Water outgassing rate* & adsorption isotherms

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***for a metallic surface**

Glossary

Coverage (θ): Ratio between occupied sites (N_m) and total amount of sites (N_s) available on a surface.
0 (empty surface) $\leq \theta \leq 1$ (full surface)

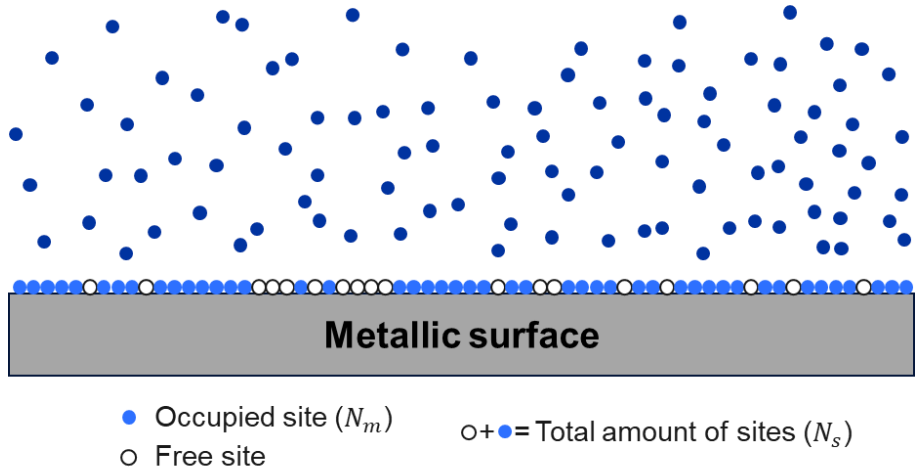
Sticking coefficient (s): probability of the surface to capture an impinging molecule ($0 \leq s \leq 1$).

Binding energy (E): energy of the bond between the water vapour molecule and the surface.

Sojourn time (τ): time spent by a molecule on a surface with a binding energy E at temperature T.

$$\tau = \tau_0 \, e^{\frac{E}{k_b T}} \text{ with } \tau_0 = 10^{13} \, s$$

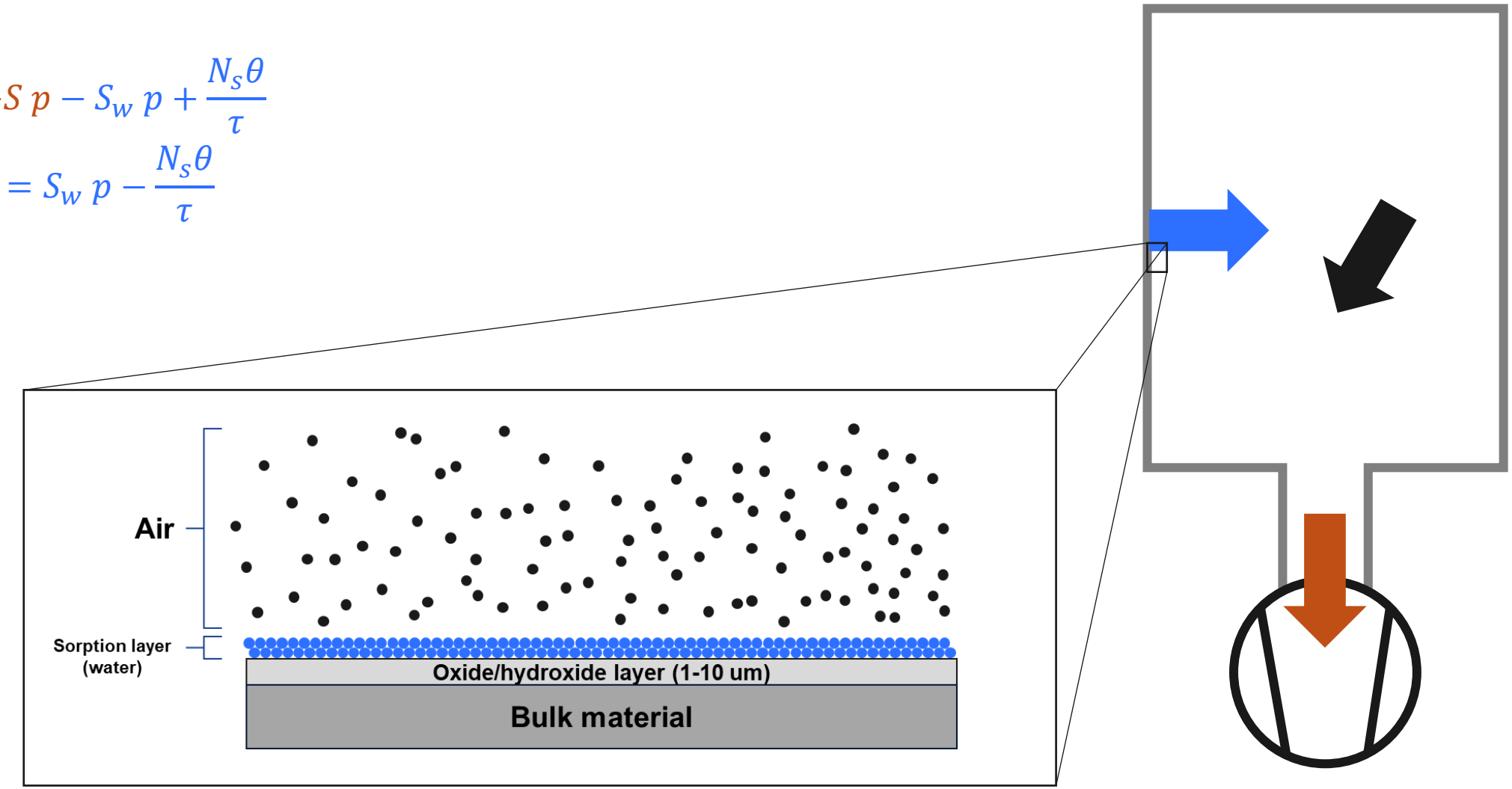
Adsorption isotherm: is a mathematical function that defines the relationship between the concentration of solute (water vapour) molecules in two phases (gas and solid) at the interface of the phases (surface), at constant temperature.



Vacuum system pumpdown: the mathematical approach

Mass balance equation [1,5]

$$\begin{cases} V\dfrac{dp}{dt} = -S\,p - S_w\,p + \dfrac{N_s\theta}{\tau} \\ N_s\dfrac{d\theta}{dt} = S_w\,p - \dfrac{N_s\theta}{\tau} \end{cases}$$



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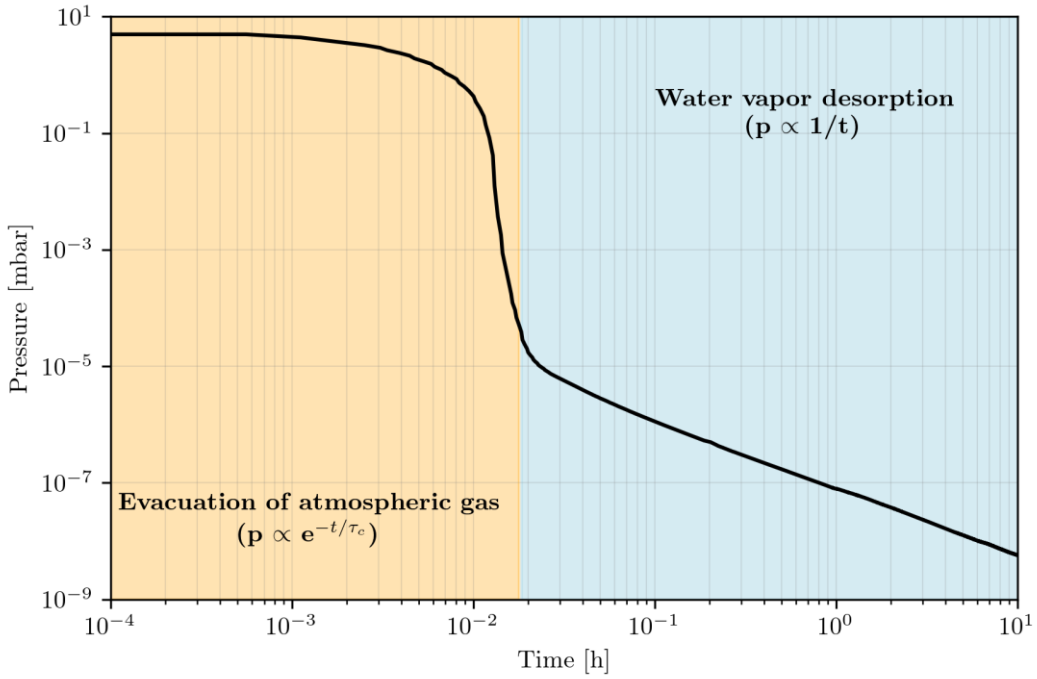
Beginning of the pumpdown $\left\{\frac{d\theta}{dt} \approx 0\right\}$:

$p(t) = p_0\, e^{-\frac{t}{\tau_c}}$ with $\tau_c = \frac{V}{S}$ characteristic pumping time

Desorption dominated pumpdown $\left\{\frac{dp}{dt} \approx 0,\ \tau_c < \tau,\ S \ll S_w\right\}$:

$$p(t) \approx \frac{N_s}{\tau\,(S + S_w)} \exp\left[-\frac{t}{\tau\left(1 + \frac{S_w}{S}\right)}\right]$$

Average time spent of a water molecule before leaving the system



Pumpdown of an AISI 304L chamber at 294 K.

Vacuum system pumpdown: the mathematical approach

The Edwards limit [1,2]

Desorption dominated pumpdown $\left\{\frac{dp}{dt} \approx 0,\ \tau_c < \tau,\ S \ll S_w\right\}$:

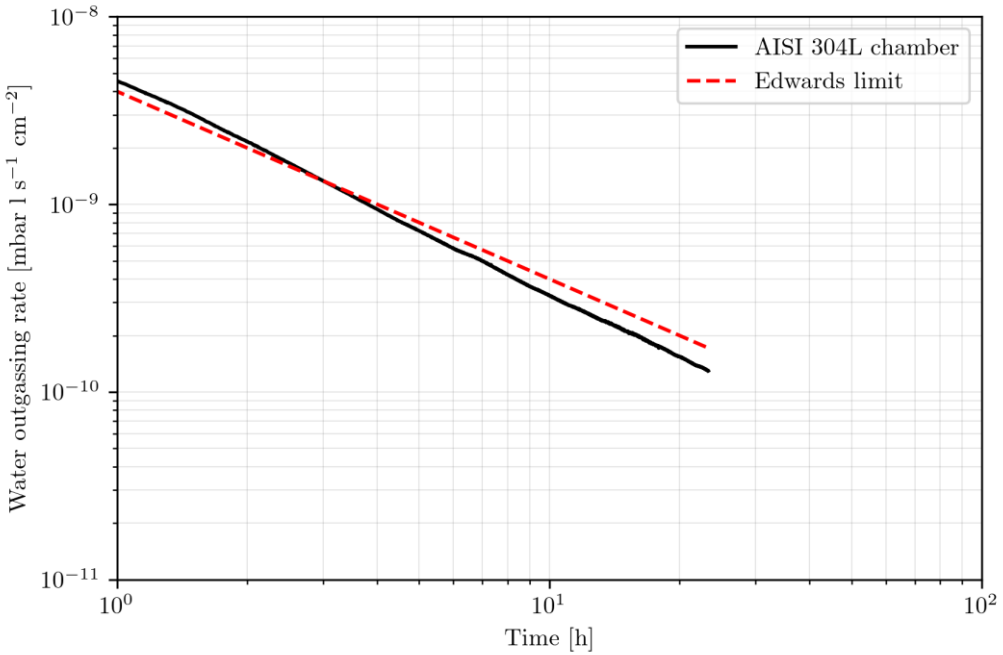
$$p(t) \approx \frac{N_s}{\tau\,(S + S_w)} \exp\left[-\frac{t}{\tau\left(1 + \frac{S_w}{S}\right)}\right]$$

Maximum pressure during pumpdown:

$$\frac{\partial P}{\partial \tau} = 0 \ \rightarrow\ \tau = \frac{t}{1 + \frac{S_w}{S}} \ \Rightarrow\ p(t)_{max} \approx \frac{N_s}{t\ e\ S}$$

Let's assume $n_m = 1\ ML\ \approx 10^{15}\ \frac{molecules}{cm^2}\ \approx 4 \times 10^{-5}\ \frac{mbar\ l}{cm^2}\ (@\ 293K)$[3,4]:

$$Q_{max} \approx \frac{4 \times 10^{-9}}{t\ [h]}\ \frac{mbar\ l}{s\ cm^2}$$



Pumpdown of an AISI 304L chamber at 294 K.

0D modelling and limitations

For most of the situations we encounter daily, we can approach with a 0D problem and apply a quasi-static equilibrium (Horikoshi-Kanazawa-Redhead condition[6-8]):

$$\left|\frac{dp}{dt}\right| \ll \frac{S_w}{V} = \frac{s\ A\ p\ \bar{v}}{4}\frac{1}{V}$$

The inequality is valid upon the satisfaction of two additional conditions:

- A surface site can be occupied by one and only one molecule at a time without dissociation.
- $s = const$ and equally probable for all the sites.

$$\theta \Longrightarrow \theta(p,T)\ fully\ reversible$$

It's a quasi-static equilibrium! Does not model very well dynamic effects (i.e. changes of pumping speed). For that, an energy distribution model as to be applied.

New formulation and possible ads. isotherms

$$V\frac{dp}{dt} = -S\,p \underbrace{- S_w\,p + \frac{N_s\theta}{\tau_w}}_{-N_s\frac{d\theta}{dt}} \quad \Rightarrow \quad V\frac{dp}{dt} = -S\,p - N_s\frac{d\theta}{dt} \quad \xRightarrow{chain\ rule} \quad V\frac{dp}{dt} = -S\,p - N_s\left(\frac{d\theta}{dp}\frac{dp}{dt} + \frac{d\theta}{dT}\frac{dT}{dt}\right)$$

$$\frac{dp}{dt} = \frac{-S\,p - N_s\frac{d\theta}{dT}\frac{dT}{dt}}{V + N_s\frac{d\theta}{dp}}$$

$\frac{dT}{dt}$: thermal cycle (bake-out)

Some adsorption isotherms that could be used:

Temkin

$$\theta(p,T) = \frac{R\,T}{E_0 - E_1} ln\left(\frac{1 + (p/p^*)\cdot e^{\frac{E_0}{R\,T}}}{1 + (p/p^*)\cdot e^{\frac{E_1}{R\,T}}}\right)$$

$$p^* = \frac{n_m\,4\,k_b T}{s\,\bar{v}\,\tau_0}$$

Dubinin-Radushkevich

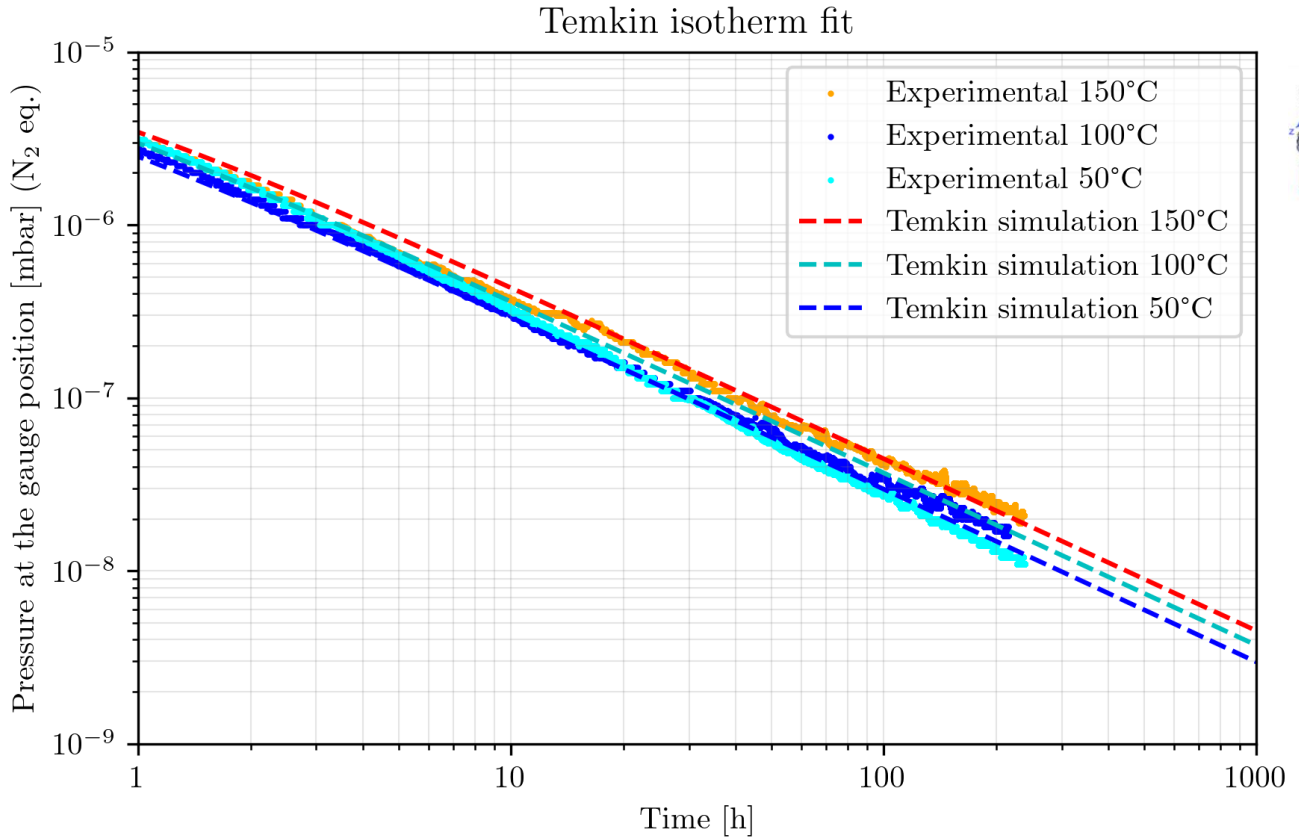
$$\theta(p,T) = \exp\left(-\left(\frac{R\,T}{\tilde{T}}\ln\left(\frac{p}{p_{sat}}\right)\right)^2\right)$$

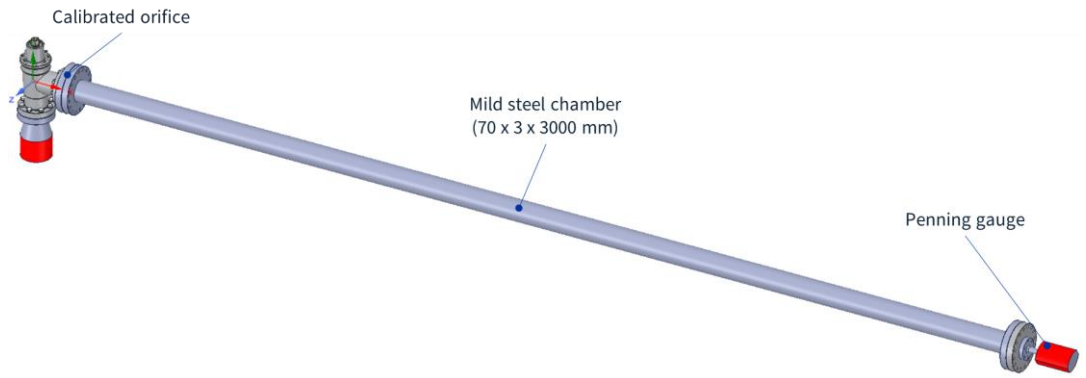
Many others (Sips, Freudlich, ..)

Experimental parameters extraction

Simplest approach:

Series of pumpdown at different temperatures to extract (and adjust) the isotherm parameters (N_m/n_m, E, etc.)





Mild steel chamber baked at 50, 100 and 150ºC.

(vented to lab conditions for 24h after each pumpdown)

Parameters extracted

n_m: 9.8×10^{15} $molecules/cm^2$

E_0: 1.5 eV

E_1: 0.3 eV

≈ 2 ML

Possible oxide contribution

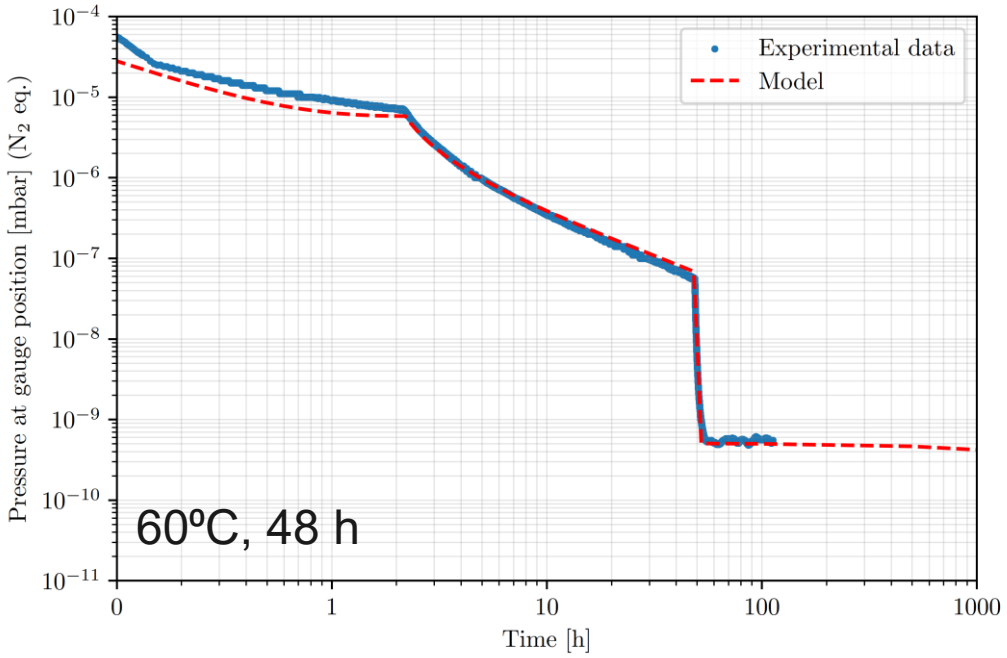
Bake-out simulation

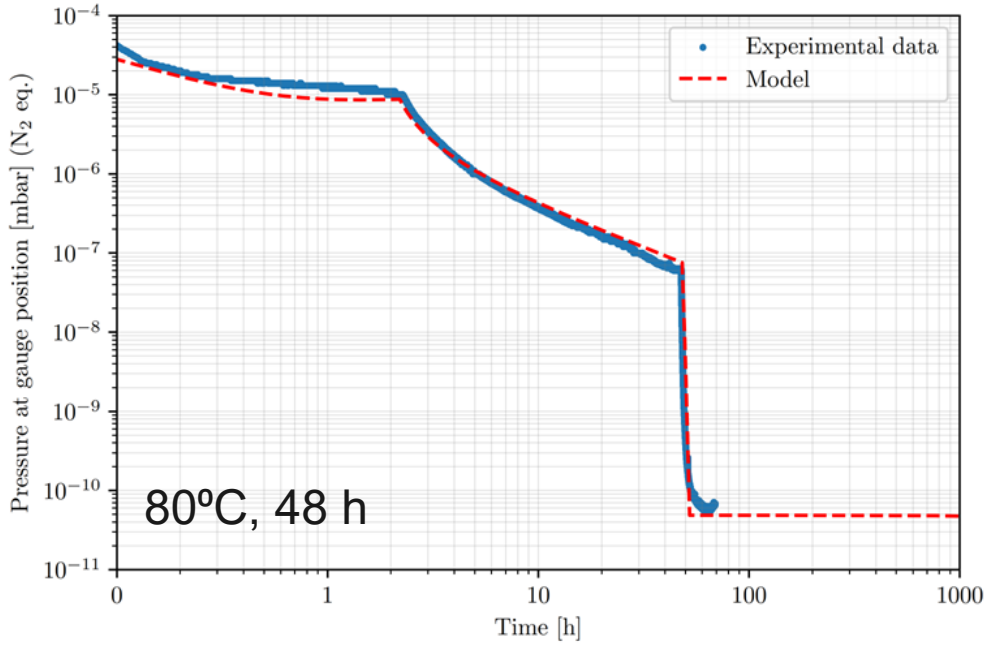
Parameters extracted

n_m: 9.8×10^{15} $molecules/cm^2$

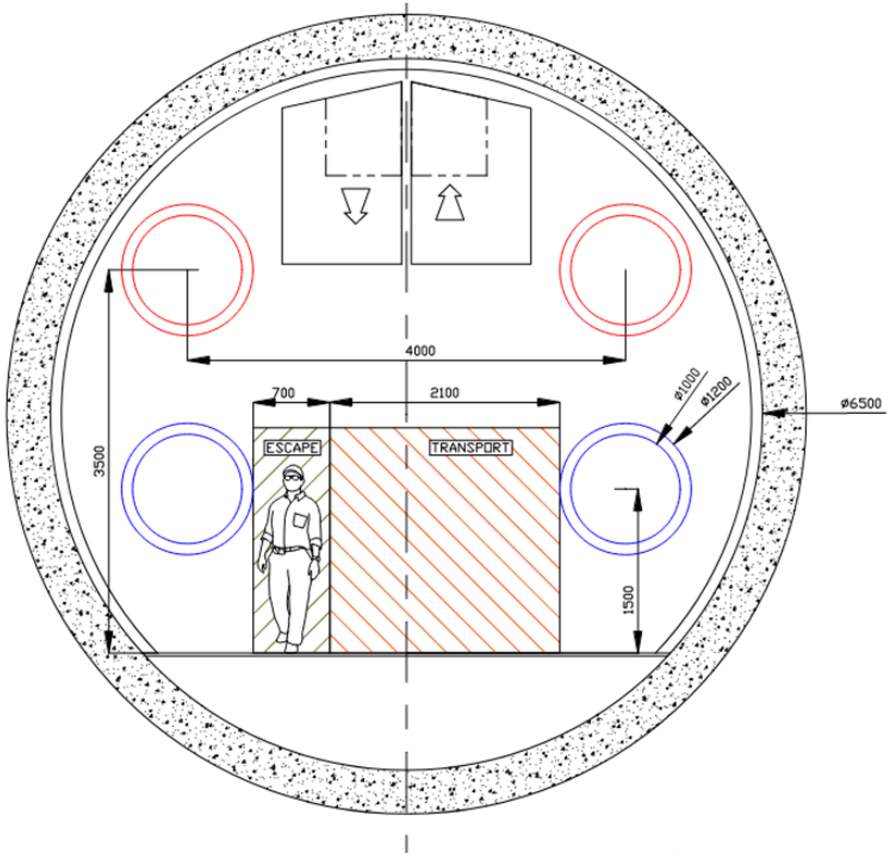
E_0: 1.5 eV

E_1: 0.3 eV





Example of application: the ET beam pipe vacuum design



Source: ET design report update 2020 and XIII ET symposium (2023)

Dimensions

- **Beampipe internal diameter: 1 m**
- **Total beampipe length: 120 km**

Partial pressure requirements

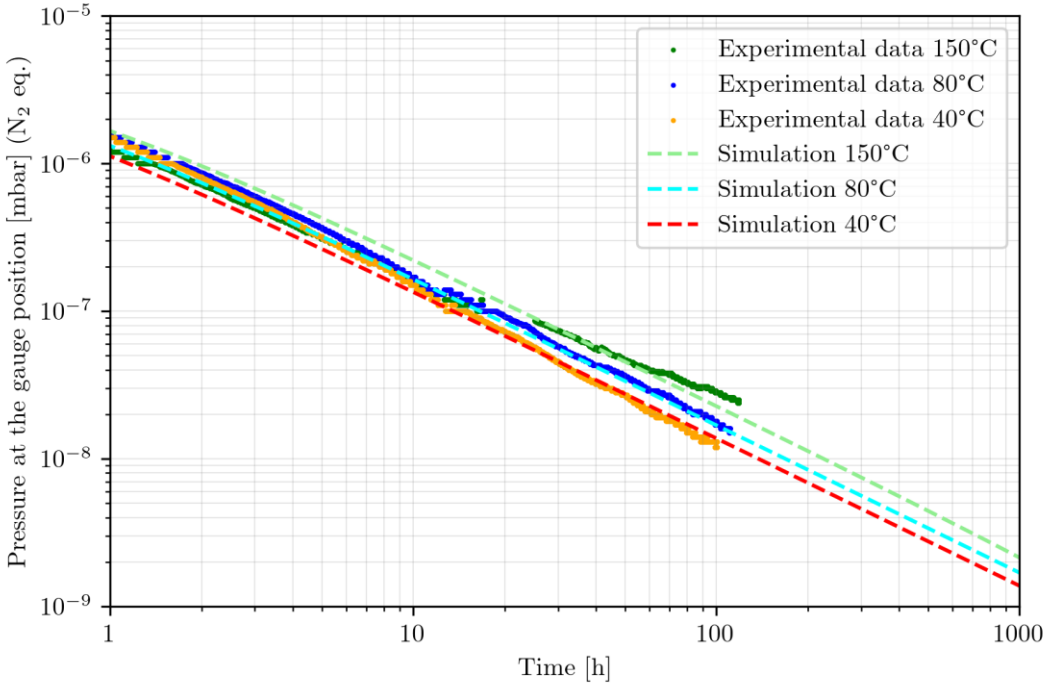
- P (H_2O) ≈ 10^{-11} mbar

Other requirements/characteristics

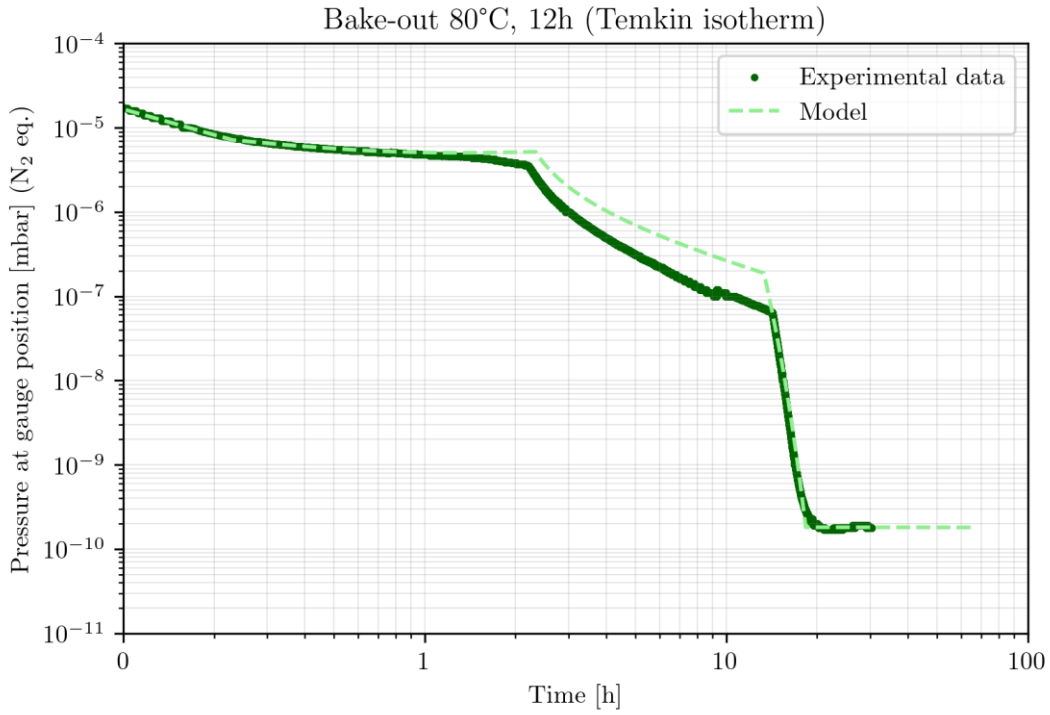
- Bakeout via direct joule effect
- Max bakeouts: 1 every 50 years [req.]
- Max bakeout temperature: 150ºC [~req.]
- Minimum sector length: 5 km
- Material: Ferritic stainless steel (AISI 441)

Example of application: the ET beam pipe vacuum design

AISI 441 H_2O partial pressure modelling with Temkin isotherm



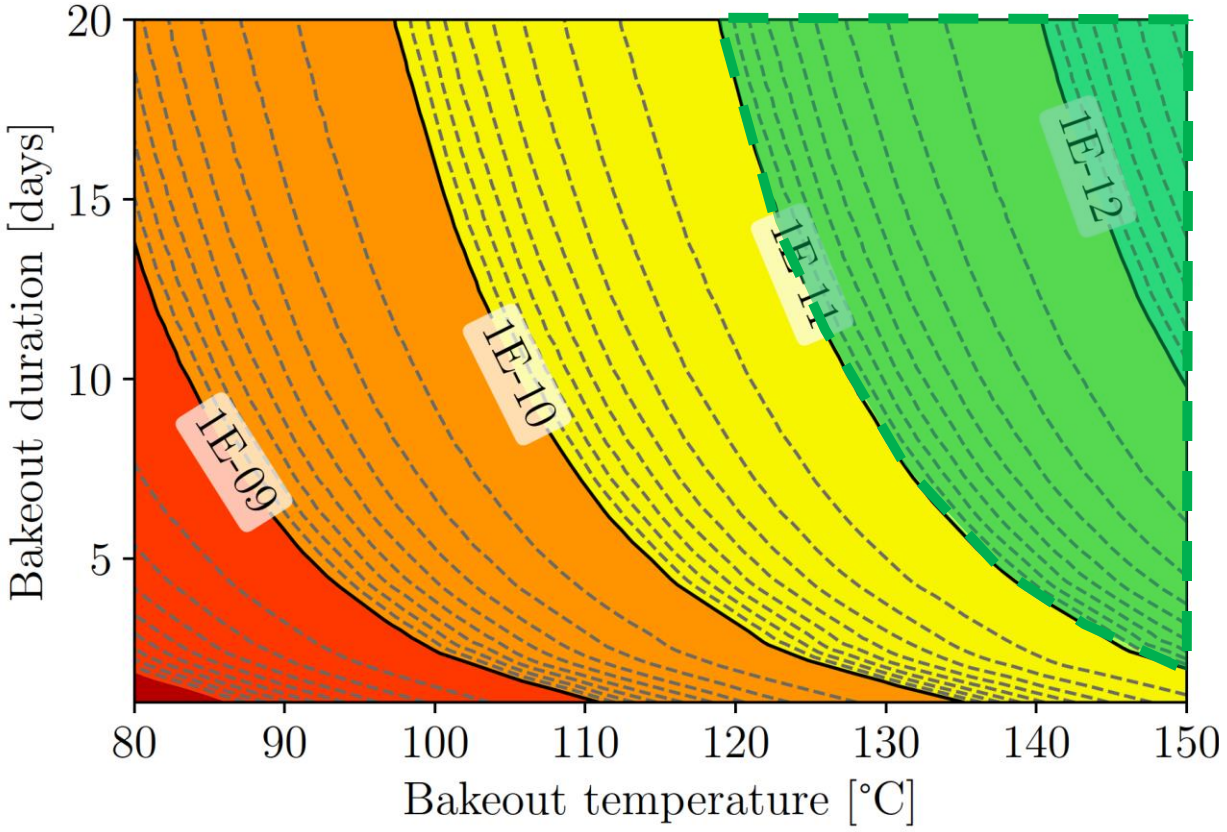
H_2O binding energy & coverage



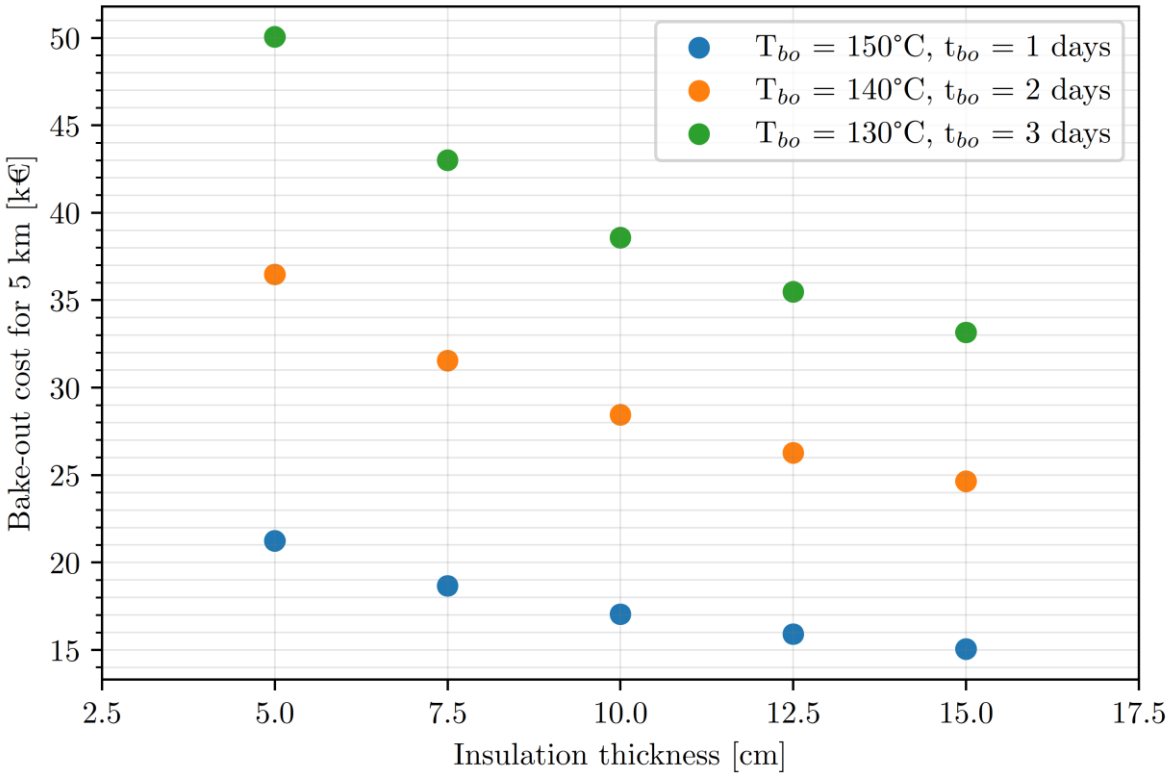
Example of application: the ET beam pipe vacuum design

Simulation of H_2O partial pressure after bakeout and insulation optimisation

H_2O pressure after bakeout between two pumps



Pumps distribution:1 Turbomolecular pump (700 l/s nominal) every 2000 m



Electricity cost per 5 km sector in function of T, duration and insulation thickness (mineral wool)

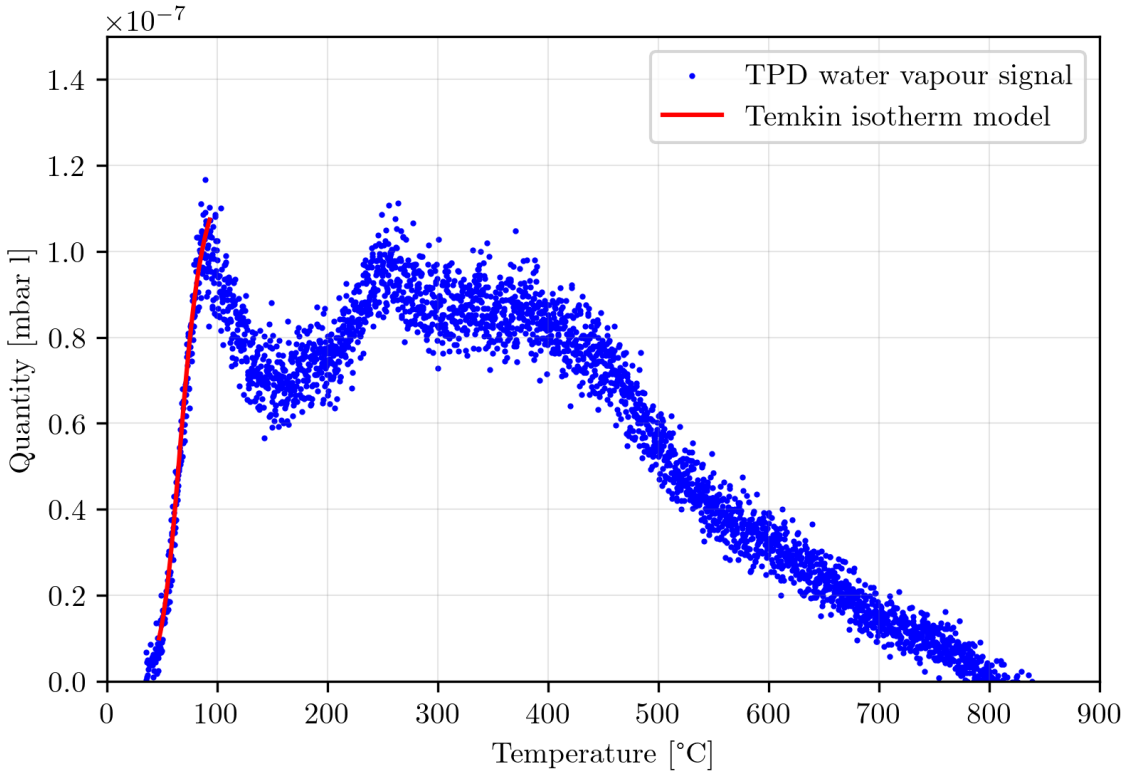
Conclusions and considerations

- **Simple first principles can get very close prediction of the water outgassing rate evolution.**
- **With a simple 0D quasi-equilibrium modelling we can model water outgassing behaviour of materials and vacuum systems at room temperature and during bakeout.**

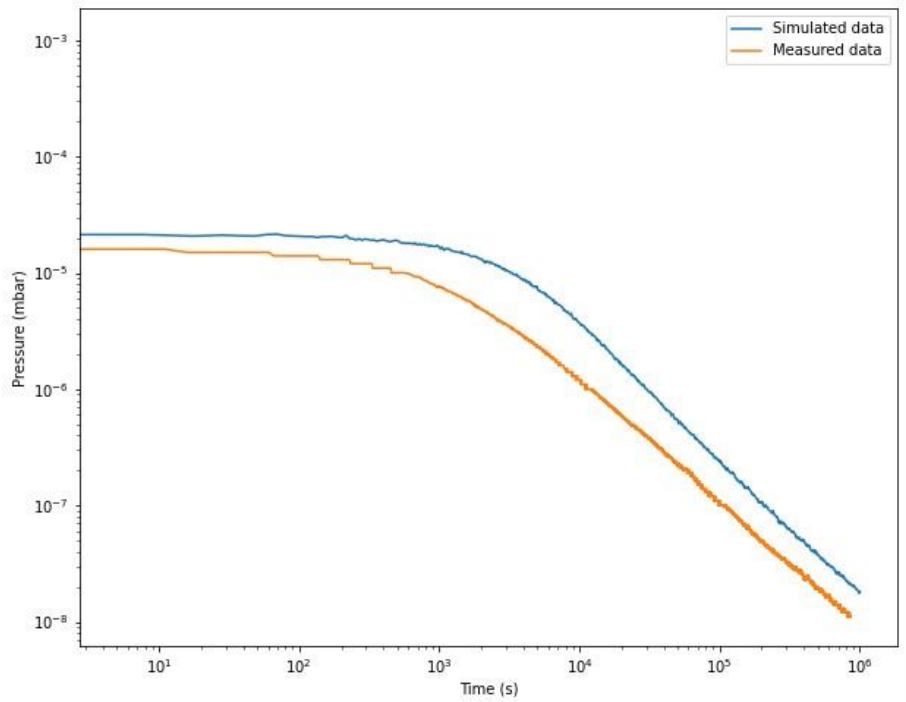
❖ **The discussed approach can be extended to 1D, 2D and 3D cases. For other applications, cryo-sorption (ice formation) and dynamic vacuum (change in pumping speed, vacuum accumulation) a more refined approach must be used for a better modelling.**

❖ **NOTE: the adsorption isotherms are a sandbox, their use without a proper experimental confirmation and reasoned evaluation might be highly misleading. Please use them wisely.**

Future developments (?)



H_2O binding energy &
coverage extraction from small samples via TPD
(useful for coatings characterisations)



Molflow+ / COST implemented isotherm to
simulate water outgassing in Molflow+
(Lindquist Henriksen – Ady – Kersevan - Scarcia)

Thank you for you attention

A special thanks goes to Jose Antonio Ferreira Somoza for the instructive talks and having introduced me to the topic

home.cern

References

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