MESURES de DEGAZAGE

G. Vandoni, CERN

Definitions, Units
Some theory and phenomenology with some tentative explanation
Methods of measurement:
  Throughput
    conductance modulation
    two path
  Pressure rate-of-rise (accumulation)
  Coupling throughput and accumulation
  Total mass loss
  TPD-TDS
“[Intrinsic] Outgassing rate is the instantaneous net amount of gas leaving the material per unit time.”

AVS 9.1-1964 Reporting of Outgassing Data

Measured outgassing rate is the difference between intrinsic outgassing rate and the rate of reabsorption of the surfaces in the test chamber.

Depending on sticking s, the desorbed gas may re-absorb on the vessel or the sample itself after multiple collisions.
Definitions

**fr. Dégazage**

- **Dégazage thermique**
- **Eng.** Degassing: (particle or thermally) induced

- **Eng.** Outgassing: spontaneous, thermal

- **Eng.** Degassing: deliberate removal of gas from a solid or liquid in vacuum as the result of the impact of molecules, electrons, ions, photons, or by heating.

**Outgassing:** spontaneous evolution of gas from a solid or a liquid in a vacuum

**Outgassing flux** is the quantity of gas leaving the surface per unit time at a specified time \( t \) after the start of evacuation

**Fr. eng.** Désorption: release of adsorbed molecules as the result of the impact of particles or by thermal energy
Glossary

\[ Q : \text{outgassing rate, total, i.e., gas released per unit time} \ (\text{should read } \dot{Q}) \]

\[ q : \text{surface specific outgassing rate, total, i.e., gas released per unit time and unit surface} \ (\text{should read } \dot{q}) \]

\[ p : \text{pressure} \quad p_o : \text{pressure at time } t_o \quad p_u : \text{pressure at time } \infty \]

\[ S : \text{pumping speed} \quad S_{eff} : \text{effective (at the vessel entrance) pumping speed} \]

\[ A : \text{surface area, effective (macroscopic)} \]

\[ V : \text{volume of the vacuum vessel} \]
Units of gas quantity

\[ p \cdot V = N \cdot k_B T = N_{\text{mol}} \cdot R \cdot T \]

\[ Q = \frac{d(pV)}{dt} = \frac{dN}{dt} \cdot k_B T = \frac{dN_{\text{mol}}}{dt} \cdot RT \]

\( N \) number of molecules
\( N_{\text{mol}} \) number of moles, i.e., of batches of \( 6.02 \times 10^{23} \) molecules

\[ R = k_B N_A \]

<table>
<thead>
<tr>
<th>molecules</th>
<th>( k_B )</th>
<th>([k_B \text{ units}])</th>
<th>((1/k_B T)) at 296 K</th>
<th>([1/(k_B T) \text{ units}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.38 \times 10^{-23}</td>
<td>Pa \cdot m^3 \cdot K^{-1}</td>
<td>2.45 \times 10^{20}</td>
<td>((\text{Pa} \cdot \text{m}^3)^{-1})</td>
<td></td>
</tr>
<tr>
<td>1.38 \times 10^{-22}</td>
<td>mbar \cdot l \cdot K^{-1}</td>
<td>2.45 \times 10^{19}</td>
<td>((\text{mbar} \cdot \text{l})^{-1})</td>
<td></td>
</tr>
<tr>
<td>1.04 \times 10^{-22}</td>
<td>torr \cdot l \cdot K^{-1}</td>
<td>3.3 \times 10^{19}</td>
<td>((\text{torr} \cdot \text{l})^{-1})</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>moles</th>
<th>( R )</th>
<th>([R \text{ units}])</th>
<th>( RT ) at 296 K</th>
<th>([RT \text{ units}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.31</td>
<td>Pa m^3 K^{-1} mol^{-1}</td>
<td>2.46 \times 10^3</td>
<td>Pa m^3 mol^{-1}</td>
<td></td>
</tr>
<tr>
<td>83.1</td>
<td>mbar l K^{-1} mol^{-1}</td>
<td>2.46 \times 10^4</td>
<td>mbar l mol^{-1}</td>
<td></td>
</tr>
<tr>
<td>62.4</td>
<td>torr l K^{-1} mol^{-1}</td>
<td>1.85 \times 10^4</td>
<td>torr l mol^{-1}</td>
<td></td>
</tr>
</tbody>
</table>
Units of outgassing rates

\[ q = \frac{Q}{A} = \frac{p \cdot V}{A \cdot \text{time}} = \frac{N \cdot k_B T}{A \cdot \text{time}} = \frac{N_{\text{mol}} \cdot R \cdot T}{A \cdot \text{time}} \]

<table>
<thead>
<tr>
<th>From</th>
<th>To</th>
<th>( \frac{Pa \cdot m^3}{s \cdot m^2} )</th>
<th>( \frac{mbar \cdot l}{s \cdot cm^2} )</th>
<th>( \frac{torr \cdot l}{s \cdot cm^2} )</th>
<th>( \frac{molecules}{s \cdot cm^2} )</th>
<th>( \frac{moles}{s \cdot cm^2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{Pa \cdot m^3}{s \cdot m^2} )</td>
<td></td>
<td>10^{-3}</td>
<td>7.5 \times 10^{-4}</td>
<td>2.5 \times 10^{16}</td>
<td>4.1 \times 10^{-8}</td>
<td></td>
</tr>
<tr>
<td>( \frac{mbar \cdot l}{s \cdot cm^2} )</td>
<td>10^{3}</td>
<td></td>
<td>0.75</td>
<td>2.5 \times 10^{19}</td>
<td>4.1 \times 10^{-5}</td>
<td></td>
</tr>
<tr>
<td>( \frac{torr \cdot l}{s \cdot cm^2} )</td>
<td>1330</td>
<td>1.33</td>
<td></td>
<td>3.3 \times 10^{19}</td>
<td>5.4 \times 10^{-5}</td>
<td></td>
</tr>
<tr>
<td>( \frac{molecules}{s \cdot cm^2} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.66 \times 10^{-24}</td>
<td></td>
</tr>
<tr>
<td>( \frac{moles}{s \cdot cm^2} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.02 \times 10^{23}</td>
<td></td>
</tr>
</tbody>
</table>

Conversion from \( pV \) to \( N \) or \( N_{\text{mol}} \) at 296K*

* standard AMBIENT temperature (and pressure) **SATP**: 296K ± 3K
standard temperature and pressure **STP**: 273.15K
Gas quantity to mass

\[ M = \frac{pV}{RT} M_{\text{mol}} \]

\[ M_{\text{mol}} : \text{molecular weight of the gas} \]

Gas flux [mbar·s\(^{-1}\)] \(\rightarrow\) mass loss rate [g s\(^{-1}\)]

\[ Q = \frac{d(pV)}{dt} = \frac{dM}{dt} \frac{RT}{M_{\text{mol}}} \]

If gas species not known, \(M_{\text{mol}}=28\text{g}\) and outgassing data in nitrogen equivalent.
Why measure outgassing rates

In absence of leaks, the total outgassing rate $Q$ at time $t$ and the applied pumping speed $S$ determine the pressure in the system at time $t$.

$$p = \frac{Q}{S} + p_u$$

(1)*

$$p(t) = \frac{Q(t)}{S} + p_u$$

$p_u$ ultimate pressure (at $\infty$ time)

$S$ can be varied by ~ 3 orders of magnitude: 1 to 1000 l·s$^{-1}$

$Q$ may vary by > 10 orders of magnitude: $10^{-5}$ to $10^{-15}$ mbar·l·s$^{-1}$·cm$^{-2}$

Sound design of a vacuum system requires knowledge and limitation of $Q$

*Strictly, (1) is valid only in a volume where gas evolves from surfaces and flows due to pumping: not where large $T$ differences exist.
## Typical outgassing rates

<table>
<thead>
<tr>
<th>Material</th>
<th>mbar l s⁻¹ cm⁻²</th>
<th>molecules s⁻¹ cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neoprene, non-baked, @10h</td>
<td>10⁻⁵ (H₂O)</td>
<td>3.3 x 10¹⁴</td>
</tr>
<tr>
<td>Viton, non-baked, @10h</td>
<td>10⁻⁷ (H₂O)</td>
<td>3.3 x 10¹²</td>
</tr>
<tr>
<td>Viton, baked</td>
<td>5 x 10⁻¹⁰ (H₂O)</td>
<td>1 x 10¹⁰</td>
</tr>
<tr>
<td>Unbaked stainless steel @10h</td>
<td>3 x 10⁻¹⁰ (H₂O)</td>
<td>6.6 x 10⁹</td>
</tr>
<tr>
<td>Baked stainless steel (150°C, 24h)</td>
<td>3 x 10⁻¹² (H₂)</td>
<td>6.6 x 10⁷</td>
</tr>
<tr>
<td>Vacuum fired stainless steel, 4 cycles 300°C, 24h</td>
<td>10⁻¹⁴ (H₂)</td>
<td>6.6 x 10⁵</td>
</tr>
<tr>
<td>Baked OFS Copper (200°C, 24h)</td>
<td>10⁻¹⁴ (H₂)</td>
<td>6.6 x 10⁵</td>
</tr>
<tr>
<td>Ti-Zr-V activated at 180°C (24h)</td>
<td>&lt;10⁻¹⁶ (CH₄)</td>
<td>&lt;3.3 x 10³</td>
</tr>
<tr>
<td>Ti-Zr-V activated at 180°C (24h)</td>
<td>≈ 10⁻¹⁸ (Kr)</td>
<td>≈ 30</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gauge</th>
<th>mbar l s⁻¹</th>
<th>molecules s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayard-Alpert gauge, SVT, W filament</td>
<td>≈ 10⁻⁹ (CO, CO₂,H₂)</td>
<td>≈ 3 x 10¹⁰</td>
</tr>
<tr>
<td>B-A gauge SVT, thoriated filament</td>
<td>≈ 10⁻¹⁰ (CO, CO₂,H₂)</td>
<td>≈ 3 x 10⁹</td>
</tr>
<tr>
<td>QMS Inficon</td>
<td>10⁻⁸ ÷ 10⁻¹⁰</td>
<td>3 x 10¹¹ ÷ 3 x 10⁹</td>
</tr>
</tbody>
</table>
## Gas specific outgassing rates

### Metals, unbaked, at 10h [torr·s⁻¹·cm⁻²]

<table>
<thead>
<tr>
<th>Gas</th>
<th>Al</th>
<th>Cu</th>
<th>St.steel</th>
<th>Be</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>7 x 10⁻¹²</td>
<td>1.4 x 10⁻¹¹</td>
<td>7 x 10⁻¹²</td>
<td>1.4 x 10⁻¹¹</td>
</tr>
<tr>
<td>CH₄</td>
<td>5 x 10⁻¹³</td>
<td>5 x 10⁻¹³</td>
<td>5 x 10⁻¹³</td>
<td>1 x 10⁻¹²</td>
</tr>
<tr>
<td>CO</td>
<td>5 x 10⁻¹²</td>
<td>1 x 10⁻¹²</td>
<td>5 x 10⁻¹²</td>
<td>1 x 10⁻¹¹</td>
</tr>
<tr>
<td>CO₂</td>
<td>5 x 10⁻¹³</td>
<td>2.5 x 10⁻¹³</td>
<td>5 x 10⁻¹³</td>
<td>1 x 10⁻¹²</td>
</tr>
<tr>
<td>H₂O</td>
<td>3 x 10⁻¹⁰</td>
<td>3 x 10⁻¹⁰</td>
<td>3 x 10⁻¹⁰</td>
<td>6 x 10⁻¹⁰</td>
</tr>
</tbody>
</table>

### Metals, baked, at 50h [torr·s⁻¹·cm⁻²]

<table>
<thead>
<tr>
<th>Gas</th>
<th>Al</th>
<th>Cu</th>
<th>St.steel</th>
<th>Be</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>5 x 10⁻¹³</td>
<td>1 x 10⁻¹²</td>
<td>5 x 10⁻¹³</td>
<td>1 x 10⁻¹²</td>
</tr>
<tr>
<td>CH₄</td>
<td>5 x 10⁻¹⁵</td>
<td>5 x 10⁻¹⁵</td>
<td>5 x 10⁻¹⁵</td>
<td>1 x 10⁻¹⁴</td>
</tr>
<tr>
<td>CO</td>
<td>1 x 10⁻¹⁴</td>
<td>1 x 10⁻¹⁴</td>
<td>1 x 10⁻¹⁴</td>
<td>2 x 10⁻¹⁴</td>
</tr>
<tr>
<td>CO₂</td>
<td>1 x 10⁻¹⁴</td>
<td>5 x 10⁻¹⁵</td>
<td>1 x 10⁻¹⁴</td>
<td>2 x 10⁻¹⁴</td>
</tr>
<tr>
<td>H₂O</td>
<td>1 x 10⁻¹⁴</td>
<td>&lt;1 x 10⁻¹⁵</td>
<td>1 x 10⁻¹⁴</td>
<td>2 x 10⁻¹⁴</td>
</tr>
</tbody>
</table>

CAUTION: Design values circulating at CERN, no reference
Pumpdown: effect of outgassing on \( p(t) \)

In a “perfect” vacuum vessel of volume \( V \), pumped with constant pumping speed \( S \), if \( p(t) \) is the pressure at time \( t \), without leaks, permeation or outgassing:

\[
V \frac{dp}{dt} = -Sp = -Q_{\text{pumped}}
\]

**Volume depletion**

\[
\ln p_{\text{ideal}} = \ln p_o - \frac{S}{V} t
\]

\[
p_{\text{ideal}} = p_o e^{-\frac{S}{V} t}
\]

\[
p_{\text{real}} = k t^{-n}
\]

with \( 0.5 < n < 1.2 \)

\[
\ln p_{\text{real}} = k - n \ln t
\]

[Graph showing \( \ln p \) versus \( t \)]
Pumpdown: effect of outgassing on $p(t)$

In a “perfect” vacuum vessel of volume $V$, pumped with constant pumping speed $S$, if $p(t)$ is the pressure at time $t$, without leaks, permeation or outgassing:

$$ V \frac{dp}{dt} = -Sp = -Q_{pumped} $$

Volume depletion

$$ \ln p_{ideal} = \ln p_o - \frac{S}{V} t $$

$$ p_{ideal} = p_o e^{-\frac{S}{V} t} $$

$$ p_{real} = kt^{-n} \quad \text{with } 0.5 \leq n \leq 1.2 $$

At constant pumping speed $S$, this is also the time dependence of $q$

$$ q(t) = \frac{q_1}{t^n} \quad \text{where } q_1 \text{ is the specific outgassing rate after 1 unit time (1h) pumping} $$

$n \sim 1$ for metallic unbaked surfaces

$n \sim 0.5$ for elastomers

Knowing $q_{1h}$ (or $q_{10h}$) $\rightarrow$ extrapolate
Outgassing rate time evolution

Let’s go for some insight into outgassing time evolution...

NB:
For baked metals, $q(t)$ goes with $n \approx 0.5$ on a short timescale and with $\exp(-t/t_o)$ on a long timescale. Of course, on a very different absolute range...

- Type III, plastics $q(t) \propto e^{-t/t_o}$
- Type II, plastics $q(t) \propto t^{-1/2}$ $n=1/2$
- Type I, unbaked metals $q(t) \propto t^{-1}$ $n=1$
Molecules deposited while exposed at atmospheric pressure desorb under vacuum. (Dissociation) and diffusion of atomic species in the near surface, through microcracks and the oxyde layer. Diffusion from the bulk of atomic H, trapped during manufacturing process, recombination at the surface and desorption as H₂. Permeation through thin walls and elastomeric seals.
**Surface bonding**

**Physisorption**
- Van der Waals
- $E_b \approx 6-40\text{kJ/mole}, \ 0.06-0.4\text{ eV/molecule}$
- $z_0 \approx 2-4\text{Å}$
- Coverage: $\sim$ multilayer

**Chemisorption**
- Electron sharing
- $E_b \approx 40-1000\text{kJ/mole}, \ 0.4-10\text{eV/molecule}$
- $z_0 \approx 1.5\text{Å}$
- Coverage $\sim 1\text{ monolayer}$

Real surface: multitude of adsorption sites, hence of binding energies
Simplified treatment (Frenkel 1924):
In a potential well of depth $E_b$, the molecule vibrates with characteristic frequency $\nu = kT/h \sim 10^{13} \text{ s}^{-1}$.

Frequency of attempts to overcome the potential barrier and break free from the surface.

Probability that fluctuation in thermal energy is $\geq E_b$: $\exp(-E_b/kT)$

Boltzmann factor

Probability per unit time that a molecule will desorb:

$$\sigma = \nu_0 \exp\left(-\frac{E_b}{kT}\right) = \frac{1}{\tau_0} \exp\left(-\frac{E_b}{kT}\right)$$

Frequency of attempts

Probability to get free in 1 attempt

Average time of stay:

$$\tau = \frac{1}{\sigma} = 10^{-13} \exp\left(\frac{E_b}{kT}\right)$$
Time of stay: binding energy

\[ \tau_a = \frac{1}{\sigma} = 10^{-13} \exp\left( \frac{E_b}{kT} \right) \]

The stronger \( E_b \), or the lower \( T \), the longer the average time of stay (sojourn time)

<table>
<thead>
<tr>
<th>( E_b ) [kJ/mol]</th>
<th>( E_b ) [eV]</th>
<th>( \tau_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.06</td>
<td>( 1.2 \times 10^{-12} ) s</td>
</tr>
<tr>
<td>15</td>
<td>0.16</td>
<td>( 5 \times 10^{-11} ) s</td>
</tr>
<tr>
<td>40</td>
<td>0.41</td>
<td>( 1.2 \times 10^{-6} ) s</td>
</tr>
<tr>
<td>60</td>
<td>0.62</td>
<td>( 5.5 \times 10^{-3} ) s</td>
</tr>
<tr>
<td>80</td>
<td>0.83</td>
<td>15 s</td>
</tr>
<tr>
<td>90</td>
<td>0.93</td>
<td>15 min</td>
</tr>
<tr>
<td>95</td>
<td>0.98</td>
<td>2 h</td>
</tr>
<tr>
<td>100</td>
<td>1.04</td>
<td>( 8 \times 10^4 ) s ( \sim ) 1 d</td>
</tr>
<tr>
<td>120</td>
<td>1.24</td>
<td>( 2 \times 10^8 ) s ( \sim ) 10 years</td>
</tr>
<tr>
<td>150</td>
<td>1.55</td>
<td>( 7 \times 10^{13} ) s ( \sim ) 20,000 years</td>
</tr>
</tbody>
</table>

kT at room temperature: 0.025eV

- physisorption
- weak chemisorption
- Neither very short nor very long times bother us.
- strong chemisorption

Dependence of stay time on binding energy at room temperature

1eV~97kJ/mole
Time of stay: temperature

\[ \tau_a = 1 / \sigma = 10^{-13} \exp\left( \frac{E_b}{kT} \right) \]

Typical binding energy of H\(_2\)O:
80kJ/mole, 0.8eV

<table>
<thead>
<tr>
<th>T [K]</th>
<th>(\tau_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>10(^{41}) s</td>
</tr>
<tr>
<td>295</td>
<td>15 s</td>
</tr>
<tr>
<td>300</td>
<td>1 (\mu)s</td>
</tr>
</tbody>
</table>

Effect of temperature on stay time

We still don’t know why \(q(t) \sim t^n\), but we may recognize several features of desorption, which then determine changes in outgassing rates:

- Effect of temperature: cryopumping, bakeout
- Quantities and coverages: \(\theta \leq 1\)ML (by stay time)
- Binding energies

Bridge between microscopic view and macroscopic observation

\[ \Rightarrow \text{TPD-TDS} \]
Unbaked metals: $t^{-1}$

Starting from the surface physics vision, several models have been attempted to explain the $t^{-1}$ behaviour and relative independence from treatments, history, composition: superposition of isotherms, surface and sub-surface diffusion through micropores in the oxide layer...

Dominated by $\text{H}_2\text{O}$, chemisorbed at the first 1÷2 layers~ binding energy 85-90 kJ/mol, stay time [min-hr]

For standard rugosity, $q(t) \approx \frac{3 \cdot 10^{-9}}{t[h]} \text{ mbar} \cdot \text{l} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$
Some initial concentration of gas is trapped in a slab of finite dimension $d$. 

The concentration of this gas is zero at the border of the slab.

The gas will get out of the solid progressively, because of concentration gradient and gradually empty the slab.
**Diffusion: polymers and baked metals**

**Fick’s laws**

Flux \( \sim \) concentration gradient

\[
q = -D \frac{dc}{dx}
\]

Conservation of mass

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

Limit at small times

\( t < 0.025 \frac{d^2}{D} \)

Concentration decays quickly close to the boundaries of the solid, remaining fairly constant in the bulk of the slab.

Outgassing rate:

\[
q \propto t^{-\frac{1}{2}} = \frac{1}{\sqrt{t}}
\]

"Volume depletion"

Limit at long times

\( t > 0.025 \frac{d^2}{D} \)

Concentration may be considered as uniform in the slab of material. It decreases exponentially with time, with time constant \( \frac{d^2}{p^2D} \)

Outgassing rate:

\[
q \propto \exp \left(-\frac{t}{t_o}\right)
\]
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 polymers is orders of magnitude larger than in metals.

Example

Water solubility:
0.1 to 0.5 wt.% (4.4 to 22x10^{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 x 10^{-9} cm^2 s^{-1}
2000 times larger than that reported for H in austenitic stainless steel.


Courtesy P. Chiggiato
Outgassing rate of materials

**Time dependence**

- **Type I, metals**
  \( q(t) \propto t^{-1} \)
  Determined by \( \text{H}_2\text{O} \) desorption

- **Type II, plastics**
  \( q(t) \propto t^{-1/2} \)
  Bulk diffusion rate limited

- **Type III, plastics**
  \( q(t) \propto e^{-t/t_0} \)
  Volume depletion

**Graph:**
- Type I, metals
  \( q(t) \propto t^{-1} \)
- Type II, plastics
  \( q(t) \propto t^{-1/2} \)
- Type III, plastics
  \( q(t) \propto e^{-t/t_0} \)
Outgassing measurement methods

Méthode par débit

\[ p \rightarrow Q \rightarrow C \rightarrow S_p \]

Méthode par accumulation

\[ p \rightarrow Q_b \rightarrow Q_s \]

Méthode par double pesée

\[ \text{22} \rightarrow \text{21} \]
Throughput method

In steady state (after an equilibration time):

\[ p = \frac{Q}{S_{\text{eff}}} \quad p(t) = \frac{Q(t)}{S_{\text{eff}}} \]

\[ Q = Q_s + Q_v \]

\( Q_v \) determined by a blank run, with \( p_v(t) \) the blank pumpdown curve.

Outgassing rate:

Calculated from raw data, by subtracting pressure readings at corresponding times:

\[ \Delta p(t) = p(t) - p_v(t) \]

\[ q_{10h} = \frac{S_{\text{eff}} \Delta p(10h)}{A_s} \]

\( A_s \) sample’s surface

Sample outgassing rate
Throughput method: choice of C

Orifice: chamfered edge, conical section transmission $\alpha = 1 \pm 0.00001$ (see K.F.Poulter 1973)

Conductance is then:

$$C = A \sqrt{\frac{RT}{2\pi M_{mol}}} = 11.8 [l/s] \ A \ in \ cm^2$$

The area of C is chosen as a function of the expected outgassing rate and taking the error sources into account.

If $C \ll S_p$, i.e. $S_p > 50C$, then $S_{eff} \approx C$

If C too small w.r. to $sA_s$, readsoption on the vessel’s walls will fake the measurement and result in estimated Q too small.

$C > 10x$ gauge pumping speed

$A_s$ sample area, $s$ sticking coeff for evolved gases
Sensitivity limits -1-

**H₂ outgassing**

Baked, stainless steel spherical vessel

\[ q_v = 3 \cdot 10^{-12} \text{ mbar} \cdot \text{l} \cdot \text{s}^{-1} \cdot \text{cm}^{-2} \]

\[ V = 10l \]

\[ Q_v = 6 \cdot 10^{-9} \text{ mbar} \cdot \text{l} \cdot \text{s}^{-1} \]

\[ S_{\text{eff}} = 10l \cdot \text{s}^{-1} \]

Gauge outgassing, W filament

\[ Q_{\text{gauge}} = 10^{-9} \text{ mbar} \cdot \text{l} \cdot \text{s}^{-1} \]

Bkg outgassing

\[ Q_{\text{bkg}} = 7 \cdot 10^{-9} \text{ mbar} \cdot \text{l} \cdot \text{s}^{-1} \]

Detection limit of outgassing rate: >25% of background

\[ Q_{\text{min}} = 1.8 \cdot 10^{-9} \text{ mbar} \cdot \text{l} \cdot \text{s}^{-1} \]

Background pressure

\[ p_{\text{bkg}} = 7 \cdot 10^{-10} \text{ mbar} \]
Sensitivity limits -2-

H₂ outgassing

Baked, vacuum fired stainless steel spherical vessel

\[ q_v \approx 10^{-14} \text{ mbar} \cdot \text{l} \cdot \text{s}^{-1} \cdot \text{cm}^{-2} \]

\[ V = 10 \text{l} \quad \Rightarrow \quad Q_v = 2.2 \cdot 10^{-11} \text{ mbar} \cdot \text{l} \cdot \text{s}^{-1} \]

\[ S_{\text{eff}} = 10 \text{l} \cdot \text{s}^{-1} \]

Gauge outgassing, thoriated filament

\[ Q_{\text{gauge}} = 10^{-10} \text{ mbar} \cdot \text{l} \cdot \text{s}^{-1} \]

Bkg outgassing

\[ Q_{\text{bkg}} = 1.2 \cdot 10^{-10} \text{ mbar} \cdot \text{l} \cdot \text{s}^{-1} \]

Detection limit of outgassing rate: >25% of background

\[ Q_{\text{min}} = 3 \cdot 10^{-11} \text{ mbar} \cdot \text{l} \cdot \text{s}^{-1} \]
Effect of readsorption

**H₂O outgassing**

Measured outgassing rate is not intrinsic outgassing rate.

\[ Q_m < Q_i \]

The vessel and the sample itself, readsorb the outgassed flux.

- \( A \) re-pumping surface
- \( s \) sticking coefficient
- \( S_A \) re-pumping speed

\[ S_A = A \cdot s \cdot \sqrt{\frac{RT}{2\pi n}} = 11.8 \cdot A \cdot s \text{[l/s]} \quad A \text{ in cm} \]

Due to readsorption, measurement will “miss” a part of the intrinsic outgassing flux.

Remember:
H₂O sticking \( s=10^{-3} \) at room temperature
Reasorption in the throughput method

\[ S_A = A \cdot s \cdot \sqrt{\frac{RT}{2\pi m}} = 11.8 \cdot A \cdot s \text{[l/s]} \quad A \text{ in cm}^2 \]

\[ S_{\text{eff}} \quad \text{effective applied pumping speed, typically 10l/s} \]

\[ S_{\text{eff}} / S_A \quad \text{Relevant parameter} \]

The gas released by the sample is not entirely evacuated. A fraction of it is reabsorbed by sample or vessel.

\[ Q_m = pS_{\text{eff}} \]

\[ Q_{\text{int}} = p(S_A + S_{\text{eff}}) = pS_{\text{eff}} \left(1 + \frac{S_A}{S_{\text{eff}}} \right) \]

\[ \frac{Q_{\text{int}}}{Q_m} = 1 + \frac{S_A}{S_{\text{eff}}} \]

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Sticking s=10⁻³ (H₂O) at 20°C
C=1cm²
\[ \frac{Q_{\text{int}}}{Q_m} \approx 3 \]

10l vessel +100cm² sample
Outgassing of gauge:
Contribution to $Q$

- W filament
  $$Q_{gauge} = 10^{-9} \text{ mbar} \cdot \text{l} \cdot \text{s}^{-1}$$

- Thoriated W filament
  $$Q_{gauge} = 10^{-10} \text{ mbar} \cdot \text{l} \cdot \text{s}^{-1}$$

Error relevant for $H_2$, when vessel background becomes comparable

Pumping effect of gauge:
Contribution to $S$

Ionic pumping
Ions are trapped at the collector and are removed from the gas phase as neutrals; and may be buried by implantation.
Affects all gases including noble gases.
$\sim 10^{-2}$ l/s

Chemical pumping
Reaction or cracking at the hot filament.
Dissociation of $H_2O$, $C_nH_{2n}$, $H_2$. Does not affect monoatomic gases.
Thoria coated filaments have lower temperature, hence lower $S$.
$\sim 1$ l/s
Fisher-Mommsen dome

...or how to reduce error due to pressure anisotropy

Fisher-Mommsen dome, used for Pumping speed measurements more generally permits a precise quantification of gas flux via pressure difference measurement:

\[ Q = C(p_2 - p_1) \]

Thermodynamically, \( p \) is defined only in an enclosed system at equilibrium. To approach isotropy, we need a “infinite volume” dome, and gauges far from the pump. The gauge should then measure a isotropic, Maxwellian gas distribution. The inlet \( C \) and pump \( S \) should have a negligible effect on the distribution.

The Fisher Mommsen dome has geometry, dimensions and position of the gauge such that measured pressures are identical to those measurable in the ideal case.

E. Fischer, H. Mommsen, Vacuum 17, 309 (1967)
A method to get rid of the measurement error in $S$ and the differential error of 2 gauges

\[ C = C_1, C_2 \quad S = S_1, S_2 \quad p = p_1, p_2 \quad Q = (p - p_{pump}) \cdot S \]

\[
\begin{align*}
\frac{1}{S} &= \frac{1}{S_p} + \frac{1}{C} \\
p &= \frac{Q}{C} + \text{const}
\end{align*}
\]

Involves ratios and not absolute values

Independent of $S_p$

$Q$, $S_p$ should not vary while the conductance is varied ($P_p$ should remain constant).

K.Terada et al, J.Vac.Sci.Technol. A7 (189) 2397
Variable stop of a aerial photography camera, embedded in a gate valve: C varies between 3.5 and 173 l/s/

R.P.Henry, Le Vide, No 82 (1959) 226; Le Vide No 144 (1969) 316
Two path method

Sample chamber

\[ Q = Q_A - Q_B = (P_{1A} - P_{2A}) \cdot C - (P_{1B} - P_{2B}) \cdot C = (P_{1A} - P_{1B}) \cdot C \]

\( P_{2A} = P_{2B} \) constant! determined by \( Q + Q_1 + Q_2 \) and \( S \).

Needs only \( G_1 \).
\( G_2 \) used just for concomitant, conventional throughput method

\[ Q_A = (P_{1A} - P_{2A}) \cdot C \]

\[ Q_B = (P_{1B} - P_{2B}) \cdot C \]

Two path method

\[ P_{1A} - P_{1B} \] cancels constant systematic error

**Single gauge method!**
Used for very low outgassing rates: by differential measurement, X-ray limit and outgassing of gauge are cancelled out.

\[ C=6 \text{ l/s}, Q_{\text{min}} \rightarrow 10^{-14} \text{ mbarl/s cm}^2 \]


**Systematic errors**
Small difference between 2 pumping paths is sought: outgassing rate of apparatus outside test chamber must be kept as low as possible.
- \( V_a, V_b \) all metal
- Connection pipes to \( V_a, V_b \): short
- Gas flux \( q_p \) from valves and connecting pipes measured by blank, with 2-path method.
Two path method

Pressure(-rate-of)-rise method

The system is pumped down to \( p_o \). At time \( t_o \), the system is suddenly isolated from the pumps. Pressure begins to rise.

\[
\begin{align*}
\left. \frac{dN}{dt} \right|_{t=t_o} &= Q(t_o) = \frac{V}{k_B T} \frac{dP}{dt} \\
Q &= Q_b + Q_s \\
\left. \frac{dp}{dt} \right|_{t=t_o} &= k_B T \frac{Q_b(t_o) + Q_s(t_o)}{V}
\end{align*}
\]

The rate of rise \( dp/dt \) is highest at the instant of isolation. It will gradually decrease to zero when outgassing rate and surface readsorption + gauge pumping balance each other.

Pumpdown may be resumed by opening the isolation valve, before the pressure has increased significantly (e.g. less than x 3).
Error sources

**Background** outgassing from the vacuum vessel, the gauges, the isolation valve
- Limit background by choosing all-metal isolation valve
- Apply a reproducible venting procedure, take measurement at the same time

To be significant, \( Q_S \geq 0.25 \times Q_B \)

**Example:**
Baked spherical vessel, \( V=10l, q_v=3\cdot10^{-12} \text{ mbar l/s.cm}^2 \) Area=2245cm²,
- \( Q_B = 6.7\cdot10^{-9} \text{ mbar l/s} \)
- \( Q_S \geq 1.7\cdot10^{-9} \text{ mbar l/s} \) \( \rightarrow \) with a sample of 100cm², \( q_S \geq 1.7\cdot10^{-11} \text{ mbar l/s.cm}^2 \)

\( \rightarrow \) Very practical if the outgassing sample is the vessel itself

**Pumping action of the gauge**
- Non-pumping gauges: spinning rotor, capacitance diaphragm
- If a hot-cathode ionization gauge is used, reduce electron current and choose a low-temperature filament
- **Switch gauge on and off intermittently**

**Readsorption** on the sample and the vessel’s walls
Effect of readsorption: pressure rise method

Pressure rise may be followed for a long period of time (sometimes even ~30 days). To minimize gauges’ pumping, gauges can be switched on/off intermittently.

If \( Q = \text{constant} \), then \( p(t) = \text{linear without repumping} \)

\[
p(t) - p_o = k_B T \frac{Q}{V} \cdot t
\]

Measurement of \( \text{H}_2 \) outgassing in a baked and vacuum fired stainless steel vessel show a linear increase of \( p(t) \):

This demonstrates that \( \text{H}_2 \) does not reabsorb on stainless steel.


In the case of \( \text{H}_2 \) outgassing, the error is then only due to gauge pumping.
Accumulation + throughput method

Extends the limits of the throughput method to lowest outgassing rates
- Limits the effect of the gauge
- Limits the effect of the system’s outgassing

The sample is in a separate vessel. After pumpdown, the sample vessel is isolated and gas is accumulated for a time \( t_a \).
At time \( t_a \) the leak valve is opened. Pressure evolves as shown below.

\[
G(t_a) = G_s + G_b = S_{\text{eff}} \int_{t_a}^{t_a+\Delta t} p(t) \, dt
\]

\( G \) total evolved gas quantity (not rate!)

\( t_a \) may be very long!
Accumulation + throughput method

\[ \int_{t_a}^{t_a+\Delta t} p(t)dt = I(t_a) \]
measured for different \( t_a \)

Linear regression of \( I(t_a) \) versus \( t_a \): slope gives \( Q \)

\[ G(t_a) = Q \cdot t_a = S_{eff} \int_{t_a}^{t_a+\Delta t} p(t)dt \]

Limitation: **repumping during** \( t_a \). For gases which are not reabsorbed and when the test vessel is the sample, very high sensitivity may be reached.

Ex. \(~30\ \text{molecules} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}\), Kr trapped during production by sputtering and evolving from NEG
Mass (or Weight) loss method

On a laboratory microbalance, a sample and its containing boat (Cu) is weighed. A collector plate is also weighed. The sample is put in a vacuum vessel, evacuated at $10^{-6}$ mbar, then heated at 125°C for 24h. After this time, the sample and the collector are weighed again.

Simultaneous measure of

Total Mass Loss

$$TML = \frac{m_o - m}{m_o} = \% m_o$$

Collected Volatile Condensable Materials

Quantity outgassed at 125°C and condensed on collector at 25°C

Water Vapor Regained

Mass of H$_2$O vapor regained after reconditioning, upon exposure to 50% humidity.

ASTM standard E-595-07 NASA database [outgassing.nasa.gov](http://outgassing.nasa.gov)
Mass (or Weight) loss method

ASTM standard test method E-595-07, based on apparatus developed at NASA

PROCEDURE:
- Conditioning (50% humidity, 23°C, 24h)
- Weighing of sample / Weighing of collector
- Evacuation at 10⁻⁶ mbar, keep at 125°C for 24h / Venting with dry inert gas
- Rapid (<2min) weighing of sample / Weighing of collector

QUANTITIES and Precision
Sample weight ~ 100 to 300mg
Balance precision: ±1μg
Theoretical limit precision: 0.002 %

Possible bias and mitigation
Cleanliness of manipulation
Inhomogeneity of sample
Control collectors are used to check cross contamination or poor technique: if these detect more than 50μg, the measure is discarded
TML system at CERN

Vacuum tank

Cooling circuit

Collector's chambers

Resistance-heated copper plate which contains 12 specimen chambers
At NASA, rate of weight loss was measured continuously, by weighing under vacuum

Podlaseck *et al*., Trans 9th AVS Symp (1962) 320
Temperature Programmed Desorption or Thermal Desorption Spectroscopy is a standard surface science technique which has been used to provide information on the binding energies of atomic and molecular species adsorbed on a solid surface.

Complementary technique to overcome sensitivity limitations of previous methods. Adapted to fundamental studies of interaction between gases and surfaces.

Requires knowledge or assumptions on the underlying physical model

Very useful on “simplified” systems, as usual in surface physics: monocrystals, few absorbed species, well-controlled preparation conditions.
Temperature Programmed Desorption

Provides information on binding energy of atoms and molecules on surfaces

\[
\frac{d\theta_m}{dt} = -\nu_0 \theta^n \exp \left( -\frac{E_d}{k_B T} \right)
\]

\( E_d \) desorption activation energy

Probability of desorption \( \sim \) frequency of attempts \( \nu_0 \), Boltzmann factor, function of coverage \( f(\theta) \).

\[
d\theta_m/dt \text{ is rate of desorption} = \text{probability of desorption} \times \text{number of molecules in monolayer } n_m
\]

Assumption: desorption rate of an adsorbate is \( \square \) to its measured partial pressure. This condition is rigorous only if pumping speed > rate of desorption.

Partial pressures are measured versus \( T \)
Analysis: rewrite Polanyi-Wigner equation

\[
\frac{d\theta_m}{dt} = -\nu_o \theta^n \exp\left(-\frac{E_d}{k_B T}\right)
\]

\[
\ln \frac{d\theta_m}{dt} = \ln \nu_o + n \ln \theta_m - \frac{E_d}{k_B T}
\]

Arrhenius plot:
Plot \(\ln(d\theta_m/dt)\) versus \(1/T\), obtain a straight line with

- slope \(-E_d/k_B\)
- intercept \(\ln(\nu_o) + n \ln(\theta_m)\)

Leading edge analysis: use only <5% of desorption trace, such that \(\theta_m\) is \(\sim\) constant.
Gauge pumping speed, readsorption, gauge and background outgassing, are all sources of error in outgassing rate measurements.

Care must be taken and case-by-case analysis, together with some knowledge of the adsorption, diffusion, outgassing physics is required to chose the best configuration.
Recommended practices for measuring and reporting outgassing data

Outgassing of vacuum materials I
R.J. Elsey, Vacuum 25 (7) 299 (1975)

Outgassing of vacuum materials II
R.J. Elsey, Vacuum 25 (8) 347 (1975)

P. Chiggiato, CAS 2006 Lecture, in pdf.

I am heartily grateful to P. Chiggiato for guiding me through the meanders of outgassing phenomenology, theory and measurement
Further reading

Measurement system for low outgassing materials by switching between two pumping paths

Accuracy of the conductance modulation method for the measurement of pumping speed and outgassing rate
Y.Tuzi, Vacuum 41, 2004 (1990)

Effects of readsorption on outgassing rate measurements

Monte-Carlo computation on molecular flow in pumping speed test domes
E.Fischer, H.Mommsen, ISR-VAC (1966)

Outgassing database NASA:
http://www.outgassing.nasa.gov

Outgassing database ESA:
http://esmat.esa.int/Services/outgassing_data/outgassing_data.html