PRD-LMD End-of-year/Kick-off meeting

Droplet ejection from liquid metals

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Sn droplet ejection can lead to unacceptable core radiation

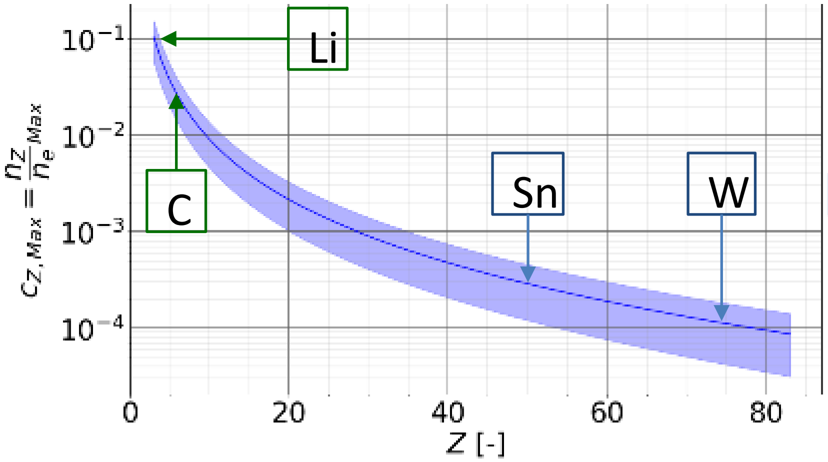
- Droplet emission observed from Sn in several different experiments[1,2,3]
- Could be strong limit on Sn CPS application due to core contamination
- Not observed for Li samples – why?
- Under what conditions happens, and how to prevent in Sn?

[1]A. Manhard *Nucl. Fusion* 60 (2020) 106007
[2]W. Ou *Nucl. Fusion* 61 (2021) 066030[3]
[3]J. G. A. Scholte *Nuclear Materials and Energy* 34 (2023) 101315

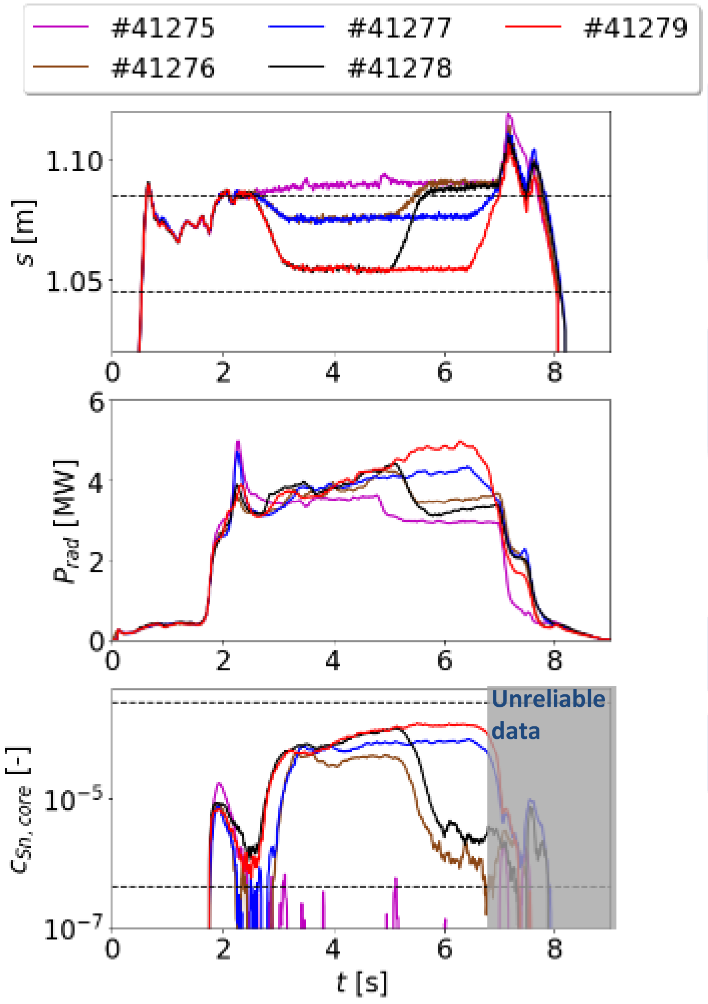
Credits to: Wei Ou

Maximum impurity concentration DEMO for different elements

Pütterich et al., 2019 NF, 0D model assuming τ*=7,5



ASDEX Upgrade with an Sn module 1. J. G. A. Scholte *et al.*, *Nucl. Mater. Energy*. **37**, 101522 (2023).



Possible reasons for droplet ejection

1. Localized boiling: Seen in welding (Spatter)

   Not possible because:
   - Should be more droplet in Li vs Sn
   - Droplets are also seen when T<500°C
2. JxB forces:

   Not possible because: Nano-PSI (and others) has no B-field
3. Other instabilities:

   Unlikely: A CPS should suppress those
4. Chemical erosion: $Sn + 4H \rightarrow SnH_4 \rightarrow Sn + 2H_2$

   Unlikely: Surface effect, how does it eject?
5. Hydrogen saturation leading to H_2 bubbles: Champagne

3. M. A. Jaworski *et al.*, *Nucl. Fusion*. 53 (2013)
4. T. W. Morgan *et al.*, *Nucl. Mater. Energy*. 12, (2017).

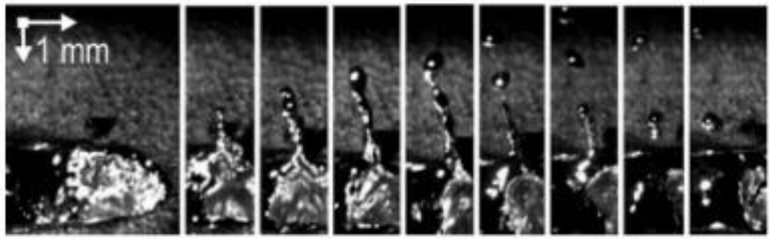


FIG. 2. A high speed imaging sequence (500 μs steps) of droplets being ejected from a laser weld pool. The acceleration of a proportion of the melt in the vertical direction creates a column of melt which later disintegrates into droplets.

2. A. F. H. Kaplan, J. Powell, *J. Laser Appl.* 23 (2011)

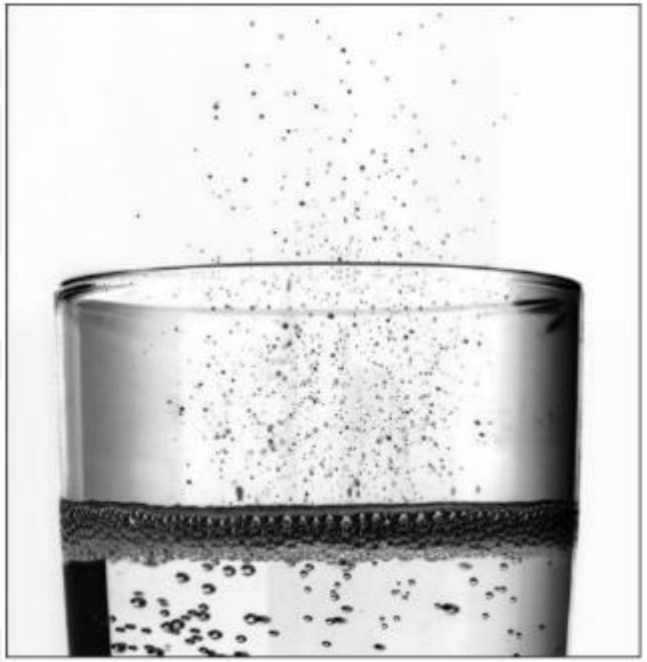


Fig. 31 The collapse of hundreds of bubbles at the free surface radiates a cloud of tiny droplets which is characteristic of champagne and sparkling wines and which complements the sensual experience of the taster (© Alain Cornu/Collection CIVC).

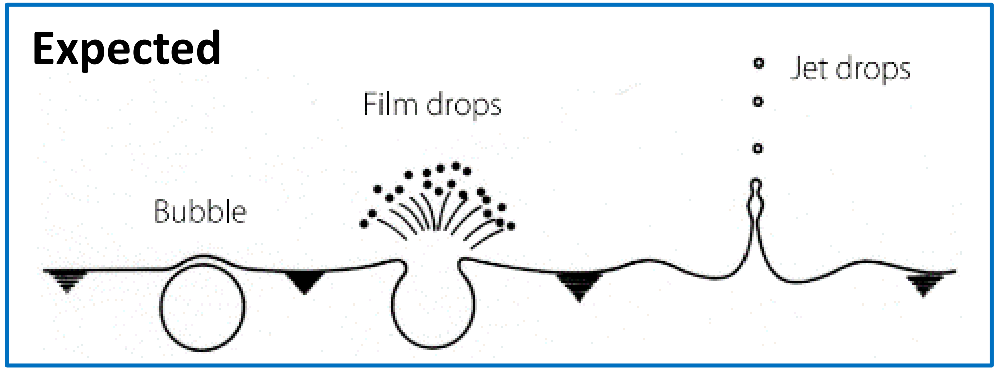
5. G. Liger-Belair, G. Polidori, P. Jeandet, *Chem. Soc. Rev.* 37 (2008).

Shadowgraphy

Goal: Test the hypothesis that:

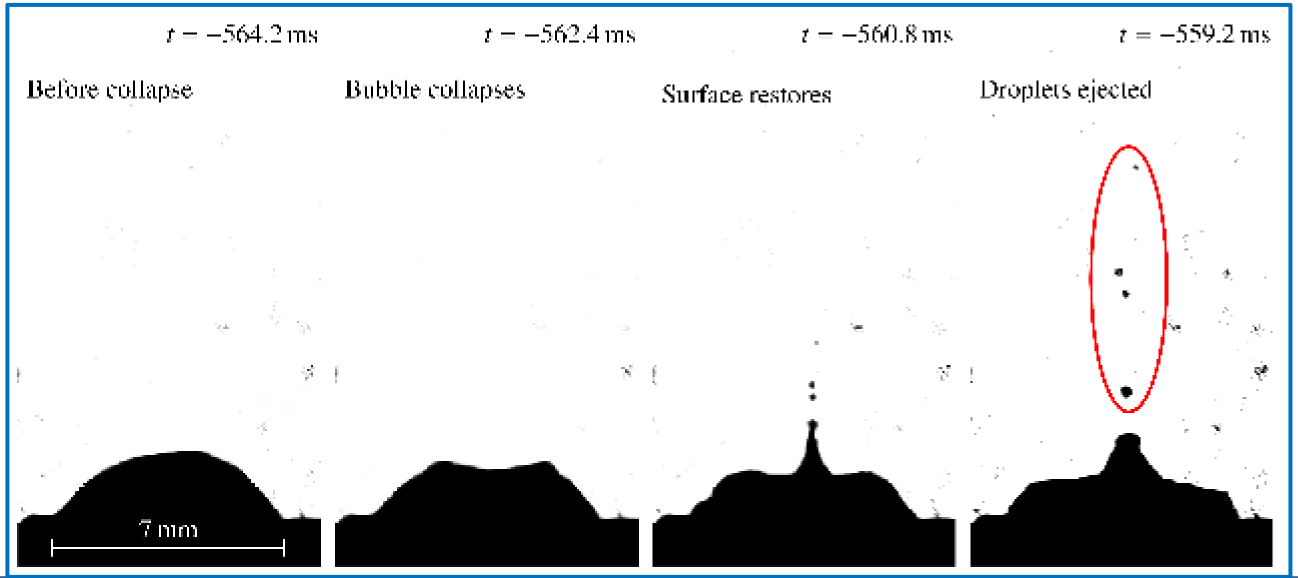
"Sn droplets eject due to a gas bubble collapse"

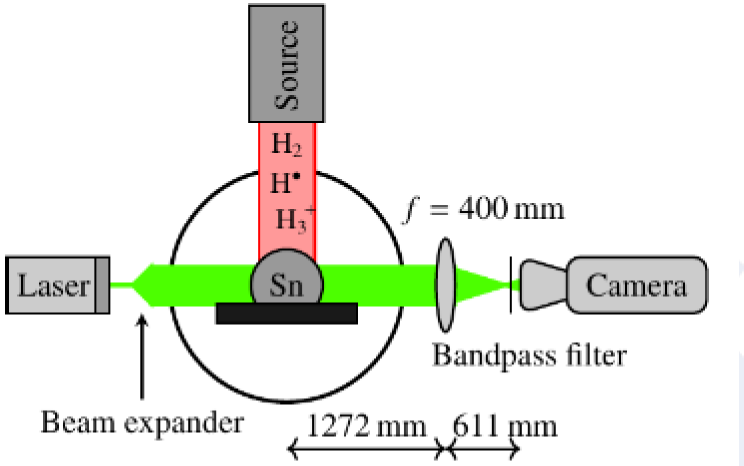
Expected

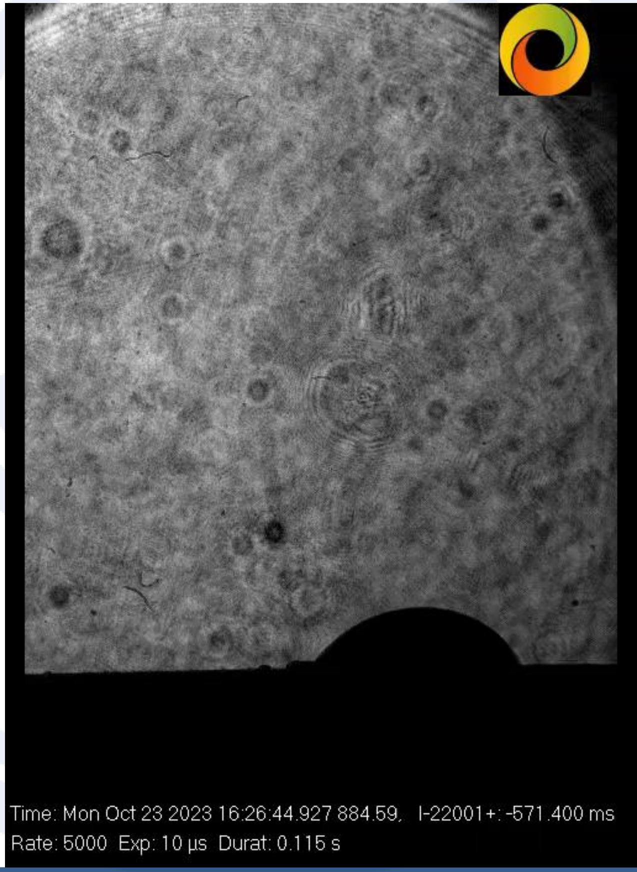


6. F. J. Resch, J. S. Darrozes, G. M. Afeti, *J. Geophys. Res. Ocean.* **91**, 1019–1029 (1986).

Result



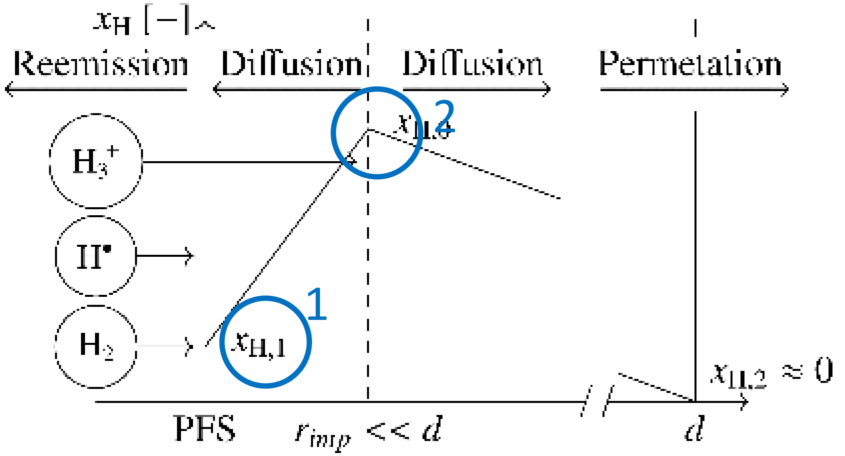




Calculation of hydrogen dissolved in a liquid metal

Calculation plan:

1. Determine x_H on the PFS
2. Determine the increase in xH in the implantation zone



Reaction equation of hydrogen dissolving in a liquid metal LM

$$\frac{1}{2}\mathrm{H}_2 \rightleftharpoons \mathrm{H}_{(\mathrm{LM})}$$

The steady-state mol fraction, using Sievert's law and assuming an ideal gas.

$$x_{H,g} = \frac{\text{Moles of H}}{\text{Total moles}} = \boxed{K_{\mathrm{H},g}}\sqrt{\frac{p_{\mathrm{H}_2}}{p^{o}}}$$

We can find this value in literature

Reaction equation of hydrogen radicals dissolving in a liquid metal LM

$$H^{\bullet} \rightleftharpoons \mathrm{H}_{(\mathrm{LM})}$$

$$x_{\mathrm{H},r} = K_{\mathrm{H},r}\frac{p_{\mathrm{H}}}{p^{o}}$$

$$K_{\mathrm{H},r} = \underbrace{\exp\left(\frac{217{,}988 - 49{,}37T}{R_g T}\right)} K_{\mathrm{H},g}$$

Independent of the material !!!!!

The influence of radicals and gas

Useful quantities

Saturation ratio: $\alpha = \frac{x_{\mathrm{H}}}{x_{\mathrm{H}\,g}}$

Supersaturation ratio: $S = \frac{x_{\mathrm{H}}}{x_{\mathrm{H}\,g}} - 1$

$$S_{\mathrm{H},1} = \exp\left(\frac{217{,}988 - 49{,}37T}{R_g T}\right)\frac{p_{\mathrm{H}}}{\sqrt{p_{H2}p^{o}}}$$

Laplace pressure bubble: $p = p_0 + \frac{2\gamma}{r}$

Sieverts Law: $\frac{x_{H,crit}}{x_{H,g}} = \sqrt{\frac{p_{crit}}{p_{\mathrm{H2}}}}$

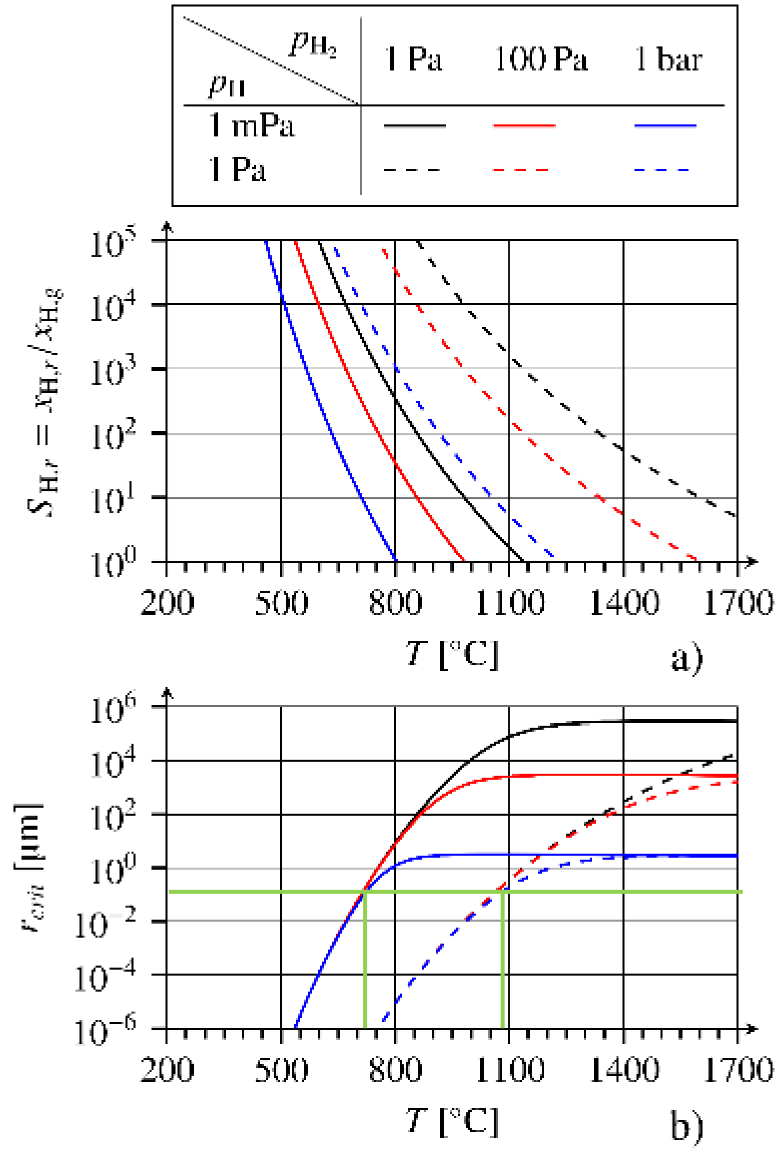
$$\boxed{r_{crit} = \frac{2\gamma}{p_{\mathrm{H2}}(\alpha^2 - 1)}}$$

Conclusion:

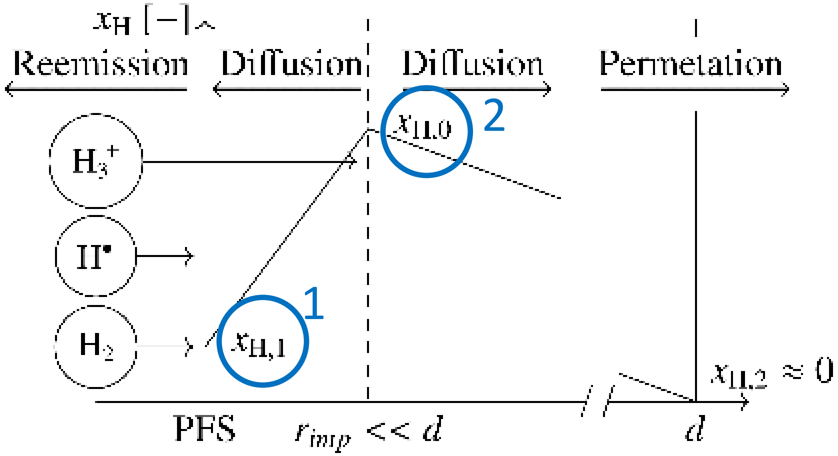
- Critical radius depends on the radical partial pressure
- A reasonable CPS will have a pore radius > 0,1µm
  - It could be stable at 750 °C, more realistically 1100°C
- Material independent*

* The critical radius depends on surface tension;
Sn is used in the figure:

	γ [N/m] @750C
Sn	0,51
Ga	0,66
In	0,50
Li	0,25



Step 2 the ions

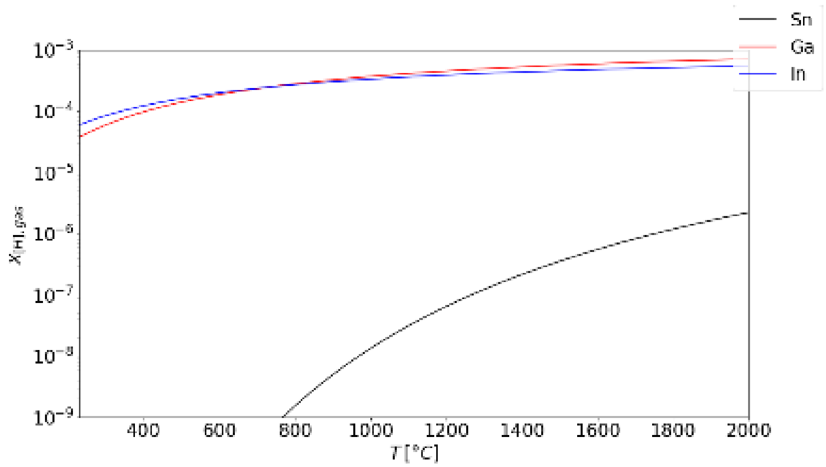


Ficks law of diffusion

$$x_{H,0} < x_{H,1} + \frac{\Gamma_{imp} r_{imp}}{N_A D} \frac{M_{LM}}{\rho_{LM}}$$

Ignoring the radicals

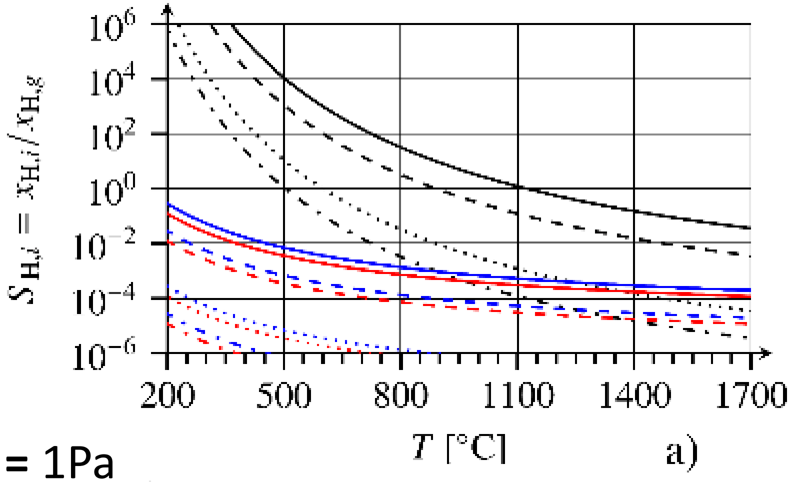
$$S_{H,0} = \frac{\frac{\Gamma_{imp} r_{imp}}{N_A D} \frac{M_{LM}}{\rho_{LM}}}{x_{H,g}}$$



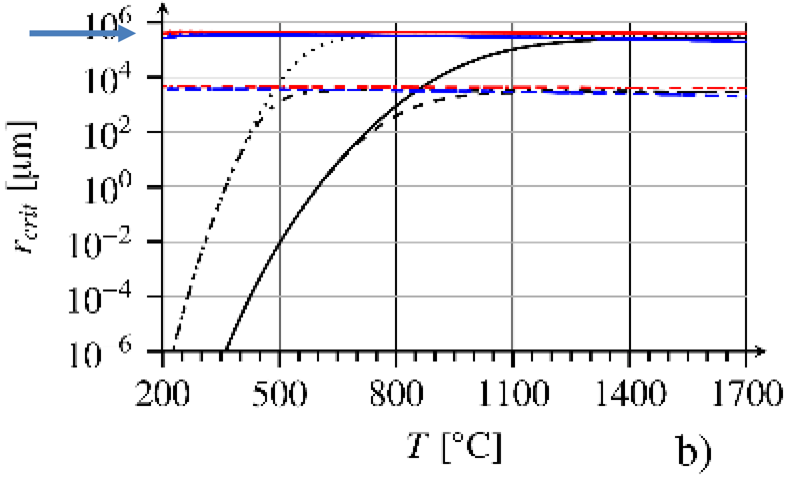
N. D. Deveau, P. S. Yen, R. Datta, *Int. J. Hydrogen Energy*. **43**, 19075–19090 (2018).
P. W. Humrickhouse, *IEEE Trans. Plasma Sci.* **47**, 3374–3379 (2019).

For **Sn**, **Ga** and **In**

p_{H_2} \ Γ_{imp}	10^{20} m^{-1} s^{-2}	10^{23} m^{-1} s^{-2}
1 Pa	⋯⋯	——
100 Pa	-·-	- - -



p_{H_2} = 1Pa



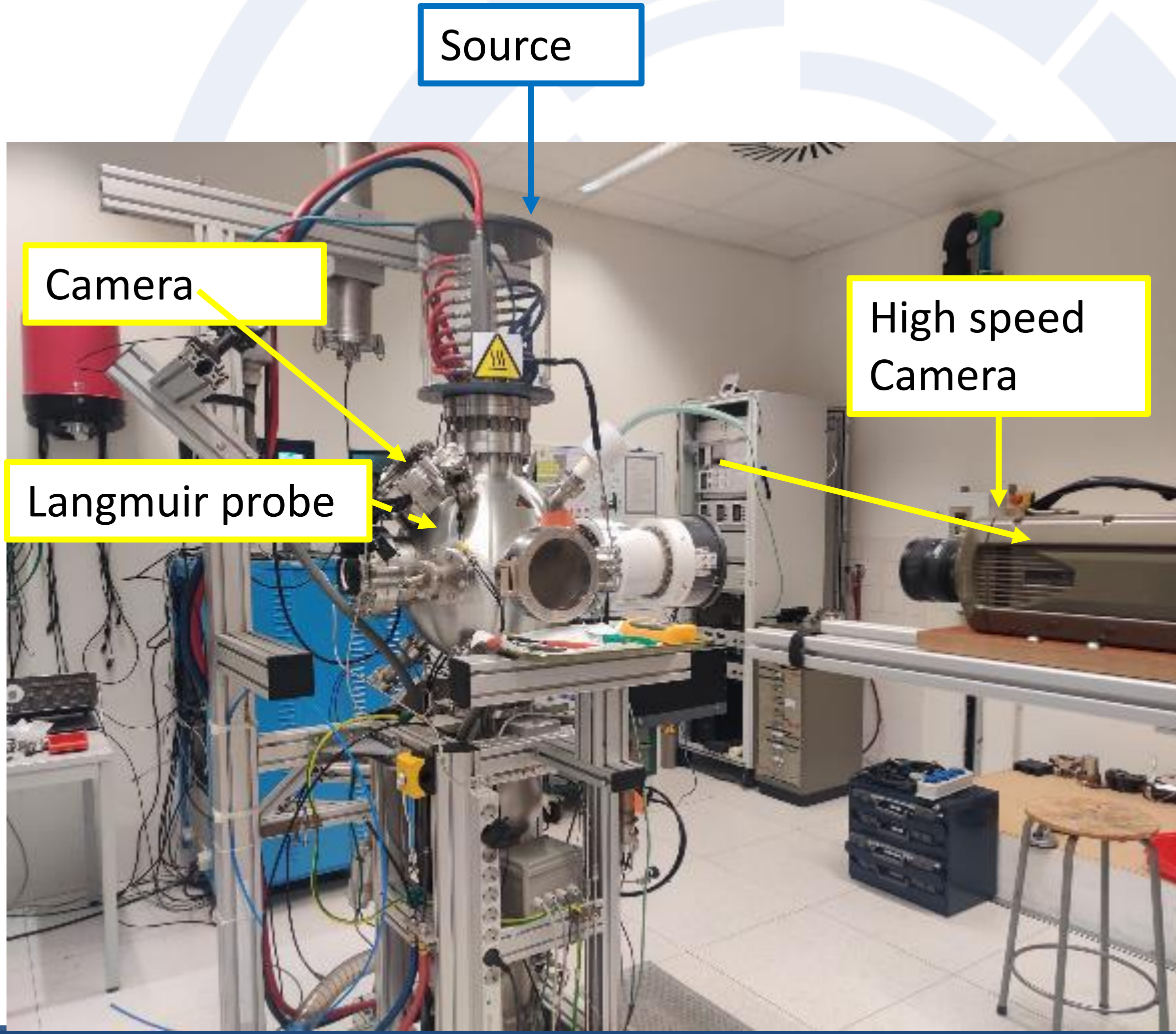
Preliminary results in Nano-PSI

Experimental plan in Nano-PSI

- Expose samples for 30min @ 500°C ±20 °C
- No bias or magnetic field
- Total fluence of ≈ $3{,}6\times10^{23}$ m^{-2}

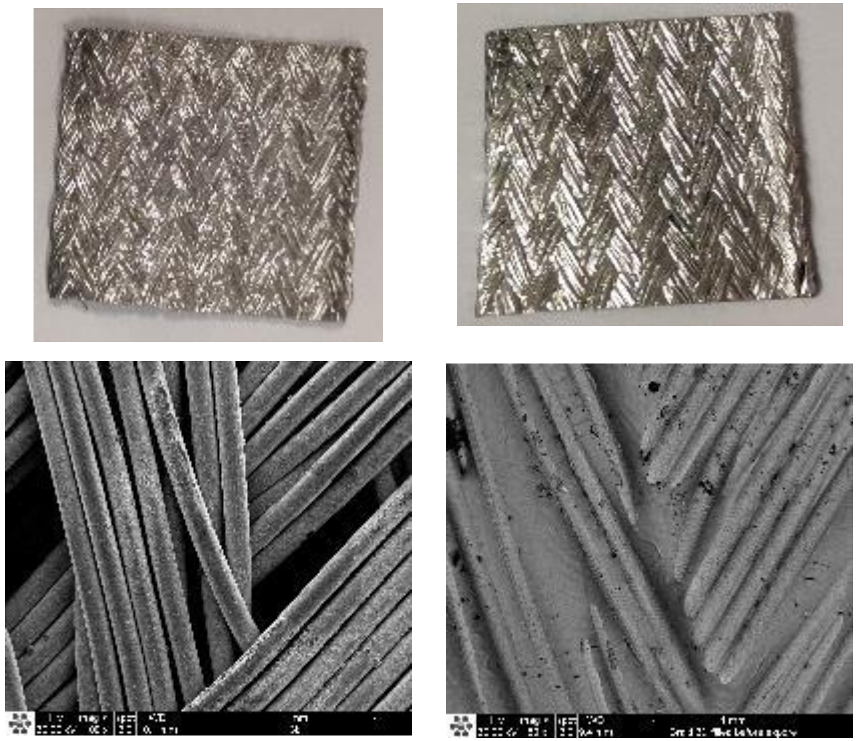
Diagnostics:

- 4 Stainless steel witness plates
- Thermocouple



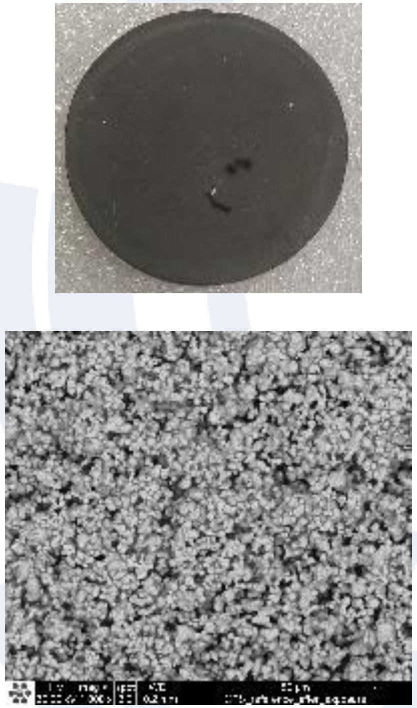
Different CPSs exposed to Nano-PSI

Braids: Hot isolating pressing (UKAEA)



Felts (ENEA)

Sintered disc (Edgetech industries)

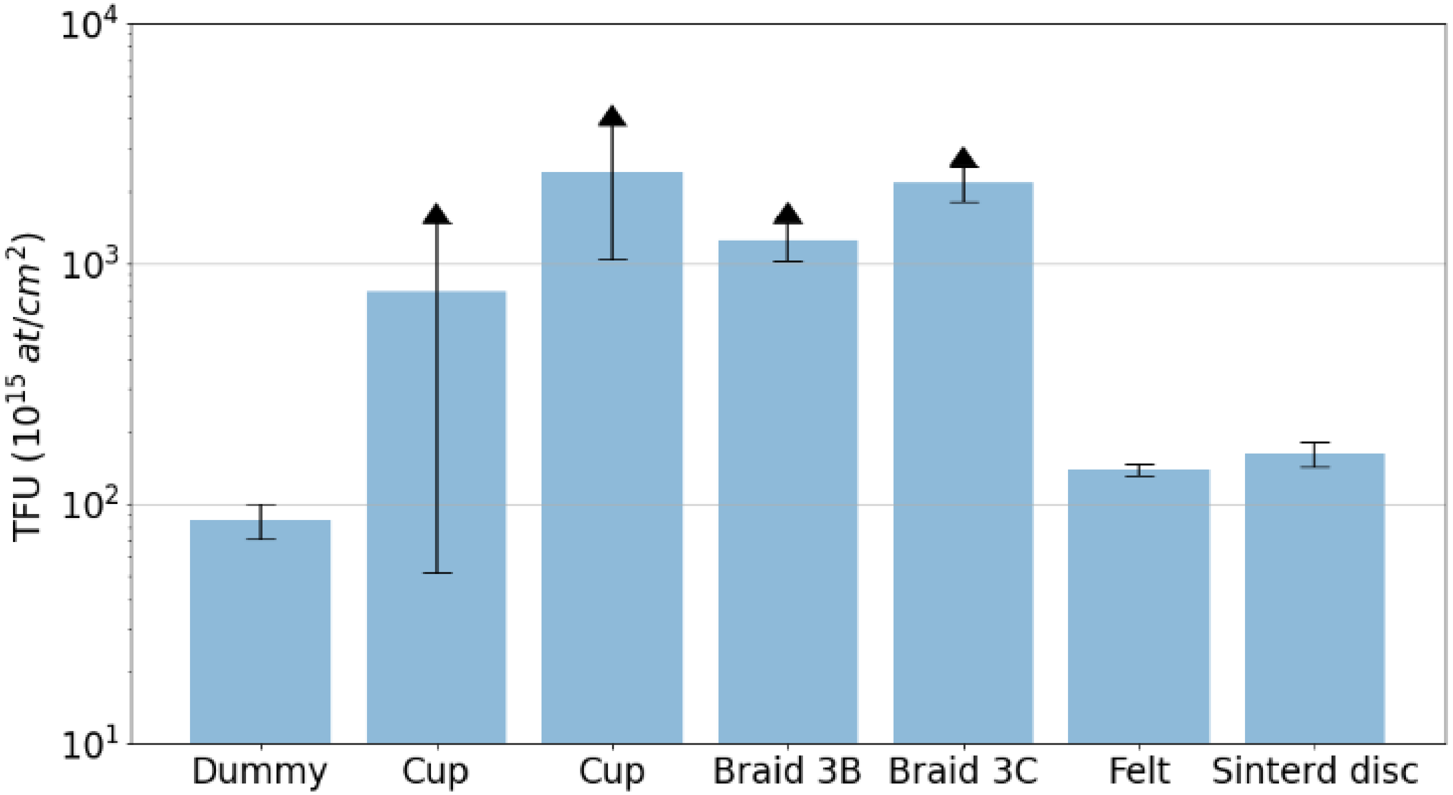


First results on Sn erosion

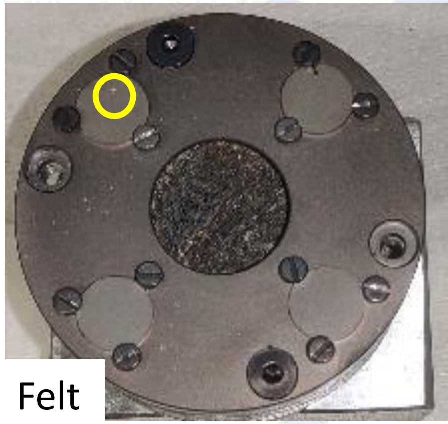
- Felt and Sintered disc: quite reasonable at droplet suppression

Sample	Mass Loss [mg]
Cup	180,7
Braid 3B	36,3
Braid 3C	108,5
Felt	1
Sintered disc	144,4

RBS Measurements




Cup, no CPS

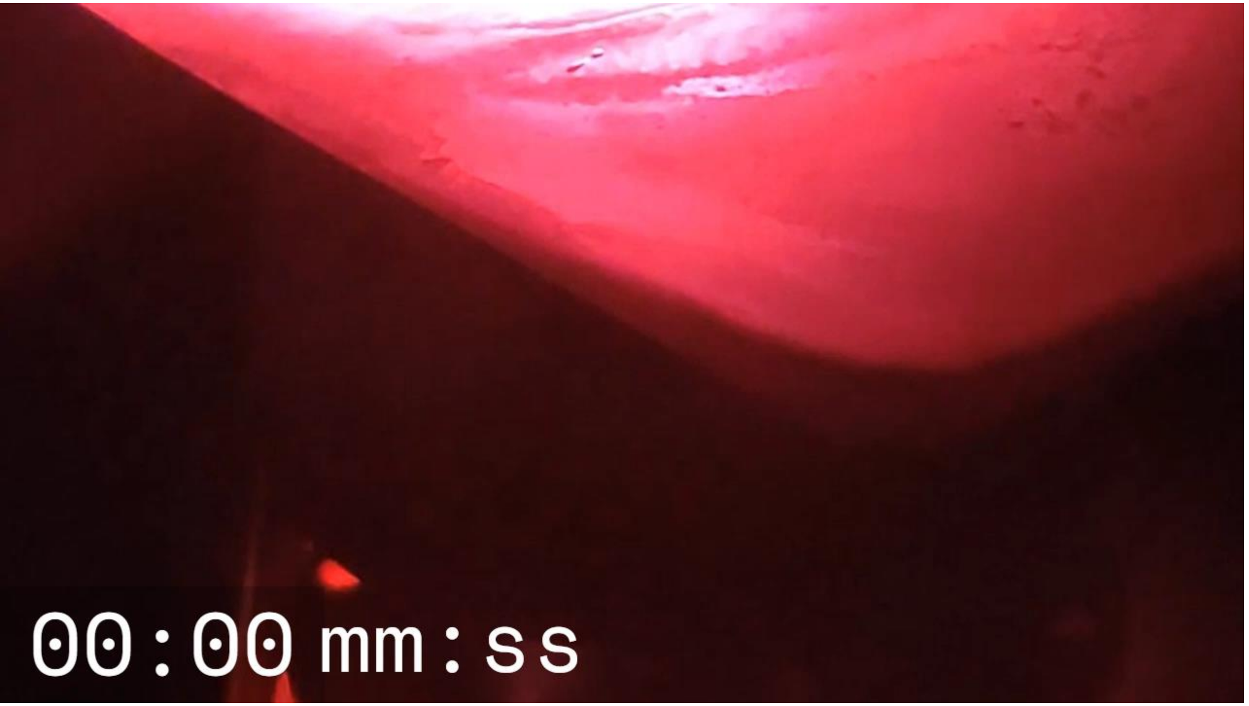

Felt

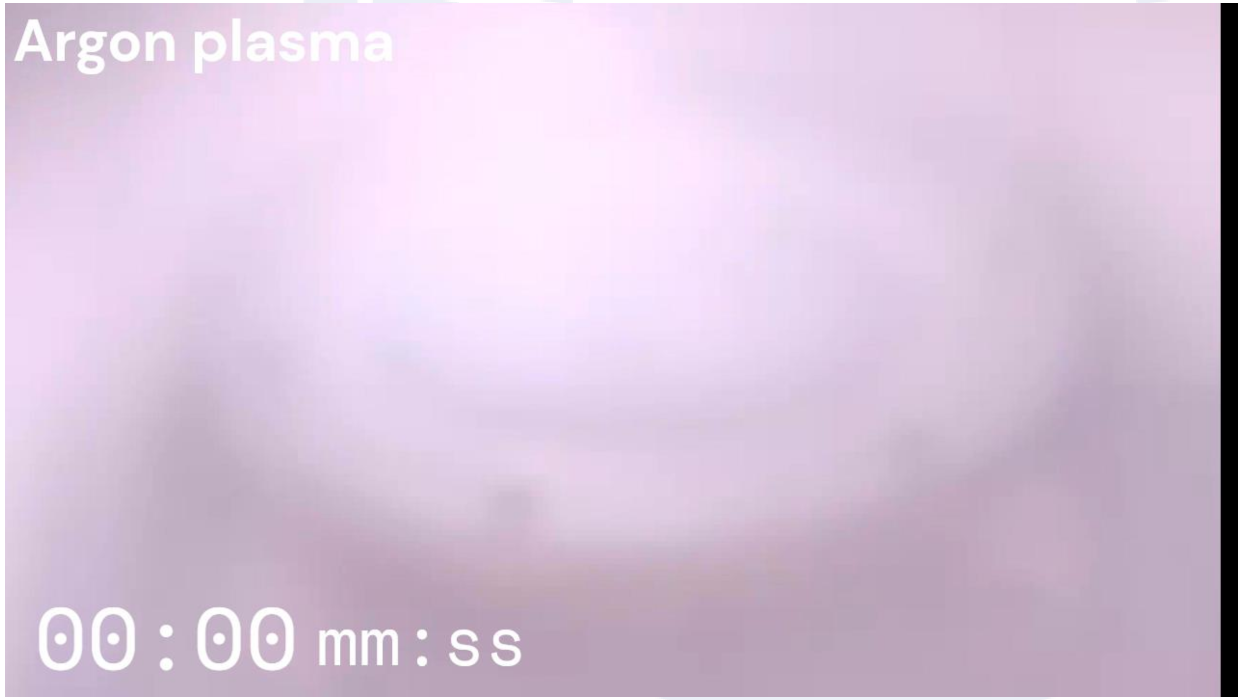

Braids


Sintered disc

Sintered disc “sweats” Sn droplets

- Immediate wettings while switching to hydrogen
- Did not sweat as much with only the heater
- Tin can form a pool on top of the CPS, from which it will spit tin.





Conclusions

- Gas bubble formation is the cause of droplet ejection
- When considering only radicals (and gas)
  - The H solubility in liquid metals are independent of the LM
  - The critical radius is restricted by the radical partial pressure and not the partial gas pressure
- When considering only ions
  - Strong material dependence
  - Sn has an extremely low hydrogen solubility
- With all CPSs Sn droplet ejection, Felt and Sintered disc most promising
- Improvement suggestions various CPS manufacturing techniques
  - Felts/Braids: Thermal connection
  - Sintered: Brittleness, leakage/pooling

To be done in 2024

- What is the influence of ions vs free radicals w.r.t. droplet ejection?
  - Use a radical source with the same flux as in the Nano-PSI.
- Do droplets only eject when using Sn or are other metals also effected
  - Ga and In have a higher solubility → less droplet ejection?
  - Ions vs radial
  - Different pore

Back-up slides

Calculation of hydrogen dissolved in a liquid metal

Calculation plan:

1. Determine x_H on the PFS
2. Determine the increase in xH in the implantation zone

Reaction equation of hydrogen dissolving in a liquid metal LM

$$\frac{1}{2}\mathrm{H}_2 \rightleftharpoons \mathrm{H}_{(\mathrm{LM})}$$

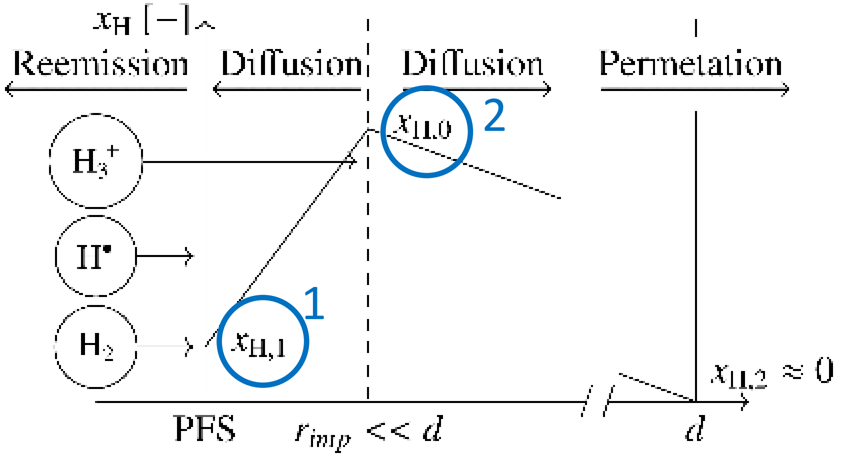
The steady-state mol fraction, using Sievert's law and assuming an ideal gas.

$$x_{H,g} = \frac{\text{Moles of H}}{\text{Total moles}} = K_{\mathrm{H},g}\sqrt{\frac{p_{\mathrm{H}_2}}{p^{o}}}$$

We can write this as:

$$\boxed{K_{\mathrm{H},g}} = \exp\left(-\frac{\Delta G^{o}_{H2}}{R_g T}\right)$$

We can find this value in literature



Reaction equation of hydrogen radicals dissolving in a liquid metal LM

$$H^{\bullet} \rightleftharpoons \mathrm{H}_{(\mathrm{LM})}$$

$$x_{\mathrm{H},r} = K_{\mathrm{H},r}\frac{p_{\mathrm{H}}}{p^{o}}$$

$$\boxed{K_{\mathrm{H},r}} = \exp\left(-\frac{\Delta G^{o}_{H}}{R_g T}\right)$$

We ***cannot*** find this value in literature

But we can calculate its value

We can find the reaction constant from first principles

$$\Delta G^{O}_{\mathrm{H2}} = \Delta G_f^{O}(\mathrm{H_{(LM)}}) - \tfrac{1}{2}\Delta G_f^{O}(\mathrm{H_2})$$

$$\Delta G^{O}_{\mathrm{H}} = \Delta G_f^{O}(\mathrm{H_{(LM)}}) - \Delta G_f^{O}(\mathrm{H^\bullet})$$

$$\Delta G^{O}_{\mathrm{H}} = \Delta G^{O}_{\mathrm{H2}} + \tfrac{1}{2}\Delta G_f^{O}(\mathrm{H_2}) - \Delta G_f^{O}(\mathrm{H^\bullet})$$

$$\Delta G_f^{O} = \Delta H_f^{O} - T\Delta S_f^{O}$$

From textbooks one can find that:
$\Delta H_f^{O}(\mathrm{H_2}) = 0$ Jmol^{-1}, $S_f^{O}(\mathrm{H_2}) = 130{,}68$ JK^{-1}mol^{-1},
$\Delta H_f^{O}(\mathrm{H^\bullet}) = 217{,}998$ kJmol^{-1}, $S_f^{O}(\mathrm{H^\bullet}) = 114{,}717$ JK^{-1}mol^{-1}

$$\Delta G^{O}_{\mathrm{H}} = \Delta G^{O}_{\mathrm{H2}} - 217{,}988 + 49{,}37T$$

$$K_{\mathrm{H},r} = \exp\left(-\frac{\Delta G^{O}_{H2} - 217{,}988 + 49{,}37T}{R_gT}\right)$$

$$K_{\mathrm{H},r} = \exp\left(-\frac{-217{,}988 + 49{,}37T}{R_gT}\right)\exp\left(-\frac{\Delta G^{O}_{H2}}{R_gT}\right)$$

$$K_{\mathrm{H},r} = \underbrace{\exp\left(\frac{217{,}988 - 49{,}37T}{R_gT}\right)}_{\text{Independent of the material !!!!!}}\boxed{K_{\mathrm{H},g}} \rightarrow \boxed{\text{We can find this value in literature}}$$

Reminder

Hydrogen gas	Hydrogen radicals/atoms
$\frac{1}{2}\mathrm{H_2} \rightleftharpoons \mathrm{H_{(LM)}}$	$H^\bullet \rightleftharpoons \mathrm{H_{(LM)}}$
$x_{H,g} = K_{\mathrm{H},g}\sqrt{\frac{p_{H_2}}{p^{\mathrm{O}}}}$	$x_{\mathrm{H},r} = K_{\mathrm{H},r}\frac{p_{\mathrm{H}}}{p^{\mathrm{O}}}$
$K_{\mathrm{H},g} = \exp\left(-\frac{\Delta G^{\mathrm{O}}_{H2}}{R_gT}\right)$	$K_{\mathrm{H},r} = \exp\left(-\frac{\Delta G^{\mathrm{O}}_{H}}{R_gT}\right)$

The supersaturation ratio and critical bubble radius without ions

Useful quantities

Saturation ratio: $\alpha = \frac{x_{\mathrm{H}}}{x_{\mathrm{H}\,g}}$

Supersaturation ratio: $S = \frac{x_{\mathrm{H}}}{x_{\mathrm{H}\,g}} - 1$

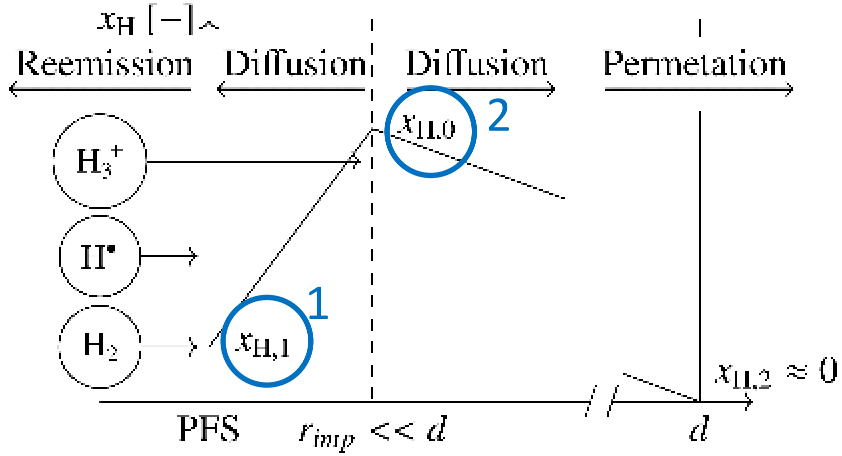
Laplace pressure bubble: $p = p_0 + \frac{2\gamma}{r}$

Sieverts Law: $\frac{x_{H,crit}}{x_{H,g}} = \sqrt{\frac{p_{crit}}{p_g}}$

$$r_{crit} = \frac{2\gamma}{p_g(\alpha^2 - 1)}$$

If a bubble is smaller than r_{crit} the surface tensions will shrink the bubble until it vanishes.

Material independent !!!



Step 1: Determine xH on the PFS

$$x_{\mathrm{H},1} = x_{\mathrm{H},r} + x_{\mathrm{H},g}$$

$$S_{\mathrm{H},1} = \frac{x_{\mathrm{H},r}+x_{\mathrm{H},g}}{x_{\mathrm{H}\,g}} - 1 = \frac{x_{\mathrm{H},r}}{x_{\mathrm{H}\,g}}$$

$$S_{\mathrm{H},1} = \frac{x_{\mathrm{H},r}}{x_{\mathrm{H}\,g}} = \frac{\exp\left(\frac{217{,}988-49{,}37T}{R_g T}\right) K_{\mathrm{H},g}\frac{p_{\mathrm{H}}}{p^{\mathrm{O}}}}{K_{\mathrm{H},g}\sqrt{\frac{p_{\mathrm{H}2}}{p^{\mathrm{O}}}}}$$

$$\boxed{S_{\mathrm{H},1} = \exp\left(\frac{217{,}988 - 49{,}37T}{R_g T}\right)\frac{p_{\mathrm{H}}}{\sqrt{p_{\mathrm{H}_2} p^{\mathrm{O}}}}}$$