Hydrogen permeation through a stainless steel membrane at small pressure differences

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**Introduction**

One of the main problems in UHV and EXV practice is to suppress the hydrogen outgassing rate $q_{\text{out}}$

- the ultimate pressure in UHV and EHV chambers
- the lifetime of sealed vacuum devices

lowest $q_{\text{out}} \Rightarrow$ baking at very high $T$?
the majority of H really expelled?
Introduction

The \( q_{\text{out}} \) is a consequence of a non-equilibrium state between in the dissolved and gas phase.

Equilibrium:

**formal condition:**

\[
\mu_{\text{diss.}} = \frac{1}{2} \mu_{\text{gas}}
\]

**experimental condition:**

\[
\frac{dp_{H_2}}{dt} = 0
\]
The theory

Equilibrium:

Sieverts law: \[ C_{\text{eq.}} = K_{S0} \exp\left(-\frac{E_S}{k_B T}\right)\sqrt{p_{H_2 \text{ eq.}}} \]

Solution \( \frac{1}{2}H_2 \rightarrow H + Me \) is endothermal reaction \((E_S > 0)\).

Example 1: \( T=1000^\circ\text{C}, \ p_{H_2} = 1\text{bar} \Rightarrow C_{\text{eq.}} = 1.2 \times 10^{19} \text{ H at./cm}^3 \)

Example 2: \( T=25^\circ\text{C}, \ p_{H_2} = 5 \times 10^{-4}\text{mbar} \Rightarrow C_{\text{eq.}} = 6.5 \times 10^{14} \text{ H at./cm}^3 \)

The relation has never been experimentally verified at low hydrogen pressures, since the equilibrium state has not been established during the time of the experiment.
Kinetics of approaching to the equilibrium:

1) Diffusion limited model (DLM) - diffusion of H atoms determines the $q_{\text{out}}$.

$$\frac{\partial C}{\partial t} = D(T) \nabla^2 C$$

Fourier characteristic time for a plate, thickness $d$:

$$F_0 = d^2 / 4D(T)$$

2) Recombination limited mod. (RLM) - $q_{\text{out}}$ determined by recombination of H atoms on the metal surface.

$$q_{\text{out}} = K_L(T)C_{\text{surf}}^2$$

$K_L(T)$ values are very scattered.

Observed $q_{\text{out}}$ values after thermal treatment much higher than predicted by DLM or RLM and seems to be pressure independent in the observation time.
The situation

- most papers report $q_{\text{out}}$ after some thermal procedure, indicating only that $\mu_{\text{diss}} > \mu_{\text{gas}}$
- little data available on measurements of the $q_{\text{out}}$ in situ at elevated $T$
- no data found about kinetics close to the equilibrium in the high vacuum range
- no data about the hydrogen concentration in the wall after the thermal procedure
The outline of our work

Verifying models of hydrogen interaction with stainless steel by:
- $q_{\text{out}}$ measurement during the 109 h processing at 200°C by the SRG
- $q_{\text{out}}$ measurement between 25°C and 55°C within 14 months by the SRG
- melting the cell in vacuum and the subsequent QMS quantitative analysis of released gases
Experimental

SS cell data:
- AISI304, AISI316L, Cu
- d=0.015 cm
- A=460 cm²
- V=125 cm³
Preprocessing - thermal outgassing:

- 109 hours at $T=200^\circ\text{C}$ $\Rightarrow$ equivalent to $F_{o}=23$

- $q_{\text{out}}$ measured by the pressure rise method using the SRG 1

- final $q_{\text{out}}(200^\circ\text{C})=4.5\times10^{-12}$ mbar l cm$^{-2}$s$^{-1}$ - before cool-down

- average H concentration decrease $\Delta C=8.8\times10^{16}$ at.H/cm$^3$

assuming that both surfaces outgassed equally
Preparation for the 14 month measurement:

1. the cell left to cool down to R.T.

2. the system was disconnected from the pumps

3. the pressure in the system increased into the $10^{-4}$ mbar range in some hours $\Rightarrow$ cell pinched-off
SRG pressure reading [mbar H₂ eq.]

- system alone
  dp/dt = 1.61 \times 10^{-8} \text{ mbar/s}
- cell alone
  dp/dt = -2.83 \times 10^{-10} \text{ mbar/s}
- pinch - off

Time [hours]
Measurements

The pressure in the cell was measured by the SRG2.

At the beginning the pressure in the cell was constantly decreasing; $\mu_{\text{diss}} < \mu_{\text{gas}}$

The $p(t)$ at the temperature jump $25^\circ\text{C} \rightarrow 55^\circ\text{C} \rightarrow 25^\circ\text{C}$
the $p(t)$ at several temperature jumps, equilibrium at 55°C
the \( p(t) \) at a longer period at 25\(^\circ\), after the jump 55\(^\circ\)C → 25\(^\circ\)
25°C→55°C jump followed by a long period at 55°C
very fast pressure rise immediately after the T jump

slow pressure rise, max. pressure, slow pressure fall
Hydrogen is permeating through the wall to the atmospheric side.

constant $\frac{dp}{dt} = -8 \times 10^{-12}$ mbar/s

$q_{perm} = 2.2 \times 10^{-15}$ mbar l cm$^{-2}$ s$^{-1}$

$q_{perm} = 4.8 \times 10^4$ molec. H$_2$ cm$^{-2}$ s$^{-1}$
The cell was kept at room temperature for the following 4 months, then...

we continued at 32°C, 42°C and 55°C.
$\Delta p (42^\circ C)$ in 8 days corresponds to $4 \times 10^{10}$ molec H$_2$/cm$^2$

Very fast pressure rise not displayed.

SRG offset has changed.

337-404d
after the long term SRG measurements, cell cut ⇒ pieces put in a quartz crucible within a quartz tubing ⇒ melted by RF in vacuum ⇒ QMS analysis
The most interesting finding

the calculated C at the upstream \( p = 1.7 \times 10^{-4} \text{ mbar} \) should be \( C = 5 \times 10^{14} \text{ at H/cm}^3 \), but in 5 melting cycles a lot of hydrogen was extracted: \( \Delta C = 7.6 \times 10^{18} \text{ at H/cm}^3 \)
Conclusions

- during the preprocessing (109h, 200°C, 23Fo)
  \[ \Delta C = 8.8 \times 10^{16} \text{ at.H/cm}^3 \ll \text{expected } C_0 \sim 10^{19} \text{ at.H/cm}^3 \]

The extraction of this tiny fraction of the total hydrogen content has an essential effect on the observed kinetics close to the equilibrium between stainless steel and H₂.

- a long-term pressure decrease indicates a permeation out of the cell to the atmosphere \( p(H_2) < 1.7 \times 10^{-4} \text{ mbar} \), (probably \( \ll \)) and thus never contributes a noticeable part to the \( q_{out} \) in UHV chamber even during the bake out.
Comparison with the DLM and RLM:

- measured $q_{\text{perm}} = 2.2 \times 10^{-15}$ mbar l cm$^{-2}$ s$^{-1}$ at 55°C, is lower than $q_{\text{perm}} = 3.4 \times 10^{-14}$ mbar l cm$^{-2}$ s$^{-1}$ (by the DLM)
- oxidised surfaces reduced the $q_{\text{perm}}$ by a factor of 15, (by the RLM), which is an acceptable agreement

DISCREPANCY IN THE PHYSICAL PICTURE

- both models apply Sievert's law, when $C \approx 5 \times 10^{14}$ at. H/cm$^3$
- the released H$_2$ during the melting $\Delta C = 7.6 \times 10^{18}$ at H/cm$^3$
  ⇒ a very low $q_{\text{out}}$ would be recorded for millenia if the UHV would be maintained in the cell by pumping!?
Our previous work


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