Materials and Properties IV
Outgassing

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CERN Accelerator School (CAS) on Vacuum for Particle Accelerators
June 18th 2017

Outline
- Gas source and main features.
- Order of magnitude.
- Outgassing of water vapour from metals
- Outgassing of water vapour from polymers
- Outgassing of H$_2$ from metals
The total outgassing rate \( Q \) and the effective pumping speed \( S \) define the pressure in a vacuum system:

\[
P = \frac{Q}{S} + P_0
\]

\( P_0 \): ultimate pressure of the pumping system.

In general, \textit{in particle accelerators}, the effective \( S \) varies between 1 to 1000 l.s\(^{-1}\)) while \( Q \) can extend over more than 10 orders of magnitude (\( \approx 10^{-5} \rightarrow 10^{-15} \) mbar l.s\(^{-1}\).cm\(^{-2}\)).

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

In this respect the \textbf{measurement of outgassing rate is an essential activity} for an ultra-high vacuum expert.
Reminder: Terminology

- **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.
Gas sources

Contamination onto surfaces is a source of gas. After production, the surface of vacuum components is always contaminated. They must be thoroughly cleaned before installation.

See Mauro Taborelli presentation on Monday 22nd

<table>
<thead>
<tr>
<th>Gross contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption layer (≈nm)</td>
</tr>
<tr>
<td>Oxide and hydroxyde layer (1-10 nm)</td>
</tr>
<tr>
<td>Damaged skin (10-100 μm)</td>
</tr>
<tr>
<td>Undamaged metal</td>
</tr>
</tbody>
</table>

Solvent or detergent cleaning

 oils, dirt, …→
 CₓHᵧ, H₂O, Cl, …→
 MeₓOᵧ, →
 excess dislocation, voids →
Outgassing: main features

Gas molecules dissolved in the bulk of **materials** are also a source of gas. They diffuse towards the surfaces and are then released.

**Polymers** dissolve a **significant quantity** of molecules, **in particular** H\(_2\)O.

**Metals** can dissolve only **limited quantities** of small atoms that, at room temperature, are immobile in the lattice, except for hydrogen.

In one day, H atoms travel in average **4 \(\mu\)m in austenitic stainless steels**, while O atoms travel the same distance in 1000 years.

Therefore, amongst the dissolved elements in the bulk of metals, **only H\(_2\)** is released at room temperature.

For comparison, in one day, **H\(_2\)O molecules move along about 20 \(\mu\)m in PEEK**, a high-performance polymer.
Outgassing rates: orders of magnitude

**Neoprene (10 h pumping):**
- $q_{\text{H}_2\text{O}} \approx 10^{-5} \text{ mbar l s}^{-1} \text{ cm}^{-2}$
- $q_{\text{H}_2\text{O}} \approx 10^{14} \text{ molecules s}^{-1} \text{ cm}^{-2}$

**Unbaked stainless steel (10 h pumping):**
- $q_{\text{H}_2\text{O}} = 3 \times 10^{-10} \text{ mbar l s}^{-1} \text{ cm}^{-2}$
- $q_{\text{H}_2\text{O}} = 7 \times 10^{9} \text{ molecules s}^{-1} \text{ cm}^{-2}$

**Baked stainless steel (150° C x 24 h):**
- $q_{\text{H}_2} = 3 \times 10^{-12} \text{ mbar l s}^{-1} \text{ cm}^{-2}$
- $q_{\text{H}_2} = 7 \times 10^{7} \text{ molecules s}^{-1} \text{ cm}^{-2}$

**Baked OFS Copper (200° C x 24 h):**
- $q_{\text{H}_2} = 3 \times 10^{-14} \text{ mbar l s}^{-1} \text{ cm}^{-2}$
- $q_{\text{H}_2} = 7 \times 10^{5} \text{ molecules s}^{-1} \text{ cm}^{-2}$

**Instruments** equipped with hot filaments are an **important source of gas**.

‘Indicative’ value for CERN instruments after standard degassing procedure:

- **Bayard-Alpert gauges (W filaments)**
  - $Q \approx 10^{-9} \text{ mbar l s}^{-1}$
  - $Q \approx 3 \times 10^{10} \text{ molecules s}^{-1}$

- **Residual gas analyzer (W filaments)**
  - $Q \approx 10^{-8} \text{ mbar l s}^{-1}$
  - $Q \approx 3 \times 10^{11} \text{ molecules s}^{-1}$

Equivalent **in quantity** to $\approx 1 \text{ m}^2$ of stainless steel.
Outgassing of water vapour from unbaked metallic alloys
Outgassing of water vapour

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

$q_{H_2O} \approx \frac{3 \times 10^{-9}}{t[h]} \left[ \frac{\text{mbar l}}{s \text{ cm}^2} \right]$  

Experimental values valid for all metals used for vacuum chamber manufacturing.

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

$A = 2067 \text{ cm}^2$

$S = 19.6 \text{ l/s}$

St. steel
Outgassing of water vapour

Water vapour outgassing rate of austenitic stainless steel that underwent four different surface treatments.

\[ q_{H_2O} \approx \frac{3 \times 10^{-9}}{t[h]} \left[ \frac{mbar \ l}{s \ cm^2} \right] \]

The most effective way to accelerate the release of water vapour is \textit{in-situ} bakeout at least at 120°C for 12 hours.

The source of H\textsubscript{2}O is recharged after each venting to air.
**Interpretation: single desorption energy**

Mean stay time at room temperature

The mean stay time (sojourn time) is given by the Frenkel law:

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

where the value of $\tau_o$ is usually assumed to be about $10^{-13}$ s ($\approx h/K_B T$).
Interpretation: single desorption energy

Pressure decrease

\[ V \frac{dP}{dt} = -SP + \frac{N_s \Theta}{\tau_d} \]

\[ \frac{d\Theta}{dt} = -\frac{\Theta}{\tau_d} \]

\[ P(t) \approx \frac{N_s}{S \cdot \tau_d} e^{-\frac{t}{\tau_d}} \text{ for } t > \tau_d \]

\[ \Theta = \text{fraction of sites occupied} \]
\[ \text{The total number of sites } N_s \text{ is assumed to be } \approx 10^{15} \text{ cm}^{-2} \rightarrow 4 \times 10^{-5} \text{ mbar l s}^{-1} \text{cm}^{-2} \]

The solution is plotted for:

\[ V = 10 \ell, \ S = 10 \ell /s, \ N_s = 2245 \times 4 \times 10^{-5} \text{ mbar } \ell \]

and different energies
**Interpretation: single desorption energy**

Pressure decrease for different adsorption energies and two values of $T$

$T=296K$  
$P(0)=0$  
$T=373K$

$1\text{Torr} = 1.33\text{ mbar}$

- $0.75\text{ eV}$
- $0.8\text{ eV}$
- $0.85\text{ eV}$
- $0.9\text{ eV}$
- $0.95\text{ eV}$
- $1\text{ eV}$

$P[\text{Torr}] \propto \frac{1}{t}$

Interpretation: single desorption energy

Pressure decrease for different adsorption energies and two values of $T$

$1\text{Torr} = 1.33\text{ mbar}$

$T=296K$  
$P(0)=0$  
$T=373K$
Interpretation: single desorption energy

Pressure decrease for different adsorption energies

\[ T = 296K \]
\[ P_0 = 1 \text{ Torr} \]

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

\[ P \propto e^{-t} \]
\[ \propto \frac{1}{t} \]
Water vapour outgassing from polymers
Outgassing of polymers

Polymers, in particular in their amorphous structures, can **dissolve huge quantities of gas, in particular water vapour.**

The **water vapour solubility is very high**; for example for common materials like Viton, PEEK, and Vespel (Kapton) the content of water in equilibrium with 50%-humidity air at 20°C is 0.21, 0.2, and 1 wt. %, respectively.

The huge quantity of dissolved gas and the **relatively high mobility** through the polymeric chains result in **much higher outgassing rates** than the ones of metals. This is particularly marked for **water vapour.**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Unbaked, 1 h pumping</th>
<th>Baked, ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoroelastomer</td>
<td>$4 \times 10^{-7} : 2 \times 10^{-5}$</td>
<td>$3 \times 10^{-11} : 2 \times 10^{-9}$</td>
</tr>
<tr>
<td>Buna-N</td>
<td>$2 \times 10^{-7} : 3 \times 10^{-6}$</td>
<td>---</td>
</tr>
<tr>
<td>Neoprene</td>
<td>$5 \times 10^{-5} : 3 \times 10^{-4}$</td>
<td>---</td>
</tr>
<tr>
<td>Butyl</td>
<td>$2 \times 10^{-6} : 1 \times 10^{-5}$</td>
<td>---</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>$5 \times 10^{-7}$</td>
<td>---</td>
</tr>
<tr>
<td>Silicone</td>
<td>$3 \times 10^{-6} : 2 \times 10^{-5}$</td>
<td>---</td>
</tr>
<tr>
<td>Perfluoroelastomer</td>
<td>$3 \times 10^{-9}$</td>
<td>$3 \times 10^{-11} : 3 \times 10^{-10}$</td>
</tr>
<tr>
<td>Teflon</td>
<td>$2 \times 10^{-8} : 4 \times 10^{-6}$</td>
<td>---</td>
</tr>
<tr>
<td>KEL-F</td>
<td>$4 \times 10^{-8}$</td>
<td>$3.5 \times 10^{-10}$</td>
</tr>
<tr>
<td>Polyimide</td>
<td>$8 \times 10^{-7}$</td>
<td>$3 \times 10^{-11}$</td>
</tr>
</tbody>
</table>


The maximum bakeout temperature depends on the type of polymer; it is limited to about 200 °C for Viton®.
Outgassing of polymers

Example:

Water solubility:
0.1 to 0.5 wt.% (4.4 to $22 \times 10^{19}$ molecules/cm$^3$) 
10 to 50 times larger than the H total content in as produced austenitic stainless steel

Water diffusivity at RT:
$5 \times 10^{-9}$ cm$^2$ s$^{-1}$
2000 times larger than that reported for H in austenitic stainless steel.

The outgassing rates of **thick slab of polymers** decrease with the inverse of the square root of the pumping time $t$:

$$q_{H_2O} \propto \frac{1}{\sqrt{t}}$$

The decrease of water vapour outgassing rate is much slower in polymer than in metals.
Outgassing of polymers

Case study: Outgassing of Axon wires, 0.2-mm-thick Kapton insulation

Exponential decay

$q_{H_2O} \propto \frac{1}{\sqrt{t}}$

$q_{H_2O} \propto \frac{1}{t}$

Courtesy of Jose Antonio Ferreira Somoza
Another important limitation of polymers used as seals is the high gas permeability.

Gas penetrates into the material and diffuses towards the vacuum system. The permeation flow may limit the ultimate water vapour pressure in vacuum systems and affect the sensitivity of helium leak-detection.

The permeation flow of atmospheric water vapour through a Viton O-ring, 5 mm cross section diameter, 6 cm torus diameter is $\approx 10^{-7}$ Torr l s$^{-1}$. The stationary condition (ultimate permeation) will be attained after about two months.
Outgassing of H$_2$ from metals used in vacuum systems for particle accelerators.
Outgassing of hydrogen

For metallic alloys, as soon as water vapour outgassing is strongly reduced, by either long pumping or bakeout, \( \text{H}_2 \) outgassing rate becomes the highest one.

This gas is dissolved in metals as single H atoms. Its diffusion is relatively fast and, after recombination on the surface, it can be released as molecular hydrogen.

Most of the H atoms are dissolved in liquid metals, during the production process.

H atom mobility and solubility in the liquid state are higher than in the solid state.

Typical sources of H are:

• metals ores;
• tools needed for fusion;
• refractory materials of furnaces;
• combustion and treatment gas;
• water vapour and fluids used for quenching (for example the hyper-quench of austenitic stainless steels is carried out from 1100°C in water, air, or oil).
Example of a process of $\text{H}_2$ dissolution in liquid Al

If the solidification is fast, the gas is trapped in the solid far from the equilibrium.

Typical $\text{H}_2$ contents are about 1 wt. ppm for copper, aluminum, and austenitic stainless steel.
Outgassing of hydrogen

As for water vapour, hydrogen-outgassing rate is **reduced by heating**.

The high temperatures **increase the H atoms mobility** and, as a result, accelerate the depletion of the residual hydrogen content.

However, there is a **crucial difference between water vapour and hydrogen**.

Each time the vacuum system is exposed to air, water molecules re-adsorb on the surface, while **hydrogen is not recharged** in the bulk of the metal.

For most of the materials used for the manufacturing of vacuum chambers, the H **solubility is very low** in the solid state.

For example, to recharge **1 wt. ppm** of hydrogen at room temperature in stainless steel, the material has to be in equilibrium with the gas at **7 bar**. The hydrogen pressure in air is roughly $10^{-4}$ mbar, which gives a maximum recharging of about $2.10^{-4}$ wt. ppm.
For **copper and aluminium alloys**, a few bakeout at 150-200°C for 24 hours are sufficient to reduce the hydrogen-outgassing rate to less than $10^{-13}$ mbar l s$^{-1}$ cm$^{-2}$.

For **austenitic stainless steel**, higher temperatures are needed to have a similar effect for a few-mm-thick vacuum chambers. Repeated bakeout at temperature higher than 200°C may have a significant influence.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Bakeout T[°C] x 24 h</th>
<th>q [mbar l s$^{-1}$ cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenitic st. steel</td>
<td>150</td>
<td>$3 \times 10^{-12}$</td>
</tr>
<tr>
<td>Austenitic st. steel</td>
<td>200</td>
<td>$2 \times 10^{-12}$</td>
</tr>
<tr>
<td>Austenitic st. steel</td>
<td>300</td>
<td>$5 \times 10^{-13}$</td>
</tr>
<tr>
<td>Copper Silver added (OFS)</td>
<td>150</td>
<td>$3 \times 10^{-12}$</td>
</tr>
<tr>
<td>Copper Silver added (OFS)</td>
<td>200</td>
<td>$\approx 10^{-14}$</td>
</tr>
<tr>
<td>Beryllium after brazing</td>
<td>150</td>
<td>$&lt; 10^{-14}$</td>
</tr>
<tr>
<td>Al alloys</td>
<td>150</td>
<td>$&lt; 10^{-13}$</td>
</tr>
</tbody>
</table>
Outgassing of hydrogen: effect of vacuum firing

For austenitic stainless steels, a radical effect is obtained by heating in a vacuum furnace to temperatures up to about 1000°C.

Such a treatment is called ‘vacuum firing’. At CERN, it is carried out at 950°C for 2 h.

The **CERN’s large furnace**: useful height and diameter: 6 m and 1 m, respectively. Maximum charge weight: 1000 Kg. Ultimate pressure: about $10^{-7}$ mbar; pressure at the end of the 950°Cx2h treatments: $10^{-5}$mbar.
Outgassing of hydrogen: effect of vacuum firing

- **$T < 500^\circ C$**
  - H atom diffusion in austenite is too slow

- **$500^\circ C \ (600^\circ C) < T < 900^\circ C$** (depending on the steel grade)
  - carbide and carbo-nitride precipitation
  - residual $\delta$-ferrite transformation into $\sigma$-phase (very brittle)

- **$T > 1050^\circ C$**
  - Solution annealing, abnormal grain growth, recrystallisation, excessive nitrogen loss
### Outgassing of hydrogen: effect of vacuum firing

<table>
<thead>
<tr>
<th>Thermal treatment</th>
<th>Outgassing rate [mbar l s(^{-1}) cm(^{-2})]</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C x 24 h</td>
<td>2 x 10(^{-12})</td>
<td></td>
</tr>
<tr>
<td>300°C x 24 h (*)</td>
<td>5 x 10(^{-13})</td>
<td>1.5 mm thick</td>
</tr>
</tbody>
</table>
| Vacuum firing (*)         | ≈ 5 x 10\(^{-15}\)                           | 950°C x 2 h 
\(\text{P}_\text{H}_2=2\times10^{-5}\) mbar 
1.5-mm-thick slabs |

(*) J-P Bojon, N. Hilleret, B. Versolatto

\(\text{H}_2\) outgassing value for vacuum-fired beam pipes assumed for **design of vacuum systems** in the ISR era: 2 x 10\(^{-13}\) mbar l s\(^{-1}\) cm\(^{-2}\).
Outgassing of hydrogen: effect of vacuum firing

Modification of mechanical and metallurgical properties after vacuum firing

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardness HB (ISO 6506)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As received</td>
</tr>
<tr>
<td>304L (UHV use)</td>
<td>150</td>
</tr>
<tr>
<td>316LN</td>
<td>155</td>
</tr>
</tbody>
</table>

No additional precipitates have been detected after vacuum firing at 950° C

No significant variation of “rupture strength” and “stretch at break”: less than 5%
Outgassing of hydrogen: effect of vacuum firing

Modification of the surface roughness induced by vacuum firing

Modification of the surface roughness induced by vacuum firing

- Vacuum firing
- Outgassing of hydrogen: effect of vacuum firing
Outgassing of hydrogen: effect of vacuum firing

Sublimation of metallic elements during vacuum firing

Vapor pressure of the pure elements

Diffusion coefficients at 950°C in austenite:

- \( D_{Cr} = 7 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1} \)
- \( D_{Mn} = 6 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1} \)
- \( D_{Fe} = 2 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1} \)
- \( D_{Ni} = 5 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1} \)

- **After vacuum firing** the oxide layer is strongly enriched with Fe: \( \text{Cr/Fe} = 0.33 \) for 316L and 0.22 for 304L (0.75 for cleaned); oxide thickness as for cleaned.

- \( \text{Cr}^{2p\,2/3} \) and \( \text{O}^{1s} \) lines indicate the presence of less hydroxides than on cleaned samples (\( \text{Cr}_2\text{O}_3 \) and \( \text{Fe}_2\text{O}_3 \))

J. Gavillet and M. Taborelli, unpublished results
Decreasing the concentration:

Vacuum firing

BN surface segregation

- At temperature higher than 700°C, boron segregates to the surface and, in N added stainless steels (316LN), can form h-BN. Heating temperatures higher than 1150°C are needed to dissolve the h-BN layer.
- BN does not form for B concentration lower than 9 ppm.
- When the concentration is equal or larger than 9 ppm BN forms only when B is free to move, namely not blocked in BN precipitates already existing in the steel bulk.
- The BN layer strongly reduces the surface wettability and may produce peel-off of thin film coatings.
- The BN layer can be effectively removed by electropolishing.
Theory of hydrogen outgassing: two models

Two limiting mechanisms are considered:

1. diffusion limited outgassing $\rightarrow q(t) \propto -\frac{\partial c}{\partial x}$

2. recombination limited outgassing $\rightarrow q(t) \propto (c_W)^2$
Diffusion, in most of the cases of interest, is described by the **Fick’s equations**:

\[
\begin{align*}
-D \frac{\partial c(x,t)}{\partial x} &= \Gamma(x,t) \\
D \frac{\partial^2 c(x,t)}{\partial x^2} &= \frac{\partial c(x,t)}{\partial t}
\end{align*}
\]

where \(c(x,t)\) is the concentration in the solid and \(\Gamma\) is the flow of molecules per \(\text{cm}^2\).

In the limit of this model, the outgassing rate is equal to a half of the flux of atoms arriving at the surface by diffusion (2 H atoms = 1 H\(_2\) molecule):

\[
q(t) = -\frac{1}{2} D \left. \frac{\partial c(x,t)}{\partial x} \right|_{x=\text{SURF}}.
\]
Theory of outgassing: diffusion of dissolved gas

Diffusion model of $H_2$ outgassing: slab approximation

Case study 1:

316 LN Stainless steel: CERN AT-VAC int. note
J-P Bojon, N. Hilleret, B. Versolatto

stainless steel sheets 1.5-mm thick

- As received
- $\times$ After vacuum firing

Each bakeout reduces the outgassing rate by a factor of $\approx 1.8$
Theory of outgassing: diffusion of dissolved gas

Diffusion model of H₂ outgassing: slab approximation

Case of study 2:

Stainless steel: CERN unpublished results (Géraldine Chuste)

Desorption energy: stainless steel

Vacuum pipe dimensions

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>200 cm</td>
</tr>
<tr>
<td>Diameter</td>
<td>3.4 cm</td>
</tr>
<tr>
<td>Thickness</td>
<td>2 mm</td>
</tr>
</tbody>
</table>

Literature:

0.5 eV/at. ≈ diffusion energy of hydrogen in austenitic stainless steel

OK!

3. 10⁻¹² Torr.l.s⁻¹.cm⁻²

Ed = 11 kCal/mol ~ 0.5 eV/at.
Theory of outgassing: diffusion of dissolved gas

\[
\frac{D(T) \cdot c_0}{\sqrt{\pi \cdot (D(T_f)t_f + D(T_{bo})t_{bo})}}
\]

Parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of the firing treatment</td>
<td>(T_f)</td>
<td>950°C</td>
</tr>
<tr>
<td>Duration of the firing treatment</td>
<td>(t_f)</td>
<td>2 hours</td>
</tr>
<tr>
<td>In situ bakeout temperature</td>
<td>(T_{bo})</td>
<td>150°C</td>
</tr>
<tr>
<td>Duration of the in situ bakeout</td>
<td>(t_{bo})</td>
<td>24 hours</td>
</tr>
<tr>
<td>Initial content of residual hydrogen</td>
<td>(c_0)</td>
<td>1 ppm wt (≈50 ppm at.)</td>
</tr>
<tr>
<td>Hydrogen equilibrium concentration on slab surfaces during firing</td>
<td>(c_w)</td>
<td>0.06 ppm wt. Equivalent to (P_{H_2}=1.3 \times 10^{-5}) mbar</td>
</tr>
</tbody>
</table>

Case of study 3:

- For zero pressure in the furnace
- 10^{-5} Torr pressure in the furnace

Semi-infinite model
Theory of outgassing: diffusion of dissolved gas

Water in polymers

Case of study 4:

Chosen value for diffusivity of water molecules in polyimide:

\[ D_{H_2O} \approx 10^{-9} \, \text{cm}^2/\text{s} \]

Thick Kapton slab; impermeable in one face.

Thin Kapton slab; impermeable in one face.
Outgassing databases: be attentive!

**Ti 6Al 4V ?**

Google: ‘outgassing vacuum materials’

**Princeton Plasma Physics Lab**


**Fermi National Accelerator Laboratory**

http://lss.fnal.gov/archive/tm/TM-1615.pdf

http://home.fnal.gov/~mlwong/outgas_rev.htm#ss

**NASA**

https://outgassing.nasa.gov/

**Vacom**

# A Compilation of Outgassing Data on Vacuum Materials

<table>
<thead>
<tr>
<th>CATEGORY II</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>KAPTON (H-FILM)</td>
<td>$1 \times 10^{-11}$</td>
<td>25-150</td>
<td>DUS</td>
<td>2</td>
</tr>
<tr>
<td>KAPTON (H-FILM)</td>
<td>$8 \times 10^{-7}$</td>
<td>300</td>
<td>DUS</td>
<td>Gen. Atomic</td>
</tr>
<tr>
<td>POLYIMIDE SD-1</td>
<td>$9 \times 10^{-9}$</td>
<td>250</td>
<td>DUS</td>
<td>Gen. Atomic</td>
</tr>
<tr>
<td>TITANIUM 6AL4V</td>
<td>$1.8 \times 10^{-9}$</td>
<td>-</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>VITON E60C</td>
<td>$1 \times 10^{-7}$</td>
<td>225</td>
<td>DUS</td>
<td>2</td>
</tr>
<tr>
<td>VITON E60C</td>
<td>$2 \times 10^{-9}$</td>
<td>144</td>
<td>DUS</td>
<td>2</td>
</tr>
<tr>
<td>VITON E60C</td>
<td>$6 \times 10^{-1}$</td>
<td>95</td>
<td>DUS</td>
<td>2</td>
</tr>
<tr>
<td>VITON - A</td>
<td>$1 \times 10^{-7}$</td>
<td>280</td>
<td>DUS</td>
<td>1</td>
</tr>
</tbody>
</table>

*Torr-lit-sec$^{-1}$cm$^{-2}$

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Printed in Great Britain

**Space environment and vacuum properties of spacecraft materials**

T J Patrick, *University College London. Mullard Space Science Laboratory, Holmbury St Mary, Dorking, Surrey RH5 6NT, UK*
<table>
<thead>
<tr>
<th>Material</th>
<th>Application</th>
<th>Manufacturer</th>
<th>TML (°,ο)</th>
<th>CVCM (°,ο)</th>
<th>Outgassing rate, 10 h Elsey²³ (torr ls⁻¹ cm⁻²)</th>
<th>(Pa m⁻¹)</th>
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<tbody>
<tr>
<td>Steel, stainless, BS 1449 321 S 12</td>
<td>Fittings</td>
<td></td>
<td>1.4 x 10⁻⁹</td>
<td>1.9 x 10⁻⁶</td>
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<td>Titanium 6 Al 4 V (IMI 318)</td>
<td>Fittings</td>
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<td>1.8 x 10⁻⁹</td>
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<td>3.5 x 10⁻⁸</td>
<td>4.7 x 10⁻⁵</td>
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<td>PTFE, Teflon</td>
<td>Wire sleeving</td>
<td>Du Pont</td>
<td>0.00</td>
<td>0</td>
<td>2.5 x 10⁻⁸</td>
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<td>PTFE-glass-MoS₂, composite, Duroid</td>
<td>Bearings</td>
<td>Rogers</td>
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<td>Perfluoroether, Fomblin</td>
<td>Oil and grease</td>
<td>Montedison</td>
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<td>FEP, Teflon, film</td>
<td>Thermal insulation</td>
<td>Du Pont</td>
<td>0.02</td>
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<td>Fiberglass woven cloth, Betadecloth</td>
<td>Thermal insulation</td>
<td>Stevens</td>
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<td>Viton A fluorocarbon rubber</td>
<td>Seals</td>
<td>Du Pont</td>
<td>0.22</td>
<td>0.02</td>
<td>10⁻⁷</td>
<td>10⁻⁴</td>
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<td>Silicone elastomer, 93500</td>
<td>Potting, seals</td>
<td>Dow Corning</td>
<td>0.30</td>
<td>E</td>
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<td>CIBA</td>
<td>0.40</td>
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<td>Polyurethane, Solithane 113/300</td>
<td>Conformal coating</td>
<td>Thiokol</td>
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<td>E</td>
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<td>Solid lubricant</td>
<td>Du Pont</td>
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<td>Polyurethane Z 306</td>
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<td>Hughson</td>
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<td>E</td>
<td>0.07</td>
<td>1.50</td>
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<td>Resin loctite AA/primer N</td>
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</tbody>
</table>
Outgassing of vacuum materials—II

R J Elsey, The Rutherford Laboratory, Chilton, England

A paper in our Education Series: The Theory and Practice of Vacuum Science and Technology in Schools and Colleges.

<table>
<thead>
<tr>
<th>Material</th>
<th>$K_1$ torr l. s$^{-1}$ cm$^{-2} \times 10^{10}$</th>
<th>$\alpha_1$</th>
<th>$K_{10}$ torr l. s$^{-1}$ cm$^{-2} \times 10^{10}$</th>
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<table>
<thead>
<tr>
<th>Material</th>
<th>Treatment</th>
<th>1 hour  $10^{10}$ s$^{-1}$ cm$^{-2}$</th>
<th>slope</th>
<th>10 hours  $10^{10}$ s$^{-1}$ cm$^{-2}$</th>
<th>slope</th>
<th>25 hours  $10^{10}$ s$^{-1}$ cm$^{-2}$</th>
<th>slope</th>
<th>50 hours  $10^{10}$ s$^{-1}$ cm$^{-2}$</th>
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<td>6</td>
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<td>1 value</td>
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<tr>
<td>Ti6Al4V</td>
<td>crude</td>
<td>1 value</td>
<td></td>
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<td>2 values</td>
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</tr>
</tbody>
</table>

1963
A Schram, Le Vide
Ti, crude, 2 values

1975
R J Elsey, Vacuum

1981
T J Patrick, Vacuum

1982
Princeton data base
Ti6Al4V, crude, 2 values

1963
Ti, crude, 2 values

1975
R J Elsey, Vacuum

1981
T J Patrick, Vacuum

1982
Princeton data base
Ti6Al4V, crude, 2 values
Conclusions

Outgassing rates depends on **materials and treatments**.

For **unbaked metals**, **water vapour is the leading outgassed** molecule. Its outgassing rate is **inversely proportional to the pumping time**. It is not strongly dependent on treatment and grade. Venting to air cancel the effect of previous gas release,

Multi-energy adsorption models explain the pressure decrease.

For **baked metals**, the outgassing process is **dominated by hydrogen**. It depends on the nature of the material and, **strongly, on the applied thermal treatment**. **Venting to air does not recharge hydrogen** into solid metal used for vacuum chambers.

**Diffusion theory explains the measured data and is predictive** for hydrogen content and wall thicknesses generally used for particle accelerators.

Organic materials absorb and release much more gas than metals; their gas release rate is higher and lasts longer than metallic alloys. **Avoid any polymer** (if you can)!
Thanks for your attention
Reminder: 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 \( k_B T \).
- The same number of molecules is expressed by different pressure-volume values at different temperatures. In general, the pressure-volume quantities are quoted at room temperature: 296 K.

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

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

for \( T = T_{RT} = 296 \) K

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

Outgassing rate of water vapour for polymers


- Unbaked Viton
- Baked Viton