C.A.S.
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Globe of Innovation

Outgassing

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Preamble

The total outgassing rate Q, together with the applied pumping speed S, defines the pressure in the vacuum system:

$$\boxed{P = \frac{Q}{S} + P_0}$$

P_0: ultimate pressure of the pumping system.

In general S varies in a range of three orders of magnitude (≈1 →1000 $l.s^{-1}$) while Q can extend over more than 10 order of magnitude (≈10^{-5} →10^{-15} Torr $l.s^{-1}.cm^{-2}$).

The right choice of materials and treatments is compulsory in the design of vacuum systems (especially those for accelerators).

In this respect the measurement of outgassing rates is a basic activity for an ultra-high vacuum expert.

Part 1: Syllabus

Thermal outgassing
P.C.
Thursday

Water outgassing
F. Dylla
Thursday

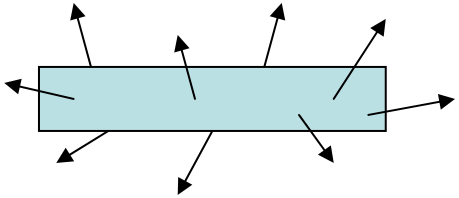
Non-thermal outgassing
N. Hilleret
Friday

Syllabus

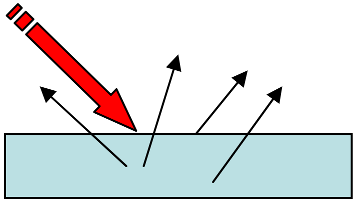
1. Definitions, units and methods
2. General features of outgassing for vacuum materials
3. Outgassing of polymers

Part 1: Definitions

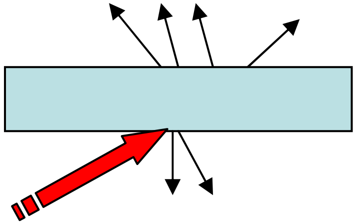
Outgassing is the spontaneous evolution of gas from solid or liquid.



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



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



Part 1: Definitions

- The intrinsic outgassing rate is the quantity of gas leaving per unit time per unit of exposed geometric surface, or per unit of mass, at a specified time after the start of the evacuation.

- The geometric surface is the visible surface without correction for roughness or open porosity.

- The measured outgassing rate is the difference between the intrinsic outgassing rate and the rate of readsorption in the test chamber. The readsorption rate depends on test chamber and on method of test.

Part 1: Units of gas quantity

The quantity of gas can be presented in number of molecules (N) or in pressure-volume (PV) units.

The two values are related by the ideal gas equation of state:

$$P \cdot V = N \cdot K_B \cdot T \rightarrow N = \frac{P \cdot V}{K_B \cdot T}$$

The pressure-volume units are transformed to number of molecules when divided by $K_B T$. A given number of molecules is expressed by different pressure-volume values at different temperatures. In general the pressure-volume quantities are quoted at room temperature

$$k_B = 1.38 \cdot 10^{-23} \left[\frac{N \cdot m}{K} = \frac{Pa \cdot m^3}{K} \right]$$

$$k_B = 1.38 \cdot 10^{-23} \left[\frac{Pa \cdot m^3}{K} \right] = 1.04 \cdot 10^{-22} \left[\frac{Torr \cdot \ell}{K} \right] = 1.38 \cdot 10^{-22} \left[\frac{mbar \cdot \ell}{K} \right]$$

$$\text{for } \mathrm{T} = \mathrm{T_{RT}} = 296\ \mathrm{K}$$

$$\frac{1}{k_B T_{RT}} = 2.45 \cdot 10^{20} \left[Pa \cdot m^3 \right]^{-1} = 3.3 \cdot 10^{19} \left[Torr \cdot \ell \right]^{-1} = 2.5 \cdot 10^{19} \left[mbar \cdot \ell \right]^{-1}$$

Part 1: Units of outgassing rate

The outgassing rate is presented in:

- ✓ $\frac{Pa \cdot m^3}{s \cdot m^2} = \frac{Pa \cdot m}{s}$
- ✓ $\frac{Torr \cdot \ell}{s \cdot cm^2}$
- ✓ $\frac{mbar \cdot \ell}{s \cdot cm^2}$
- ✓ $\frac{molecules}{s \cdot cm^2}$
- ✓ $\frac{mol}{s \cdot cm^2}$

↱	$\frac{\text{Pa m}}{\text{s}}$	$\frac{\text{Torr l}}{\text{s cm}^2}$	$\frac{\text{mbar l}}{\text{s cm}^2}$	$\frac{\text{molec}}{\text{s cm}^2}$	$\frac{\text{mol}}{\text{s cm}^2}$
$\frac{\text{Pa m}}{\text{s}}$		7.5×10^{-4}	10^{-3}	2.5×10^{16}	4.1×10^{-8}
$\frac{\text{Torr l}}{\text{s cm}^2}$	1330		1.33	3.3×10^{19}	5.5×10^{-5}
$\frac{\text{mbar l}}{\text{s cm}^2}$	10^{-3}	0.75		2.5×10^{19}	4.1×10^{-5}
$\frac{\text{molec}}{\text{s cm}^2}$	4×10^{-17}	3×10^{-20}	4×10^{-20}		1.7×10^{-24}
$\frac{\text{mol}}{\text{s cm}^2}$	2.4×10^{7}	1.8×10^{4}	2.4×10^{4}	6.02×10^{23}	

Part 1: Units of outgassing rate

Neoprene (10 h pumping):

$q_{H2O} \approx 10^{-5}$ Torr ℓ s^{-1} cm^{-2}

$q_{H2O}=3.3\times10^{14}$ molecules cm^{-2}

Unbaked stainless steel (10 h pumping):

$q_{H2O}=2\times10^{-10}$ Torr ℓ s^{-1} cm^{-2}

$q_{H2O}=6.6\times10^{9}$ molecules cm^{-2}

Baked stainless steel (150º C x 24 h):

$q_{H2}=2\times10^{-12}$ Torr ℓ s^{-1} cm^{-2}

$q_{H2}=6.6\times10^{7}$ molecules s^{-1} cm^{-2}

Baked OFS Copper (200º C x 24 h):

$q_{H2}=2\times10^{-14}$ Torr ℓ s^{-1} cm^{-2}

$q_{H2}=6.6\times10^{5}$ molecules s^{-1} cm^{-2}

Some examples

Bayard-Alpert gauges (W filaments)

$Q\approx10^{-9}$ Torr ℓ s^{-1}

$Q\approx3\times10^{10}$ molecules cm^{-2}

Bayard-Alpert gauges (Thoria coated W filaments)

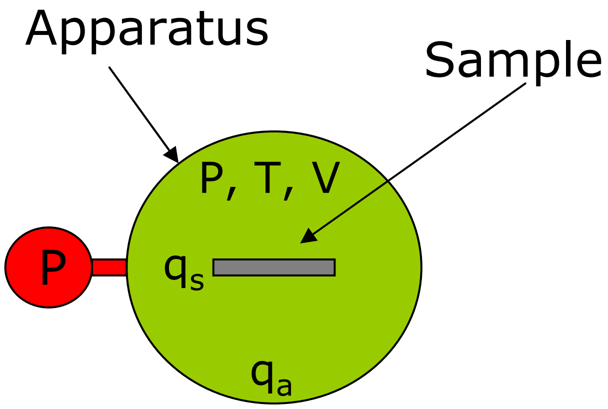
$Q\approx10^{-10}$ Torr ℓ s^{-1}

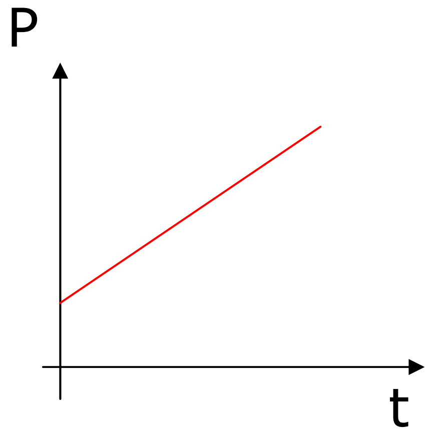
$Q\approx3\times10^{9}$ molecules cm^{-2}

Residual gas analyzer (W filaments)

$Q\approx10^{-8}$ Torr ℓ s^{-1}

$Q\approx3\times10^{11}$ molecules cm^{-2}





Pressure-rise (accumulation) method

No external pumping during the measurement

$$\frac{dN}{dt} = Q \text{ and } \frac{dN}{dt} = \frac{V}{k_B T}\frac{dP}{dt} \rightarrow \frac{dP}{dt} = \frac{k_B T}{V} Q$$

$$Q = A_a q_a + A_s q_s$$

$$\Delta P = k_B T \frac{(A_a q_a + A_s q_s)\left[\frac{molecule}{s}\right]}{V} \cdot t$$

$$\Delta P[Torr] = \frac{(A_a q_a + A_s q_s)\left[\frac{Torr \cdot l}{s}\right]}{V[l]} \cdot t[s]$$

If repumping is negligible, the pressure in the system increases linearly and the total outgassing rate is obtained from the slope of the curve.

The sensitivity of the method is limited by the outgassing of the apparatus (walls, valves and gauges) and by the sensitivity of the pressure gauge.

Part 1: Methods for measurement

Example: for a baked spherical system made of regular stainless steel containing the sample to be measured:

$$V = 10\ \ell$$

$$q_a = 2 \cdot 10^{-12} [\frac{Torr \cdot l}{s \cdot cm^2}]$$

System contribution ⇨

$$\Delta P_a[Torr] = \frac{2245[cm^2] \cdot 2 \cdot 10^{-12} [\frac{Torr \cdot l}{s \cdot cm^2}]}{10[l]} \cdot t[s] = 4.5 \cdot 10^{-9} t$$

The signal of the sample has to be at least 25% of that of the apparatus to be significant.

$$\longrightarrow \quad q_s \cdot A_s > 1.1 \cdot 10^{-9} [\frac{Torr \cdot l}{s}]$$

Optimistic

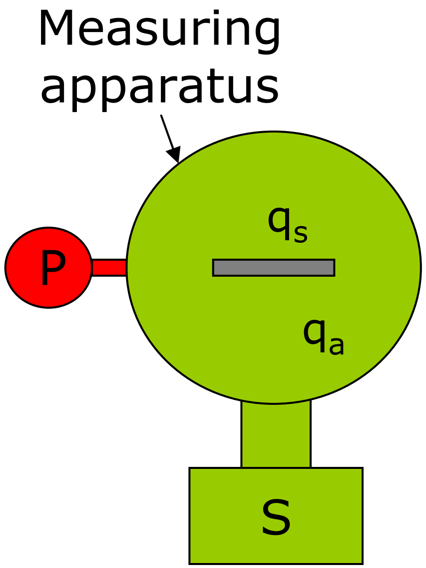
For a sample area of 100 cm^2:

$$q_s > 1.1 \cdot 10^{-11} [\frac{Torr \cdot l}{s \cdot cm^2}]$$

This excludes most of the metals applied in the UHV. This methods is used for metals when: upper limits of outgassing rate are needed, the sample is the system itself, or the sample surface is very large

Part 1: Methods for measurement

Throughput method



$$S_{eff}\left[\frac{l}{s}\right]=\sigma\cdot C_a\left[\frac{l}{s}\right]$$

C_a is the conductance of the pump opening in the system

σ is the pump capture probability in the system

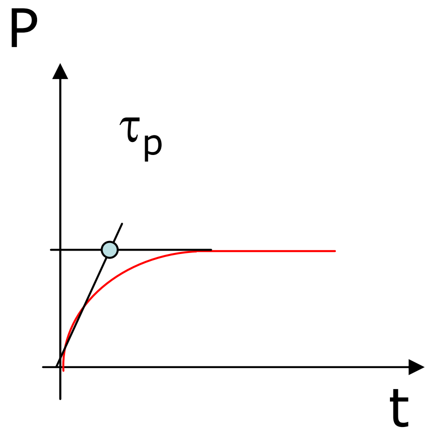
Continuous pumping is applied during the measurement

$$\frac{dN}{dt}=Q-\sigma\cdot A_P\cdot\left(\frac{1}{4}n\cdot v\right)$$ and $$\frac{dN}{dt}=\frac{V}{k_BT}\frac{dP}{dt}\rightarrow\frac{dP}{dt}=\frac{k_BT}{V}Q-\sigma\cdot A_P\cdot\left(\frac{1}{4}v\right)P$$

$$Q=A_aq_a+A_sq_s$$

$$V\frac{dP[Torr]}{dt}=Q\left[\frac{Torr\cdot l}{s}\right]-\sigma\cdot C_a\left[\frac{l}{s}\right]P[Torr]$$

$$\Delta P=\frac{Q}{S_{eff}}\left(1-e^{-\frac{t}{\tau_p}}\right)\qquad\tau_p=\frac{V}{S_{eff}}$$



In general τ_p is very small compared to the time scale of the measurement, so:

$$\Delta P[Torr]=\frac{Q\left[\frac{Torr\cdot l}{s}\right]}{S_{eff}\left[\frac{l}{s}\right]}=\frac{A_aq_a+A_aq_a}{S_{eff}}$$

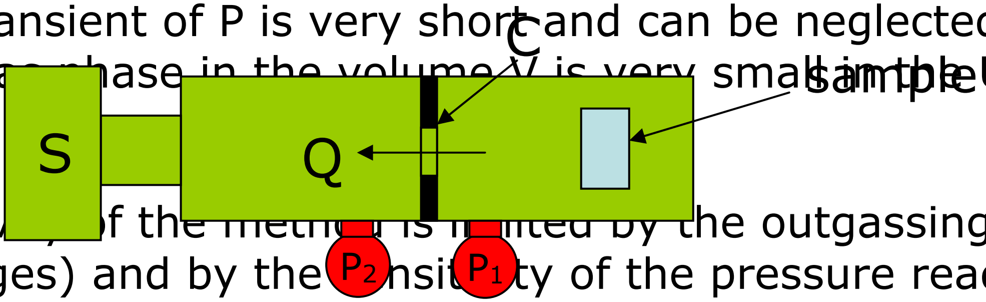
Part 1: Methods for measurement

Throughput method

τ_p is the characteristic time of pumping.
Typical values for τ_p for test systems are less than one minute.

Example: V=10 ℓ S=10 ℓ/s→ $\tau = 1$ s

This implies that the transient of P is very short and can be neglected → the quantity of gas to built up the gas phase in the volume V is very small in the UHV range.



Here again, the sensitivity of the method is limited by the outgassing of the apparatus (walls, valves and gauges) and by the sensitivity of the pressure reading.

Example 1: for a baked spherical apparatus made of regular stainless steel (V=10ℓ) evacuated by an effective pumping speed of 10 ℓ/s.
The contribution of the system is $\Delta P = 4.5\times10^{-10}$ Torr. The detection limit of the outgassing rate is 1.1×10^{-9} Torr ℓ s^{-1} (25% of the system background). If the outgassing of a standard BA gauge is also taken into account the detection limit is 1.4×10^{-9} Torr ℓ s^{-1}.

Throughput method

Example 2: Extreme conditions.

Same apparatus as before, but made of high temperature treated stainless steel:

$q \approx 10^{-14}$ Torr ℓ cm^{-2} s^{-1} → $Q_a = 2.2\text{x}10^{-11}$ Torr ℓ s^{-1}

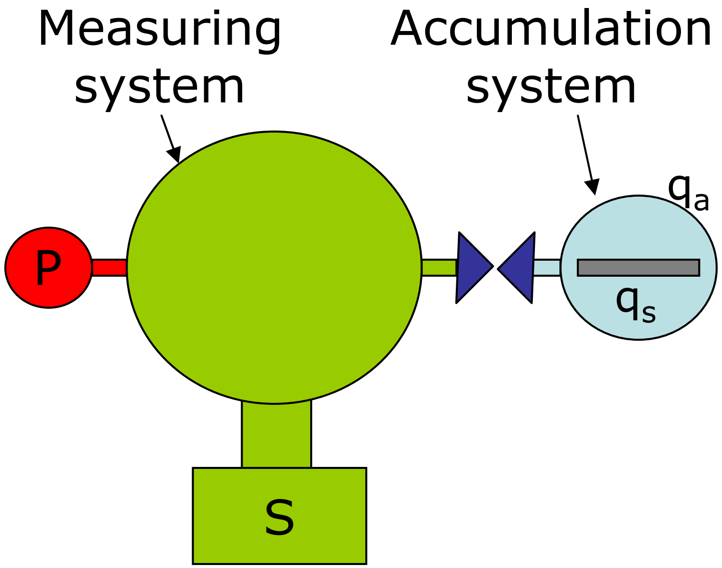
and equipped with a very low outgassing rate BA gauge

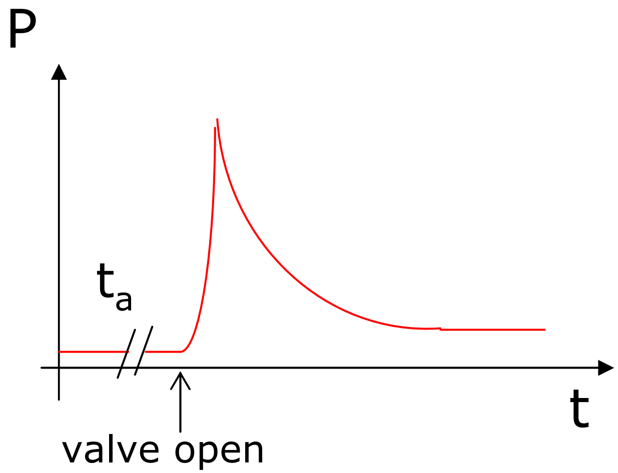
$Q_{BA} = 1\text{x}10^{-10}$ Torr ℓ s^{-1}

The system background is $Q = 1.2\text{x}10^{-10}$ Torr ℓ s^{-1} , dominated by the effect of the gauge.

The detection limit (25% of the system background) for the outgassing rate is $3\text{x}10^{-11}$ Torr ℓ s^{-1}. This limit can be attained by increasing the surface area of the sample (whenever possible) or by coupling the accumulation and the throughput methods.

Part 1: Methods for measurement





Coupled method

The sample is isolated by a valve in a separated vessel where the gas is accumulated for a time t_a. Then the valve is opened and the quantity of accumulated gas is measured in the test dome.

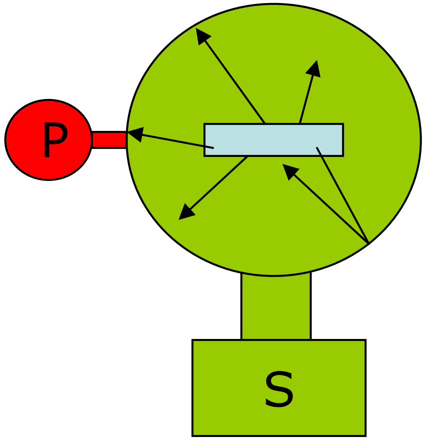
$$Q = S_{eff} \cdot \int_{t_a}^{t_a+\Delta t} P(t)\,dt$$

This method can be applied only if the outgassing rate is constant in the time of accumulation and repumping is negligible.

The detection limit is defined by the outgassing of the accumulation system and by the sensitivity of the pressure reading.
The advantages of this method are two:

- no effects of gauge on the quantity of gas accumulated
- t_a can be long enough to attain gauge sensitivity

Part 1: Methods for measurement



Ion gauges remove molecules from the gas phase through two mechanisms:

-Cracking on the hot filaments (does not affect monoatomic molecules like rare gases).

-Ionization by electrons (affects all gases).

For ordinary B-A gauges typical values are ≈1 ℓ/s and ≈10^{-2} ℓ/s respectively.

Effect of readsorption

The gas released by the sample, instead of being evacuated by the pumping system, can be adsorbed by the system wall, pumped by the gauge, or eventually reabsorbed by the sample itself.

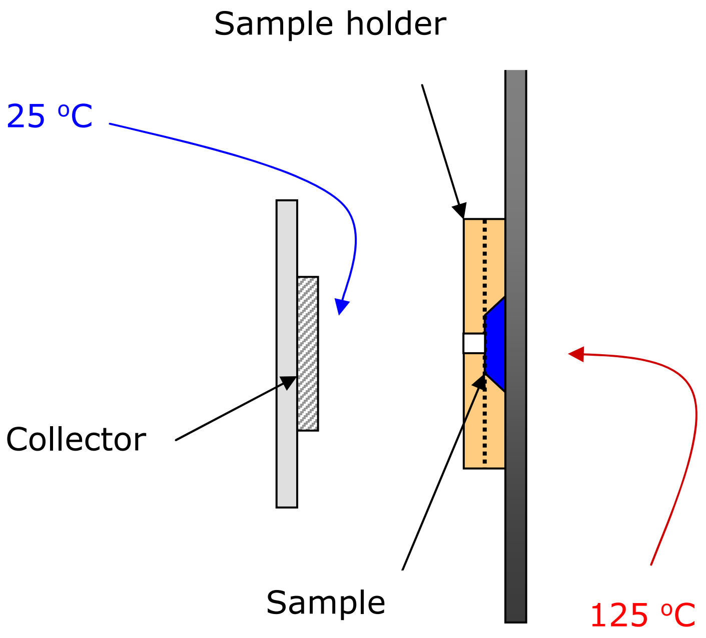
Let's call S_{add} the resulting additional pumping speed:

$$Q_{\text{int}} = P\left(S_{add} + S_{eff}\right) = PS_{eff}\left(1 + \frac{S_{add}}{S_{eff}}\right) \Rightarrow \frac{Q_{\text{int}}}{Q_m} = 1 + \frac{S_{add}}{S_{eff}}$$

Example: for a 10 ℓ spherical chamber, supposing a sticking probability of 10^{-3} for water on the system wall and a sample surface area of 100 cm^2:

$$\frac{Q_{\text{int}}}{Q_m} \cong 3$$

Weight loss



This method is used for high outgassing rate materials only, namely organics.

The test consists in measuring the weight loss of a sample following a defined thermal cycle in vacuum (TML total mass loss) and the weight gain of a collector cooled at room temperature and placed in front of the sample (CVCM Collected Volatile Condensable Material) .

The set-up and procedure are described in the ASTM E595-93 standard.

If the throughput method is applied in the same apparatus, data are obtained about the evolution of the outgassing rate at room temperature and at the temperature of the treatment.

This method is used largely in space applications and a wide database is available through the NASA’s web site. http://outgassing.nasa.gov/

Part 1: Methods for measurement

Key points

1. The quantity of gas are presented in number of molecules or in pressure-volume units. K_BT converts the former to the latter.

2. Pressure-volume values are always referred to the temperature of measurement.

3. Outgassing rates are measured by the accumulation or by the throughput method. For both methods gas repumping has to be taken into account.

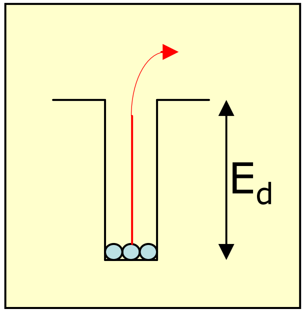
4. Pressure gauges interfere with the outgassing measurements by pumping and releasing gas molecules.

Part 2: General features of outgassing

The surface and the bulk of materials are both source of gas molecules:

- Those from the surface have to overcome an energy barrier before being released.
- Those from the bulk in addition have to diffuse along the material lattice before encountering the surface.

Single desorption energy: mean stay time



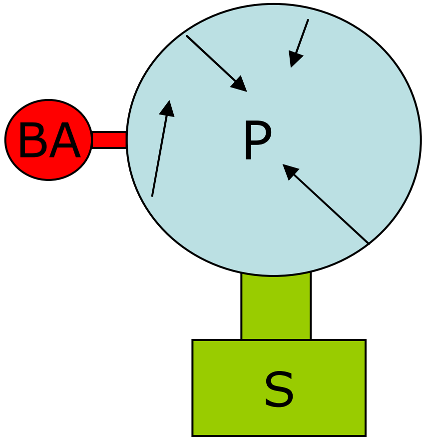
The mean stay time (sojourn time) is given by the Frenckel's law:

$$\tau_d = \tau_o e^{\frac{E_d}{k_B T}}$$

where the value of τ_o is usually assumed to be about 10^{-13} s ($\approx h/K_B T$).

E_d [Kcal/mole]	Cases	τ_d [s]
0.1	Helium	1.2×10^{-13}
1.5	H_2 physisorption	1.3×10^{-13}
3-4	Ar, CO, N_2, CO physisorption	1×10^{-11}
10-15	Weak chemisorption	3×10^{-6}
20	H_2 chemisorption	100
25		6×10^{5} one week
30	CO/Ni chemisorption	4×10^{9} 100 years
40		1×10^{17} age of Earth
150	O/W chemisorption	> age of universe

Single desorption energy: pressure evolution without repumping



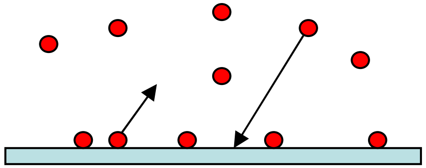
variation of the quantity of gas in the gas phase

$$\left\{ \begin{array}{l} V\dfrac{dP}{dt} = -SP + \dfrac{N_s\Theta}{\tau_d} \\ \dfrac{d\Theta}{dt} = -\dfrac{\Theta}{\tau_d} \end{array} \right.$$

quantity of gas leaving the surface

quantity of gas removed by the pump

$$P(t) \cong \frac{N_s}{S\cdot\tau_d} e^{-\frac{t}{\tau_d}} \quad \text{for} \quad t > \tau_d$$



Θ= fraction of sites occupied
The total number of sites is assumed to be ≈10^{15} cm^{-2} → 3×10^{-5} Torr l s^{-1}cm^{-2}

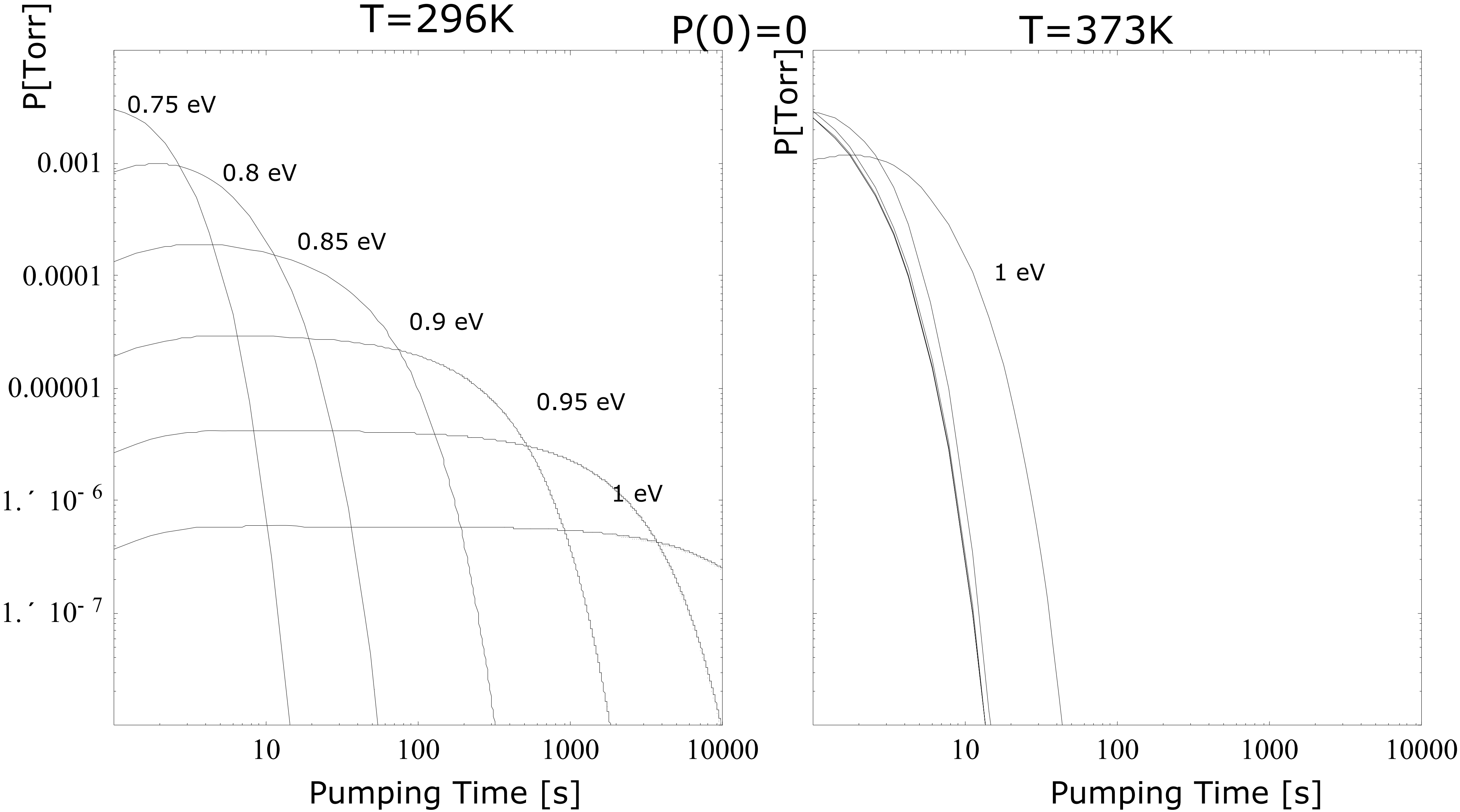
The solution is plotted for:

V=10 ℓ, S=10 ℓ /s, N_s=2245x3x10^{-5} Torr ℓ

and different energies

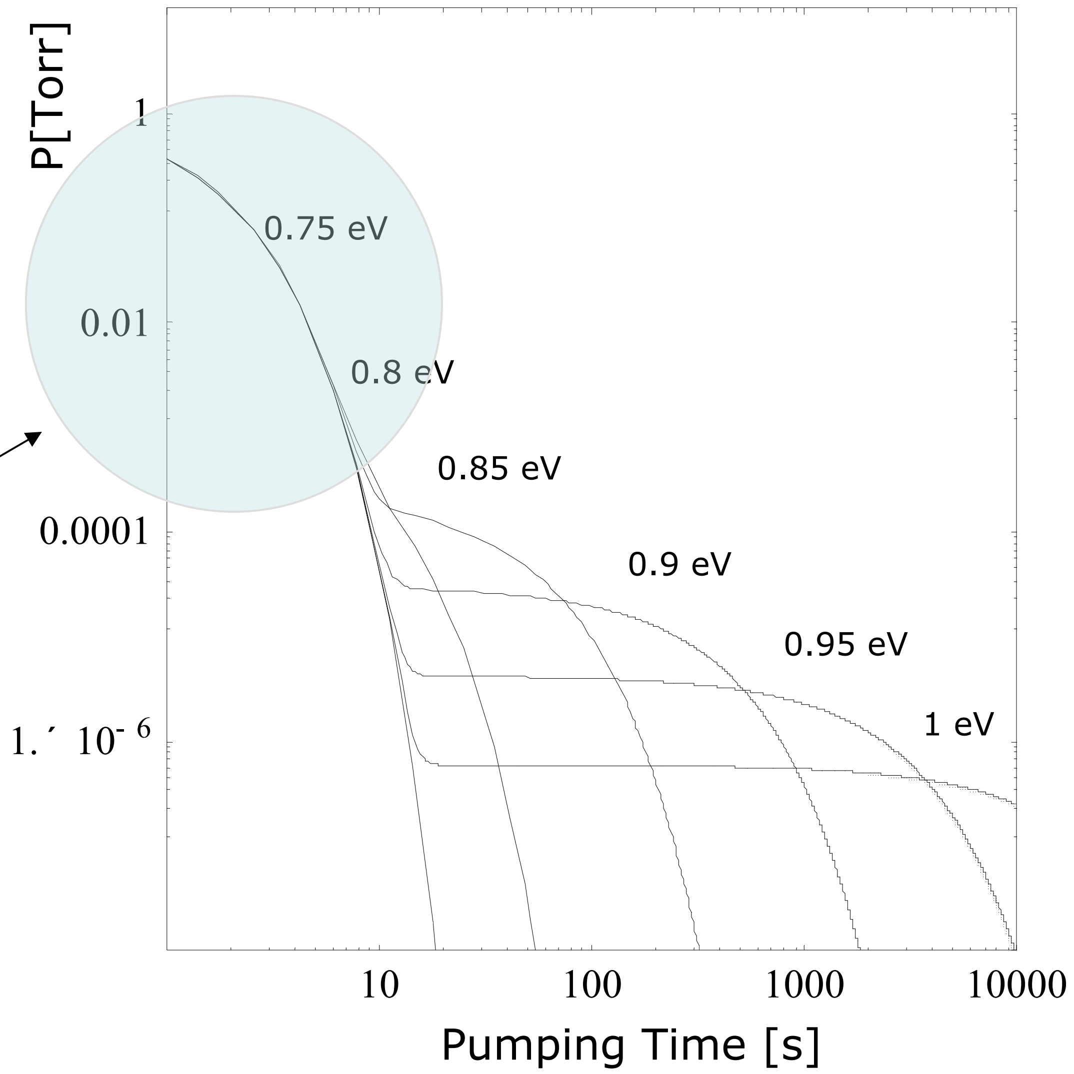
Part 2: General features of outgassing

P(0)=0



Part 2: General features of outgassing

T=296K
P_o=1 Torr



Effect of the molecules already in the gas phase at t=0

Single desorption energy: pressure evolution with repumping

$$\begin{cases} V\dfrac{dP}{dt} = -SP + \dfrac{N_s\Theta}{\tau_d} \boxed{-S_W P} \\ \dfrac{d\Theta}{dt} = -\dfrac{\Theta}{\tau_d} \boxed{+S_W P} \end{cases}$$

quantity of gas reabsorbed by the walls

The general solution exists and for the following hypothesis:

$$\frac{\tau_p}{\tau_d} < 1 \quad \text{and} \quad \frac{S_W}{S} >> 1$$

the pressure can be approximated to:

$$\boxed{P(t) \cong \frac{N_s}{\tau_d \cdot (S + S_W)} e^{-\frac{t}{\tau_d \cdot \left(\frac{S_W + S}{S}\right)}}}$$

It is again an exponential function

Part 2: General features of outgassing

The same result can be obtained by simple arguments:

- the probability that a molecule leaving the surface is pumped outside the system is: $\dfrac{S}{S+S_W}$
- the probability for a molecule to leave the surface in one second is: $\dfrac{1}{\tau_d}$
- therefore, the probability for a molecule to be definitively removed in one second is: $\dfrac{S}{S+S_W}\dfrac{1}{\tau_d}$
- the average time the molecule stays in the system is: $\boxed{\tau_d \dfrac{S+S_W}{S}}$

The increased residence time of the molecule in the system is due to the surface readsorption and reemission.

For t $<< \tau_d$ → $P(0) \cong \dfrac{N_s}{\tau_d \cdot \left(S+S_W\right)}$

$$⇨ \quad P(t) \cong \frac{N_s}{\tau_d \cdot \left(S+S_W\right)} e^{-\frac{t}{\tau_d \cdot \left(\frac{S_W+S}{S}\right)}}$$

Part 2: General features of outgassing

Which is the τ_d that, at time "t", gives the maximum value of P(t)?

$$\frac{dP(t)}{d\tau_d} \cong \frac{N_s}{\tau_d^2 \cdot (S+S_W)} e^{-\frac{t}{\tau_d \cdot \left(\frac{S_W+S}{S}\right)}} \cdot \left(1-\frac{t}{\tau_d \cdot \left(\frac{S_W}{S}+1\right)}\right)=0$$

$$\tau_{d,\max}=\frac{t}{\left(\frac{S_W}{S}+1\right)}$$

Hence, the maximum pressure that can be obtained in a desorption process (at constant temperature) is:

$$P_{MAX}(t) \cong \frac{N_s}{S \cdot e} \cdot t^{-1}$$

In the case of one monolayer coverage $N_s=10^{15}/3.3\text{x}10^{19}$:

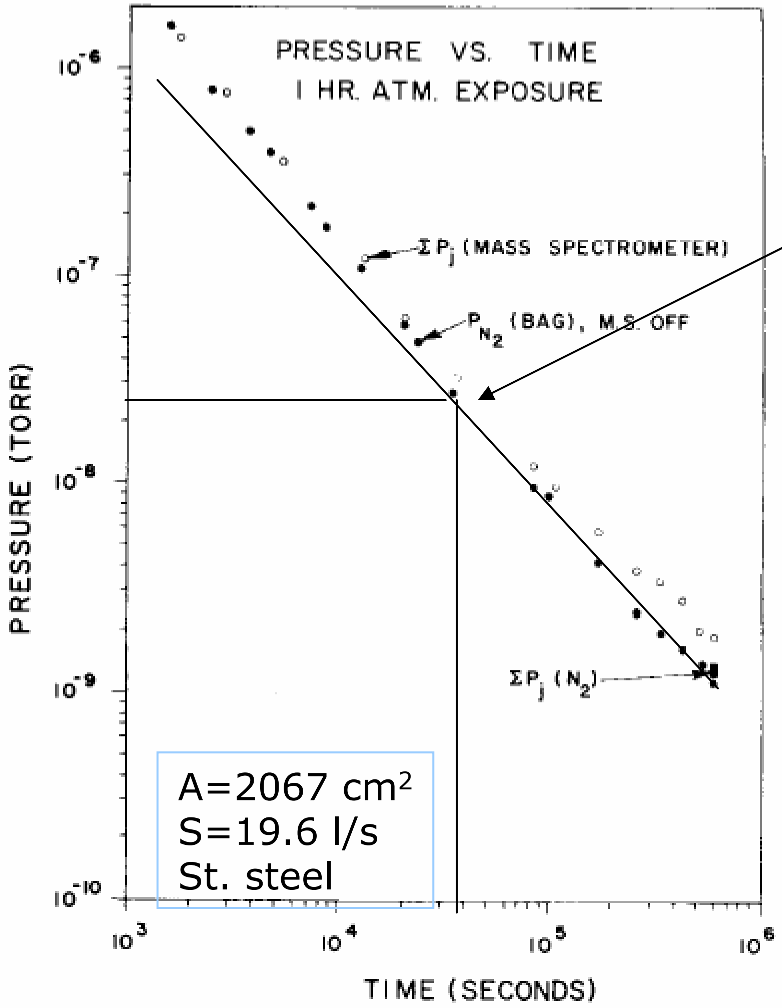
$$\boxed{q_{MAX}(t) \cong \frac{N_s}{e} \cdot t^{-1} = \frac{1.1 \cdot 10^{-5}}{t[s]} = \frac{3 \cdot 10^{-9}}{t[h]} \qquad [\frac{\text{Torr l}}{\text{s cm}^2}]}$$

Edwards' upper limit

This behavior could be that of a real system only if adsorption sites of different energy exist and they are in the worst possible combination at each pumping time.

Part 2: General features of outgassing

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



$A=2067\ cm^2$
$S=19.6\ l/s$
St. steel

$q(10h)=2.8\times10^{-10}$ Torr l s^{-1} cm^{-2}

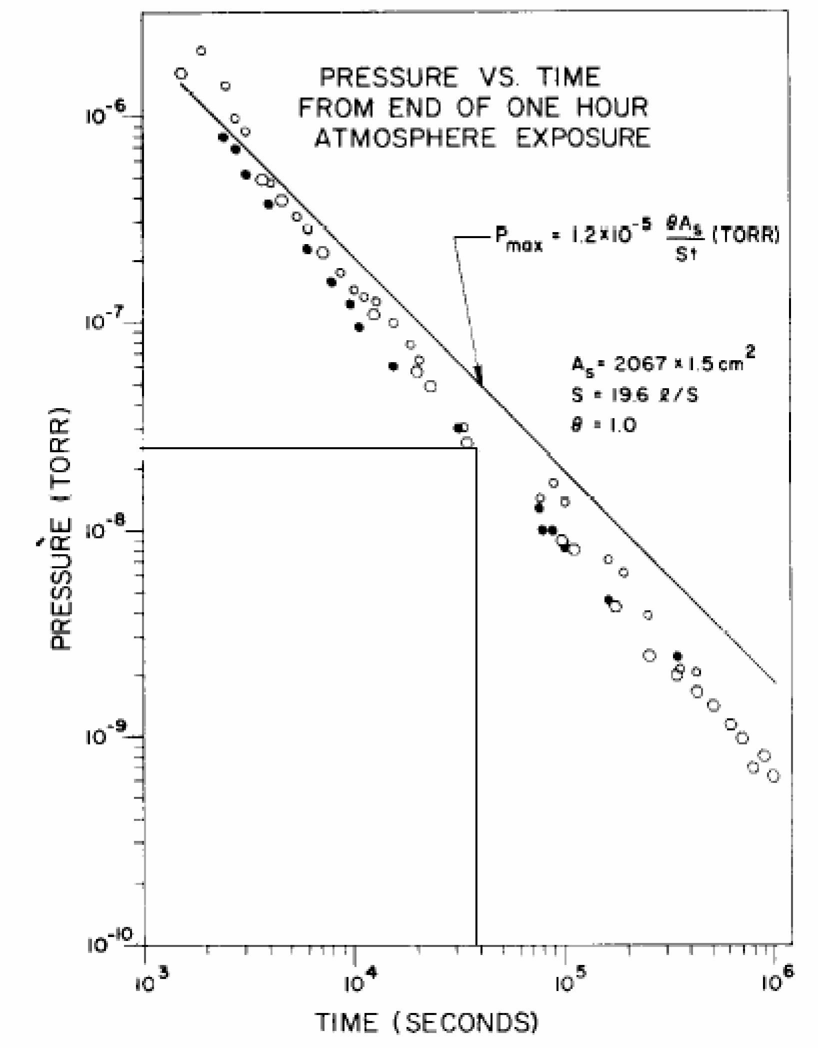
Experimental value valid for most of the metals:

$$q(t) \cong \frac{2 \cdot 10^{-9}}{t[h]} \quad \frac{Torr\ l}{s\ cm^2}$$

The outgassing rate of an unbaked material depends on pumping time, it is not an intrinsic value!

Part 2: General features of outgassing

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



The Edwards' upper limit is very close to the experimental values. In the context of the analysis reported in page 25 it could mean that:

1. water should be adsorbed on many energy states
2. the distribution of the water molecules in the different sites is, at any time, the worst.
3. this is true for all the metals!

Other models explain the 1/t variation; they are based on diffusion from the bulk of ad hoc initial distribution, adsorption in small porosity in the oxide layer, and quasi-equilibrium approximations allowing the application of standard isotherms.

Part 2: General features of outgassing

The simple models presented suppose the existence of a single desorption site or the coexistence of many but completely independent desorption sites.
In addition, when readsorption is considered, the pumping speed of the wall is assumed constant.

Much more complicate models are needed to take into account variable pumping speed of the wall and the interdependence of the population of the different adsorption sites.

However, the essential feature of desorption are already underlined by the simplest models:

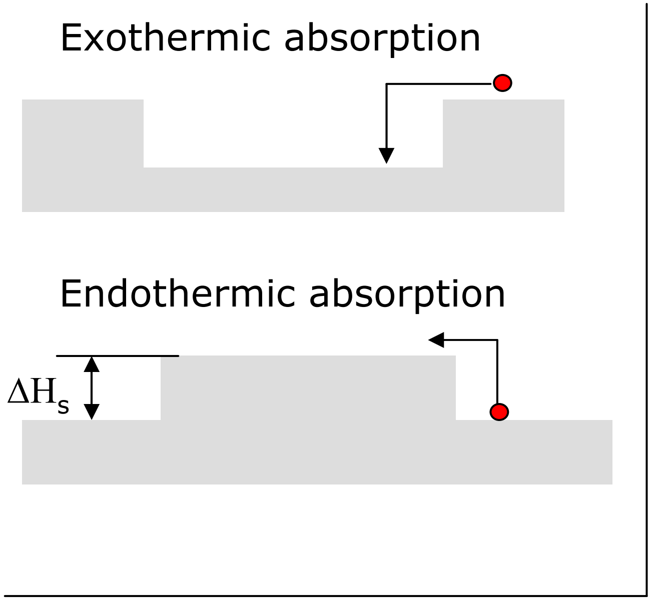
1. The outgassing rate of a single desorption site decreases as an exponential function of time, whose decay time is the desorption time.

2. Higher temperatures allow a faster degassing.

3. The decay time increases in case of repumping by the system walls.

4. The outgassing rate has a t^{-1} evolution only if desorption from sites of different energy is considered.

Outgassing of molecules dissolved in the bulk of materials: solubility



Molecules of A in gas phase and in solid are in thermodynamic equilibrium when:

A (gas) = A (solid)

The equilibrium constant K is:

$$K = e^{-\frac{\Delta G^0}{k_B T}} = \frac{a_A}{P_A}$$

where a_A is the activity of A in the solid. For diluted solution :

$$K = \frac{x_A}{P_A} \rightarrow x_A = K \cdot P_A$$

where x_A is the molar fraction and K the solubility of A in the solid. The temperature dependence is obtained:

$$x_A = B \cdot e^{-\frac{\Delta H_s{}^0}{k_B T}} \cdot P_A$$

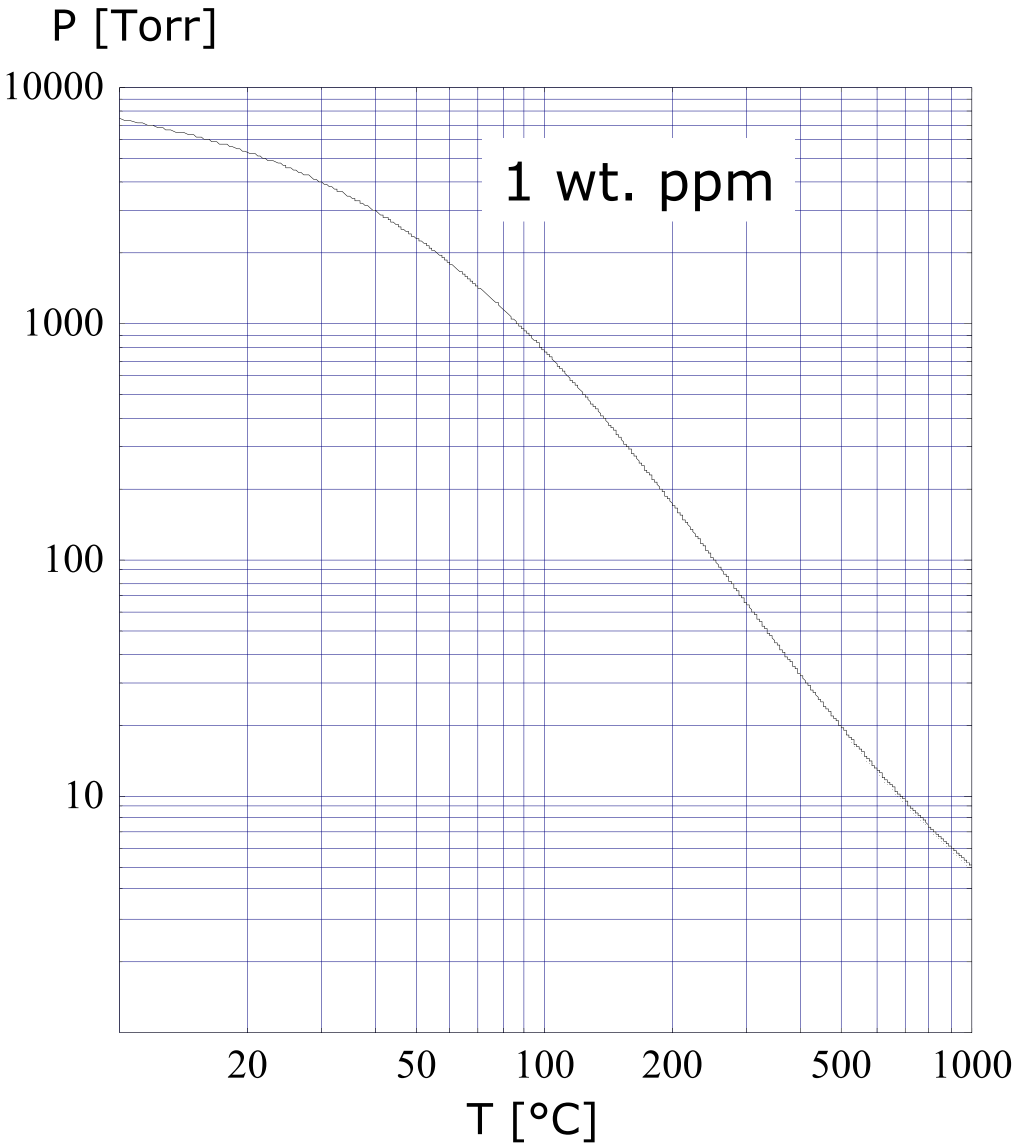
For diatomic molecules adsorption: A_2 (gas)= 2 A (solid):

$$K = \frac{x^2{}_A}{P_A}$$

$$\boxed{x_A = B \cdot e^{-\frac{\Delta H_s{}^0}{2 k_B T}} \cdot \sqrt{P_A}}$$

Sievert’s law

Part 2: General features of outgassing



Solubility of H_2 in stainless steel:

$$x_H[at.ppm] = 71.8 \cdot \sqrt{P[Torr]} \cdot e^{-\frac{0.114\,[eV]}{k_B \cdot T}}$$

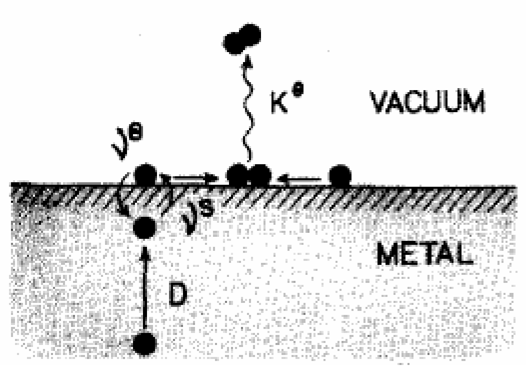
The H content in standard austenitic stainless steels is about 1 ppm in weight (≈56 ppm atomic H).

After evacuation, in an isolated stainless steel vessel the hydrogen equilibrium pressure is about 7 bar at RT !

But no humans will measure it. Why?

Part 2: General features of outgassing

Outgassing of molecules dissolved in the bulk of metals



Gas molecules are dissolved into the bulk of materials during the production processing and during their permanence in air.
In vacuum, the lighter molecules diffuse and, after reaching the surface, they are released.

- Only H atoms have enough mobility in metals to attain the surface where they recombine to form H_2.
On the other hand, in organics most of the lighter molecules quickly diffuse toward the surface where they are released.
- The models that take into account all the steps in the outgassing process are quite complicate and, in general, they give only asymptotic solution for limit conditions.
Two mechanisms are considered:

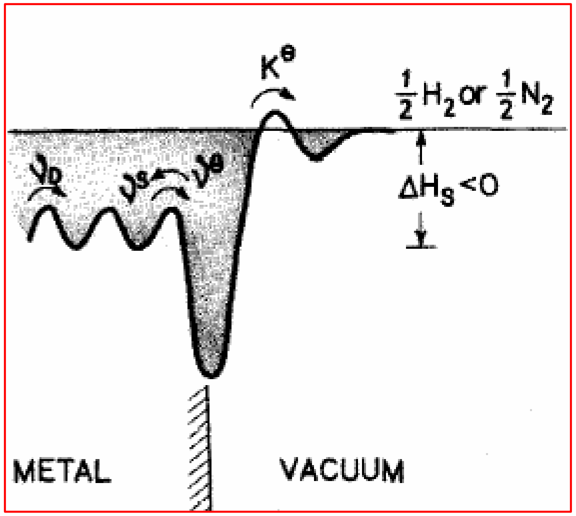
1. diffusion limited outgassing→ $q(t) \propto -\frac{\partial c}{\partial x}$ ← Concentration gradient
2. recombination limited outgassing→ $q(t) \propto c_s^{\,2}$ ← Square of the concentration on the surface

Part 2: General features of outgassing

B.M. Shipilevsky and V.G. Glebovsky have shown that, for each metal, a characteristic critical number of dissolved monolayers defines the limit between the two stages; below it, recombination becomes the controlling mechanism.

exothermic metals

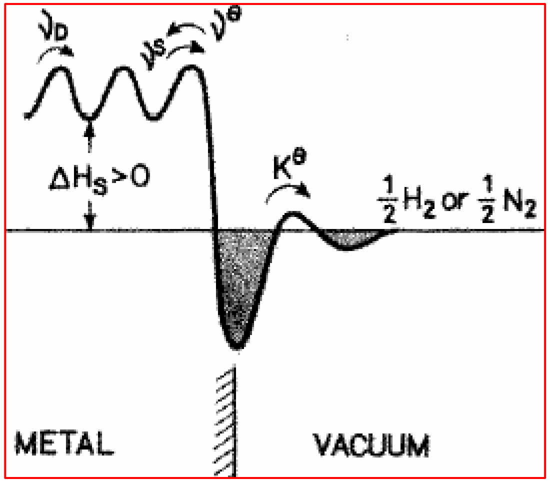
Nb,Ti,
Pd,Zr,
…



The recombination and desorption energy is higher than the dissolution energy. Recombination has to be taken into account in most of the problems.

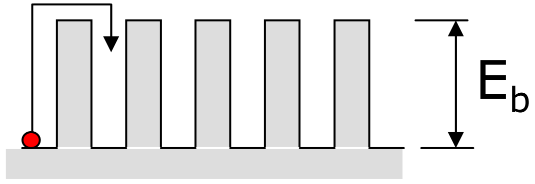
endothermic metals

Fe, Ni,
Cu, Mo,
st. steel



The recombination and desorption energy is lower than the dissolution energy.
The desorption barrier is transparent.
Kinetics is controlled by diffusion, except when concentration is very low (much less than 1 ML dissolved; do not forget that the recombination rate is ≈ $(c_s)^2$).

Diffusion limited outgassing



$$D(T) = D_0 \cdot e^{-\frac{E_b}{k_B T}}$$

Diffusion is a random process and in most of the cases of interest is described by the **Fick's equations**:

$$\left.\begin{aligned} -D\frac{\partial c(x,t)}{\partial x} &= \Gamma(x,t) \\ D\frac{\partial^2 c(x,t)}{\partial x^2} &= \frac{\partial c(x,t)}{\partial t} \end{aligned}\right\}$$

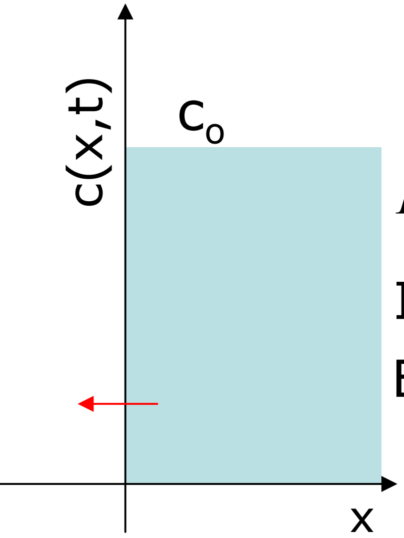
where c(x,t) is the concentration in the solid and Γ is the flux of molecules per cm^2

In the limit of this model, the outgassing rate is equal to the flux of molecules arriving at the surface by diffusion:

$$\boxed{q(t) = -D\left.\frac{\partial c(x,t)}{\partial x}\right|_{x=SURF.}}$$

Part 2: General features of outgassing

Semi-infinite solid approximation:



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

I.C. $c(x,0)=c_o$

B.C. $c(0,t)=0$

$$\boxed{c(x,t)=c_o\cdot erf\frac{x}{2\sqrt{Dt}}}$$

diffusion length

$$erf(z)=\frac{2}{\sqrt{\pi}}\int_0^z e^{-\eta^2}d\eta$$

the gaussian character of the solution reflects the brownian nature of diffusion

$$\boxed{q(t)=-D\frac{\partial c(x,t)}{\partial x}\bigg|_0=\frac{D\cdot c_o}{\sqrt{\pi\cdot D\cdot t}}\propto t^{-0.5}}$$

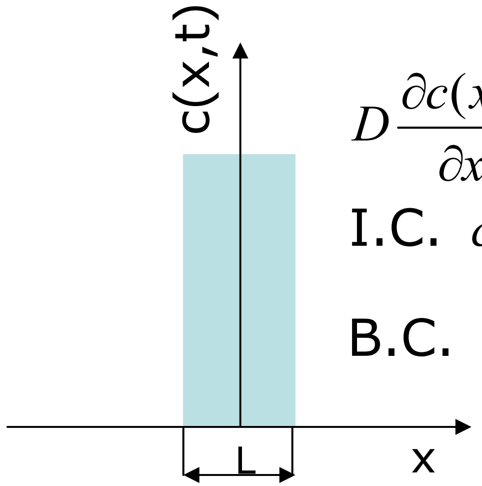
The $t^{-0.5}$ evolution holds also for solid of finite dimension L (slab) when $L>>(Dt)^{0.5}$

The total amount of substance M(t) which has left the solid is:

$$\boxed{M(t)=\frac{2c_o}{\sqrt{\pi}}\cdot\sqrt{D\cdot t}}$$

Part 2: General features of outgassing

Slab approximation



$$\left.\begin{array}{l} D\dfrac{\partial c(x,t)}{\partial x^2} = \dfrac{\partial c(x,t)}{\partial t} \\ \text{I.C.}\quad c(x,0) = c_o \\ \text{B.C.}\quad c(\pm\dfrac{L}{2},t) = c_w \end{array}\right\} \quad \boxed{\frac{c(x,t)-c_o}{c_w-c_o} = 1-\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n-1}\cos\frac{(2n+1)\pi\cdot x}{L}\, e^{\frac{-D\cdot(2n+1)^2\pi^2 t}{L^2}}}$$

$$\boxed{q(t) = \frac{4\cdot\left(c_0-c_w\right)\cdot D}{L}\sum_{n=0}^{\infty} e^{-(2n+1)^2\pi^2\cdot\frac{D\cdot t}{L^2}}}$$

For Dt>0.05 L^2 only the first term of the series is relevant :

For diatomic molecules

$$\boxed{q(t) \approx \frac{4\cdot\left(c_0-c_w\right)\cdot D}{L} e^{-\pi^2\cdot\frac{D\cdot t}{L^2}}}$$

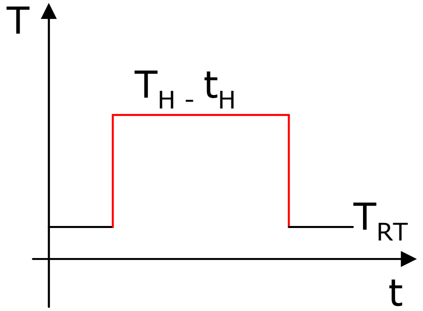
When equilibrium is assumed between gas and surface, the Sievert’s law defines the surface concentration c_w:

$$\boxed{c_w = K\sqrt{P}}$$

Part 2: General features of outgassing

Slab approximation: thermal history

If the slab is heated to a temperature T_H for a time t_H, the outgassing rate, when back at room temperature is:



$$q \approx \frac{4 \cdot (c_0 - c_w) \cdot D}{L} \exp\left[-\pi^2 \cdot \frac{D(T_H) \cdot t_H}{L^2} \right]$$

For an arbitrary thermal cycle it can be show that:

$$q \approx \frac{4 \cdot (c_0 - c_w) \cdot D}{L} \exp\left[-\pi^2 \cdot \frac{\int_0^{t_H} D(T) \cdot dt}{L^2} \right]$$

The dimensionless number: $F_o = \frac{\int_0^{t_H} D(T) \cdot dt}{L^2}$ is called the Fourier number

F_o records the thermal history of the material and determines how much of the initial concentration is depleted.
When thermal treatment of $F_o \approx 3$ are applied, the solid is actually emptied or in equilibrium with the surrounding gas phase.

Part 2: General features of outgassing

Recombination limited outgassing

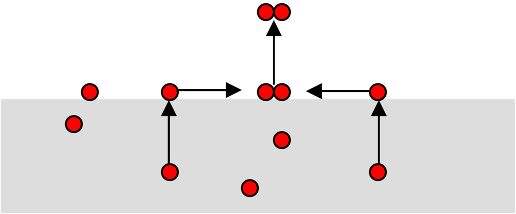
In a pure recombination limited process, the concentration in the bulk is flat and the outgassing rate is given by:

$$q(t) = K_R(T) \cdot c(t)^2$$

where K_R is called recombination coefficient. Recombination is an activated process and so:

$$K_R(T) = K_{R,0} \cdot e^{-\frac{E_R}{k_B T}}$$

In this model, the hydrogen concentration in the solid can be obtained in the following way:



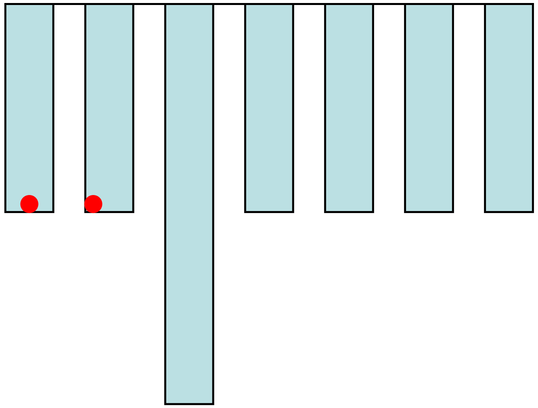
$$L\frac{dc(t)}{dt} = -K_R c^2 \rightarrow \frac{dc}{c^2} = -\frac{K_R}{L}dt \rightarrow \frac{1}{c(t)} - \frac{1}{c_0} = \frac{K_R}{L}t$$

$$c(t) = \frac{c_0}{1+\left(\frac{K_R c_0}{L}\right)\cdot t}$$

Part 2: General features of outgassing

Trapping sites are present in metals: they can block the hydrogen migration to the surface, hence providing a sort of **internal pumping**.

The trapping effect can be taken into account by introducing an effective diffusion coefficient D_{eff}



Assuming local equilibrium between the traps and the interstitial sites:

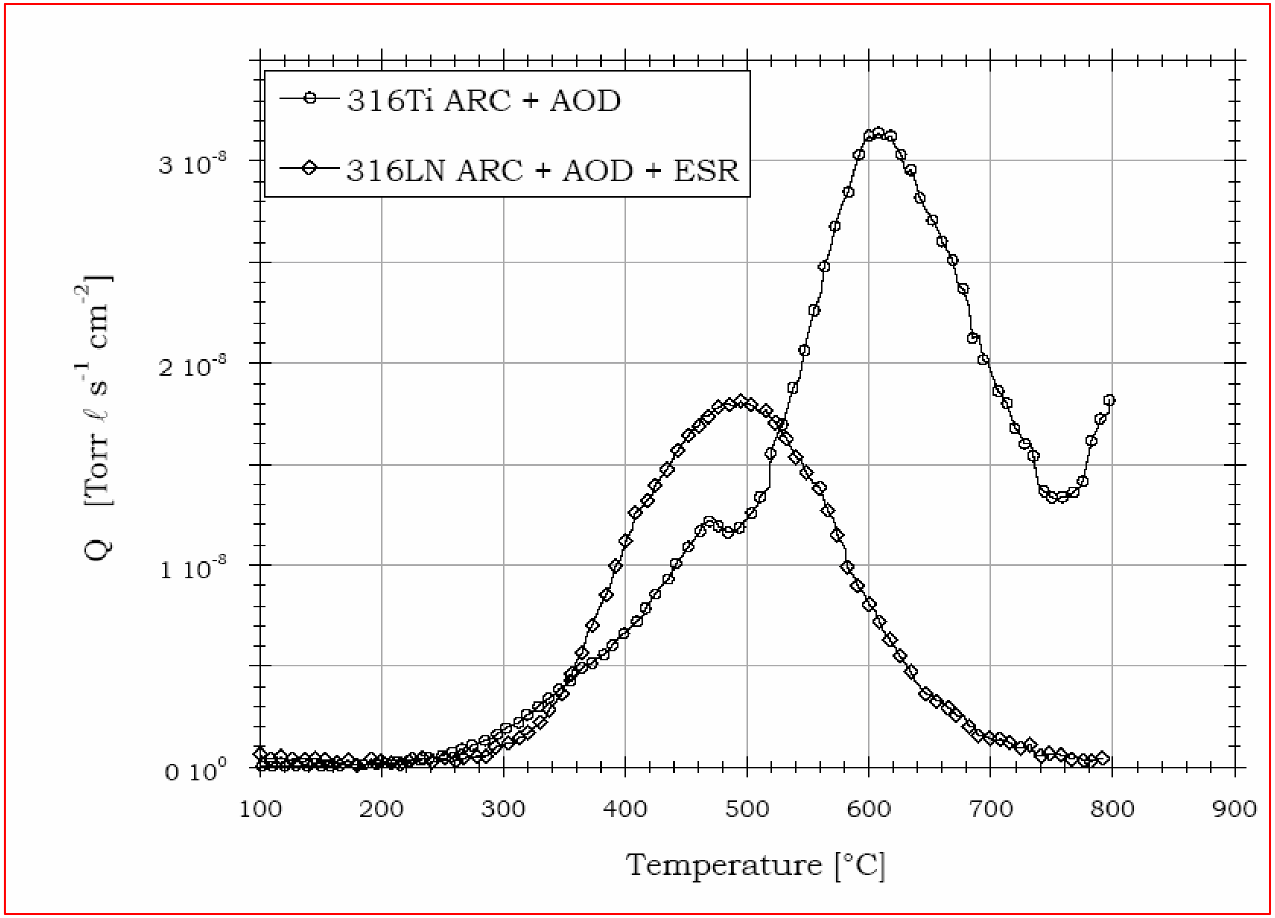
$$D_{eff} = D\frac{c_L}{c_L + c_{Trap}\left(1-\theta_{Trap}\right)}$$

For $\theta << 1$:
$$D_{eff} = D\frac{c_L}{c_{TOT}}$$

c_L, c_{Trap}: *H atoms in the regular interstitial site, trapping sites*

Part 2: General features of outgassing

Carbides and nitride are deep **trapping sites** in austenitic stainless steels



Part 2: General features of outgassing

Key points

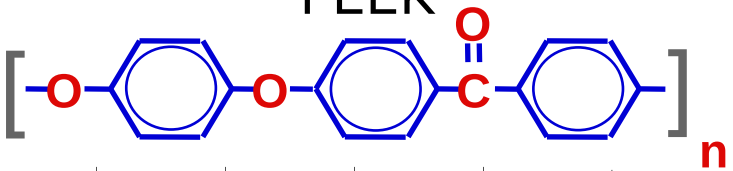
1. Both surface and bulk of materials are source of gas.
2. The desorption of gas molecules from the surface defines an exponential decay of the pressure. The decay time is related to the desorption energy by the Frenckel’s law.
3. When repumping is considered, the molecules remain in the test chamber for a longer time.
4. An upper limit to the outgassing rate of adsorbed molecules can be obtained. It is very similar to that of water in metallic systems!
5. The outgassing of molecules dissolved in the bulk is described by diffusion limited or recombination limited models. Endothermic metals should be well depicted by the former model, except for very low concentration
6. In the diffusion limited model, the Fourier number records the thermal history of the samples, and the diffusion length gives an indication of the penetration in the solid of the diffusion process.

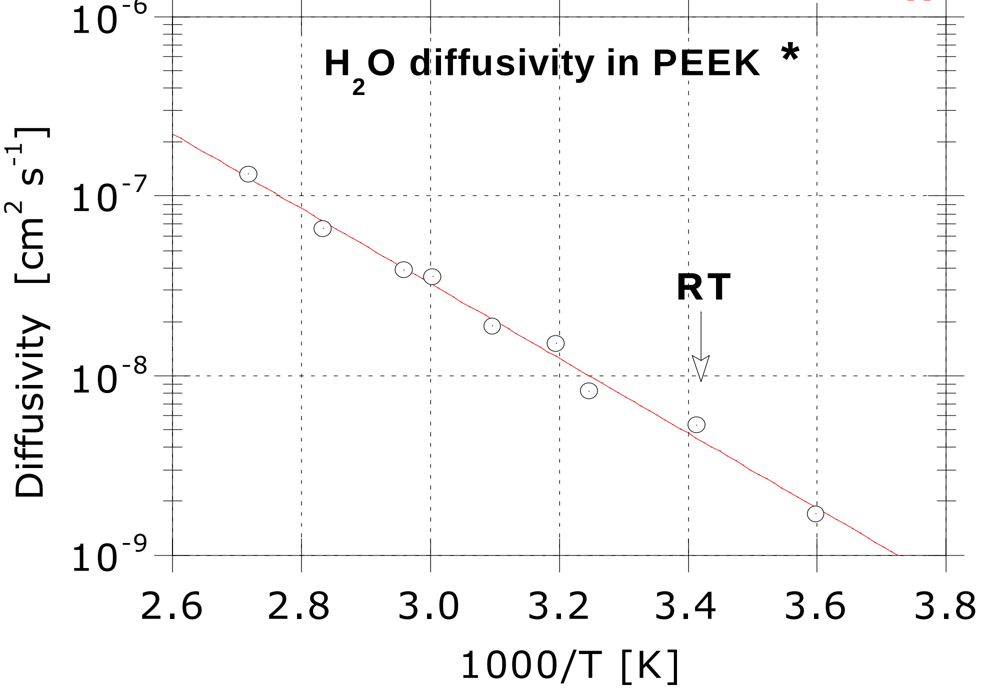
Part 3: Outgassing of polymers

Outgassing rate of polymers is known to be much higher than that of metals. Two reasons explain this phenomenon: a polymer contains much more gases than a metal, and the gas mobility in polymer is orders of magnitude larger than in metals.

Example

PEEK





Water solubility:

0.1 to 0.5 wt.% (4.4 to 22×10^{19} molecules/cm^3)

10 to 50 times larger than the H total content in as produced austenitic stainless steel

Water diffusivity at RT:

5×10^{-9} cm^2 s^{-1}

2000 times larger than that reported for H in austenitic stainless steel.

* After G.Mensitieri et al., J.Appl.Polym.Sci., **37**, 381, (1989)

Transport of gas in polymers

In the rubbery state the gas molecules are dragged by the thermal movement of the chain.
In the glassy state the gas molecules diffuse through the volume of the polymer and also through the excess volume.

The diffusion process in amorphous or semicrystalline polymers is not always well described by Fick's law. The diffusion process can be distinguished by evaluating the **Deborah number**

$$D_e = \frac{\tau}{\nu}$$

where τ is the polymer-penetrating molecule relaxation time, and $\nu = L^2/D$ is the characteristic time for diffusion.

For De>>1 the time for diffusion is shorter than the time for relaxation, the diffusing molecules does not record change in the polymer structure → Fick's law is valid. (He)

For De<<1 the penetrating molecules swell the polymer and hence allow the adsorption of additional molecules→ non fickian process.(H_2O)

Outgassing of Elastomers

In elastomers the molecular chains are reticulated by vulcanization.
The process of vulcanization was developed by Goodyear and Hancock (1844) by heating natural rubber with sulfur. Chemical bonds are formed by chains of sulfur atoms which react with the unsaturated bonds of the primary macromolecules. Modern elastomers utilize a wide variety of chemicals to produce the permanent network.

Fluorocarbon rubbers are prepared by cross linking a copolymer of tetrafluoro-ethylene and hexafluoro-propylene. These rubbers are thermally stable and have very low coefficient of friction.

Viton®

Viton is a fluorocarbon rubber typically employed for O-ring in vacuum technology.
Typical elements of the Viton composition are:

• Viton resin	100 parts by wt.	
• Carbon black	25	//
• MgO	15	//
• curing agent	1.5	//

Outgassing of Elastomers

The MgO is added as an acid acceptor to remove small amount of HF which results from the curing of the resin. The reaction is:

$$MgO + HF \rightarrow MgF_2 + H_2O$$

Therefore, Viton is created with a built-in source of water.

Three simple **warnings**:

1. Viton should never be cleaned with solvents, because the solvent is dissolved in the material and its outgassing could remain for long time.
2. Ozone can cause cracking of O-rings.
3. Pre-baking of O-ring gaskets at 200°C for some hours in air or vacuum is a necessary operation when possible contaminants need to be removed.

Part 3: Outgassing of polymers

The outgassing rates for polymers reported in the literature have a large spread. This could be due to:

1. The large spreading in the composition and the source of the resin
2. Different history of the samples
3. The relative humidity of the laboratory

In case of seals, the benefit of the baking is hindered by atmospheric gas permeation.

$3x10^{-10}$ for 100°Cx16 h

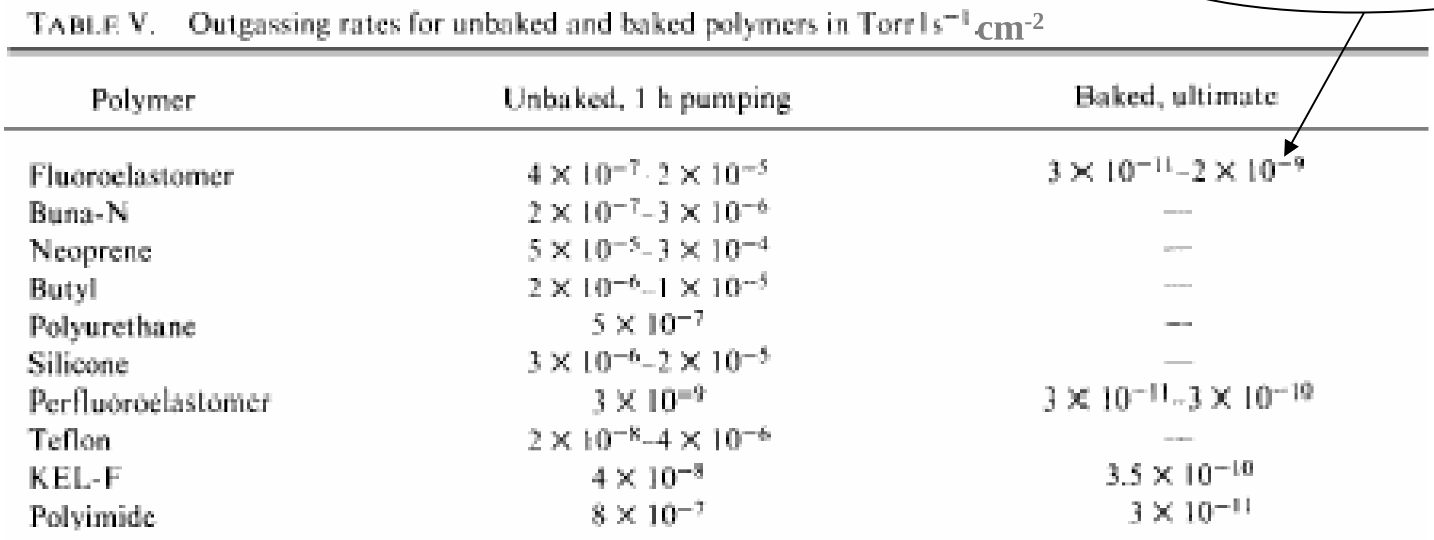


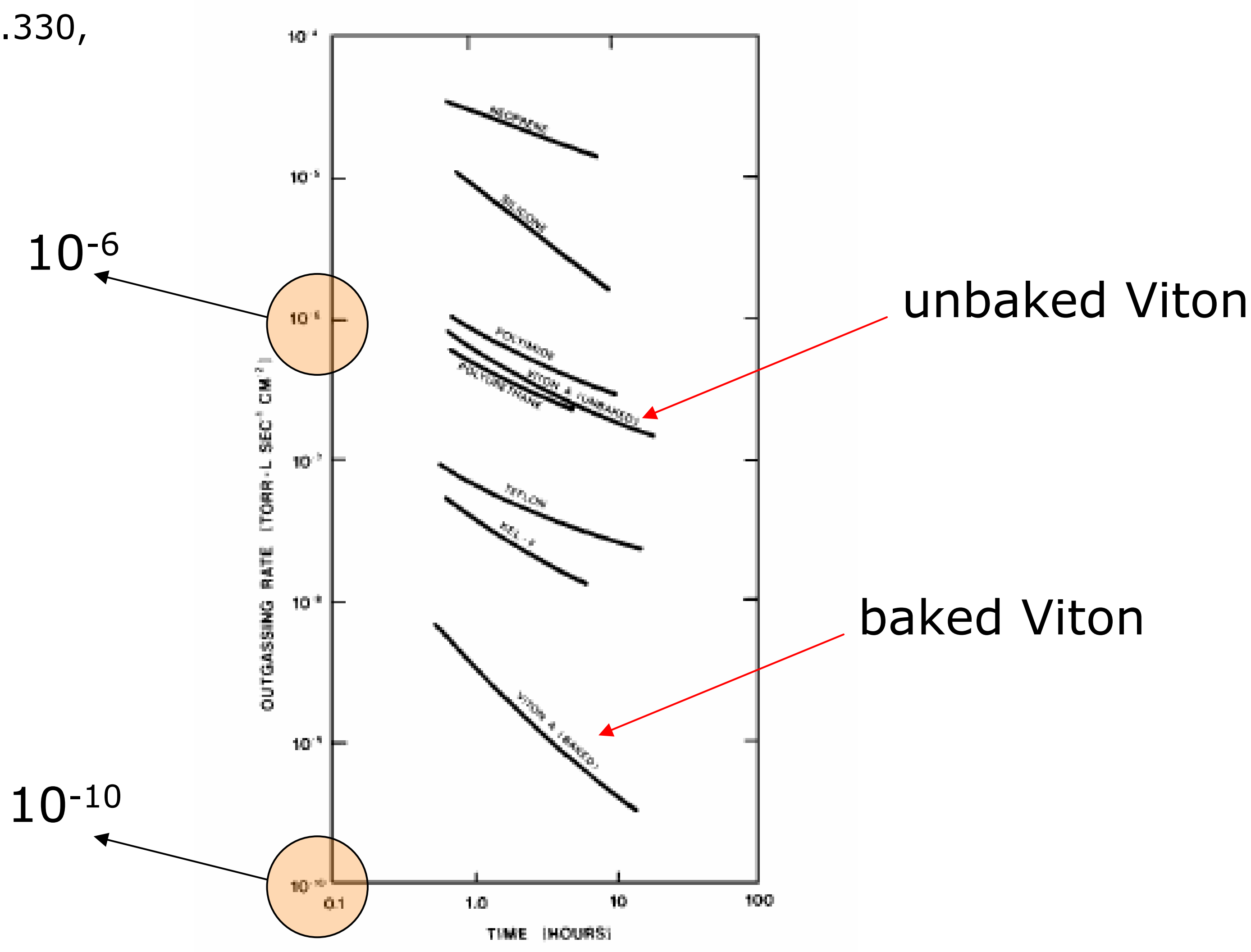
TABLE V. Outgassing rates for unbaked and baked polymers in Torr l s^{-1} cm^{-2}

Polymer	Unbaked, 1 h pumping	Baked, ultimate
Fluoroelastomer	4×10^{-7}–2×10^{-5}	3×10^{-11}–2×10^{-9}
Buna-N	2×10^{-7}–3×10^{-6}	—
Neoprene	5×10^{-5}–3×10^{-4}	—
Butyl	2×10^{-6}–1×10^{-5}	—
Polyurethane	5×10^{-7}	—
Silicone	3×10^{-6}–2×10^{-5}	—
Perfluoroelastomer	3×10^{-9}	3×10^{-11}–3×10^{-10}
Teflon	2×10^{-8}–4×10^{-6}	—
KEL-F	4×10^{-8}	3.5×10^{-10}
Polyimide	8×10^{-7}	3×10^{-11}

R. N. Peacock, J. Vac. Sci. Technol., 17(1), p.330, 1980

Part 3: Outgassing of polymers

R. N. Peacock, J. Vac. Sci. Technol., 17(1), p.330, 1980



10^{-6}

unbaked Viton

baked Viton

10^{-10}

Permeability of elastomers

The permeation flux of atmospheric **water** through a Viton O-ring, 5 mm cross section diameter, 6 cm torus diameter is 10^{-7} Torr l s^{-1}. The **stationary condition** (ultimate permeation) will be attained **after about two months**.

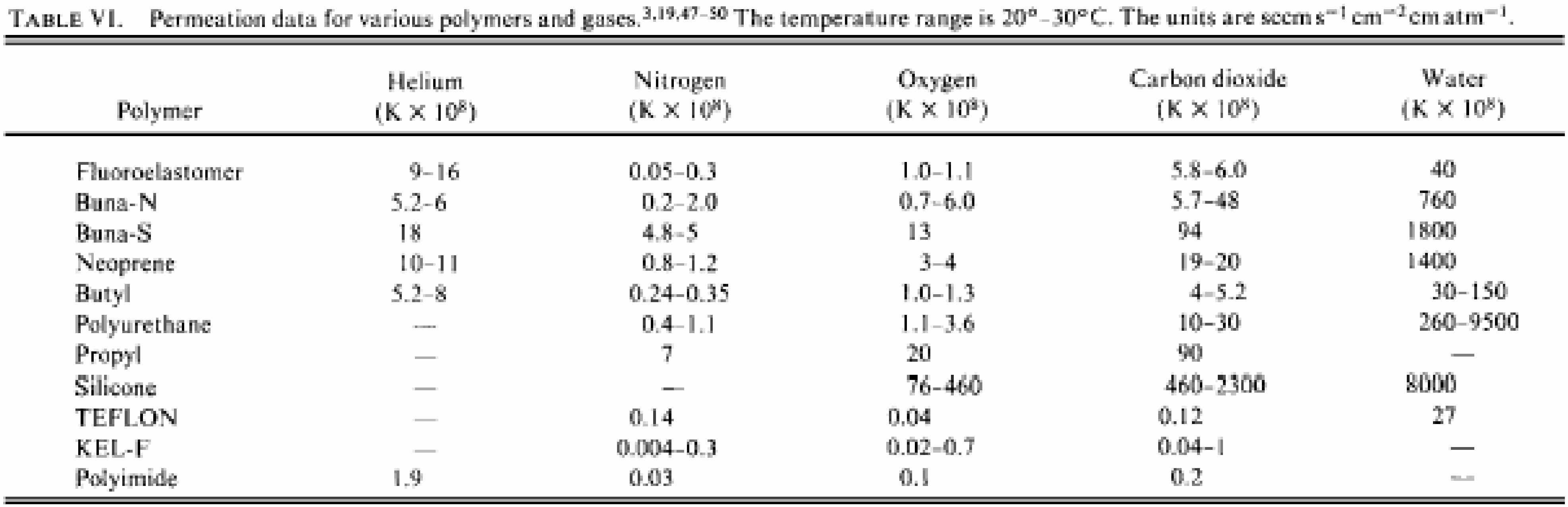


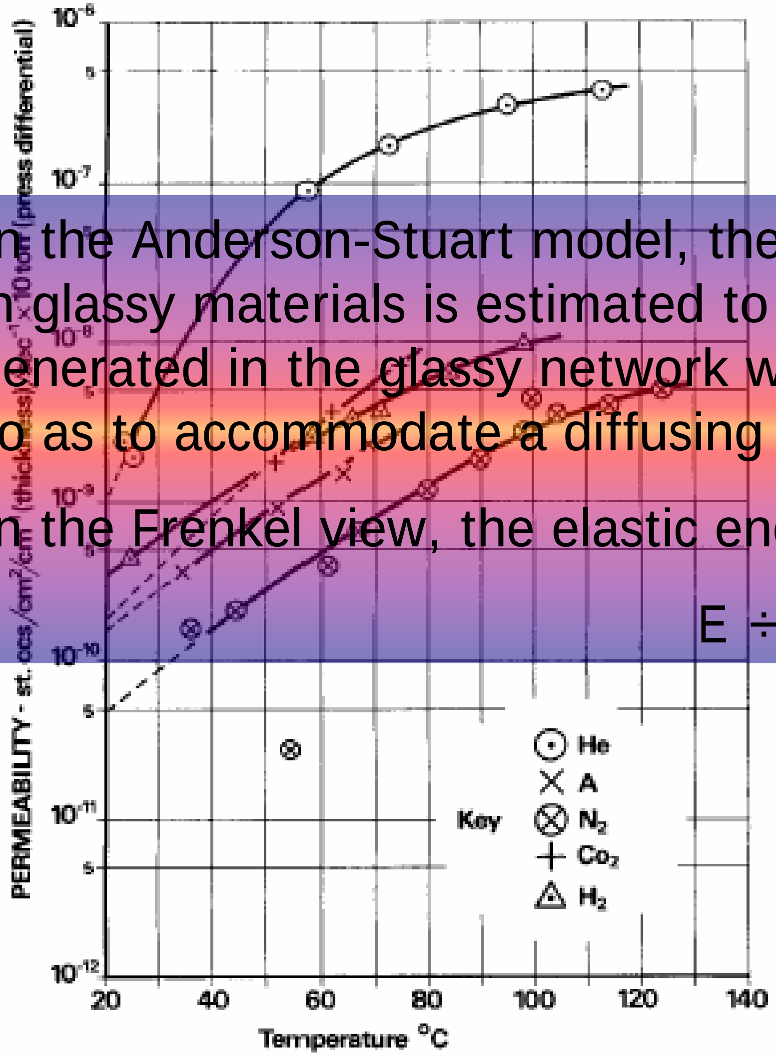
TABLE VI. Permeation data for various polymers and gases.[3,19,47–50] The temperature range is 20°–30°C. The units are $\mathrm{sccm\,s^{-1}\,cm^{-2}\,cm\,atm^{-1}}$.

Polymer	Helium ($K \times 10^8$)	Nitrogen ($K \times 10^8$)	Oxygen ($K \times 10^8$)	Carbon dioxide ($K \times 10^8$)	Water ($K \times 10^8$)
Fluoroelastomer	9–16	0.05–0.3	1.0–1.1	5.8–6.0	40
Buna-N	5.2–6	0.2–2.0	0.7–6.0	5.7–48	760
Buna-S	18	4.8–5	13	94	1800
Neoprene	10–11	0.8–1.2	3–4	19–20	1400
Butyl	5.2–8	0.24–0.35	1.0–1.3	4–5.2	30–150
Polyurethane	—	0.4–1.1	1.1–3.6	10–30	260–9500
Propyl	—	7	20	90	—
Silicone	—	—	76–460	460–2300	8000
TEFLON	—	0.14	0.04	0.12	27
KEL-F	—	0.004–0.3	0.02–0.7	0.04–1	—
Polyimide	1.9	0.03	0.1	0.2	—

R. N. Peacock, J. Vac. Sci. Technol., 17(1), p.330, 1980

Part 3: Outgassing of polymers

L. Laureson and N.T.M. Dennis, J. Vac. Sci. Technol. A3(3), p.1707, 1985



In the Anderson-Stuart model, the activation energy for molecular diffusion in glassy materials is estimated to be equivalent to the strain energy generated in the glassy network when an orifice of radius r_d is distended so as to accommodate a diffusing atom of radius r.

In the Frenkel view, the elastic energy of this dilatation is:

$$E \div (r - rd)^2$$

TABLE VII. Gas permeabilities for several polymers and for vitreous silica.

Membrane material	Gas	T(°C)	$\times 10^8 K^a$	Q_K kcal/mole	Reference
Viton	Air	24	0.1	…	Du Pont brochure
	[illegible]	24	[illegible]	…	
	N_2	24	0.05	…	
	CO_2	[illegible]	[illegible]	…	
	O_2	30	1.1	…	
[illegible]	H_2	[illegible]	[illegible]	…	[illegible]
	He	23	1.9	…	
	O_2	23	0.1	…	
	N_2	23	0.03	…	
	CO_2	23	0.2	…	
Kel-F	O_2	24	0.7	…	Thorne
	[illegible]	24	0.3	…	
Polyethylene	He	30	5.8	8.1	Ash, Barrer, and Palmer
	Ne	30	2.3	9.0	
	Ar	30	3.3	10.2	
	H_2	30	9.1	8.6	
	N_2	30	0.9	11.3	
	CO_2	30	15.2	8.2	
Polytetra-fluoroethylene	H_2	25	0.10	5.1	Pasternak, Christensen and Heller
	N_2	25	0.01	5.8	
	O_2	25	0.04	4.6	
	CO_2	25	0.12	3.3	
Vitreous Silica	He	24	0.04	5.2	Perkins and Begeal

[a] Units of K are cm^3 (STP) sec^{-1} cm^{-1} atm^{-1}.

W. G. Perkins, J. Vac. Sci. Technol., 10(4), p. 543, 1973

Part 3: Outgassing of polymers

Case study 1: Outgassing of 4 different glues

SAMPLES
Araldite 103 with hardener HY 991
Araldite 106 with hardener HV 953 U
Dow Corning R4-3117 RTV
Nuvovern LW polyurethane

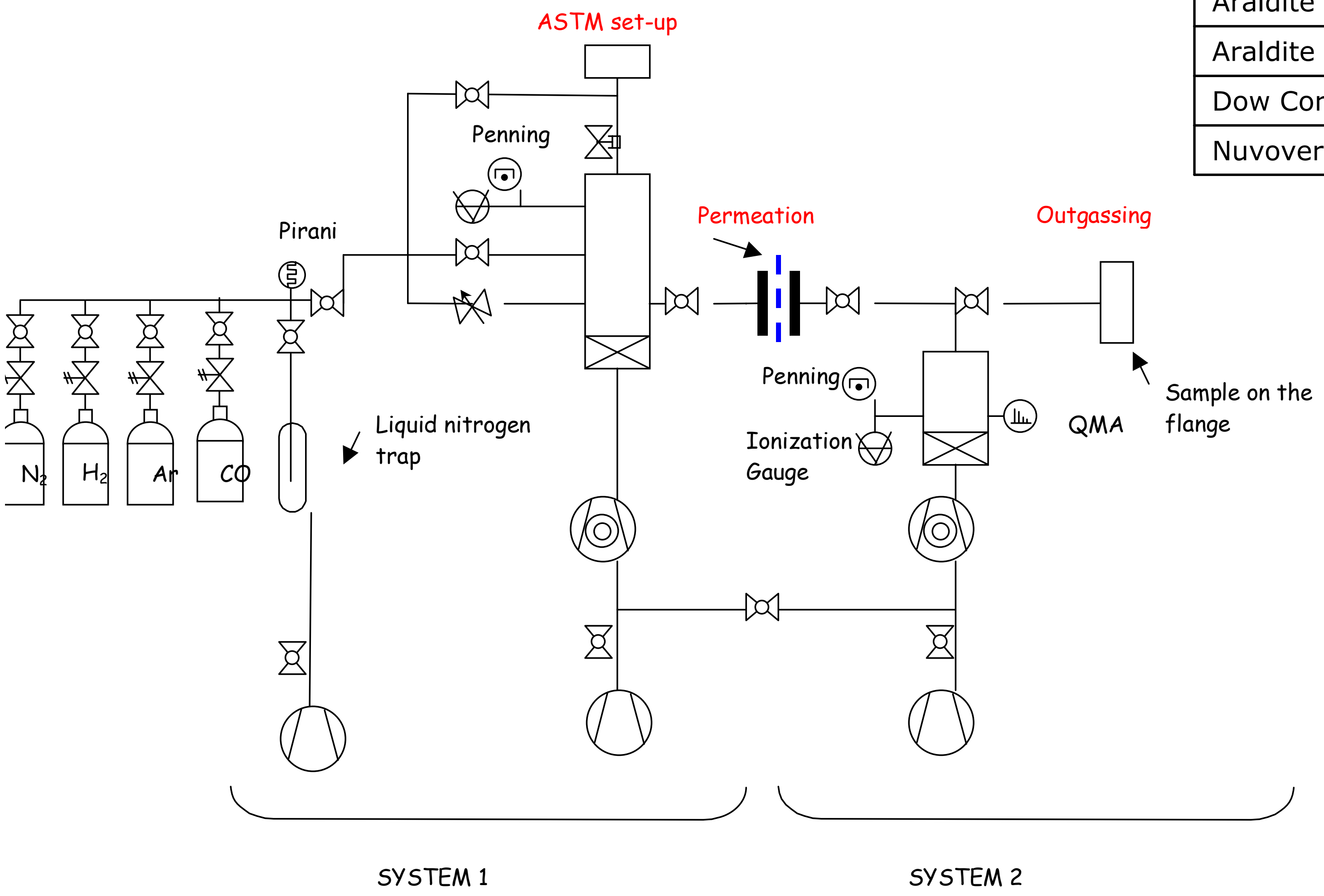
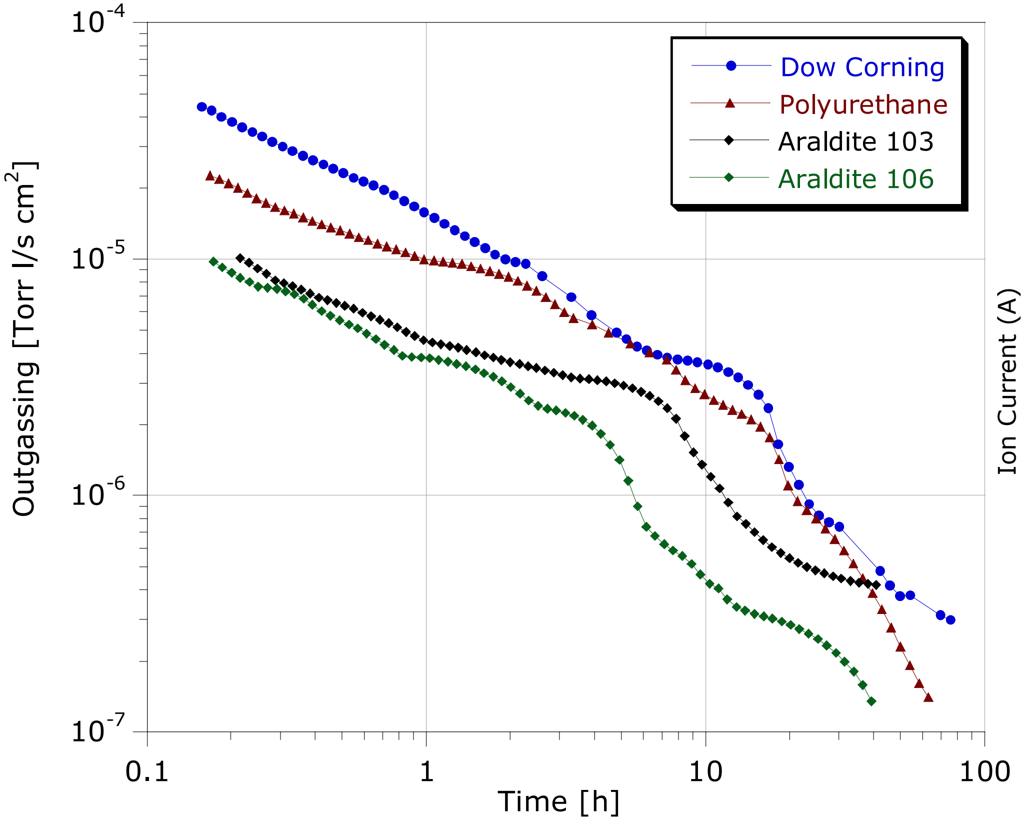
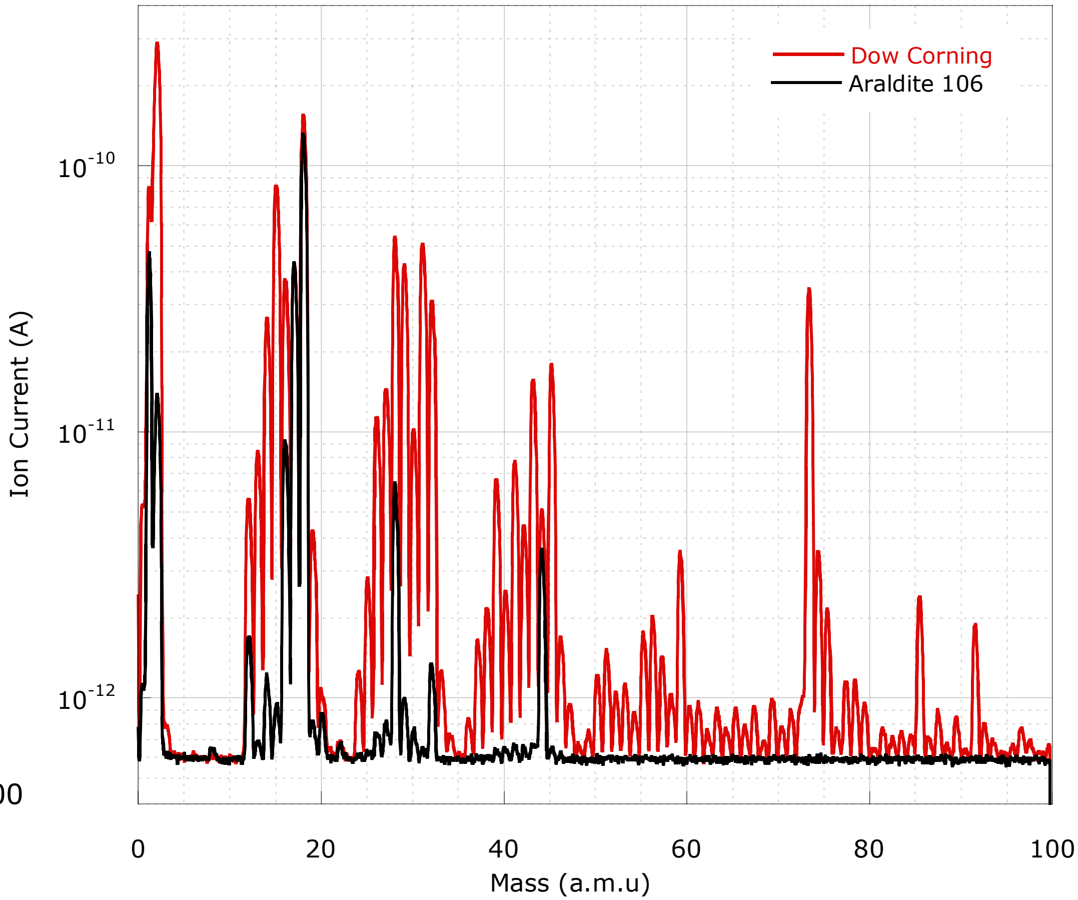


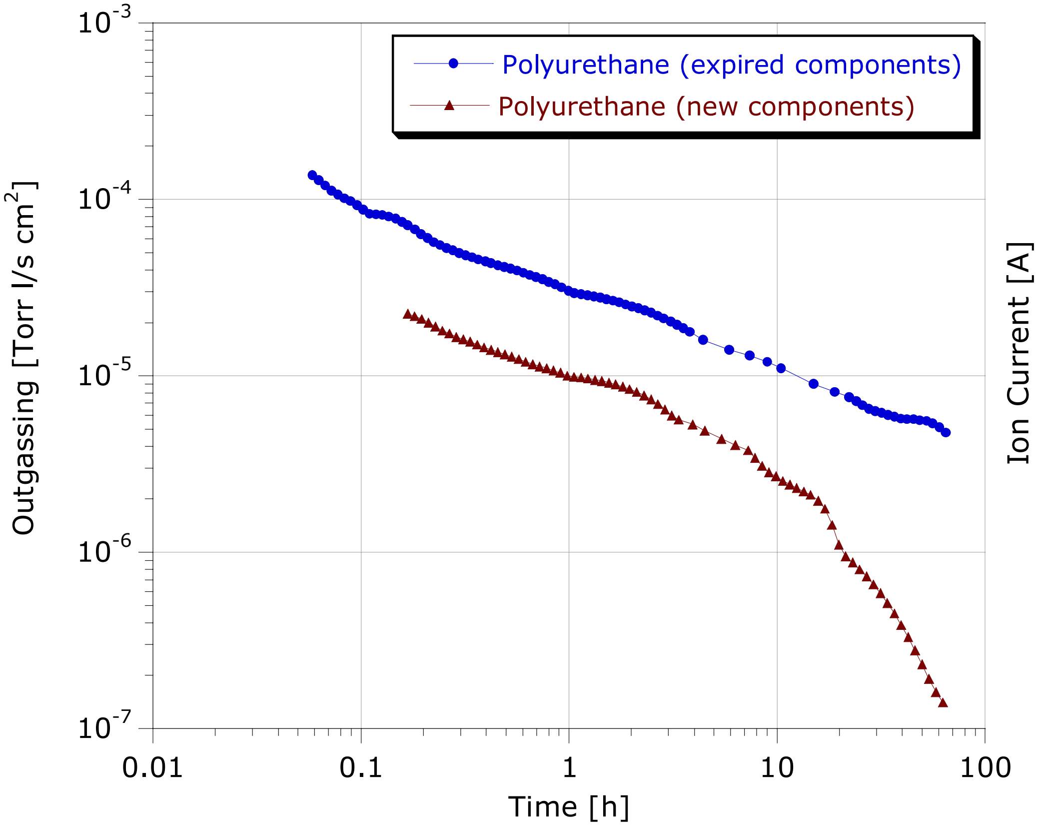
Figure 1: Experimental set-up

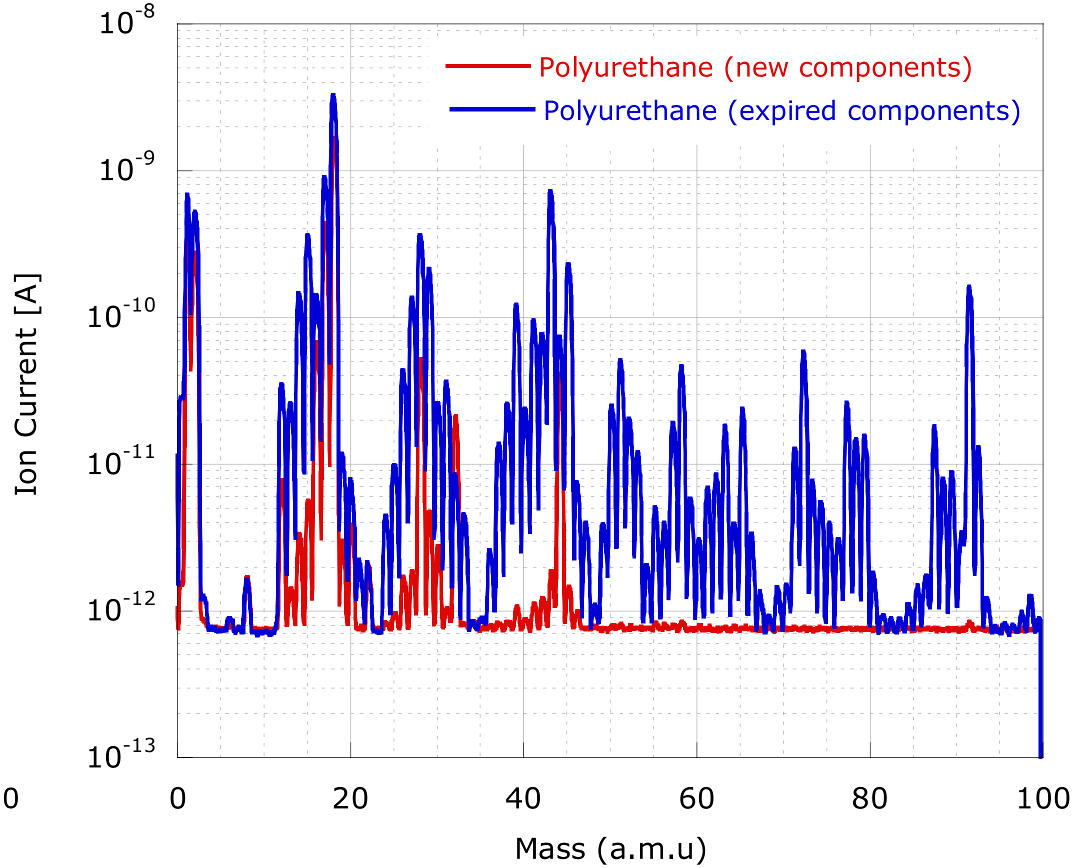
Part 3: Outgassing of polymers





Part 3: Outgassing of polymers





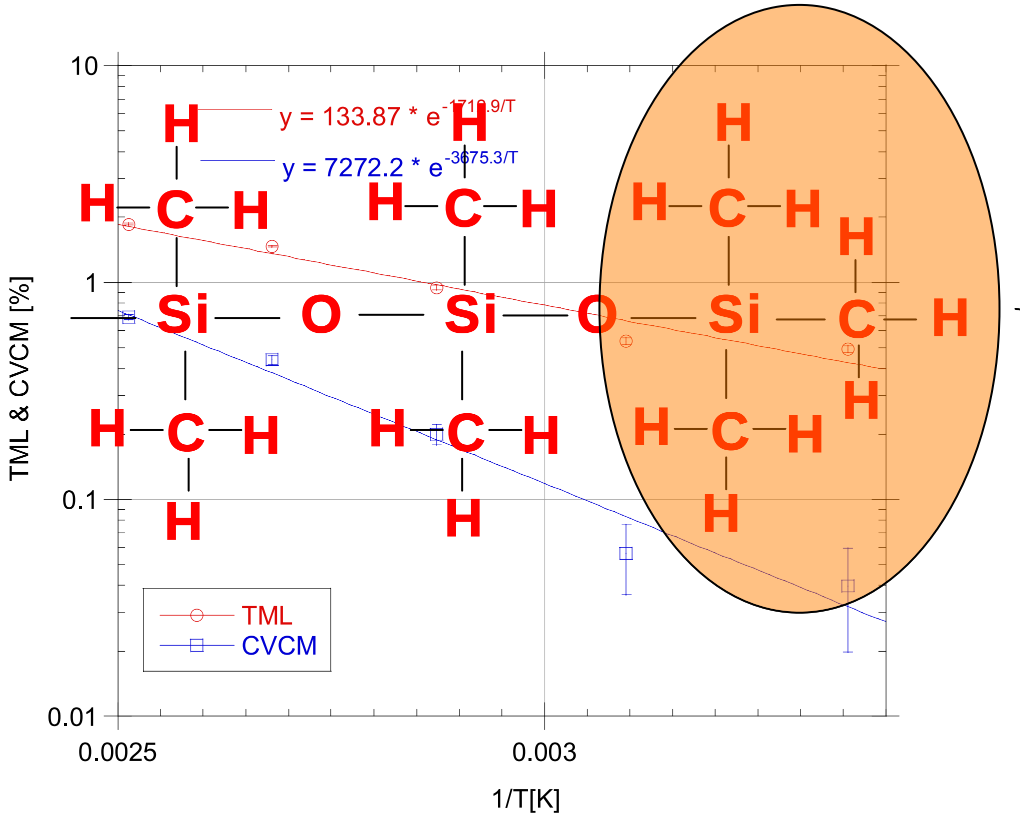
Part 3: Outgassing of polymers

Case study 2:

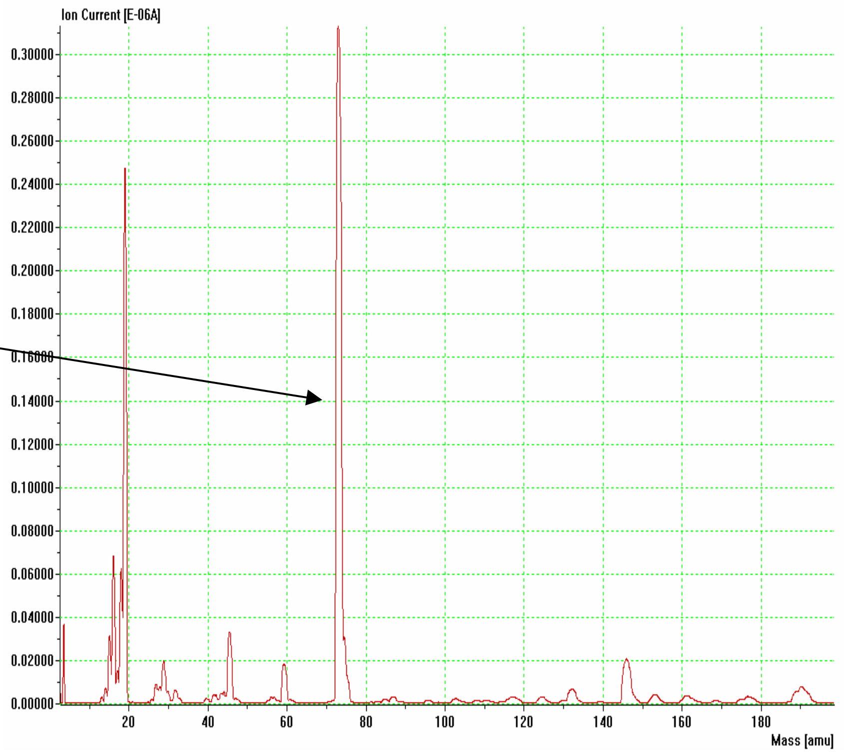
Outgassing of silicone rubber

The CERN weight loss system:
ASTM E595-93

Part 3: Outgassing of polymers



TML and CVCM as a function of the temperature of the heating treatment applied to the sample. The heating duration is 24 hours. The experimental data are fitted by Arrhenius like exponential curves



The feature of the spectra does not depend on the pumping time, except for a general reduction of the peak intensities. The main peak corresponds to 73 amu suggesting the presence of methyl-silane with a missing methyl group
(termination of silicone chain).

Part 3: Outgassing of polymers

Application of polymers in UHV technology is hindered by the **huge outgassing and permeability**.

This drawback has been partially overcome in other technological domains (i.e. packaging) by **coating polymers with metals** or metal oxides (more recently also with a:C-H).

How effective are coatings in reducing outgassing and permeation rate?

Part 3: Outgassing of polymers

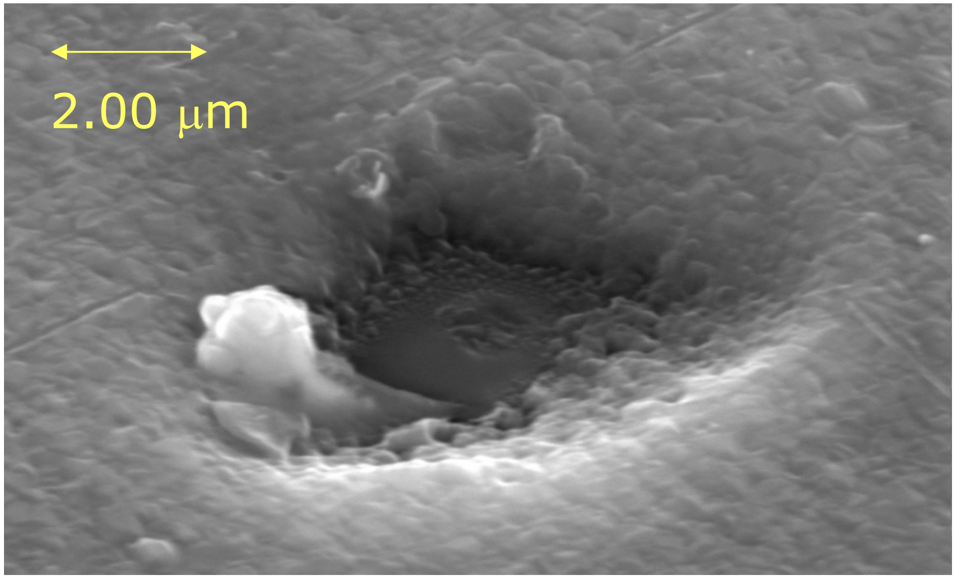
In materials made of several layers the total permeability depends on the permeability and thickness of each layer through the equation:

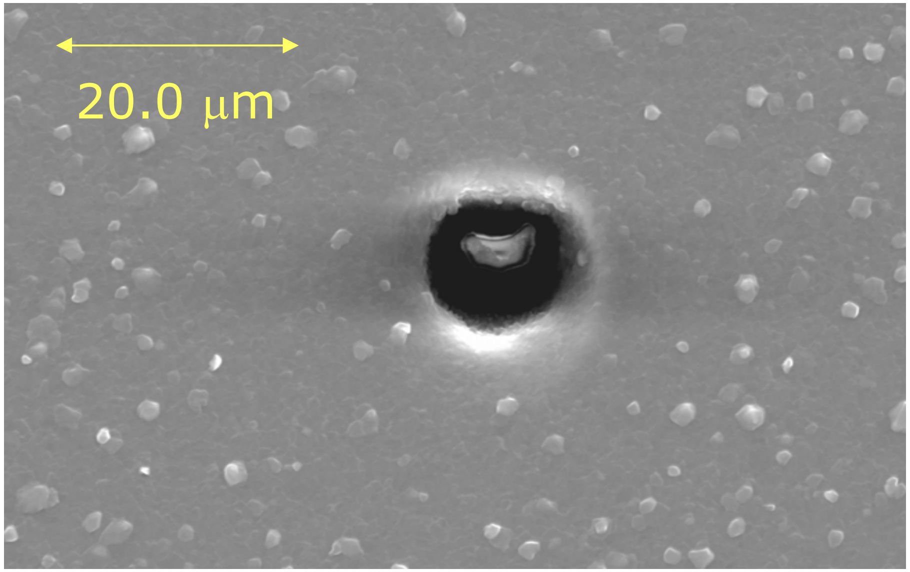
$$\frac{L_{TOT}}{\Pi_{TOT}} = \frac{L_1}{\Pi_1} + \frac{L_2}{\Pi_2} + \frac{L_3}{\Pi_3} + \ldots$$

- Since the permeability of metals is negligible for all gases, metallic coatings should entirely block the polymer outgassing and permeation.
- However, experimental results show that only a partial reduction of the flux is attained.
- This is attributed to defects on the coating (pinholes or scratches) that cause discontinuity on the surface coverage.
- Pinholes are produced during the deposition process and they are presumably due to atmospheric dust particles.

Part 3: Outgassing of polymers

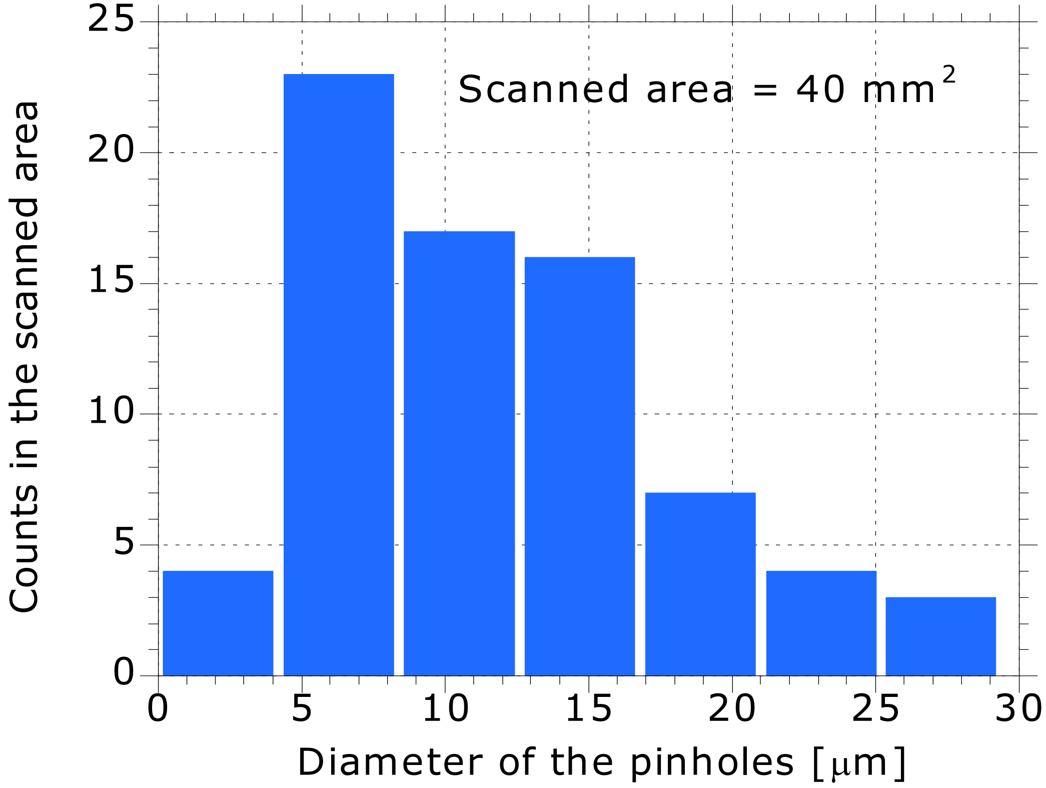
Examples of pinholes on Al coating deposited on PEEK





Part 3: Outgassing of polymers

Transmitted light optical microscopy has been used to detect uncoated surfaces on metal films, showing that they mainly consist of pinholes of different diameters.



Al/PEEK

Normalised uncoated surface areas of the order of 10^{-4} are measured

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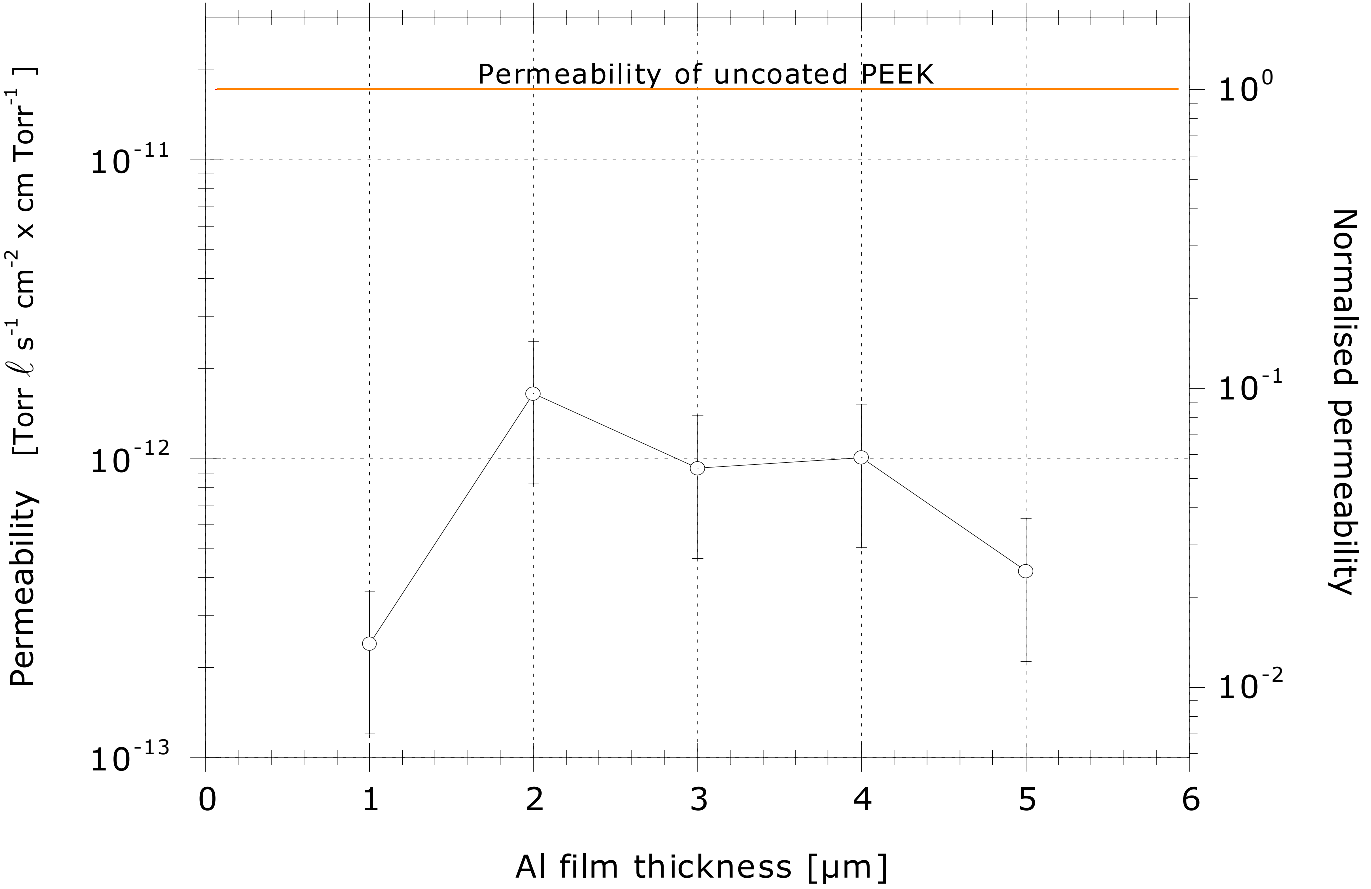
Part 3: Outgassing of polymers

However, experiments have shown that the permeability is reduced much less than expected from the uncoated fraction



Example:
Al/PEEK(0.125 mm thick)
The uncoated fraction is 10^{-4}, but the permeability of He is 10^{-2} of that of the uncoated polymer.

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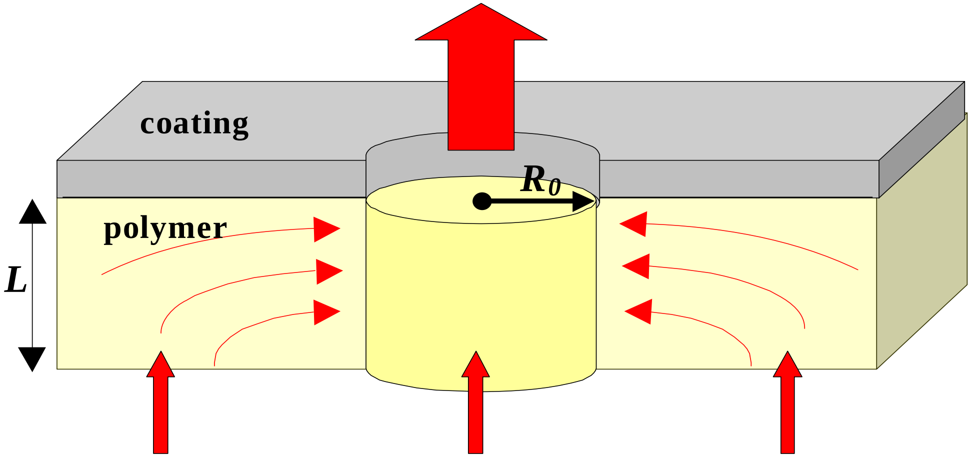
Part 3: Outgassing of polymers

This apparent inconsistency can be justified considering that the pinhole gas throughput is enhanced by lateral diffusion.

ρ =Normalised permeability → order of 10^{-2}

Θ =Normalised uncoated area → order of 10^{-4}

For $L/R_0 > 0.3$:



$$\rho = \Theta \times \left(1 + 1.18 \frac{L}{R_0} \right)^{*}$$

Amplification factor

[*] After W.Prins and J.J.Hermans, J.Phys.Chem., **63** (1959) 716.

Part 3: Outgassing of polymers

In the literature the barrier efficiency is called “barrier improvement factor” or BIF. It is the inverse of normalized permeability.

Normalized permeability:

$$\rho = \Theta \times \left(1 + 1.18 \frac{L}{R_0} \right)$$

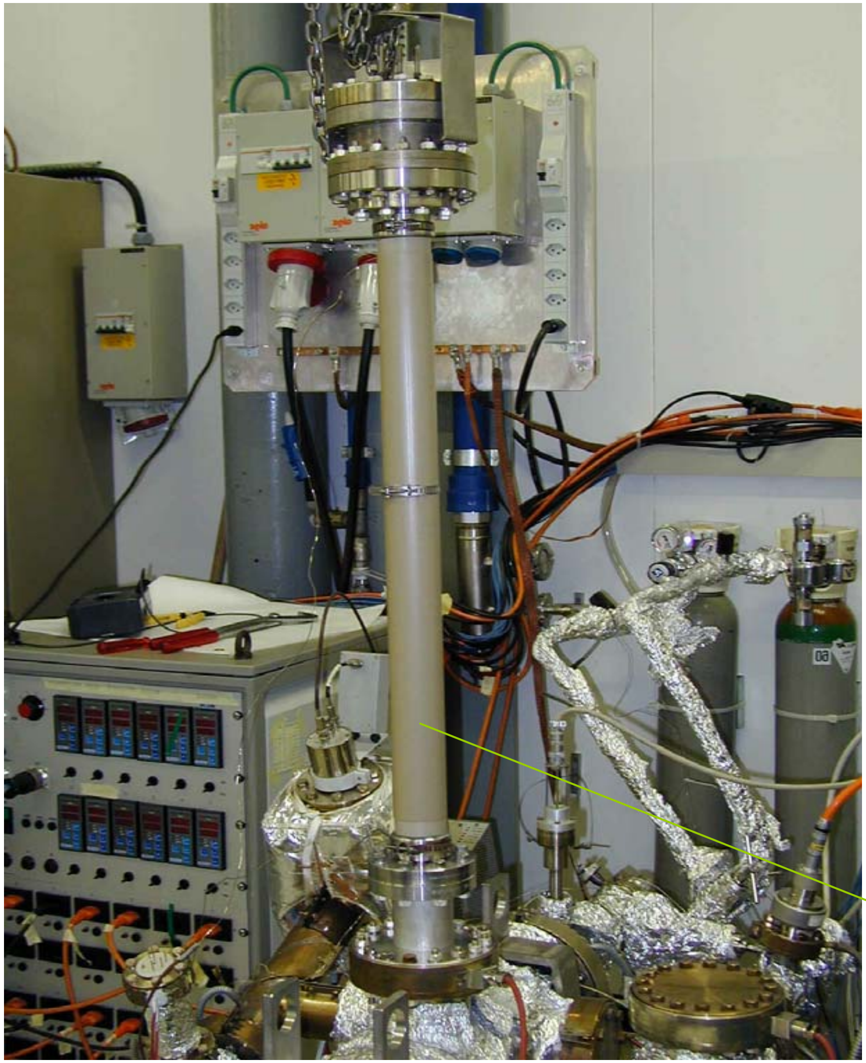
Barrier improvement factor:

$$BIF = \frac{1}{\rho} = \frac{1}{\Theta \times \left(1 + 1.18 \frac{L}{R_0} \right)}$$

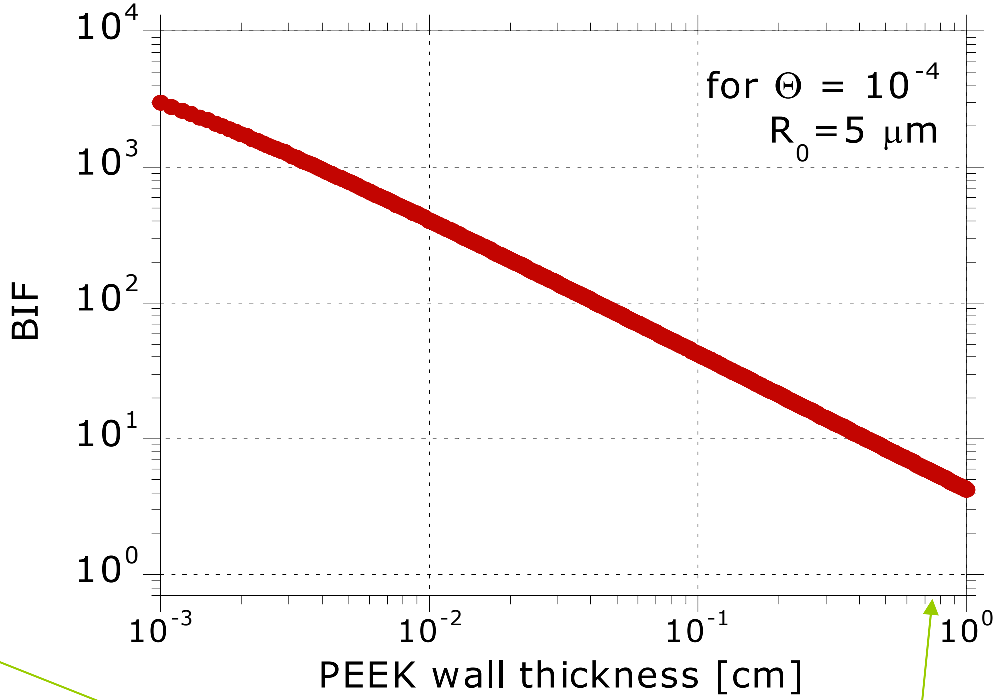
The fact that ρ depends on L means that for L>10R the flux value does not depend on the polymer thickness. In other terms, all the concentration gradient is localized near the pin-hole.

It follows also that, for similar coating, the improvement due to the coating is less significant for thicker polymer substrates.

Part 3: Outgassing of polymers



The BIF for Al coated PEEK.
For thickness larger than 5 mm, the coating is useless.



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Part 3: Outgassing of polymers

Key points

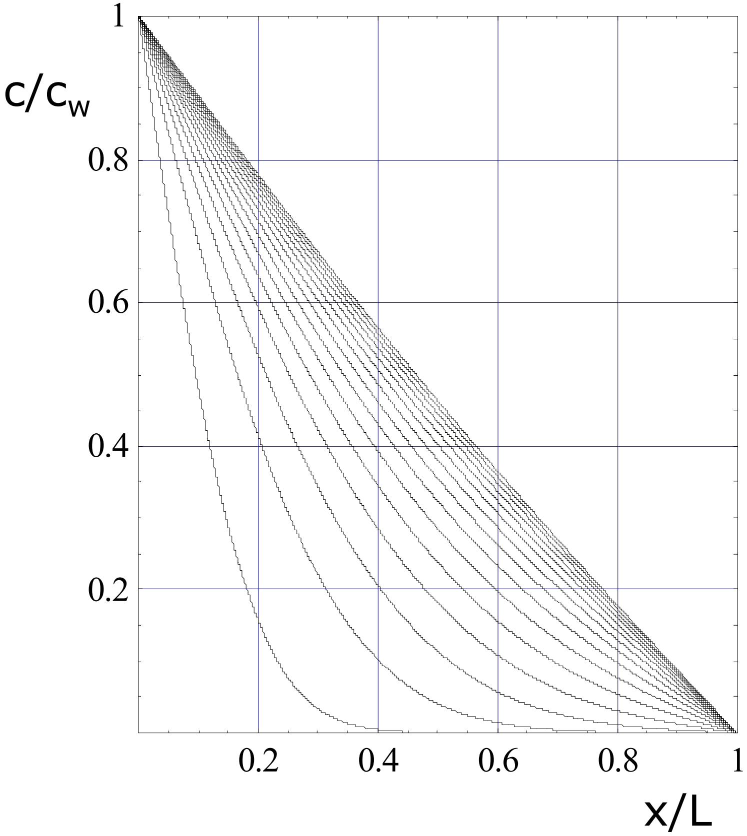
1. Polymers have a much higher gas content and gas mobility than metals. As a consequence their outgassing is order of magnitude higher.
2. Permeation of atmospheric gases is not anymore negligible as it is in metals. Helium is the gas with the higher diffusivity and water is the molecule with the higher solubility.
3. The gas transport mechanism in polymers depend on the structure. In rubbery polymers gas molecules are drained by the macromolecule chains. In glassy polymers the gas molecules jump from void to void, and excess volume has an important role. The Deborah number defines the limit of validity of the Fick's laws in polymers.
4. Elastomers should be heat treated in air or in vacuum before any application in high vacuum.
5. Metal coatings act as gas barrier, but their efficiency is strongly reduced by pinholes and scratches.
6. The effect of metal coating is negligible for thick polymer substrates.

Part 3: Complementary techniques

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

I.C. $c(x,0)=c_o$

B.C. $c(0,t)=c_w \quad c(L,t)=0$



Permeation

If the whole permeation process is considered to be dominated by diffusion through a uniform lattice, the following equation can be applied:

$$\frac{q}{q_\infty}=1+2\sum_{n=1}^{\infty}(-1)^n e^{-\frac{n^2\pi^2 D\cdot t}{L^2}}$$

Where q_∞ is the steady-state flux through the membrane.
This function, its integral and its derivative give a number of characteristic points and limiting values from which the diffusion coefficient can be evaluated.

The steady-state flux is:

$$q_\infty=\frac{c_w D}{L}=\frac{K\cdot P^a\cdot D}{L}=\frac{P^a\cdot\Pi}{L}$$ where $$\boxed{\Pi=K\cdot D=\frac{q_\infty\cdot L}{P^a}}$$

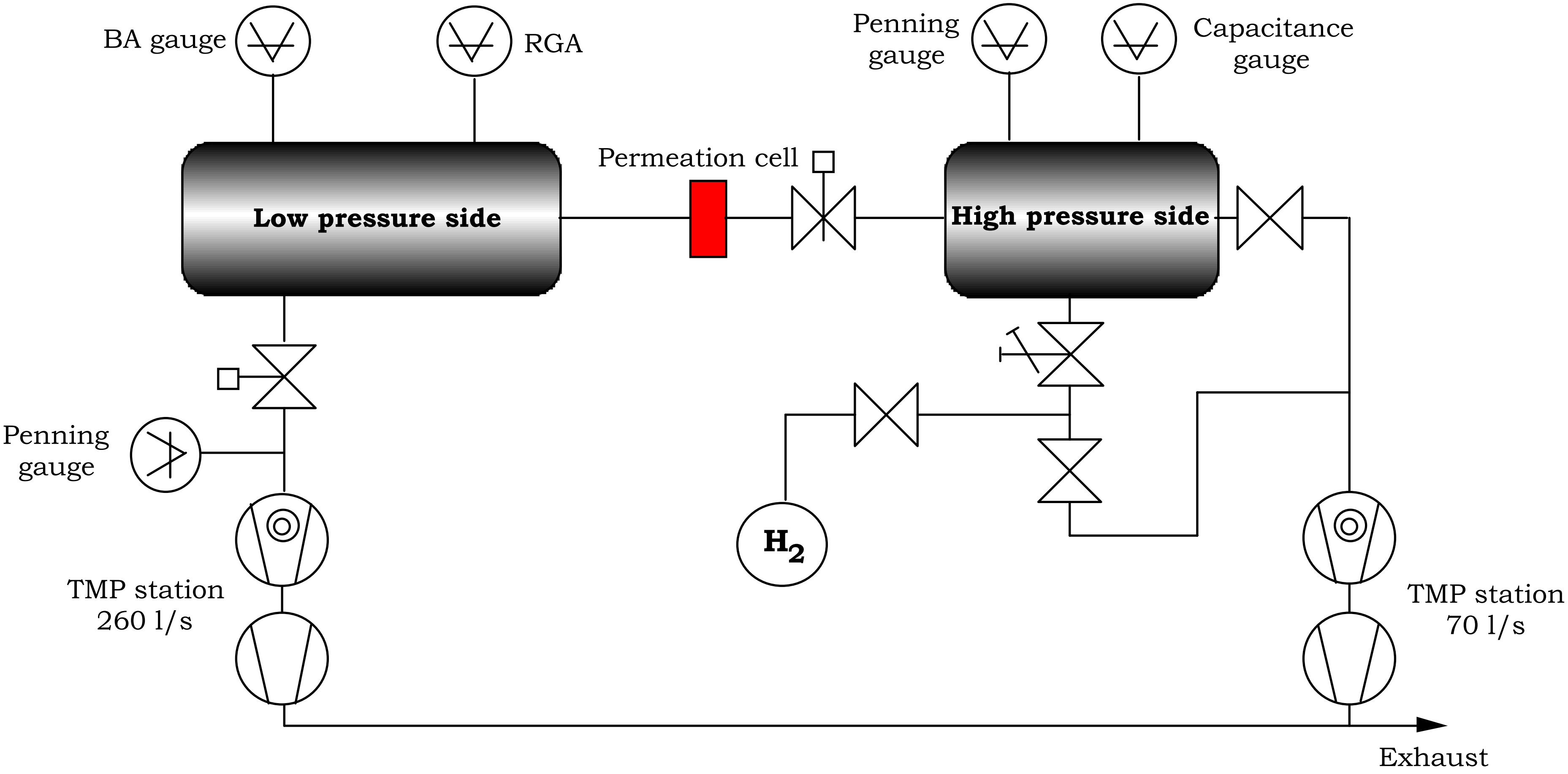
is the permeability. a=0.5 for dissociating diatomic molecules. a=1 for non dissociating molecules.

Part 8: Work in progress

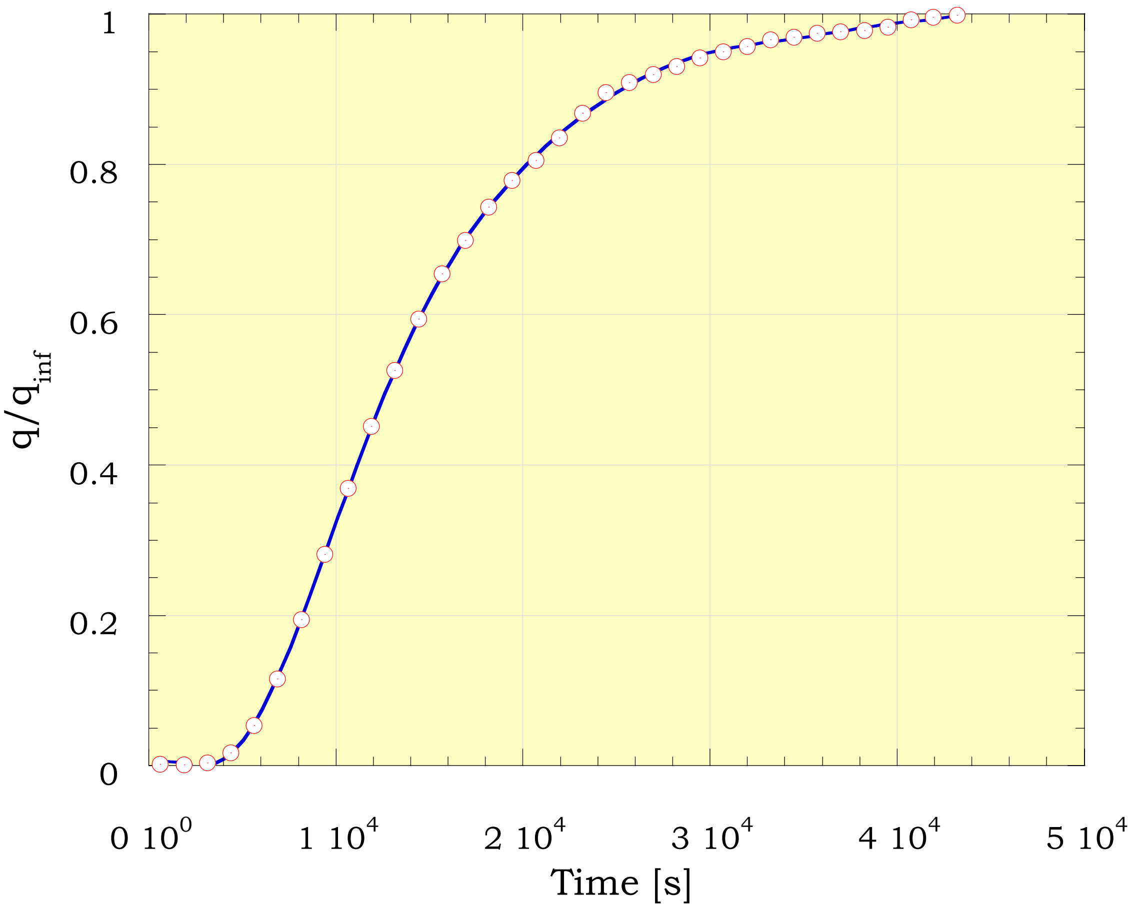
Work in progress

- Calculation of pressure profiles with localised and distribited outgassing and pumping
- Discharge cleaning (Calder, Mathewson, Dylla)
- Ougassing of graphite, ceramics.
- Glasses: outgassing and permeation
- Special polymers outgassing

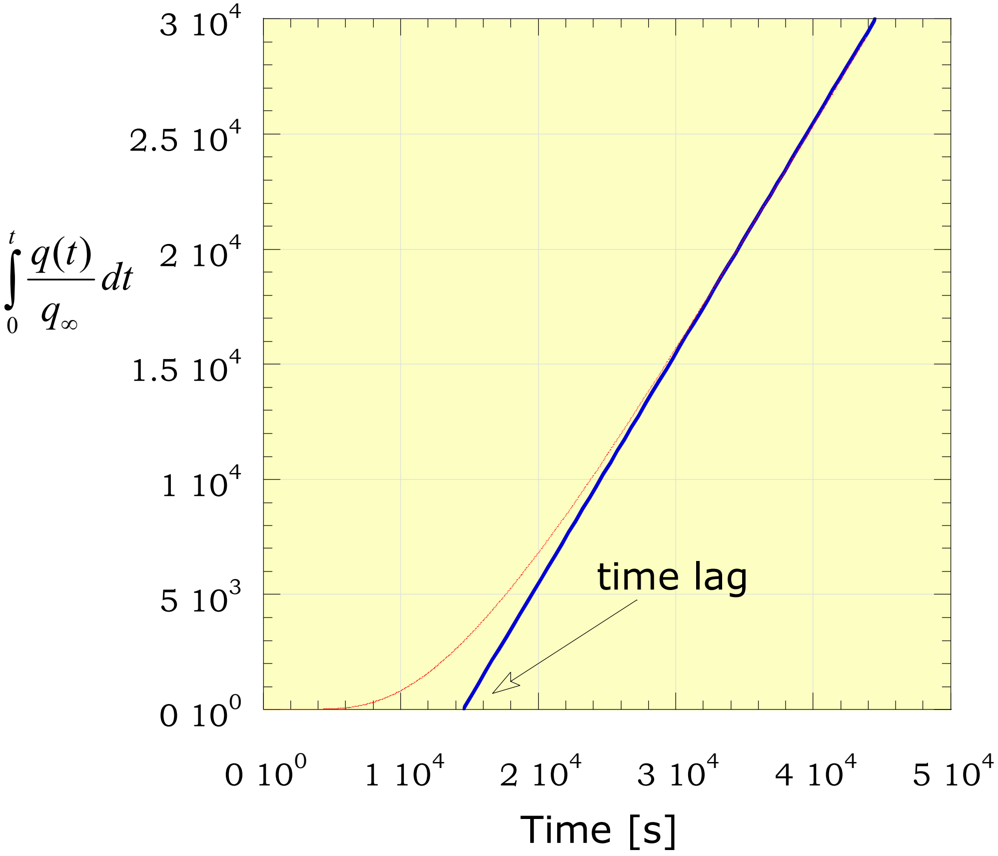
SCHEMATIC VIEW OF THE PERMEATION SYSTEM



Typical permeation curve: H_2 through stainless steel



Evaluation of the diffusion coefficient: time lag



The following relation gives the asymptotic behavior of the quantity of gas permeated

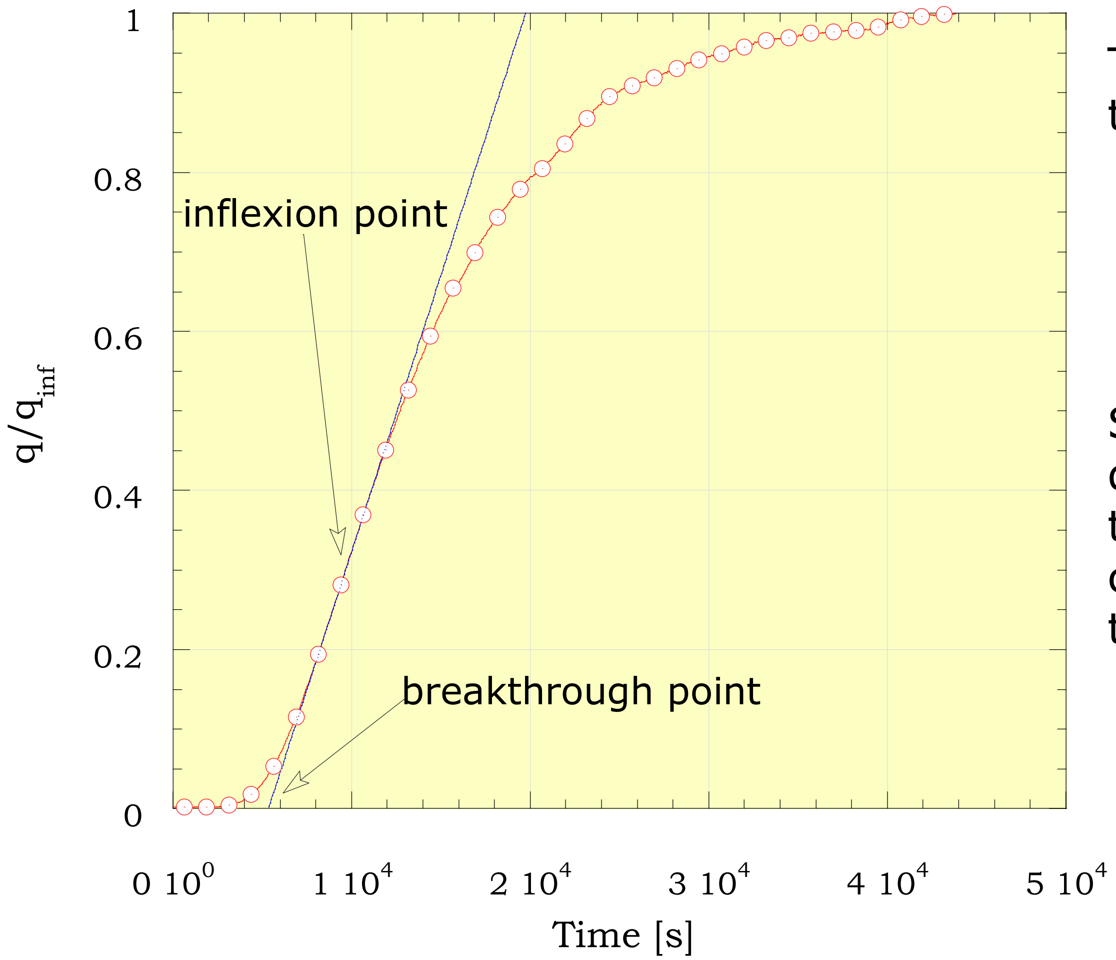
$$Lim_{t\to\infty} \int_0^t \frac{q(t)}{q_\infty} dt = Lim_{t\to\infty} \left(t - \frac{\ell^2}{6D} \right)$$

This is a straight line that intersects the time axis at:

$$\tau_L = \frac{L^2}{6D}$$

This quantity is known as the **time lag**, and gives a simple method to calculate the diffusion coefficient. It is quoted in most of the literature on permeation measurements.

Evaluation of the diffusion coefficient: inflexion and breakthrough points



The inflexion time is the time at which the derivative of q/q_∞ is a maximum.

$$\tau_i = Ln(16)\frac{L^2}{3\pi^2 D}$$

Similarly the breakthrough time is defined as the time at which the tangent to the normalized permeation curve at the inflexion point intersects the time axis

$$\tau_b = 0.5\frac{L^2}{\pi^2 D}$$

Part 3: Complementary techniques

Other methods are available for the evaluation of the diffusion coefficient D from the permeation curve.

The D values obtained with the different methods should be equal. If it is not the case, it means that the permeation process does not follow exactly Fick's law, and so diffusion model is not enough to characterize the gas transport process.

Surface recombination or internal trapping could also play an important role in metals.

Strong deviation from the Fick's law has been observed in amorphous vitreous polymers. For example linear time dependence of the flux, instead of square root, was measured; in other cases oscillations in the permeating flux were recorded.

TDS

TDS is a very useful technique to provide an insight on both the thermodynamics and the kinetics of gas-metal systems.

It consists in measuring the desorbing gas spectrum obtained while heating a sample at a constant rate of temperature rise.

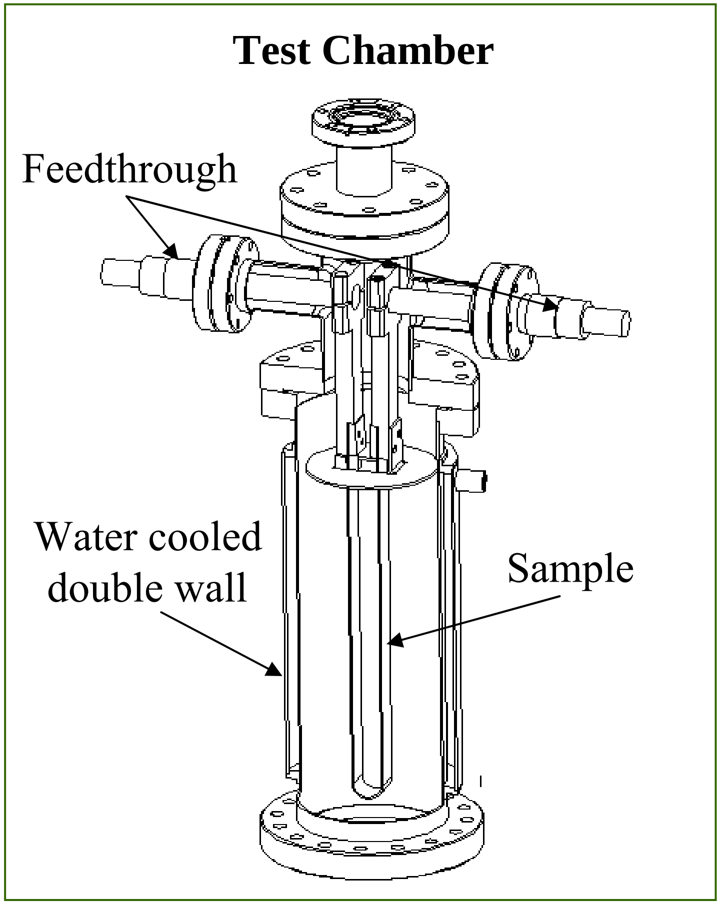
In particular, **the diffusion coefficient** may be quantified by varying the heating rate of the sample. In the assumption of an initial uniform concentration, the diffusion model gives:

$$q(t) = \frac{4 \cdot c_0 \cdot D(t)}{L} \sum_{n=0}^{\infty} e^{-(2n+1)^2 \pi^2 \cdot F_o(t)} \quad \text{where} \quad F_0(t) = \int_0^t \frac{D(t)dt}{L^2} = \frac{D_0 \int_0^t e^{-\frac{E_b}{k_B T(t)}} dt}{L^2}$$

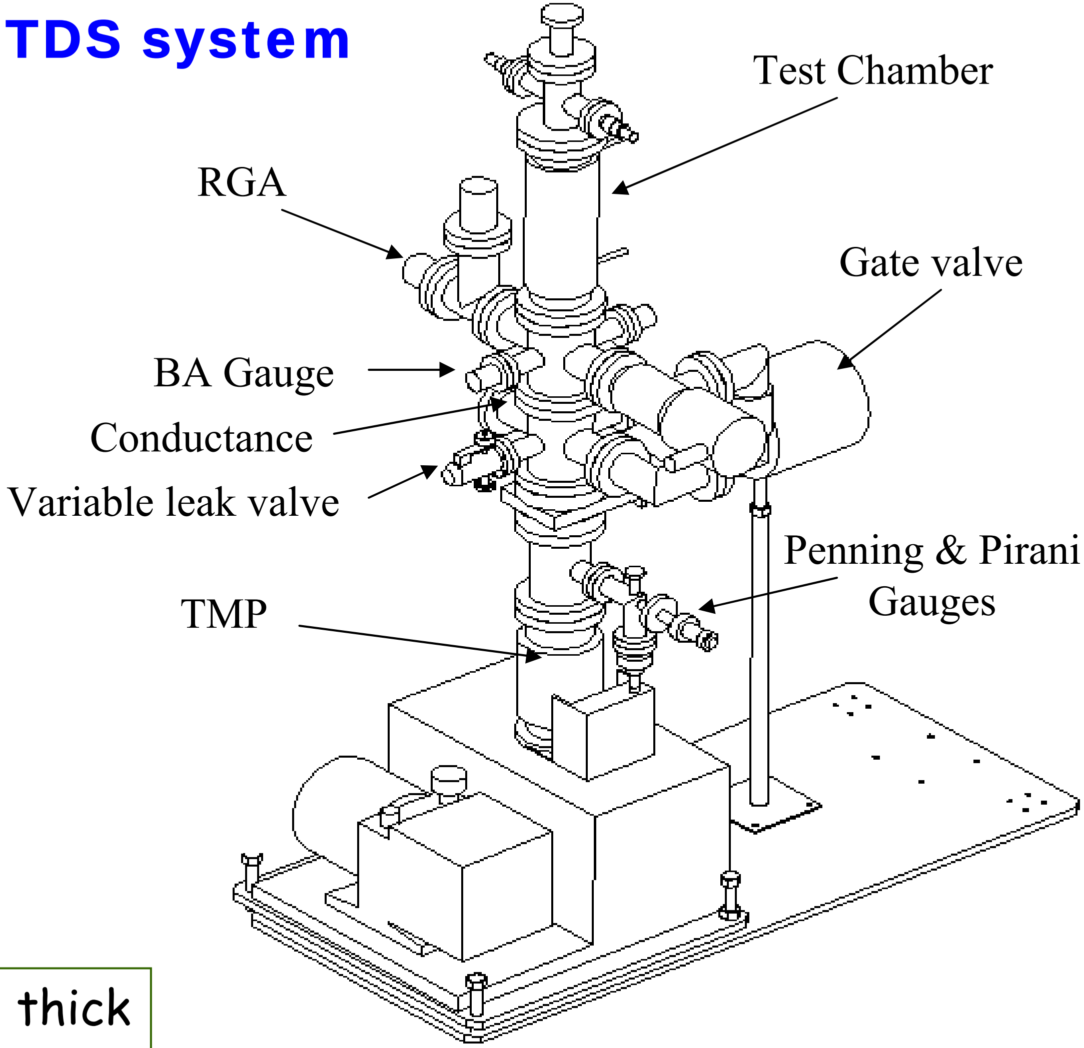
The degassing rate has a maximum when (considering the first term of the series only):

$$\frac{dq(t)}{dt} = 0 \rightarrow \frac{b}{T_{MAX}^2} = \frac{k_B \cdot D_0 \cdot \pi^2}{E_b \cdot L^2} e^{-\frac{E_b}{k_B T_{MAX}}} \quad \text{"b" is the heating rate}$$

In the plot $Ln\left[\frac{b}{T_{MAX}^2}\right] = f\left(\frac{1}{k_B \cdot T_{MAX}}\right)$ the slope of the linear function is the diffusion energy.

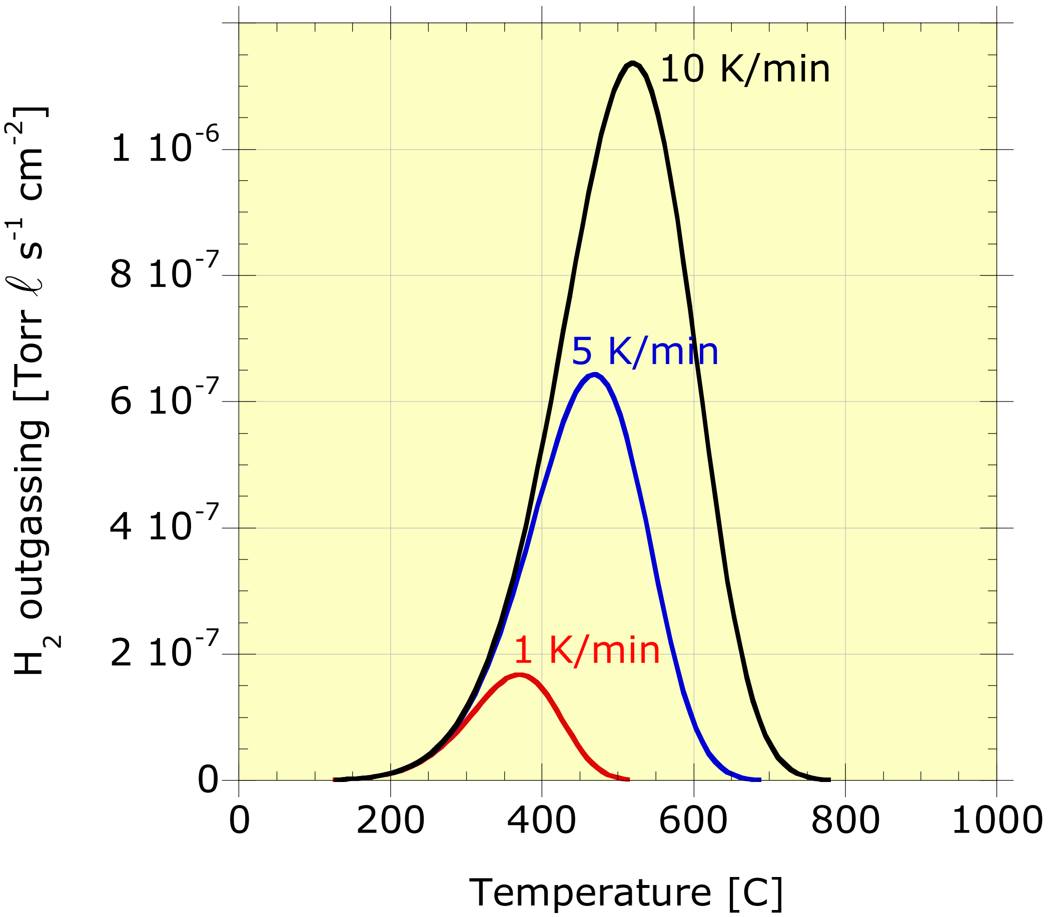


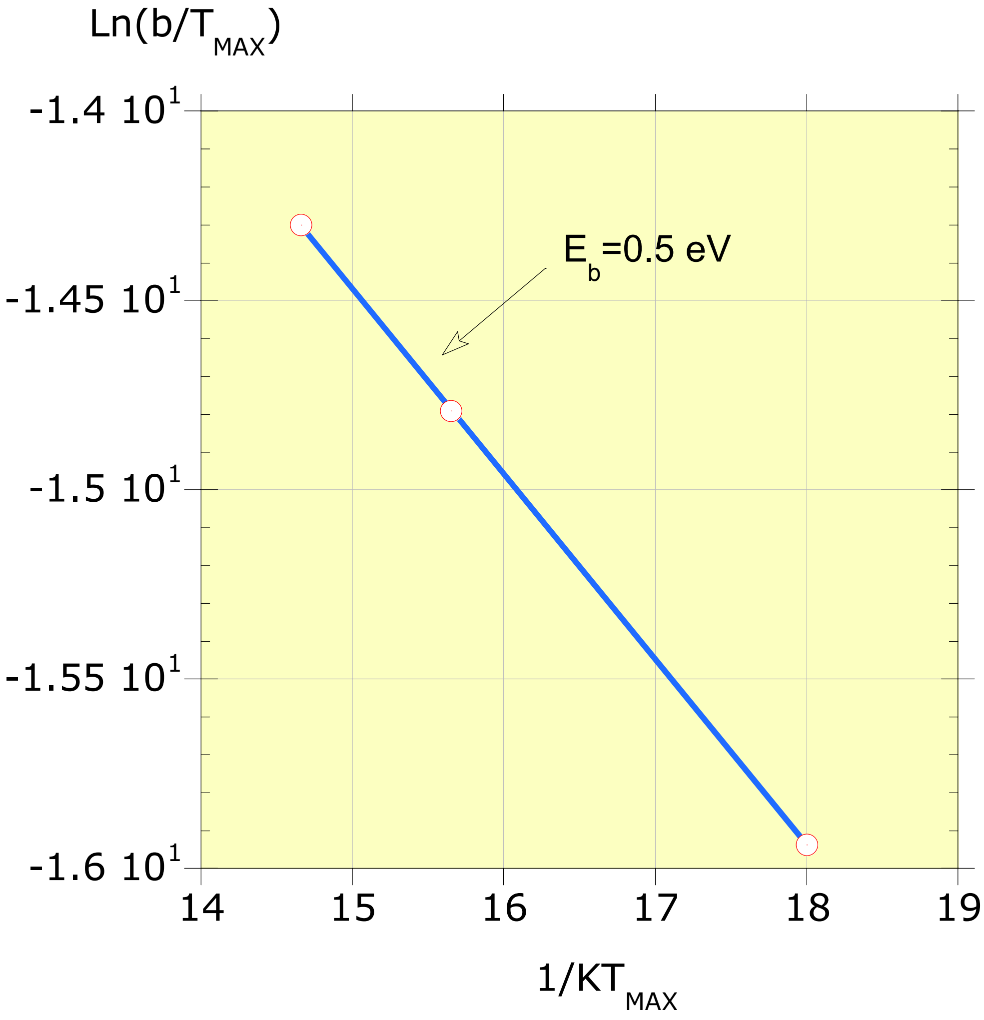
TDS system



Sample: 60 cm long, 1 cm wide, 1 mm thick
Thermocouple: 0.1 mm diameter S type

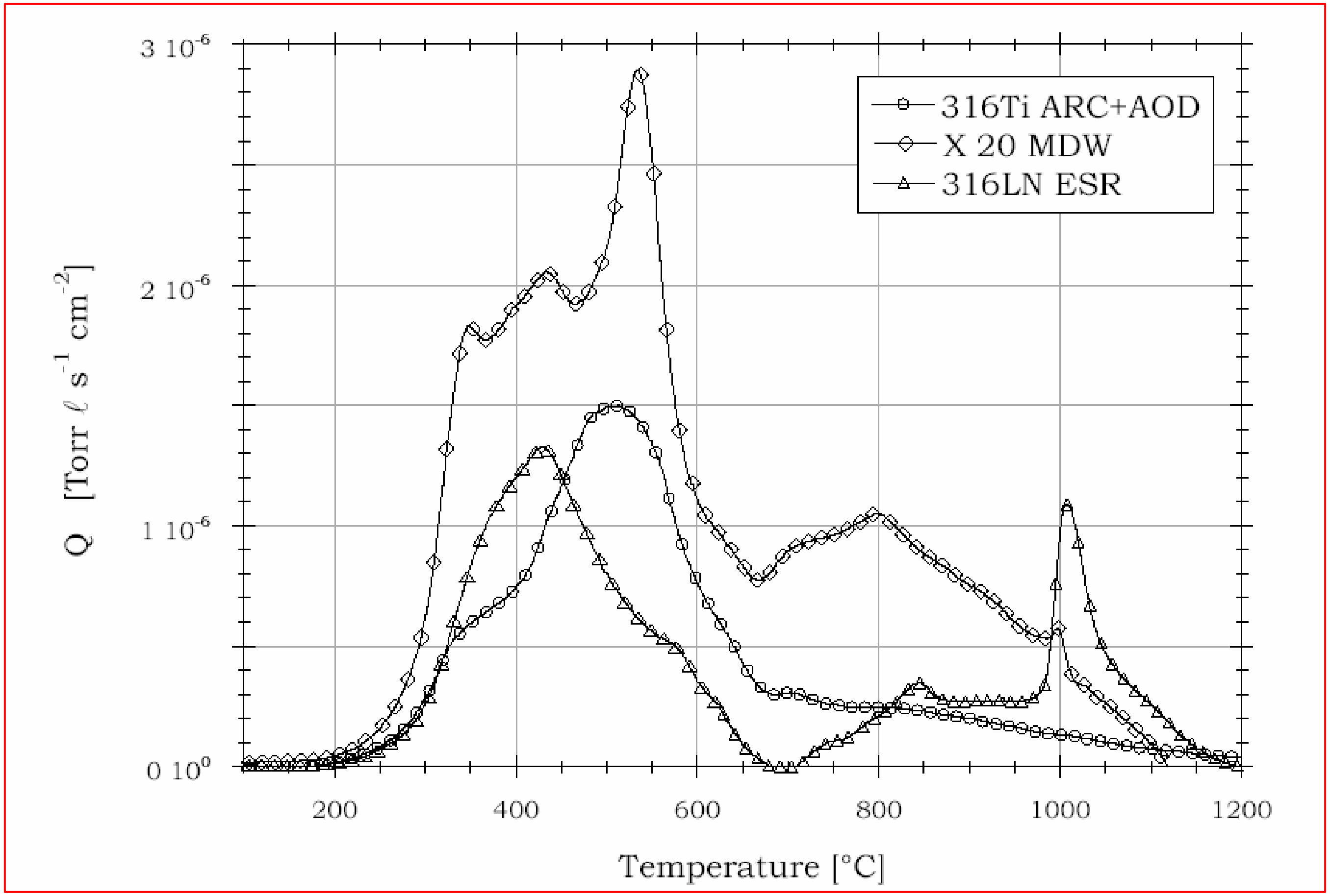
TDS peaks calculated for H_2 in stainless steel





TDS spectra could indicates the presence of multiple interactions between the gas and the solid; some of them are surface blocking and bulk trapping

5 K/min



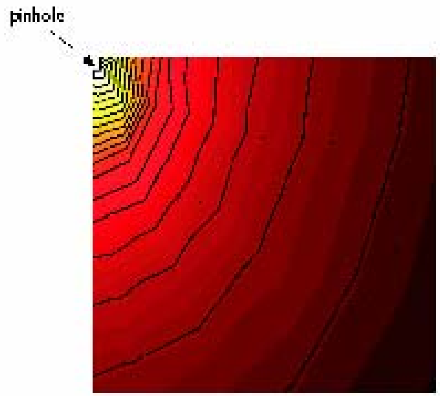
J-P. Bacher et al., J. Vac. Sci. Technol. A **21**, 167 (2003)

Key points

1. Permeation and thermal desorption experiments can clarify the mechanism of gas transport in solids. Very important intrinsic properties of materials can be obtained, namely solubility, permeability and diffusivity.

2. Permeation and thermal desorption measurements can identify deviation from the classical Fick's laws and underline the role of trapping centers and surface oxide.

Part 7: Outgassing of polymers



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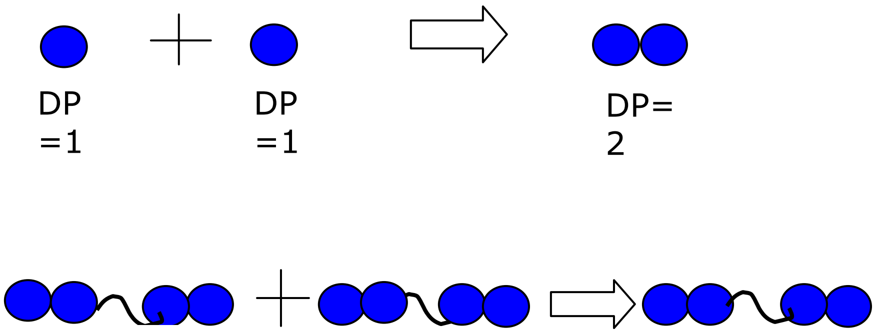
Polymers

The term polymer was introduced by Berzelius in 1830. Its etymology is from Greek πολι–many μεροσ –parts. Actually polymers are made of basic unit (monomer) repeated to form chain. The degree of polymerization is the number of monomers in the polymeric chain.



DP =1

DP =1

DP= 2

n-mer

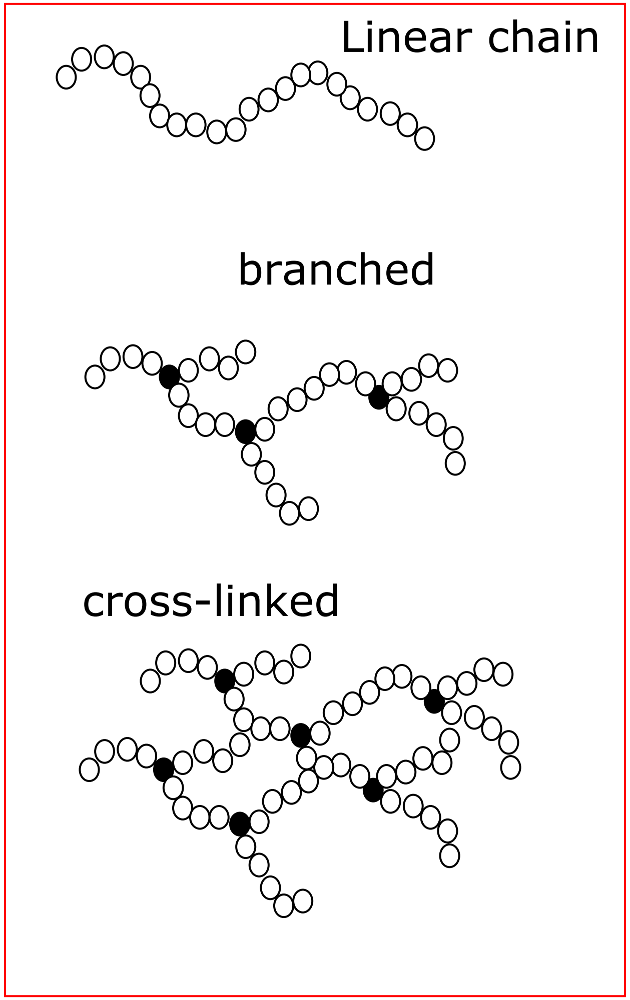
DP= N

m-mer DP= M

(n+m)-mer DP=(N+M)

Part 7: Outgassing of polymers

Polymer classification



According to topology:

- -Linear
- -Branched
- -Cross-linked

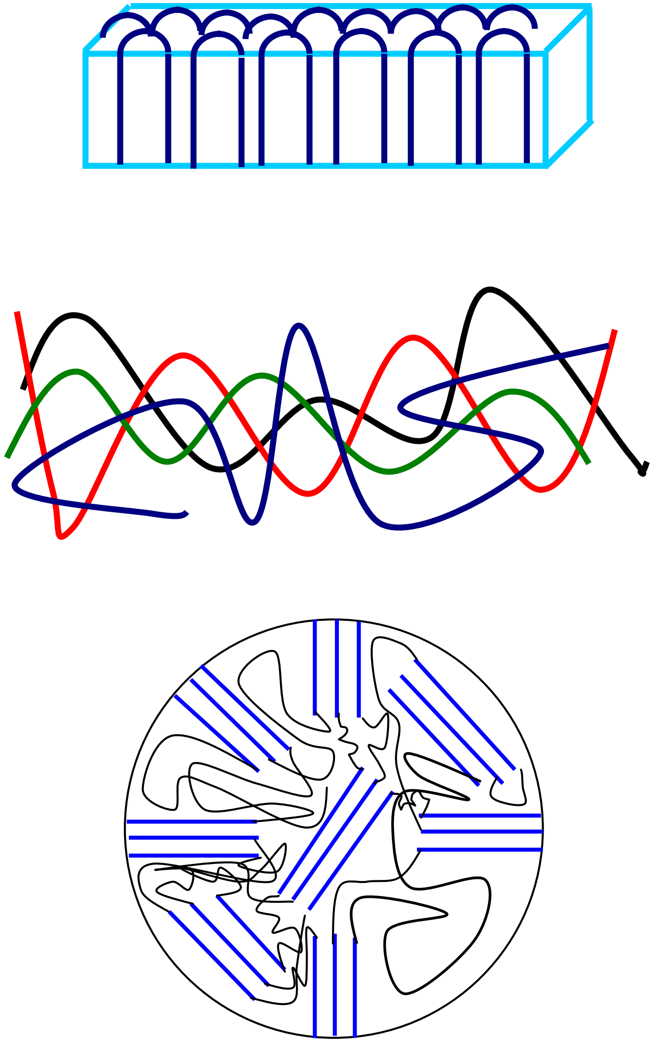
According to morphology:

- -Thermoplastics: soften when heated and return to original condition when cooled
- -Thermosets: solidify or "sets" irreversibly when heated
- -Elastomers: can be stretched to several times their length and rapidly return to their original dimension when the applied stress is released.

According to polymerization reactions:

- -Chain reaction (polyaddition)
- -Step reaction (polycondensation)

Part 7: Outgassing of polymers



The polymer structure can be:

Crystalline: macromolecules form three-dimensionally ordered arrays: **lamellar** (plate-like) crystals with a thickness of 10 to 20 nm in which the parallel chains are perpendicular to the face of the crystals.

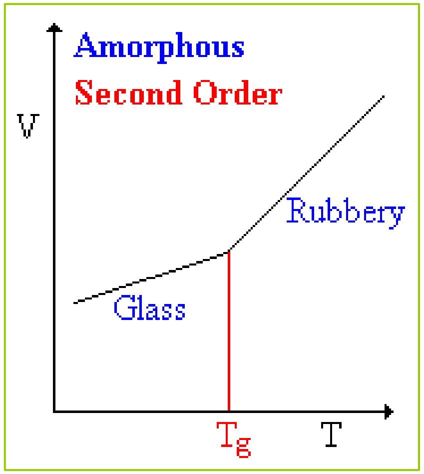
Amorphous: no long-range order (spaghetti like material) amorphous polymers are softer, have lower melting points, and are penetrated by solvents more than are their crystalline counterparts.

Semicrystalline: mixing of crystalline and amorphous regions; crystals are small and connected to the amorphous regions by polymer chains so there may be no sharp well-defined boundaries between the two types of regions

Only amorphous and semicrystalline polymers will be considered.

T_g and excess volume

-Semi-crystalline solids have both amorphous and crystalline regions. According to the temperature, the **amorphous regions** can be either in the glassy or rubbery state. The temperature at which the transition, in the amorphous regions, between the glassy and rubbery state occurs is called the **glass transition temperature**.



-Below T_g, amorphous polymers are stiff, hard and often brittle; in this state the molecules are frozen on place. This generates stable empty space called excess volume.

-Above T_g, portions of molecules can start to wiggle around: the polymer is in the **rubbery state**, which lends softness and flexibility .

Transport of gas in polymers

In the rubbery state the gas molecules are dragged by the thermal movement of the chain.
In the glassy state the gas molecules diffuse through the volume of the polymer and also through the excess volume.

The diffusion process in amorphous or semicrystalline polymers is not always well described by Fick's law. The diffusion process can be distinguished by evaluating the **Deborah number**

$$D_e = \frac{\tau}{\nu}$$

where τ is the polymer-penetrating molecule relaxation time, and $\nu = L^2/D$ is the characteristic time for diffusion.

For De>>1 the time for diffusion is shorter than the time for relaxation, the diffusing molecules does not record change in the polymer structure → Fick's law is valid.

For De<<1 the penetrating molecules swell the polymer and hence allow the adsorption of additional molecules→ non fickian process.