SYSTEMS}$$

$$\Rightarrow q_{\text{H}_2\text{O}} \approx \frac{2 \times 10^{-9}}{t_p [\text{h}]} \frac{\text{Torr} \cdot \text{L}}{\text{s} \cdot \text{cm}^2}$$

The water vapour outgassing rate depends on pumping time !!



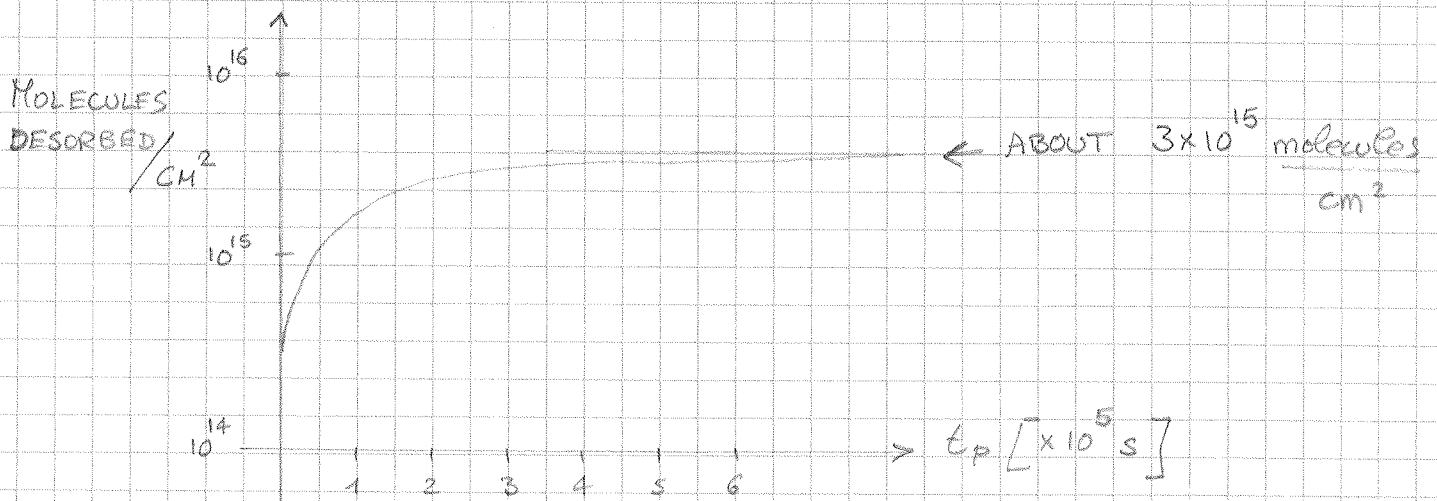
To reduce the outgassing rate by one order of magnitude, the pumping time has to be multiplied by a factor of 10.

To get: $10^{-11} \frac{\text{TorrL}}{\text{s} \cdot \text{cm}^2} \rightarrow$ week(s) of pumping
 $10^{-12} \frac{\text{TorrL}}{\text{s} \cdot \text{cm}^2} \rightarrow$ months of pumping

The total quantity of water molecules released during pumping is

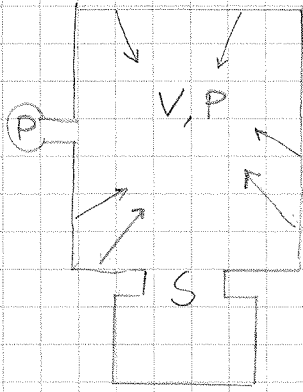
$$N \propto \int_0^{\infty} \frac{1}{t_p} dt \rightarrow \infty, \text{ of course this is not true.}$$

There is experimental evidence that N tends to about 1 to 2 monolayers.



(see D. Edwards Jr, Journal of Vacuum Science and Tech, 14 (1977) 606 and 14 (1977) 1030)

Can the $1/t$ outgassing rate trend be obtained by simple mathematical model? \Rightarrow



Θ = fraction of sites occupied

The total number of site for a molecule on the surfaces is limited and assumed to be roughly

$$N_s \approx 10^{15} \frac{\text{molecules}}{\text{cm}^2} = 3 \times 10^{-5} \frac{\text{Torr} \cdot \text{e}}{\text{s} \cdot \text{cm}^2}$$

variation of the quantity of gas

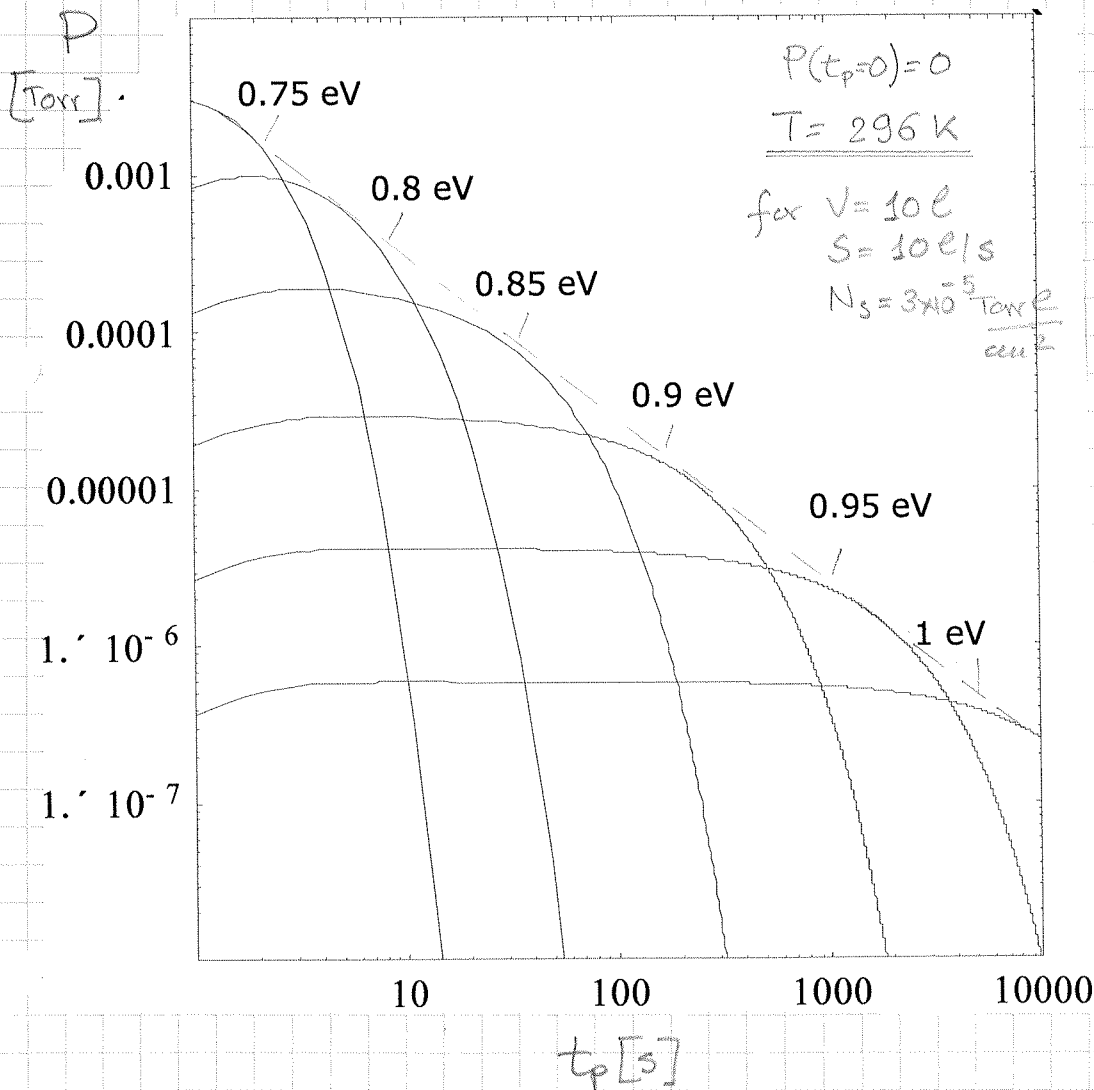
$$V \frac{dP}{dt_p} = -SP + \frac{N_s \Theta}{\tau_d} \rightarrow \text{quantity of gas leaving the surface}$$

$$\frac{d\Theta}{dt} = -\frac{\Theta}{\tau_d} \rightarrow \text{quantity of gas removed by the pump}$$

$$\tau_d = \tau_0 \cdot \exp\left(\frac{E_d}{k_B T}\right)$$

$$\tau_0 \approx \frac{h}{k_B T} \approx 10^{-13} \text{ s}$$

$$\Rightarrow P(t) \approx \frac{N_s}{S \cdot \tau_d} \cdot e^{-\frac{t_p}{\tau_d}} \Rightarrow \varphi_{H_2O} \approx \frac{N_s}{\tau_d} \cdot e^{-\frac{t_p}{\tau_d}} \text{ for } t_p > \tau_d$$



The resulting function is an exponential \Rightarrow far to be $1/t$

Two oversimplifications have been introduced:

- ① Only 1 adsorption energy.
- ② No readsorption on the system walls.

It can be shown that many adsorption energies are necessary to model the 1/t behaviour. The 1/t curve is seen as the convolution of many exponential decays.

For a given pumping time " \bar{t}_p ", the adsorption sites of low energy does not contribute anymore to the pumpdown process because their are emptied in a time much lower than " \bar{t}_p ":

$$\tau_d = \tau_0 \cdot e^{\frac{+E_d}{kT}}$$

The adsorption sites of high energy do not contribute neither, because the molecules are too tightly bounded and are desorbed only after longer times. In other words, for every " \bar{t}_p " there are adsorption sites which have a dominant role in the outgassing process.

$$q = \frac{N_s}{\tau_d} \cdot e^{-\bar{t}_p/\tau_d} \Rightarrow \frac{dq}{d\tau_d} = -\frac{N_s}{\tau_d^2} \cdot e^{-\bar{t}_p/\tau_d} + \frac{N_s}{\tau_d} \cdot e^{-\bar{t}_p/\tau_d} \cdot \frac{\bar{t}_p}{\tau_d^2} = 0$$

$$\Rightarrow \tau_d = \bar{t}_p$$

In this condition: $q_{MAX} = \frac{N_s}{\bar{t}_p} \cdot e^{-1} = \frac{N_s}{e} \cdot \frac{1}{\bar{t}_p}$

$$\frac{N_s}{e} = 1,1 \times 10^{-5} \Rightarrow q_{MAX} = \frac{1,1 \times 10^{-5}}{\bar{t}_p [s]} = \frac{3 \times 10^{-9}}{\bar{t}_p [h]} \quad \left[\frac{\text{Tor} \cdot e}{\text{s} \cdot \text{cm}^2} \right]$$

Edwards' upper limit

Compare: \rightarrow experimental $\sim \frac{2 \times 10^{-9}}{\bar{t}_p [h]}$

Edwards' upper limit $\frac{3 \times 10^{-9}}{\bar{t}_p [h]}$

\Rightarrow Water molecule are at any pumping time adsorbed in the worst possible energetic state!

The Edwards' upper limit is a very good estimation of the water outgassing rate for "technically" smooth surfaces made of Cu, Al, ..., stainless steel. For normal steel the outgassing rate can be up to 2 orders of magnitude higher depending on the roughness of the oxide layer.

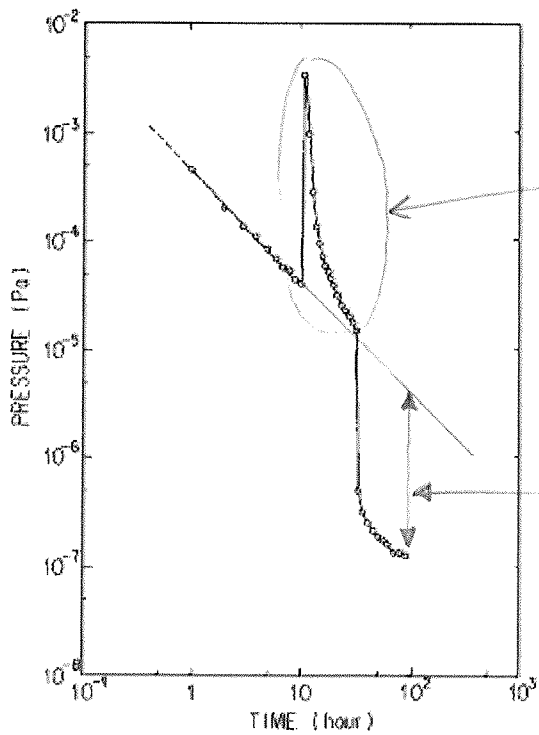
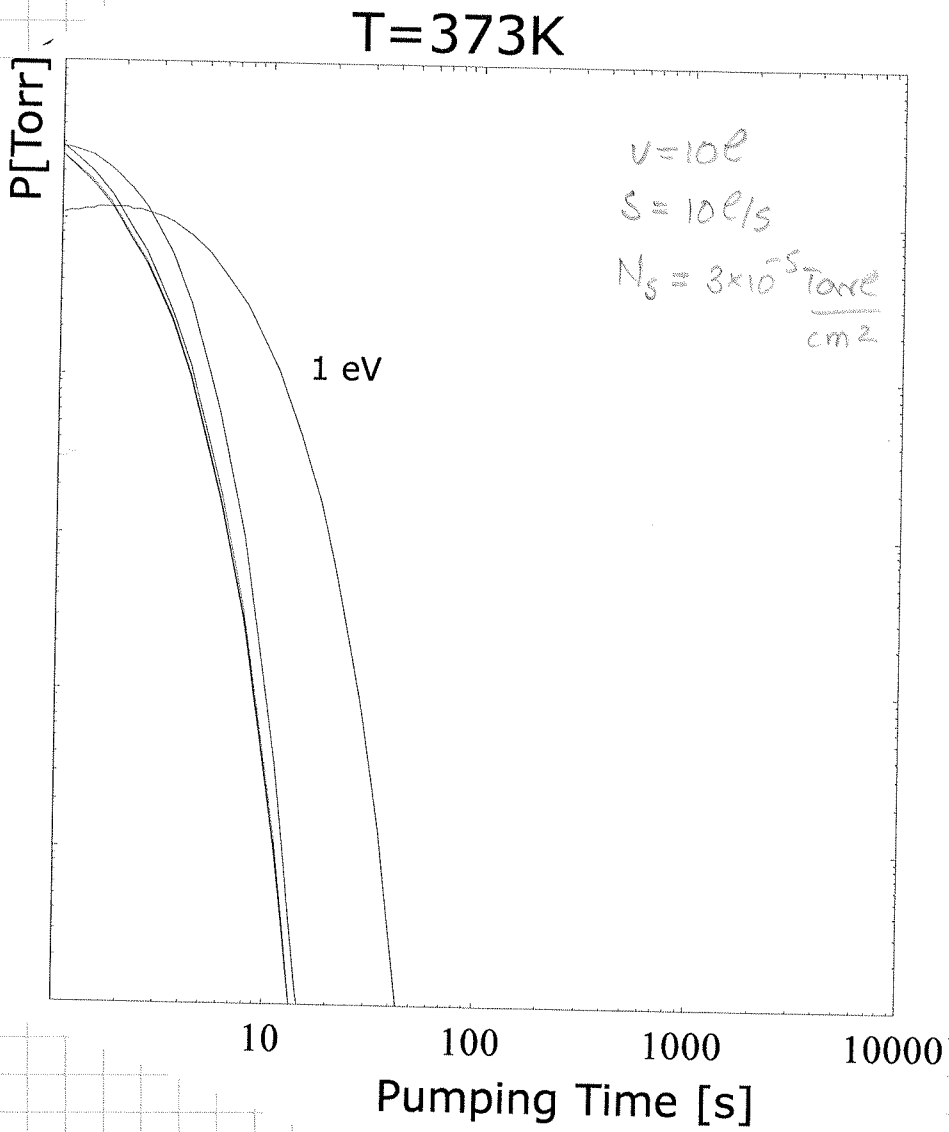
Water desorption could be accelerated, and lower pressures obtained more rapidly, by:

smooth surf. → a) Reducing the number of adsorption sites.
cooling or heating → b) Reducing or increasing the sojourn time

- The reduction of q by smoothing is limited because, for "technically" smooth surfaces, the effective surface area is not far from minimum that can be achieved. Maybe a reduction of a factor 3 can be obtained for mirror like surfaces.
- The total number of sites could be reduced by changing the nature of the surface: coatings, special chemical treatments ⇒ work for the future!
- Cooling and heating are widely used in particle accelerators. The first is in most of the cases a bonus of cryogenic system installed for other purposes (superconductivity) ⇒ LHC arcs. The second is intentionally applied. The whole vacuum system is equipped with heating elements or an oven is installed around the vacuum chamber. Cold spots must be avoided.

The in situ heating is very effective if the heating temperature is higher than 100°C . A typical duration is about 24 h.

This is BAKEOUT in the vacuum technology jargon.



accelerated desorption due to heating

effective reduction

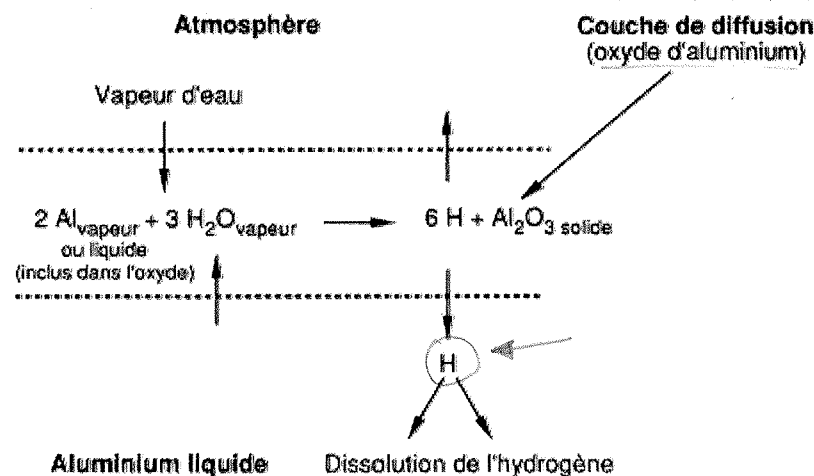
5.2 OUTGASSING OF H₂ FROM METALS

Whenever water vapour outgassing is strongly reduced, either by long pumping or bakeout, H₂ becomes the gas molecule with the highest outgassing rate.

Hydrogen is dissolved in metals as a single atom (H). Its diffusion is relatively fast and, after recombination onto the surface, it can be released as a molecule.

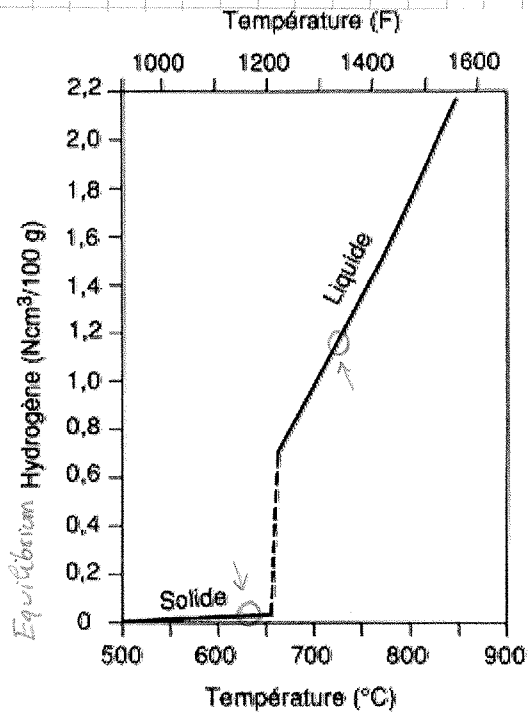
Most of the H atoms are dissolved in metals at the liquid state, during the production process. The liquid metal reacts easily with hydrogenated molecules and the transport and solubility of H are facilitated.

- Source of H₂ :
- the metal ores
 - the tools needed for fusion
 - the refractory materials of the furnace
 - the combustion gas; the treatment gas
 - water vapour



For most of the metals used in vacuum technology, the solubility of hydrogen in the liquid state is much higher than in the solid state.

If the cooling is too fast, H atoms are blocked in the solid at a concentration far above the expected equilibrium value.



Al

Example of H source ;
 → some austenitic stainless steel are hyperquenched from 1100°C to RT in water, air or oil !!

1 Ncm³ correspond à 1 cm³ de gaz mesuré dans les conditions normales de température (°C) et de pression (10⁵ Pa).

After solidifications, the metals used in vacuum technology have a residual content of hydrogen lower than 10 ppm (Wt.), except for very reactive metals (Ti, Nb, Zr).

For austenitic stainless steels typical values are around 1 ppm (Wt.), namely ≈ 50 ppm at. For Al, values 10 times lower are reported.

Typical H₂ outgassing rates are reported here below :

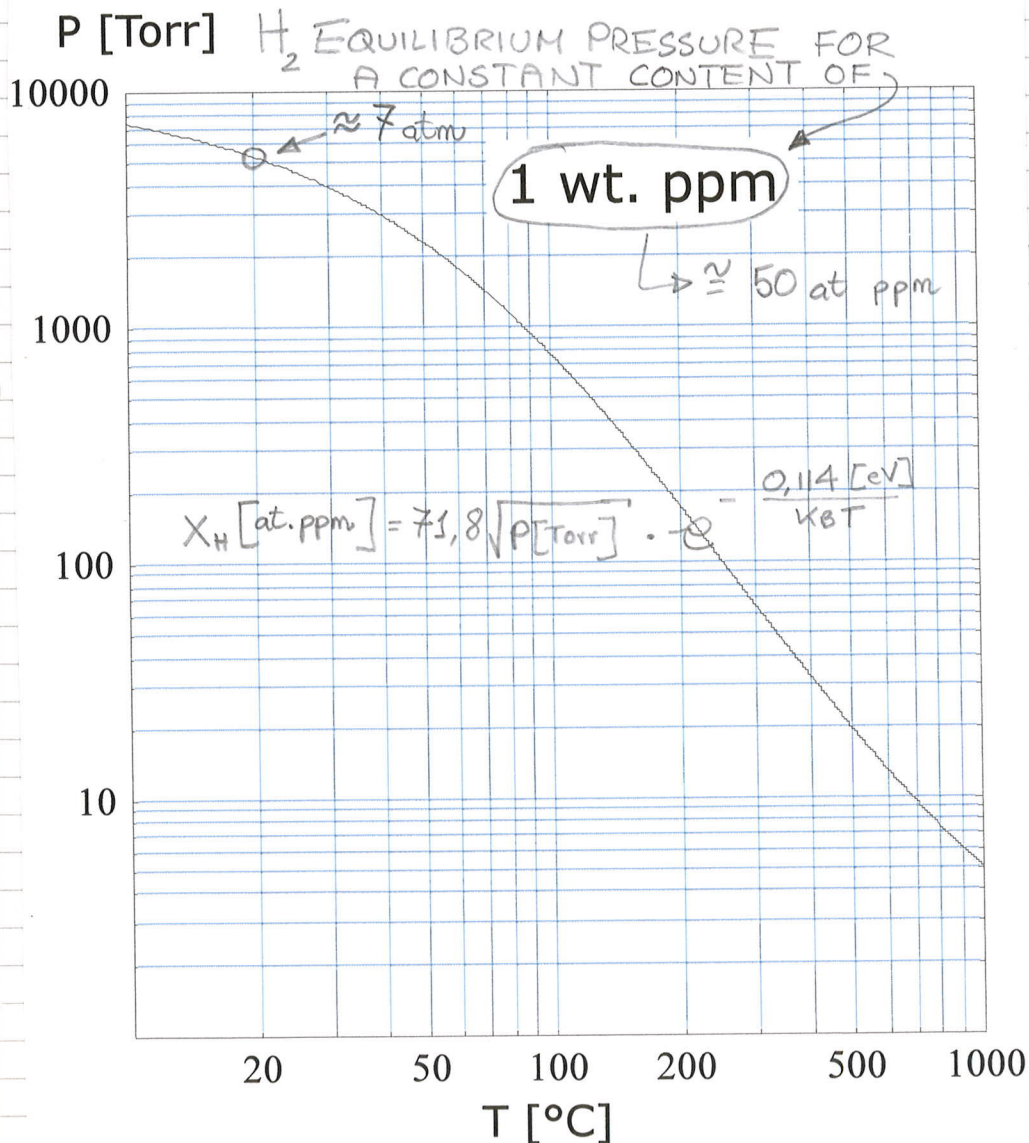
Metals	Bakeout	q [Torr/s.cm ²]	q [molecules/s.cm ²]
Austenitic St. Steel	150°C x 24h	3 × 10 ⁻¹²	1 × 10 ⁺⁸
Austenitic St. Steel	200°C x 24h	2 × 10 ⁻¹²	7 × 10 ⁺⁷
Austenitic St. Steel	300°C x 24h	4 × 10 ⁻¹³	1,3 × 10 ⁺⁷
Copper Silver added (OFS)	150°C x 24h	2 × 10 ⁻¹²	7 × 10 ⁺⁷
Copper Silver added (OFS)	200°C x 24h	≈ 10 ⁻¹⁴	3 × 10 ⁺⁵
Beryllium	150°C x 24h	< 10 ⁻¹⁴	< 3 × 10 ⁺⁵
Al alloys	150°C x 24h	≈ 10 ⁻¹³	≈ 3 × 10 ⁺⁶

As for water vapour, hydrogen outgassing can be reduced by heating the vacuum components. Increasing the temperature the H mobility is higher and the metal is emptied faster. Then, cooling the vacuum component at room temperature, a lower outgassing rate is measured.

However, there is a crucial difference: water molecules are recharged any time the vacuum system is vented to air, while H₂ is not.

H₂ recharging is hindered by the dissociation of the molecule on the oxide layer and by the low solubility at room temperature of most of the metals used in vacuum technology. The H solubilities fix the content of H in equilibrium with a defined pressure of H₂. For example, to recharge 1 wt. ppm at room temperature, 7 atm

IN STAINLESS STEEL



of H₂ are needed if the H₂ molecules could dissociate without limitation.

The H₂ pressure in air is 10⁻⁴ Torr; the ⇒ maximum recharging. ≈ 2 × 10⁻⁴ wt. ppm

CONSEQUENCE

Vacuum materials

Keep memory of

previous thermal treatments



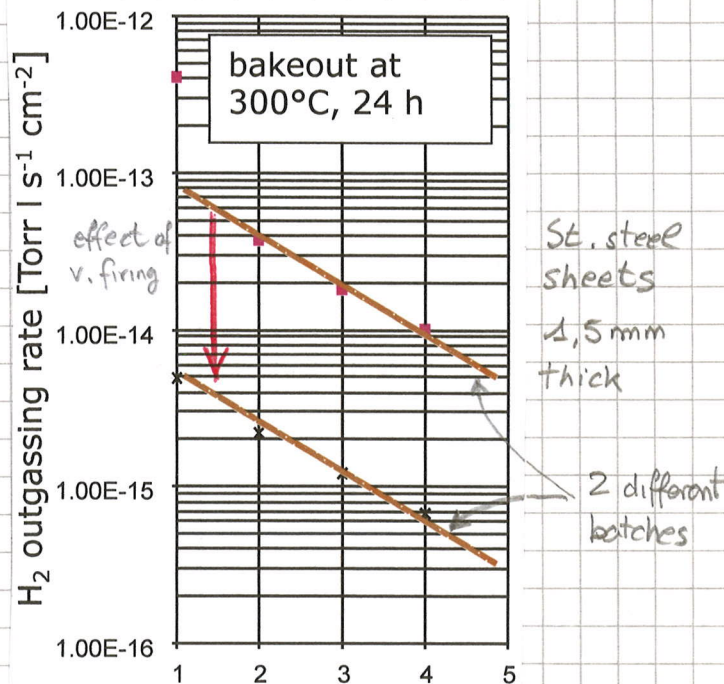
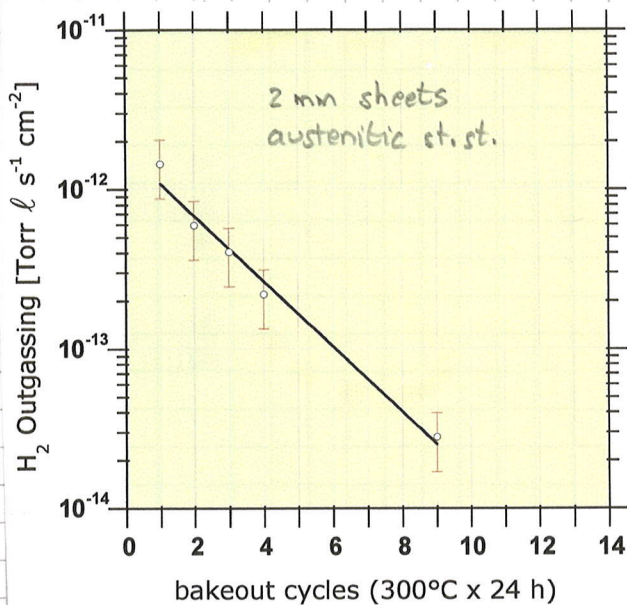
Thermal treatment

can be done ex-situ.

In general, for Cu and Al alloys a few bakeouts at $150 \div 200^\circ\text{C}$ (24h) are sufficient to reduce the outgassing rate of H_2 to less than 10^{-13} Torr l/(s.cm²).

Austenitic stainless steels are less prone to release H_2 and so low temperature bakeouts have a limited efficiency \Rightarrow higher temperatures are needed. To avoid excessive surface oxidation, the vacuum materials are then inserted in a vacuum furnace \Rightarrow in vacuum jargon this is a "VACUUM FIRING".

- The effect of repeated bakeout and vacuum firing are shown here below:

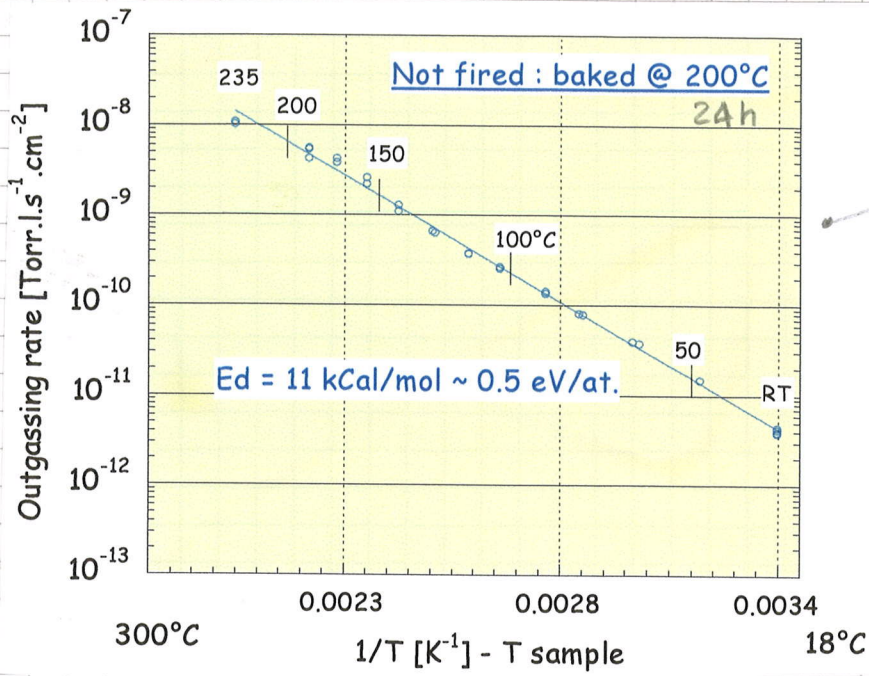


Experiment result : $\frac{q_{n+1}}{q_n} = \text{constant}$ for a given temperature cycle and material.
 $n = \text{number of bakeout cycles}$

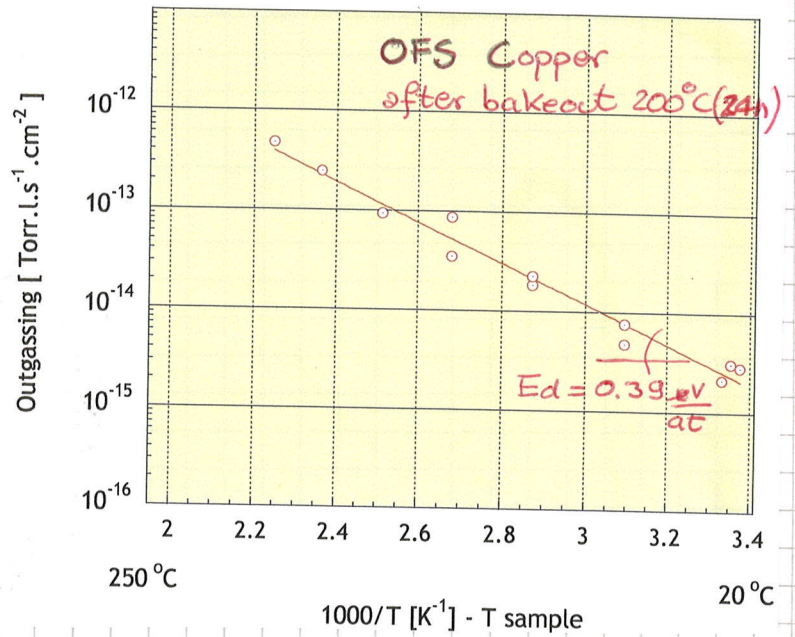
- The H_2 outgassing rate of most of the vacuum materials has a typical variation with temperature :

$$q = q_0 \cdot e^{-\frac{E}{k_B T}} \Rightarrow \ln \frac{q}{q_0} = -\frac{E}{k_B T}$$

Examples :



Austenitic st. steel
Wall thickness 2 mm



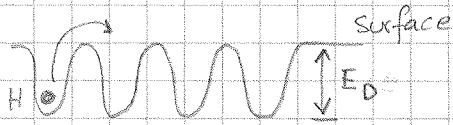
5.3 THE DIFFUSION LIMITED MODEL OF H₂ OUTGASSING

H₂ outgassing can be estimated by means of a simple diffusion model. This implies that the bottleneck of the outgassing process is the diffusion of H atoms to the surface. The recombination of two H atoms to form a molecule is neglected.

The diffusion model predicts quantitatively the measured values for

most of the metals used in vacuum

(endothermal metals: st. steel, copper, Al...)



$$D(T) = D_0 \cdot \exp\left(-\frac{E_D}{k_B T}\right)$$

Fick's equations

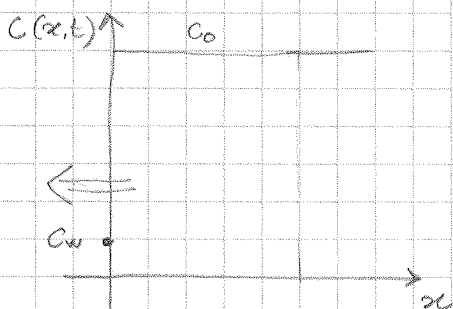
$$M(x,t) = -D \frac{\partial C(x,t)}{\partial x}$$

$C(x,t)$ = H concentration

$$\frac{\partial C(x,t)}{\partial t} = D \cdot \frac{\partial^2 C(x,t)}{\partial x^2}$$

$$q(t) = -D \frac{\partial C(x,t)}{\partial x} \Big|_{x=\text{SURFACE}}$$

SEMI-INFINITE SOLID APPROXIMATION:



$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t}$$

$$\text{I.C. } C(x,0) = C_0$$

$$\text{B.C. } C(0,t) = C_w$$

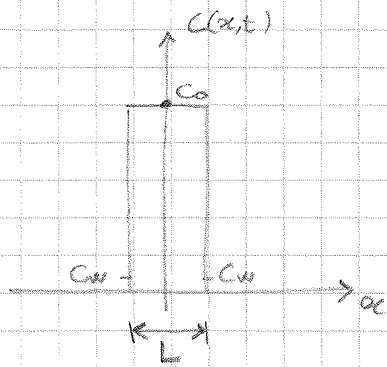
$$C(x,t) = (C_0 - C_w) \cdot \operatorname{erfc} \frac{x}{2\sqrt{Dt}}$$

$$q(t) = \frac{D(C_0 - C_w)}{\sqrt{\pi D t}} \propto t^{-0,5}$$

In general, the $t^{-0,5}$ behaviour is valid even for a finite slab when its thickness L is much larger than \sqrt{Dt} (the diffusion length).

$$L \gg \sqrt{Dt}$$

SLAB APPROXIMATION



$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t}$$

$$\left. \begin{array}{l} \text{I.C. } C(x, 0) = C_0 \\ \text{B.C. } C(\pm \frac{L}{2}, t) = C_w \end{array} \right\} q(t) = \frac{4(C_0 - C_w)}{L} D \sum_{n=0}^{\infty} e^{-\frac{(2n+1)^2 \pi^2 D t}{L^2}}$$

For $Dt > 0,05 L^2$ only the first term of the series is relevant:

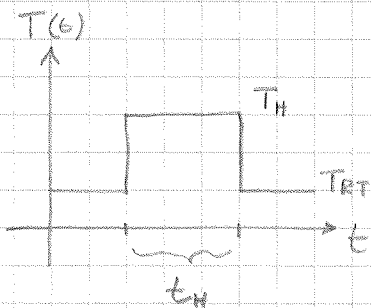
$$q(t) \approx \frac{4(C_0 - C_w) D}{L} \cdot e^{-\frac{\pi^2 D t}{L^2}}$$

C_w can be calculated in the hypothesis of equilibrium between H_2 in gas and solid phase:

$$C_w = k_s \sqrt{P} \rightarrow \text{Sievert's Law}$$

↑
solubility

THERMAL MEMORY

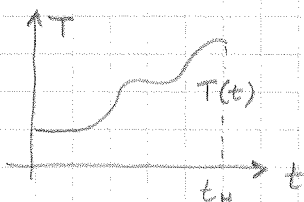


The diffusion equations can be used to calculate the outgassing rate of slabs after an arbitrary thermal cycle.

In the simplest case, namely heating at a constant temperature T_H for a duration t_H , the solution is:

$$q \approx \frac{4(C_0 - C_w)}{L} D(T_{RT}) \exp \left[-\pi^2 \frac{D(T_H) \cdot t_H}{L^2} \right]$$

For an arbitrary temperature profile:



$$q \approx \frac{4(C_0 - C_w)}{L} D(T_{RT}) \cdot \exp \left[-\pi^2 \frac{\int_0^{t_H} D(T(t)) \cdot dt}{L^2} \right]$$

The dimensionless number :

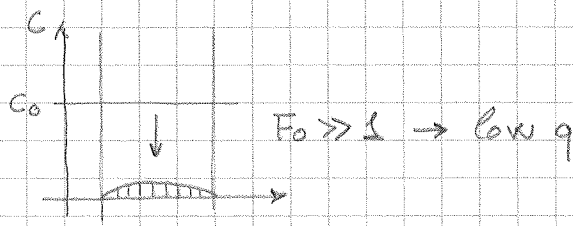
$$F_0 = \frac{\int_0^{t_H} D(T) dt}{L^2}$$

(diffusion length² = average distance of the random atomic movement²)

(thickness of the vacuum chamber wall)²

is called Fourier number (for the analogy with thermal transmission).

F_0 records the thermal history of the material and determines how much the initial concentration is depleted.



If $F_0 > 3$ the material can be considered as emptied or in equilibrium with the surrounding gas phase.

For multiple bakeout at T_h for $t_h \Rightarrow$

$$\frac{q_{n+1}(t)}{q_n(t)} = \exp\left[-\pi^2 \cdot \frac{D(T_{bo}) \cdot t_{bo}}{L^2}\right]$$

Each bakeout reduces the outgassing rate by the same factor as shown experimentally.

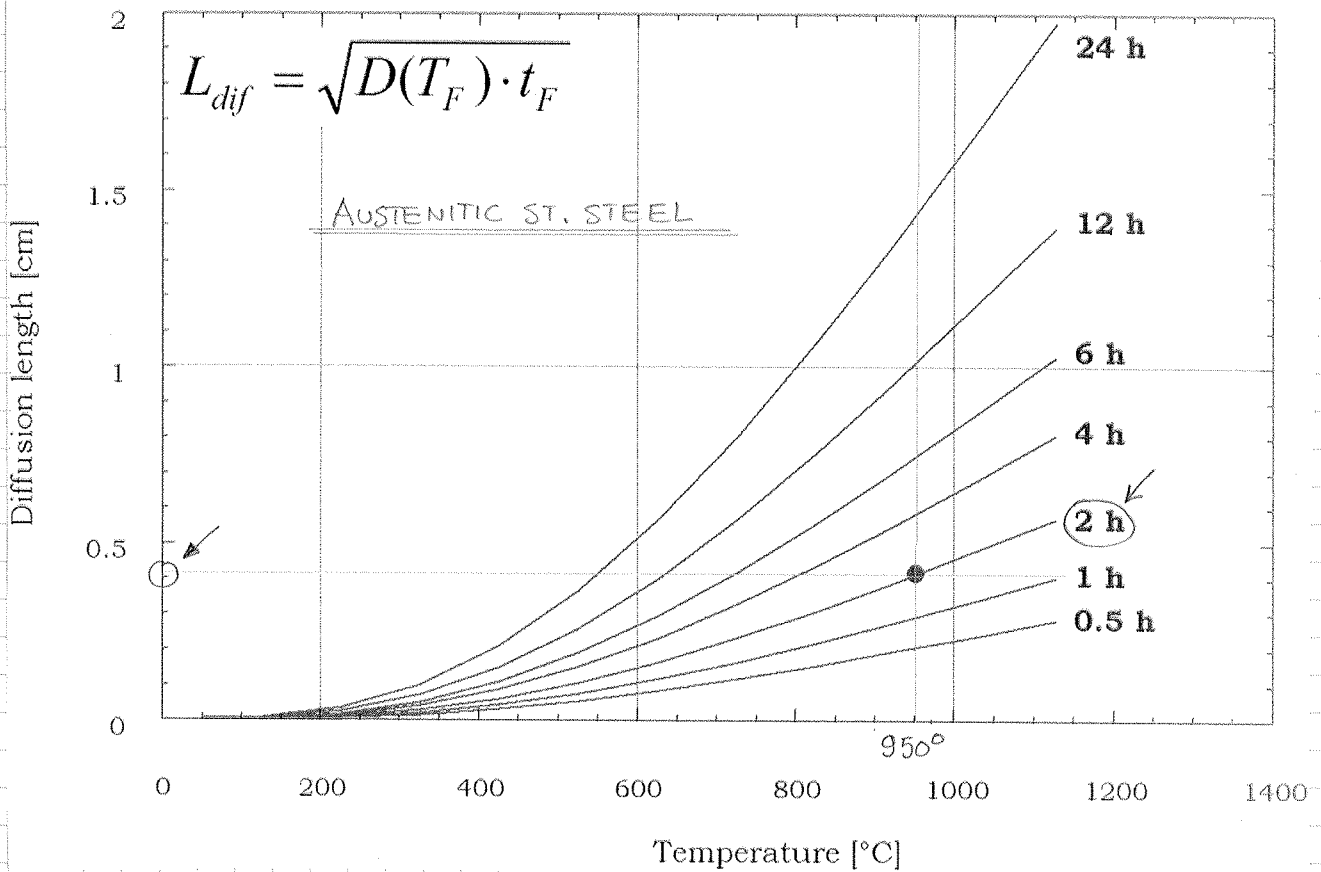
DIFFUSION MODEL OF VACUUM FIRING

As already written, vacuum firing aims at removing as much as possible H from the bulk of austenitic stainless steels components before their installation in vacuum systems.

The temperature of heating is higher than that of in situ bakeouts.

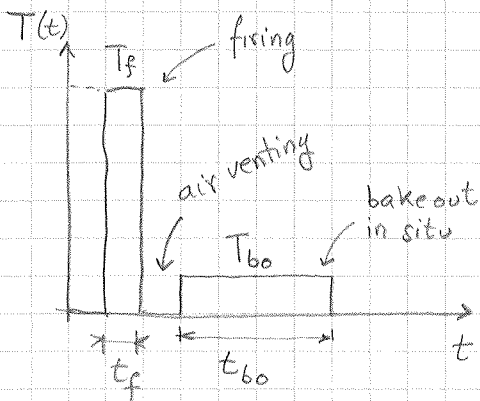
To be effective the thermal treatment should result in a diffusion length longer than the slab thickness.

$$\sqrt{D(T_F) \cdot t_F} > L$$



At CERN, $950^\circ\text{C} \times 2\text{h}$ is considered as a standard treatment.

- The diffusion model can predict the H_2 outgassing rate of stainless steel components of different wall thickness.

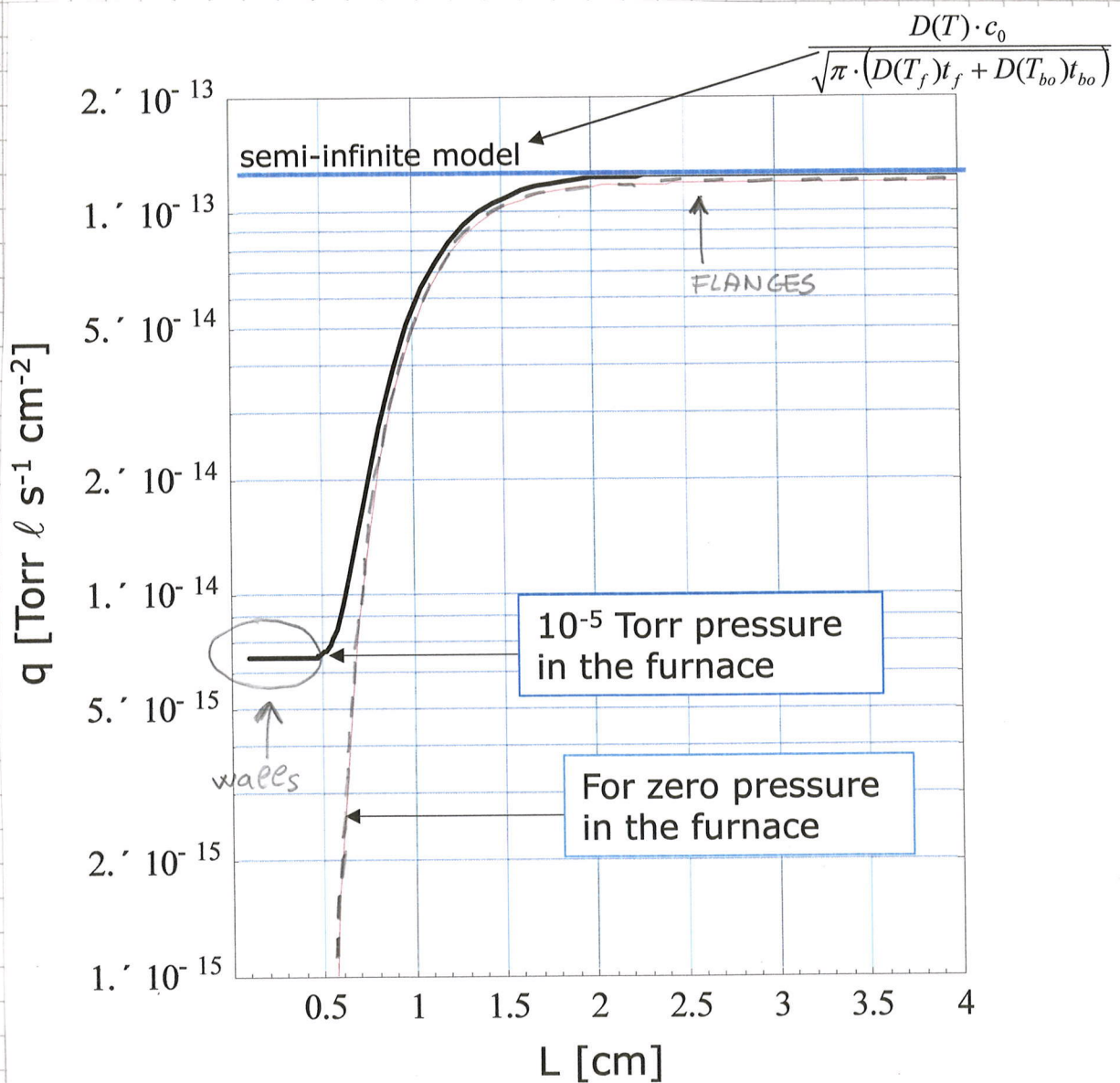


For thick slab ($L \gg \sqrt{D_F t_F}$) the results should converge to the semi-infinite solid approximation. In this case the pressure in the furnace is not relevant if $P_F \ll 1 \text{ Torr}$ (equilibrium pressure of H at 950°C for $C_0 \approx 1 \text{ wt. ppm}$)

For thin slab ($F_0 > 3$), the initial residual hydrogen is completely removed during vacuum firing. The slab reaches equilibrium with the H_2 pressure in the furnace. For a typical vacuum of 10^{-5} Torr during the thermal treatment a concentration of 6×10^{15} H atoms/cm³ is attained.

In both limits the outgassing rate does not depend on the slab thickness.

A detailed calculation is shown in the following curve:



Outgassing rates in the 10^{-15} Torr l/s · cm² are obtained for typical vacuum chambers; 20 times more for flanges \Rightarrow experimentally verified !!

6. AIR BAKEOUT

The methods for the reduction of H outgassing presented in the previous pages rely on heating in vacuum.

However other methods based on heating in air or in pure oxygen are also very effective.

- The air bakeout of austenitic stainless steels was proposed in the sixties. Such processing is reported to decrease the outgassing rate at room temperature by 3 orders of magnitude. Typical heating temperatures are $400^{\circ}\text{C} \div 450^{\circ}\text{C}$ for tens of hours.
- During the air heating an oxide layer 10 times thicker than the native oxide is formed. The oxide is essentially iron oxide (99%).

This treatment is rarely used in particle accelerators.