

Vacuum Systems

Slot 3

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<https://indico.cern.ch/event/1470062/timetable/?view=standard#day-2025-02-17>

Outline

1. Elements of adsorption/desorption
2. Outgassing
3. Bake-out

1. Elements of adsorption/desorption

Reminder: Pressure in a system

- The **Pressure**, is the ratio of the flux of molecules in the vacuum vessel to the pumping speed

$$P = \frac{Q}{S}$$

mbar →

mbar.l/s

l/s

- S ranges from 10 to 20 000 l/s
- Q ranges from 10^{-14} mbar.l/s for metallic tubes to $10^{-5} - 10^{-4}$ mbar.l/s for plastics

3 orders of magnitude for pumping

vs

10 orders of magnitude for outgassing

Outgassing MUST be optimised to achieve UHV

Reminder: Mass flow & quantities

- The mass flow can be derived from the ideal gas law

$$Q = p \frac{dV}{dt} = \frac{1}{N} \frac{dn}{dt} RT$$

$$R = N k = 8.31 J mol^{-1} K^{-1}$$

- It has the unit of [Pa.m³/s] which is equivalent to a number of molecules/s (or Watt)

PV	G
1 mbar.ℓ	2.46 10 ¹⁹ molecules
1 Torr.ℓ	3.27 10 ¹⁹ molecules

at 300 K

- Langmuir: 1 L = 10⁻⁶ Torr for 1 s.
- 1 monolayer ~ 10¹⁵ molecules/cm²



1 Torr.ℓ injected inside a 10m long, 10 cm diameter chamber corresponds to 1 monolayer adsorbed on the surface!

=> the LHC experimental **NEG beam pipe would be saturated** and unusable

Material for Vacuum Technology

- Metals are used for vacuum chambers building parts:
 - Stainless steels, coppers, aluminums, beryllium
- Insulating material are used for instrumentation or assembly:
 - Minerals:
 - Ceramics, Macor, glass
 - Polymers (plastics):
 - Kapton, PEEK, Teflon
 - Glues
 - Elastomers eg Viton, Neoprene, EPDM



Alumina feedthrough



Alumina balls

- During the manufacturing process of these materials, atoms and molecules are sorbed *i.e.* **adsorbed** or **absorbed** on the material surface or the bulk
- The surface can be very rough and the material highly porous
- **Quantities** of gas adsorbed / absorbed in materials can be very large:
 - 1 cm³ of stainless steel can contain 0.05 – 0.5 mbar.l of hydrogen
 - Under vacuum, Nylon can lose 4% of its weight *i.e.* 5 mbar.l per cm³



Viton o-rings

Long term pump down of a vessel

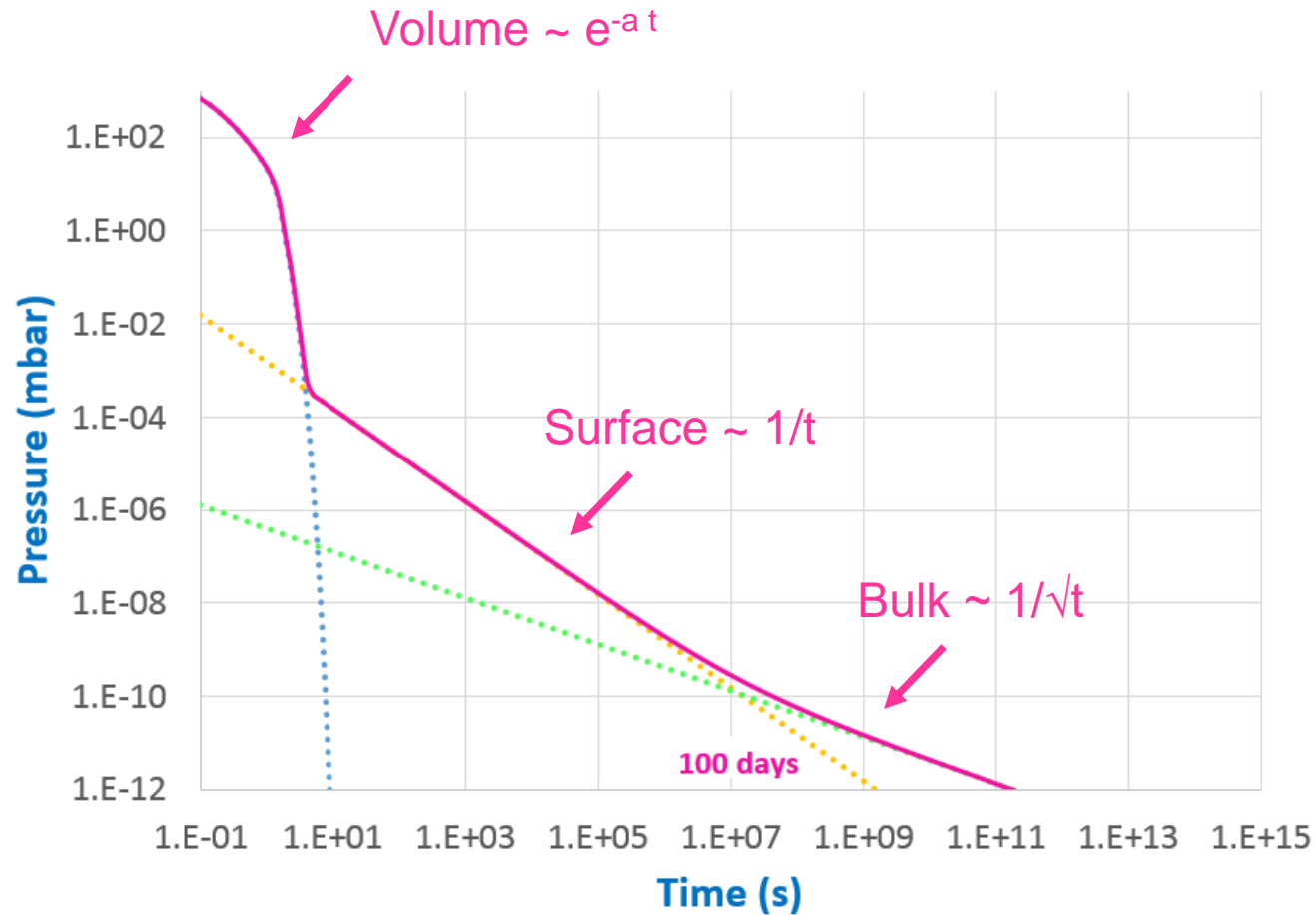
- Consider 1 m long, Ø10 cm stainless steel tube pumped by 30 l/s
- 4 regimes

1) Volume pumping

2) Surface desorption

3) Diffusion from the bulk

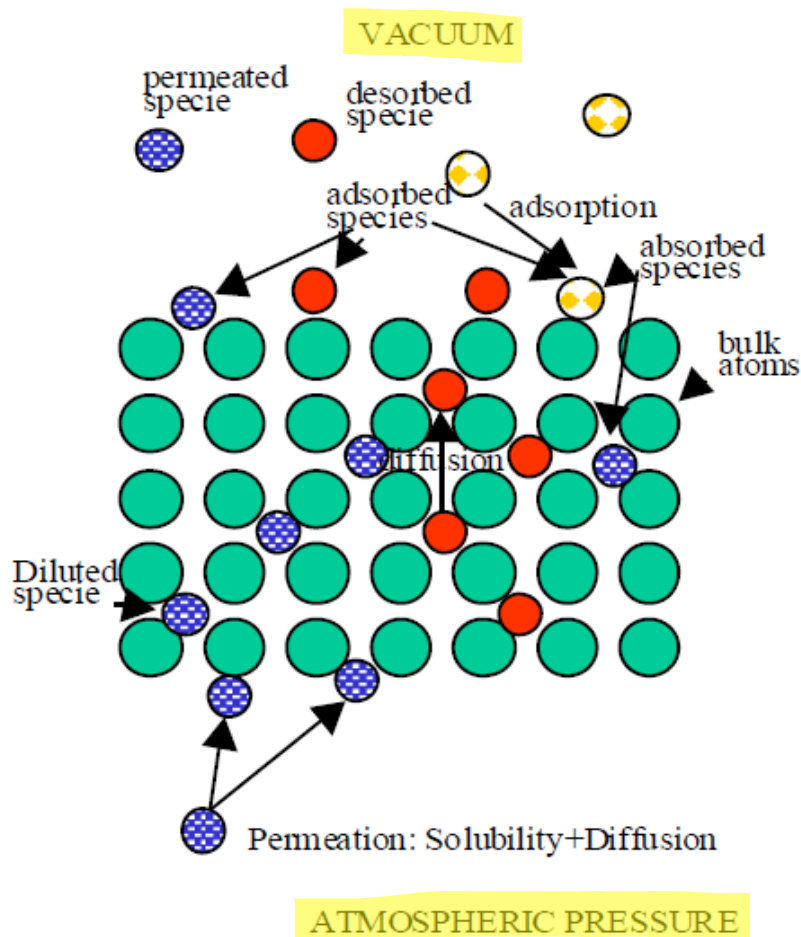
4) Permeation through the wall (solubility+diffusion)



A schematic description

• Desorbed molecules originates from:

- Adsorption
- Absorption
- Diffusion
- Permeation



The release of these molecules into the vacuum is named **OUTGASSING**

Fig. 1 Surface and bulk phenomena in vacuum.

J De Segovia, Physics of Outgassing, CAS, CERN-99-05

Adsorption-Desorption

- The process is driven by the interaction energy between the molecule or atom with the surface
- Weakly bounded molecules are **physisorbed** ($\sim 0,1$ eV), strongly bounded are **chemisorbed** (~ 1 eV)
- **Several monolayers** of gas can be physisorbed on a surface
- Chemisorption can be dissociative (H_2) and non dissociative ($C=O$), **a monolayer** can be adsorbed
- The order of desorption and the desorption energy can be evaluated from **Temperature Programmed Desorption** or **Thermal Desorption Spectroscopy**



Hiden TPD/TDS station

1st order desorption

- Applicable for **physisorbed** molecules and **non-dissociated chemisorbed** molecules
- The **rate of molecular desorption** from a surface is given by:

$$-\frac{d\theta}{dt} = \nu_1 \theta e^{-E_D/kT}$$

- θ , surface coverage, ν_1 frequency of vibration of an adsorbed molecule (10^{13} Hz), E_D , activation energy for desorption
- The solution describes the surface coverage evolution with time:

$$\theta(t) = A e^{-t/\tau}$$

→ time constant: $\tau = \frac{1}{\nu_1} e^{E_D/kT} = \tau_0 e^{E_D/kT}$



Sojourn time – residence time

Sojourn time

- This is the characteristic time for a first order desorption process
- The **sojourn time** (residence time) of a molecule on a surface is a function of the desorption energy, E_D , and the surface temperature, T :


$$\tau = \tau_0 e^{\left(\frac{E_D}{kT}\right)}$$

- With τ_0 the oscillation period of the molecules on the surface $\sim 10^{-13}$ s.
- The inverse of the sojourn time is the desorption probability of a molecule
- For **some binding energies** the residence time of a molecules is of the order of a week
- **Increasing** the temperature decrease the residence time
- **Decreasing** the temperature, increase the residence time
- **Strongly bound** molecules have long residence time

2. Outgassing

Units of outgassing rate

- The (intrinsic) outgassing rate is the **quantity** of gas leaving the surface per unit time per unit of exposed geometric surface: $\text{Pa m}^3 \text{s}^{-1} \text{m}^{-2}$ (or Pa m s^{-1} or W m^{-2})

 Pa m s^{-1}	Pa m s^{-1}	$\text{Torr l s}^{-1} \text{cm}^{-2}$	$\text{mbar l s}^{-1} \text{cm}^{-2}$	$\text{molecules s}^{-1} \text{cm}^{-2}$
1 Pa m s⁻¹	1	7.5×10^{-4}	10^{-3}	2.46×10^{16}
1 Torr l s⁻¹ cm⁻²	1.33×10^3	1	1.33	3.27×10^{19}
1 mbar l s⁻¹ cm⁻²	10^3	0.75	1	2.46×10^{19}

- Examples:
 - 3×10^{-10} Torr l/(s cm²) is converted to $1.33 \times 10^3 \times 3 \times 10^{-10} = 4 \times 10^{-7}$ Pa m s⁻¹
 - 5×10^{-13} Torr l s⁻¹ cm⁻² is converted to $1.33 \times 5 \times 10^{-13} = 6.7 \times 10^{-13}$ mbar l s⁻¹ cm⁻²
 - 5×10^{-15} mbar l s⁻¹ cm⁻² is converted to $10^3 \times 5 \times 10^{-15} = 5 \times 10^{-12}$ Pa m s⁻¹
 - 5×10^{-15} mbar l s⁻¹ cm⁻² is converted to 123 000 molecules / (s cm²)

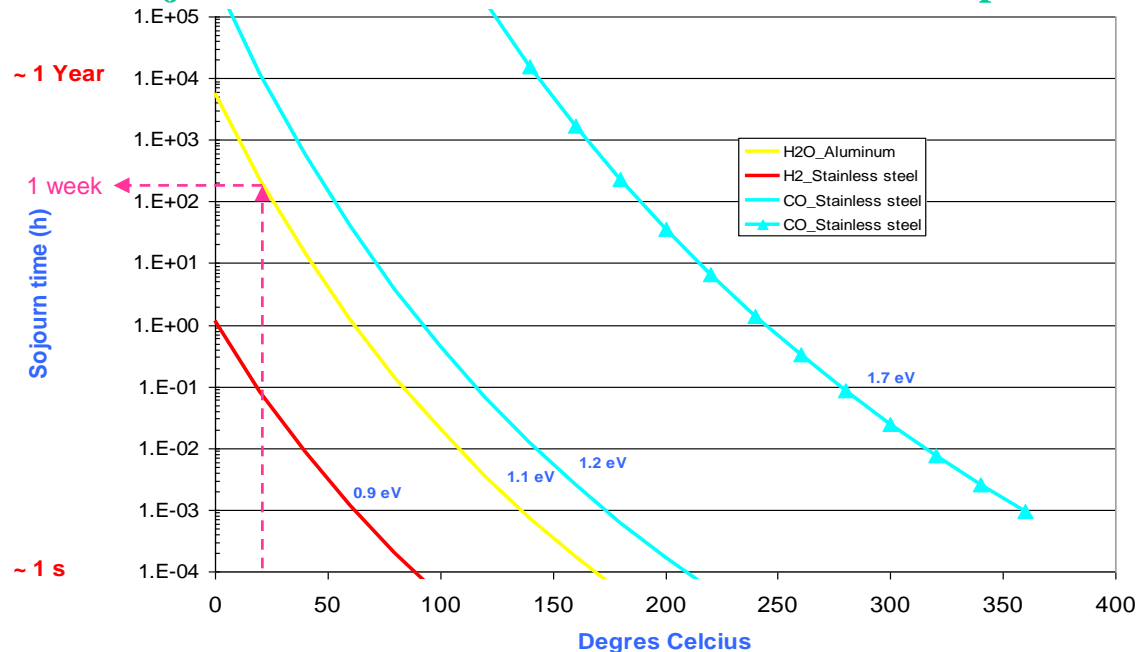
P. Redhead, Recommended practices for measuring and reporting outgassing data, J. Vac. Sci. Technol. A 20(5), Sep/Oct 2002, 1667-1675

H₂O - Sojourn time

- At room temperature (i.e. for unbaked vacuum systems), the sojourn time of water on the surface is very large ~ 1 week
 - The surface coverage of water is therefore reduced by 1/e in a week
- Water desorption is dominating the pumping process and several months are needed to fully evacuated the water adsorbed on the surface
- Water originates from previously adsorbed molecules and from reaction with oxides:



Sojourn time of a molecule as a function of temperature



Unbaked system: water outgassing

- It is observed that the desorption of water follows an inverse power law form, with $a \sim 1$ for metals and metal oxides:

$$q(t) = q_0 t^{-a}$$

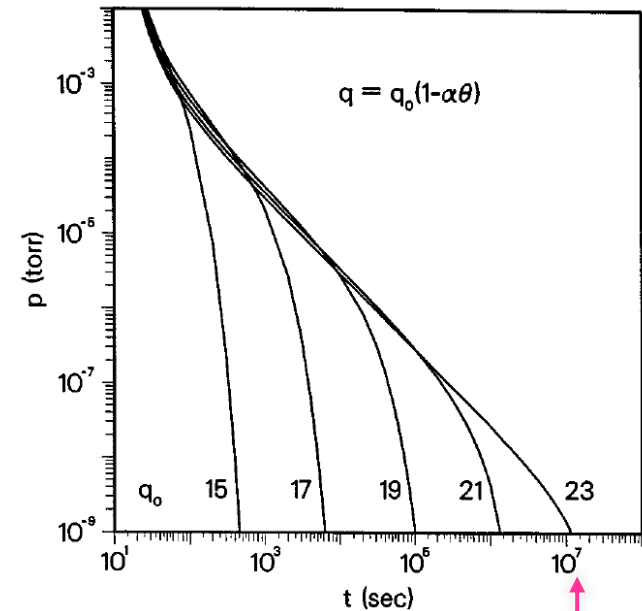
- In practical units

$$q(t) = \frac{3 \cdot 10^{-9}}{t [h]} \text{ mbar} \cdot \text{l} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$$

- Model of Redhead:

- Desorption/adsorption is assumed to be reversible
- The surface coverage can be expressed as a function of pressure by a suitable isotherm
- A Temkin like isotherm with several possible adsorption energies, q_i , due to the complexity of the technical surface (15-23 kcal/mole *i.e.* 0.6 - 1 eV)

$$P(t) = \frac{\theta_m RT V/S}{GV(q_0 - q_1)} t^{-1}$$



100 days

P.A. Redhead, J. Vac. Sci. Technol. A 13(2), Mar/Apr 1995

Impact of roughness

- Case of unbaked a-C coated stainless steel tube, 450-500 nm thick:

Mass spectrum is water dominated

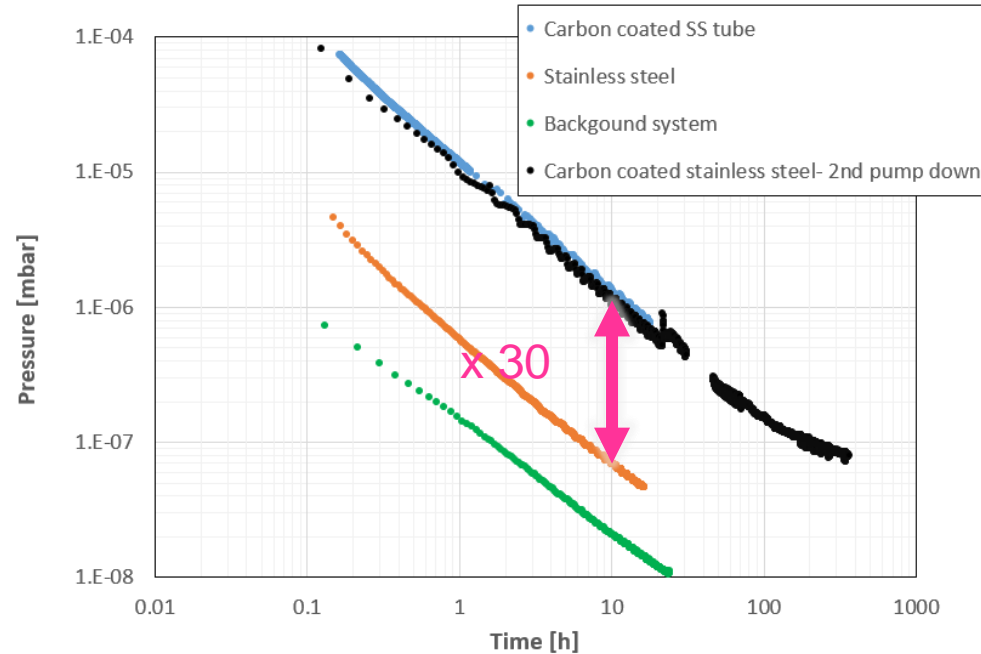
~ x 30 unbaked stainless steel

2nd pump down very similar to 1st one

After 10h pumping:

Stainless steel = $2 \cdot 10^{-10}$ mbar.l/s/cm²

a-C coating = $6 \cdot 10^{-9}$ mbar.l/s/cm²



Courtesy I. Wevers

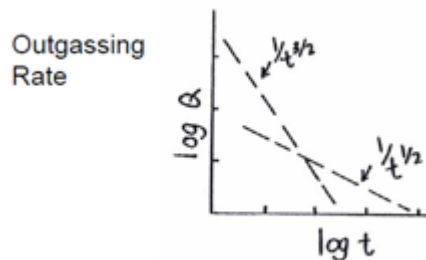
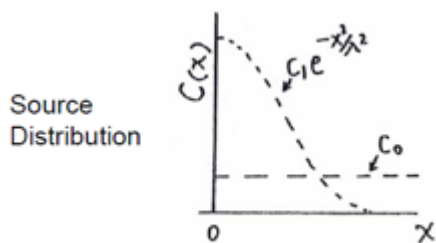
The amount of water chemisorbed on the surface increases when increasing the surface roughness

- Mechanical polishing or electropolishing are used to reduce the outgassing rate of materials

Water outgassing & venting

$$Q(t) = Q_0 t^{-a} = \frac{q_1}{t^{3/2}} + \frac{q_0}{t^{1/2}}$$

- The exponent, a , varies with the quantity of water absorbed:
 - ambient air (8 ML): 1.2
 - large water exposure (17 ML): 1.3
 - low water exposure (0.02 ML): 0.65
- The observation can be modeled by the superposition of:
 - a water surface concentration $\Rightarrow a \sim 3/2$
 - a water bulk concentration $\Rightarrow a \sim 1/2$



F. Dylla, CAS 2006 & J. Vac. Sci. Technol. A 11(4), Jul/Aug 1993

Venting with dry N₂ reduces pump down times

TABLE I. H₂O absorption/desorption data for various venting conditions of the stainless-steel (304) test chamber.^a

Trial	H ₂ O absorbed (ML)	H ₂ O exposed (ML)	$Q = Q_{10}/t^a$		$Q = q_1/t^{3/2} + q_0/t^{1/2}$		Venting gases
			Q_{10} ($\times 10^4$)	a	q_1 ($\times 10^5$)	q_0 ($\times 10^8$)	
T010	7.8		2.67	1.22	1.96	3.73	Ambient air
T020	16.8	600	8.21	1.30	4.23	3.86	Controlled mixture of H ₂ O and N ₂
T021	9.2	400	3.12	1.18	3.15	5.86	
T022	7.2	200	2.36	1.19	2.11	6.11	
T023	3.6	100	0.87	1.09	1.55	6.33	
T024	2.3	10	0.52	1.07	0.86	5.89	
T030	0.7		0.12	0.96	0.29	14.0	N ₂ gas (> 10 ppm H ₂ O)
T040	0.017		5.07 $\times 10^{-4}$	0.65	8.91 $\times 10^{-2}$	1.05	Highly dry N ₂ gas

^aNote: The unit for the outgassing rate (Q) is (Torr ℓ/cm^2 s) and the unit of time (t) is (s).

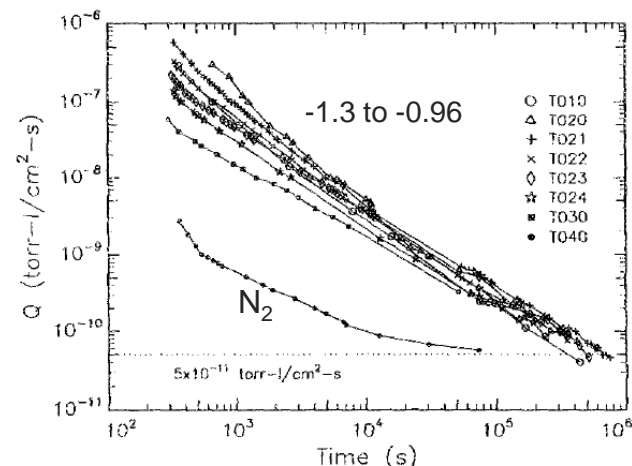


FIG. 2. Outgassing measurements for different H₂O exposures in a log (Q) vs log(t) plot. (See Table I for key to trial numbers, T010-T040.)

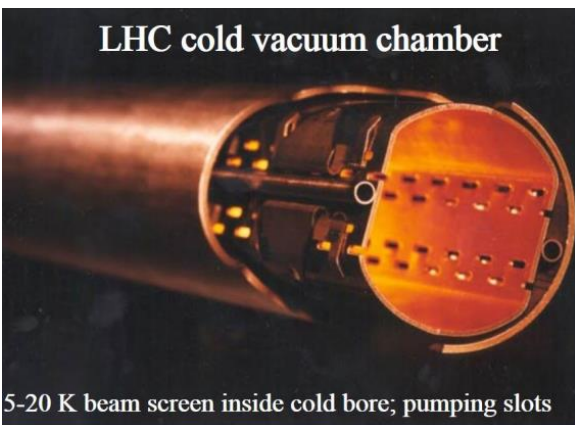
Typical design value of outgassing rates

- The outgassing rate of unbaked surfaces is **dominated by H₂O**.
- For metallic surfaces, unbaked after 10h of pumping (Torr.l.s⁻¹.cm⁻²)

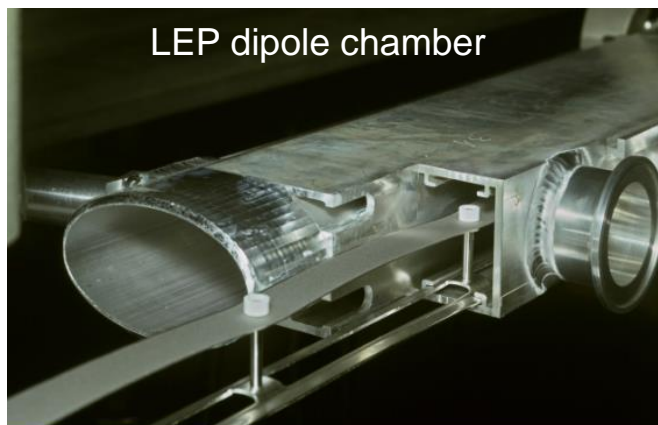
Gas	Al	Cu	St. Steel	Be
H ₂	7 10 ⁻¹²	1.4 10 ⁻¹¹	7 10 ⁻¹²	1.4 10 ⁻¹¹
CH ₄	5 10 ⁻¹³	5 10 ⁻¹³	5 10 ⁻¹³	1 10 ⁻¹²
H ₂ O	3 10 ⁻¹⁰	3 10 ⁻¹⁰	3 10 ⁻¹⁰	6 10 ⁻¹⁰
CO	5 10 ⁻¹²	1 10 ⁻¹²	5 10 ⁻¹²	1 10 ⁻¹¹
CO ₂	5 10 ⁻¹³	2.5 10 ⁻¹³	5 10 ⁻¹³	1 10 ⁻¹²

A.G. Mathewson *et al.* in Handbook of Accelerator Physics and Engineering, World Scientific, 1998

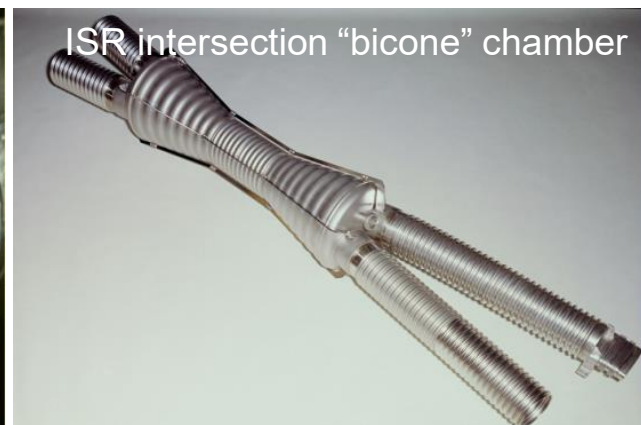
LHC cold vacuum chamber



LEP dipole chamber

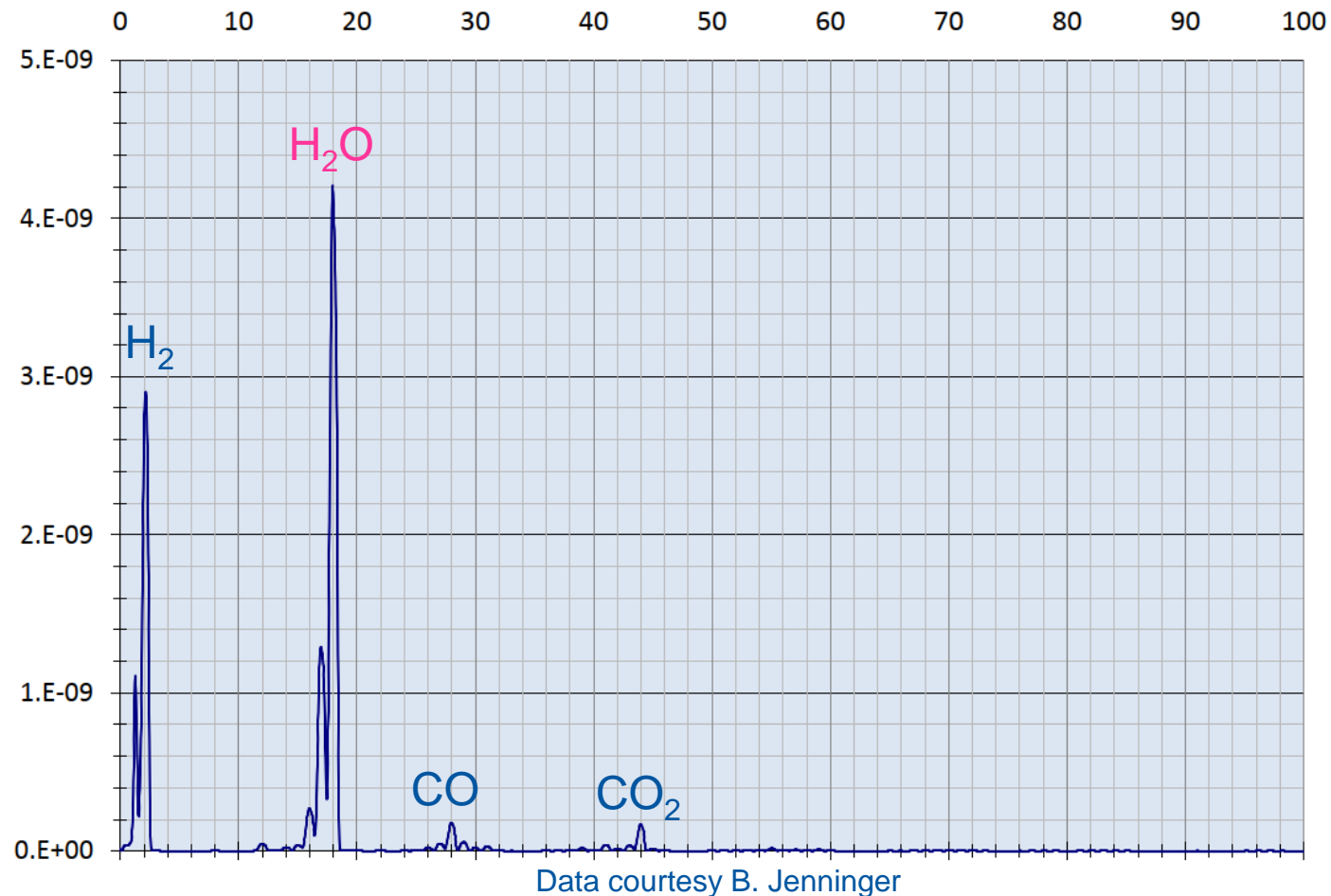


ISR intersection "bicone" chamber



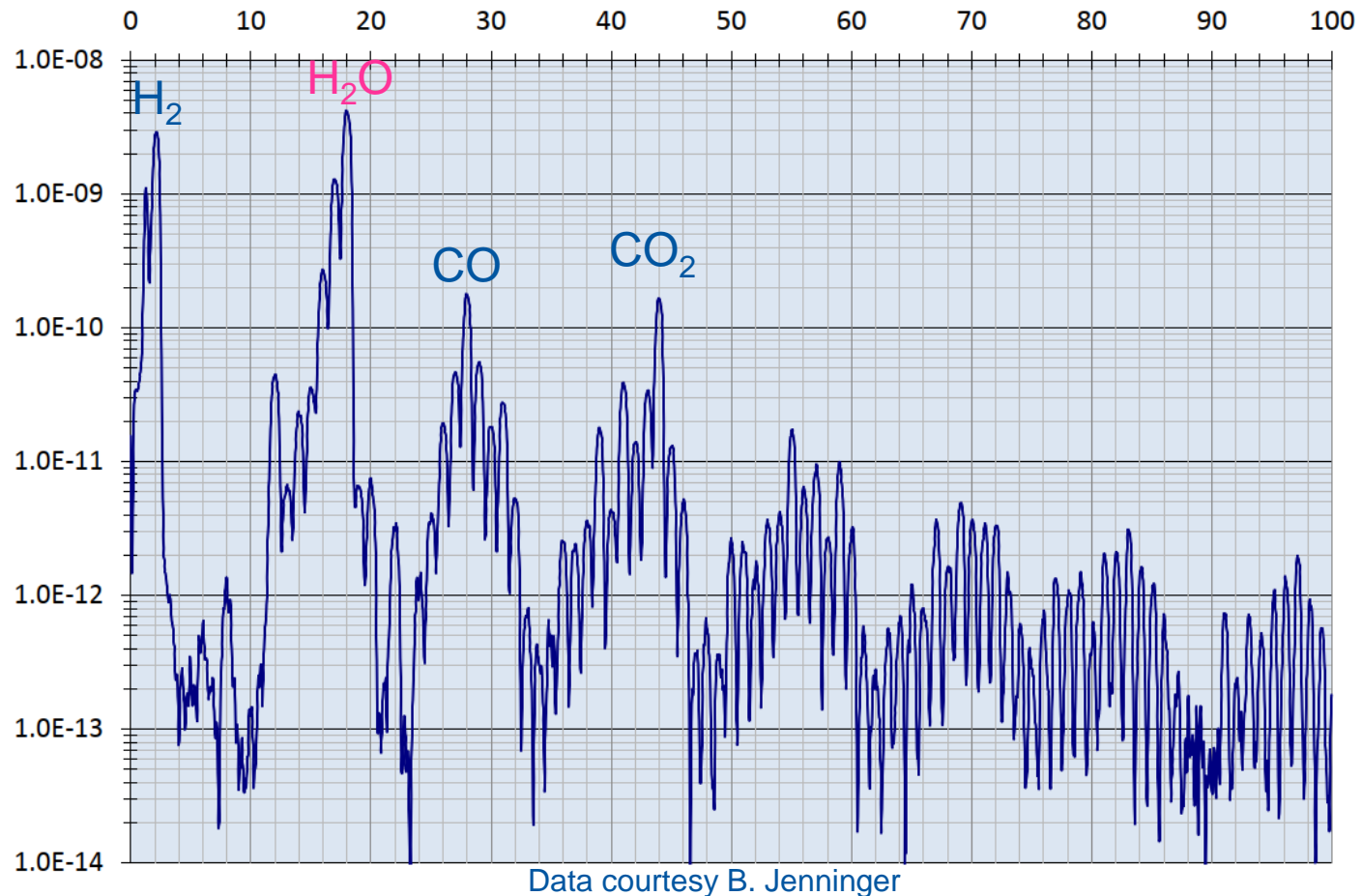
Gas composition of un-baked system

- $P = 4 \cdot 10^{-9}$ mbar after 30h turbomolecular pumping of a 1 m long, 10 cm diameter tube
- Dominated by **Water**, then hydrogen, carbon monoxide, carbon dioxide



Gas composition of un-baked system

- $P = 4 \cdot 10^{-9}$ mbar after 30h turbomolecular pumping of a 1 m long, 10 cm diameter tube
- Dominated by **Water**, then hydrogen, carbon monoxide, carbon dioxide
- Presence of alkanes up to high masses (C_nH_{2n+2}) from **cutting fluids and/or lubricants**
- Traces of **ethanol from cleaning**: C_2H_5OH



3. Bake-out

Next: Chapter 3



Sojourn time at high temperature

$$\tau = \frac{E}{kT} \frac{1}{V_0}$$

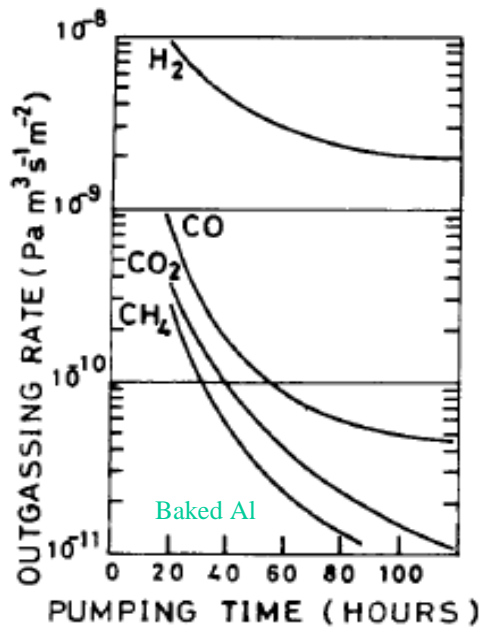
- The sojourn time **decrease strongly** with increasing temperature
- Heating the material allows a degassing of the molecules having binding energies **< 2 eV**

E(eV)	120°C	200°C	300°C	400°C
0.9	4 10 ⁻² s	4 10 ⁻⁴ s	8 10 ⁻⁵ s	6 10 ⁻⁷ s
1.1	13 s	5 10 ⁻² s	5 10 ⁻⁴ s	2 10 ⁻⁵ s
1.7	20 years	1.5 days	88 s	0.5 s
2.0	1 10 ⁵ years	6 years	10h	95 s
2.8	3 10 ¹⁵ years	2 10 ⁹ years	1 10 ⁴ years	3 years

- Molecules with larger binding energies than 1.7-2 eV will not be depleted by a bake-out
→ However, those molecules will be available for **subsequent** desorption by e.g. ion bombardment !!

In Situ Bake Out

- A bake-out above 150°C increase the desorption rate of H₂O and reduce the H₂O sojourn time in such a way that H₂ becomes the dominant gas for baked vacuum systems

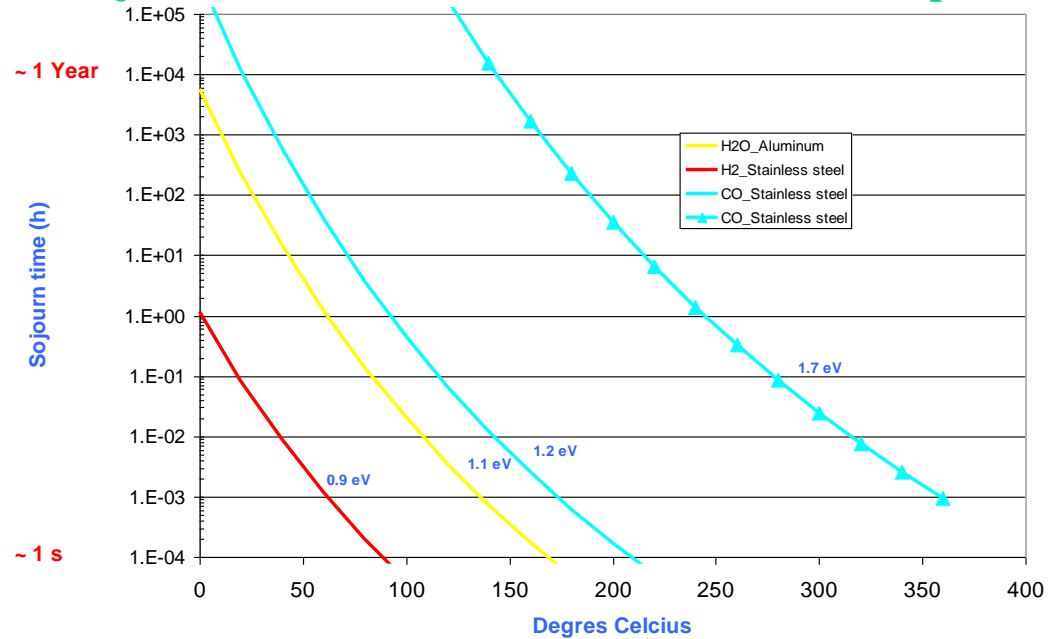


$$\tau = \frac{e^{\frac{E}{kT}}}{V_0}$$

Sojourn time (h)

~ 1 s

Sojourn time of a molecule as a function of temperature



A.G. Mathewson *et al.*

J.Vac.Sci. 7(1), Jan/Fev 1989, 77-82

Material for bakeout



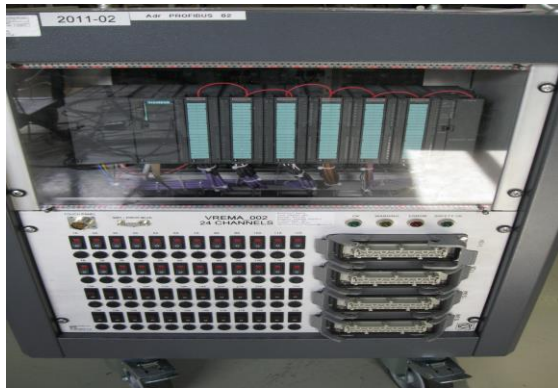
Collars



thermocouples



bakeout jackets



racks



heating tape



Storage area

All parts shall be baked (including in vacuum assemblies) : cold spots are forbidden !

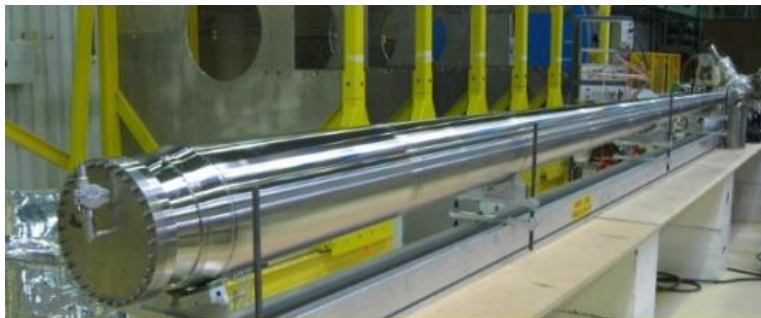
Typical design values of outgassing rates

- The outgassing rate of baked surfaces is **dominated by H₂**
- Metal, baked (24 h at 150°C for Cu and Al, 300°C for SS) after 50h of pumping (Torr.l.s⁻¹.cm⁻²)

Gas	Al	Cu	St. Steel	Be
H ₂	5 10 ⁻¹³	1 10 ⁻¹²	5 10 ⁻¹³	1 10 ⁻¹²
CH ₄	5 10 ⁻¹⁵	5 10 ⁻¹⁵	5 10 ⁻¹⁵	1 10 ⁻¹⁴
H ₂ O	1 10 ⁻¹⁴	<1 10 ⁻¹⁵	1 10 ⁻¹⁴	2 10 ⁻¹⁴
CO	1 10 ⁻¹⁴	1 10 ⁻¹⁴	1 10 ⁻¹⁴	2 10 ⁻¹⁴
CO ₂	1 10 ⁻¹⁴	5 10 ⁻¹⁵	1 10 ⁻¹⁴	2 10 ⁻¹⁴

A.G. Mathewson *et al.* in Handbook of Accelerator Physics and Engineering, World Scientific, 1998

Outgassing rate of baked materials are 2-3 order of magnitude less than unbaked materials



CMS End cap chamber



Copper tubes

Amount of gas removed after a bake-out

- After a laboratory bake-out of a stainless-steel chamber at 200°C for 20 h

Gas species	H ₂	CH ₄	H ₂ O	CO	CO ₂	Total
Molecule.cm ⁻² x 10 ¹⁵	11	0.7	7	4.4	5.7	28.8

C. Herbeaux *et al.*, J. Vac. Sci. Technol. A 17(2), Mar/Apr 1999, 635

Several monolayers of gas are removed from the vacuum system during a bake out

Model of diffusion

- The diffusion coefficient is a strong function of the diffusion energy and temperature:

$$D(T) = D_0 e^{-E_{diff}/kT}$$

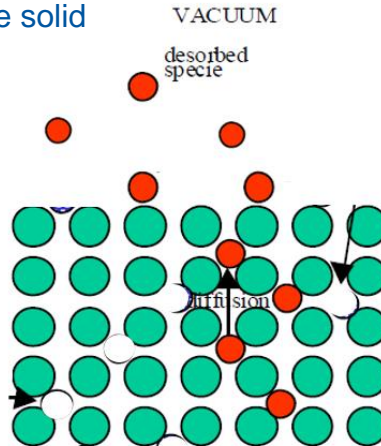
- The **hydrogen diffusion** in materials is governed by **Fick Laws**:

- 1st Law: The gaseous flux, q , is equal to the product of the diffusion coefficient, D , by the gradient of hydrogen concentration

$$q(x, t) = -D \frac{\partial c(x, t)}{\partial x}$$

- 2nd Law: The time variation of the hydrogen concentration is equal to the product of the diffusion coefficient by the second derivative of the hydrogen concentration in the solid

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



➔ These simple laws explain the hydrogen outgassing of materials

Hydrogen outgassing versus time

- During a pump down, the hydrogen concentration on the surface and in the material is reduced with time
- The time variation of the hydrogen concentration can be computed using the 2nd Law which allows to compute the hydrogen outgassing rate from the first law.
- The hydrogen outgassing rate, q , after a pumping time, t is (C_0 being the initial hydrogen concentration assumed to be uniform):

$$q(t) = D \left(\frac{\partial c(x,t)}{\partial x} \right)_{x=0} = C_0 \sqrt{\frac{D}{\pi}} \frac{1}{\sqrt{t}} \propto \sqrt{D} t^{-1/2}$$

The H₂ outgassing rate varies inversely with the square root of the pumping time

- During the pump down, the hydrogen naturally embedded in the material is depleted from it => re-exposure to air do not recharge the bulk

R.J. Elsey, Vacuum 25, 7 (1975), 299

Bake-out

- During an in-situ bake-out, the temperature of the material is increased to several 100°C (T_{BO}) for several hours (t_{BO}) in such a way the hydrogen diffusion is increased to stimulate its depletion from the material of thickness L .

- As a result, the **outgassing rate at room temperature** is greatly reduced and almost **constant** vs time

$$q_{RT}(t) \approx \frac{4 c_o D(T_{RT})}{L} e^{-\left(\frac{\pi}{L}\right)^2 D(T_{BO}) t_{BO}}$$

- In practice, increasing the **bake out temperature** is more efficient than increasing the bake out duration time: $D(T) = D_o e^{-E_{diff}/kT}$

Table of equivalences between bake out temperature

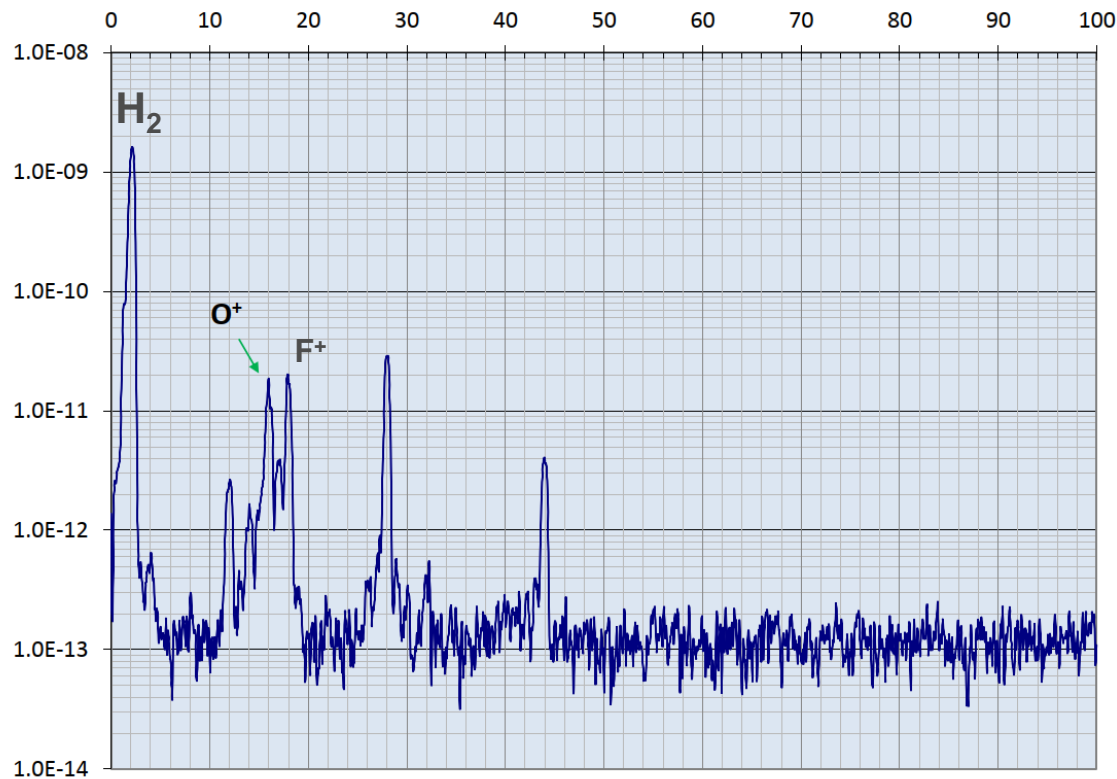
200°C	250°C	300°C
1 day	7h	2h
4 days	1 day	8h
10 days	2 days	1 day

R.J. Eley, Vacuum 25, 7 (1975), 299

R. Calder, G. Lewin, Br J Appl. Phys, 18, 1967, 1459

Gas composition after bakeout

- Baked system $P = 4 \cdot 10^{-11}$ mbar
- Clean spectrum
 - **Hydrogen dominated**, traces of H_2O , CO , CO
 - No contamination (no masses above 50 i.e. no hydrocarbons)
 - Spurious peaks following the grid bombardments by electrons (16: O^+ , 19: F^+)



Data courtesy B. Jenninger



1 mA
 $Q \sim 2 \cdot 10^{-9}$ mbar-l/s

Successive bake-outs

- n successive bakeouts at T_{BO} give the following outgassing rate at room temperature:

$$q_n(t) = \frac{4 c_o D(T_{RT})}{L} e^{-n \left(\frac{\pi}{L}\right)^2 D(T_{BO}) t_{BO}}$$

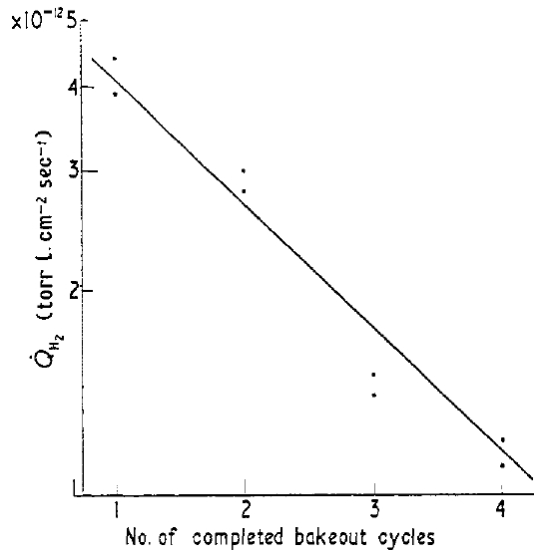
R. Calder, G. Lewin, Br J Appl. Phys, 18, 1967, 1459

- A plot $\ln(q)$ vs number of bakeout cycles, n, is **linear** with a slope proportional to the diffusion coef.

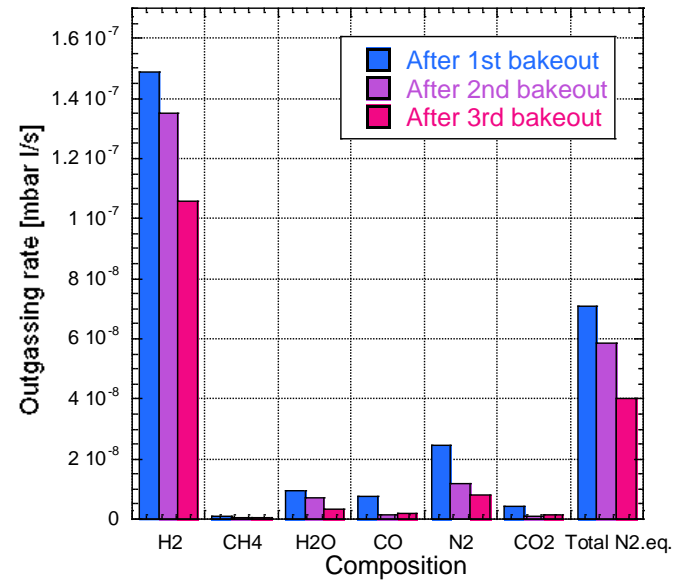
$$\frac{q_{n+1}(t)}{q_n(t)} = e^{-\left(\frac{\pi}{L}\right)^2 D(T_{BO}) t_{BO}}$$

→ each bakeout cycle **reduce** the outgassing at room temperature by a **constant value**

Stainless steel sample: a reduction of x1.3-1.5 after each cycle



LHC collimator: a reduction of x1.3 after each cycle



R. Calder, G. Lewin, Br J Appl. Phys, 18, 1967, 1459

J. Kamiya *et al.*, Vacuum 85 (2011) 1178-1181

Slot 3 summary

- The pressure in a vacuum vessel is **determined** by the outgassing of its **surface**
- The **sojourn time** of a molecule on a surface is a strong function of its binding energy and the temperature of the surface
- Unbaked materials are dominated by **water** outgassing. The desorption rate is $1/t$
- Baked material are dominated by **hydrogen** outgassing. The desorption rate is $1/\sqrt{t}$ limited by diffusion

Thank you for your attention !!!



Some References

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