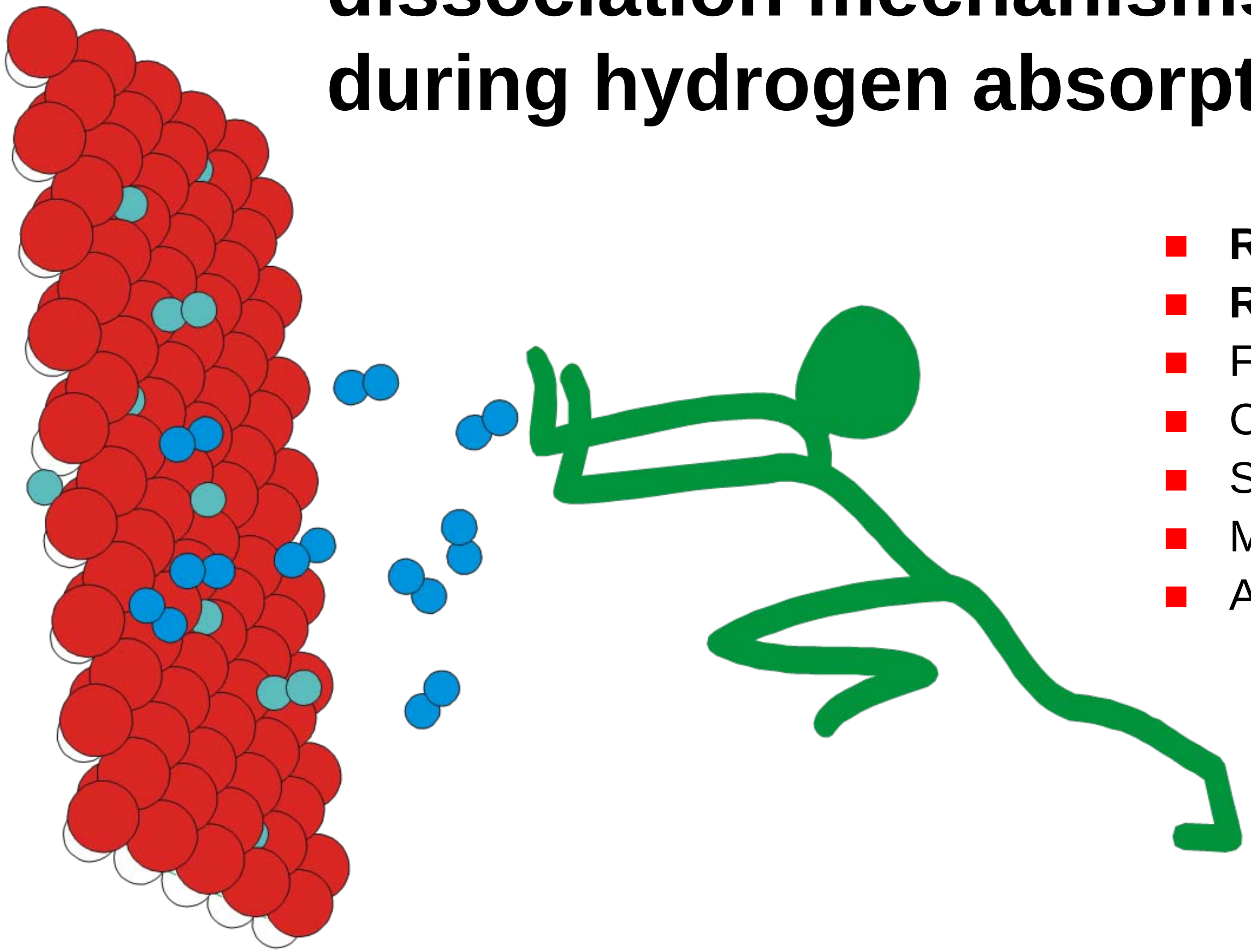
Interplay of diffusion and dissociation mechanisms during hydrogen absorption



- **Ronald Griessen**
- **Robin Gremaud**
- Flavio Pendolino
- C. Rongeat,
- S. Kato
- M. Bielmann
- Andreas Züttel

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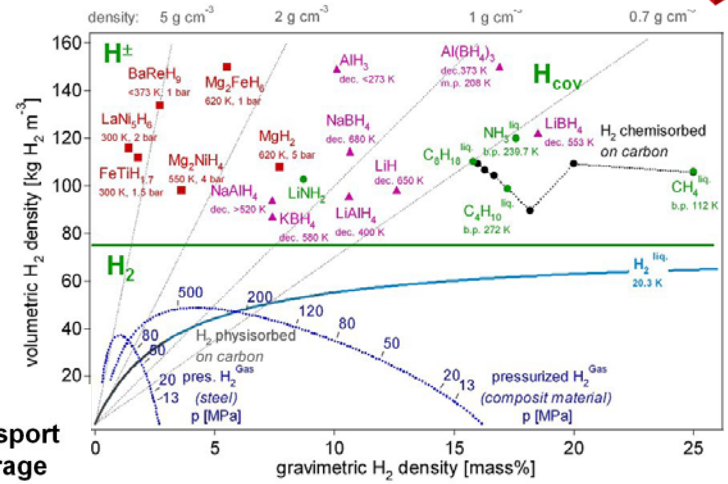
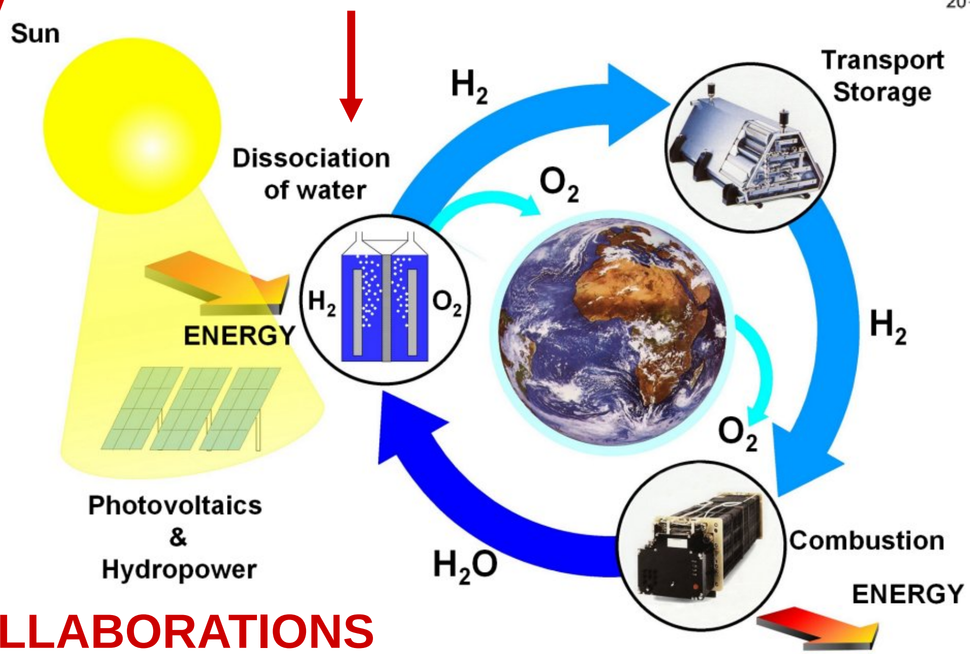
Activities

RESEARCH

EDUCATION

R&D PROJECTS





DEMONSTRATIONS

COLLABORATIONS

BFE OFEN UFE SFOE · Universitas Friburgensis · TOYOTA · Tohoku University · GfE Metalle und Materialien GmbH · Universiteit Leiden · GKSS Forschungszentrum · PSI · montena condis products · Forschungszentrum Karlsruhe in der Helmholtz-Gemeinschaft

OUTLINE

- How to measure hydrogen content in metal hydrides: **static/dynamic experiments**

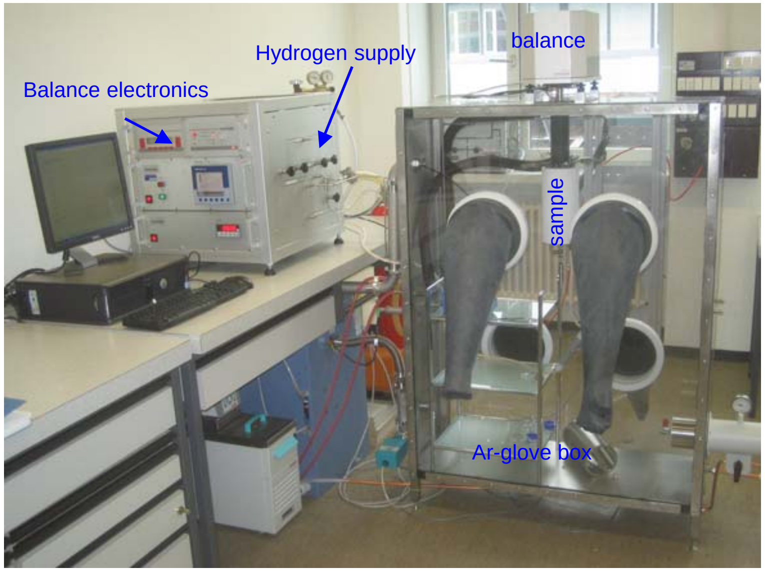
- **Thin film experiments**

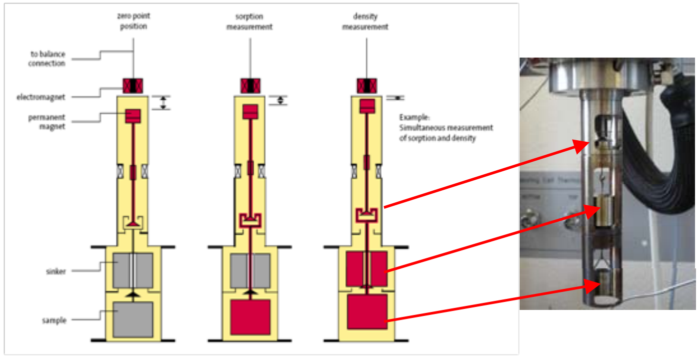
- Connecting **surface** and **bulk**:

  The **Two Layers model** – derivation and thin film experiments

- **outlook**

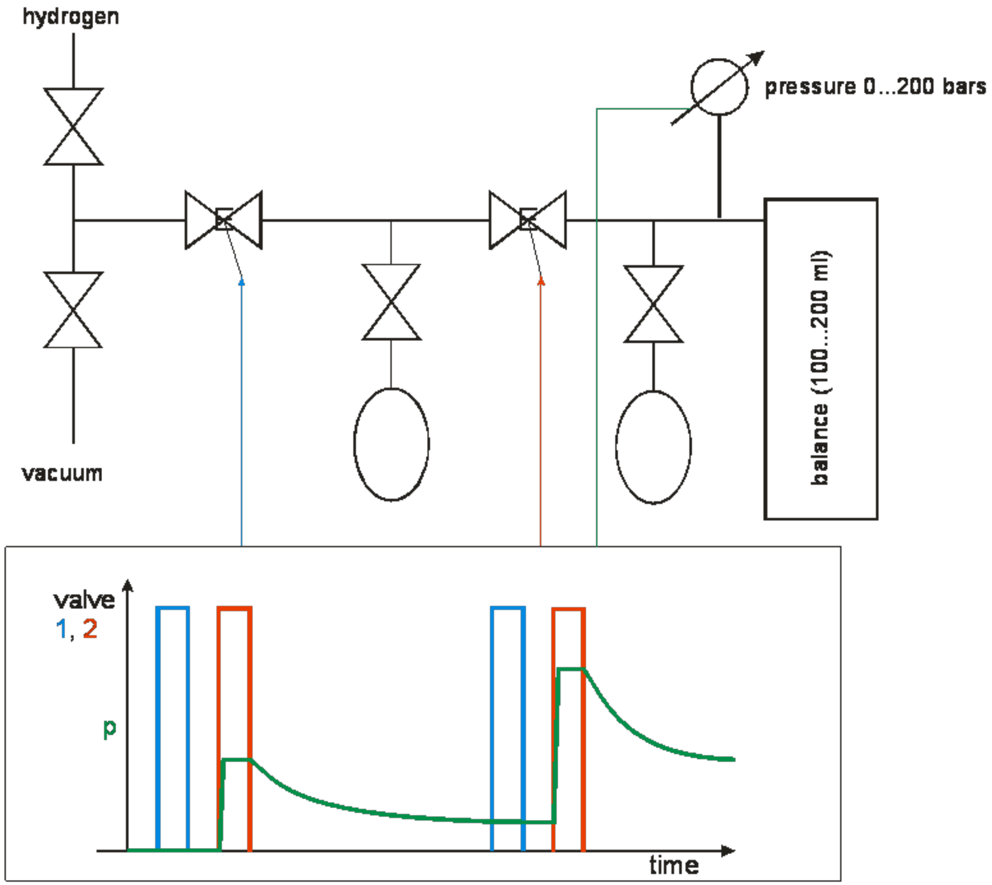
Gravimetric hydrogen sorption measurements



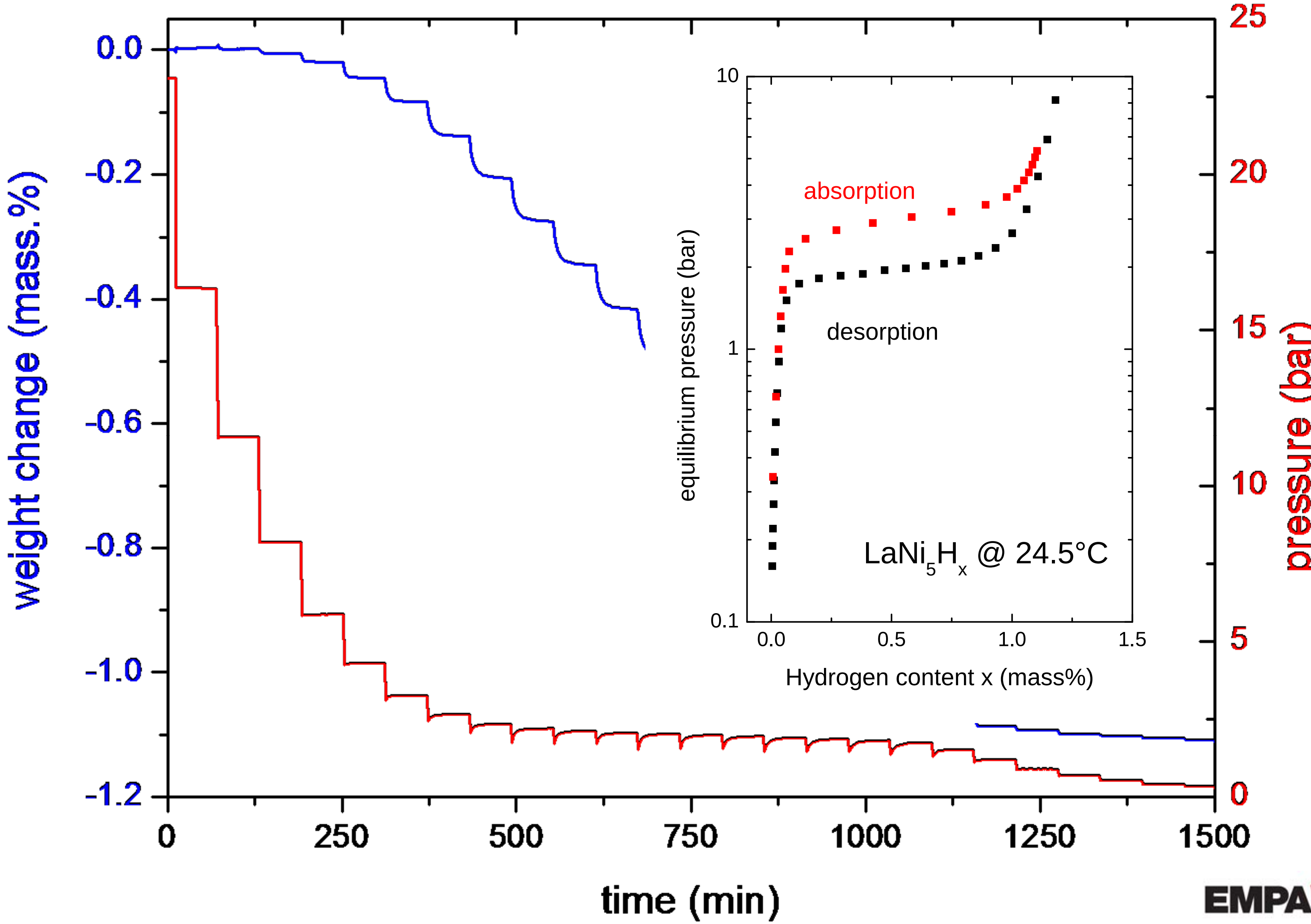


Measurement principle to correct for buoyancy contribution to the sample mass.

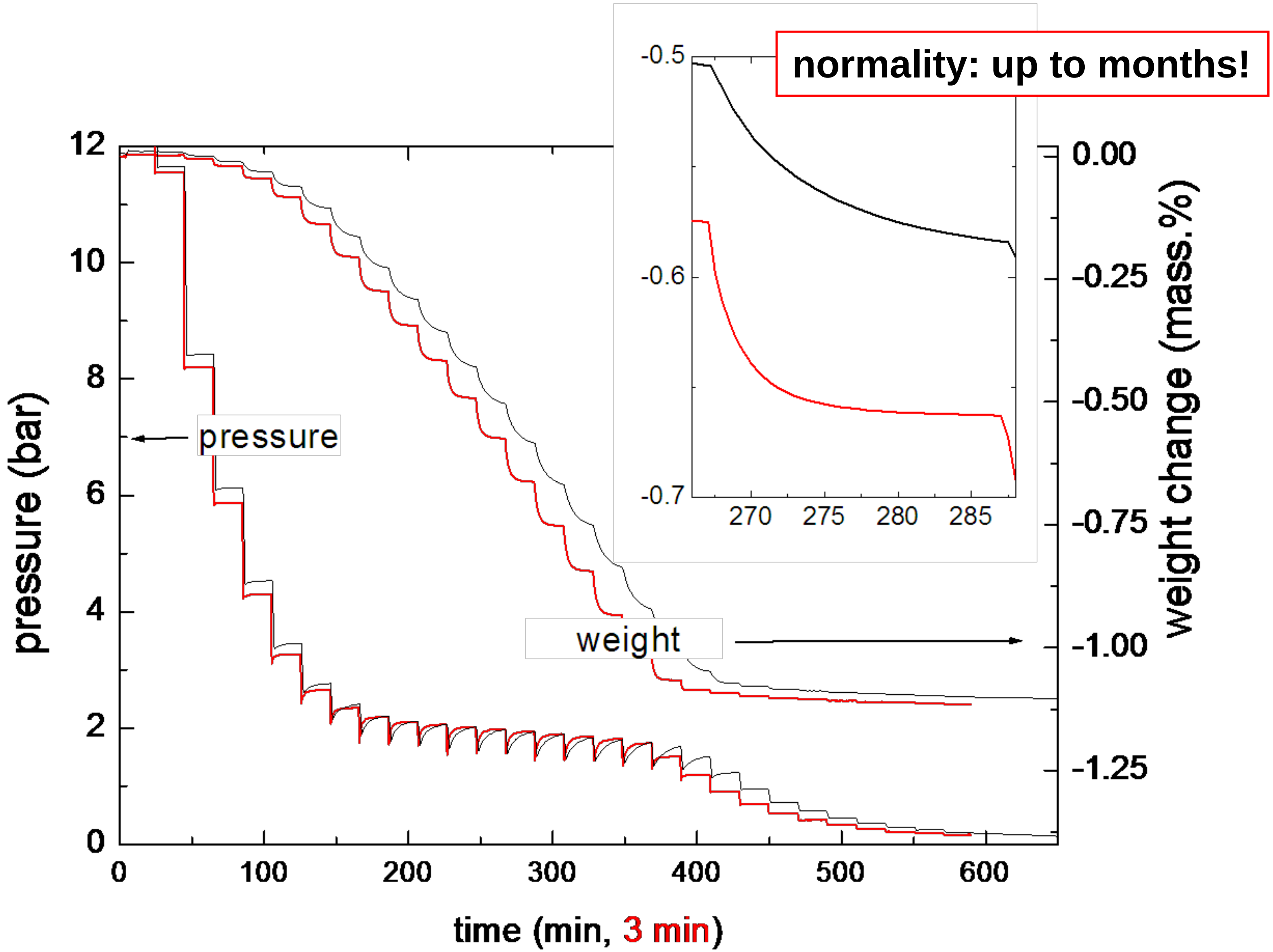
"Sieverts" Pressure automation



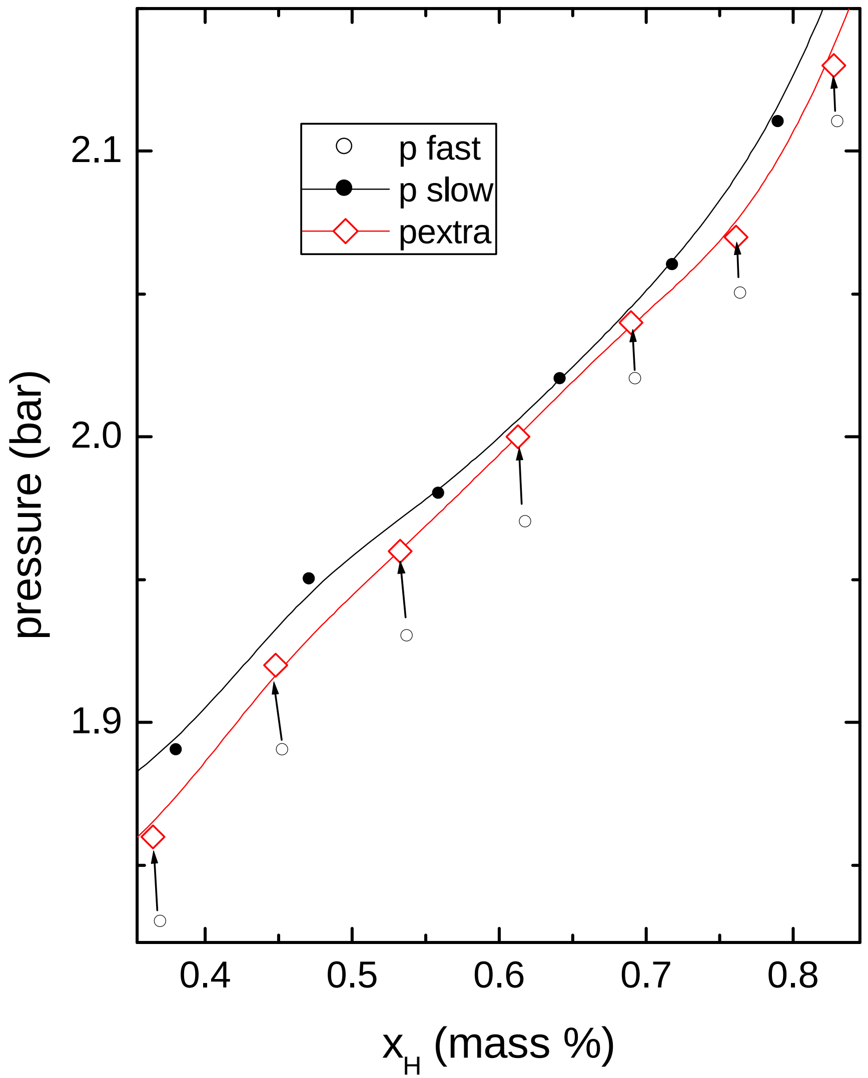
Gravimetric pcT measurements on $LaNi_5$

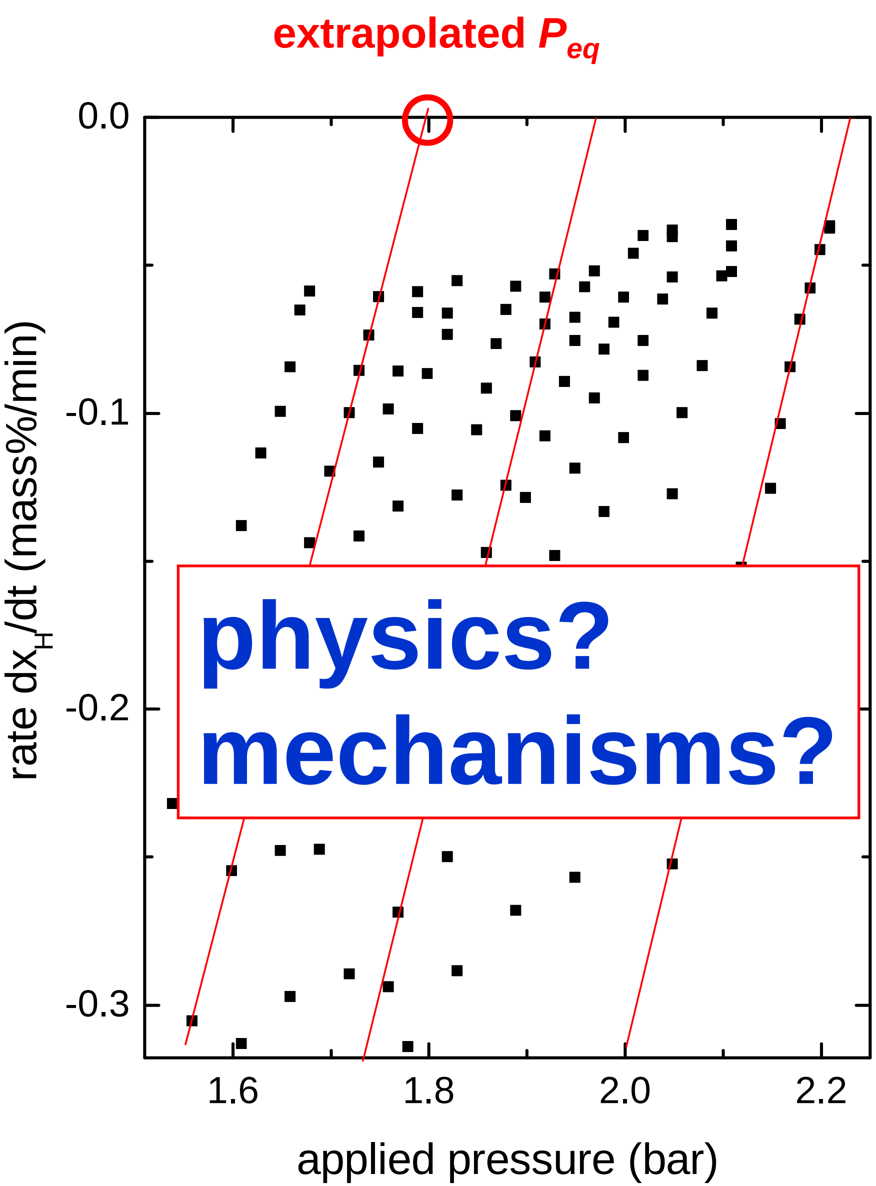


Non-equilibrium pcT-measurements



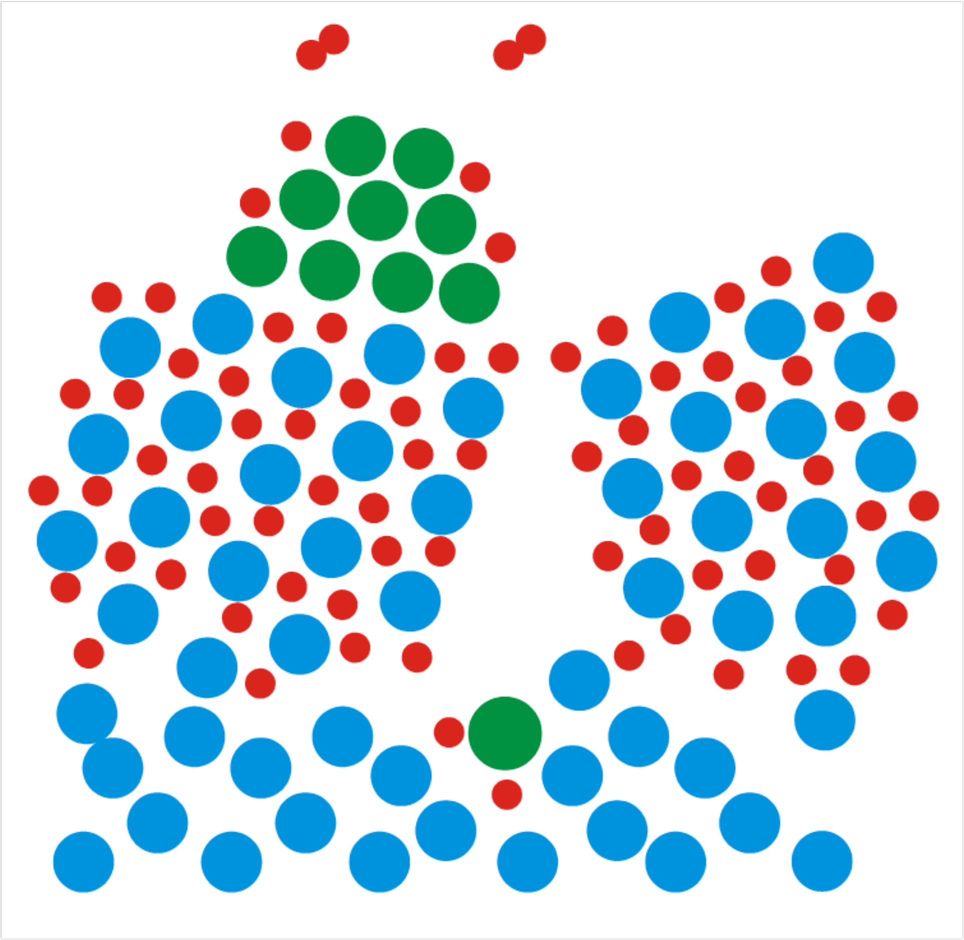
Extrapolation to equilibrium?





Mechanisms of Kinetics of Hydride formation

splitting the H_2 molecule
ΔE_{diss} ~ 0…1 eV



diffusion into bulk
$\Delta E_{diss} > \Delta E_{diff}$ ~ 0…1 eV

nucleation and growth

Hydrogen Diffusion

$$x = \sqrt{6Dt}$$

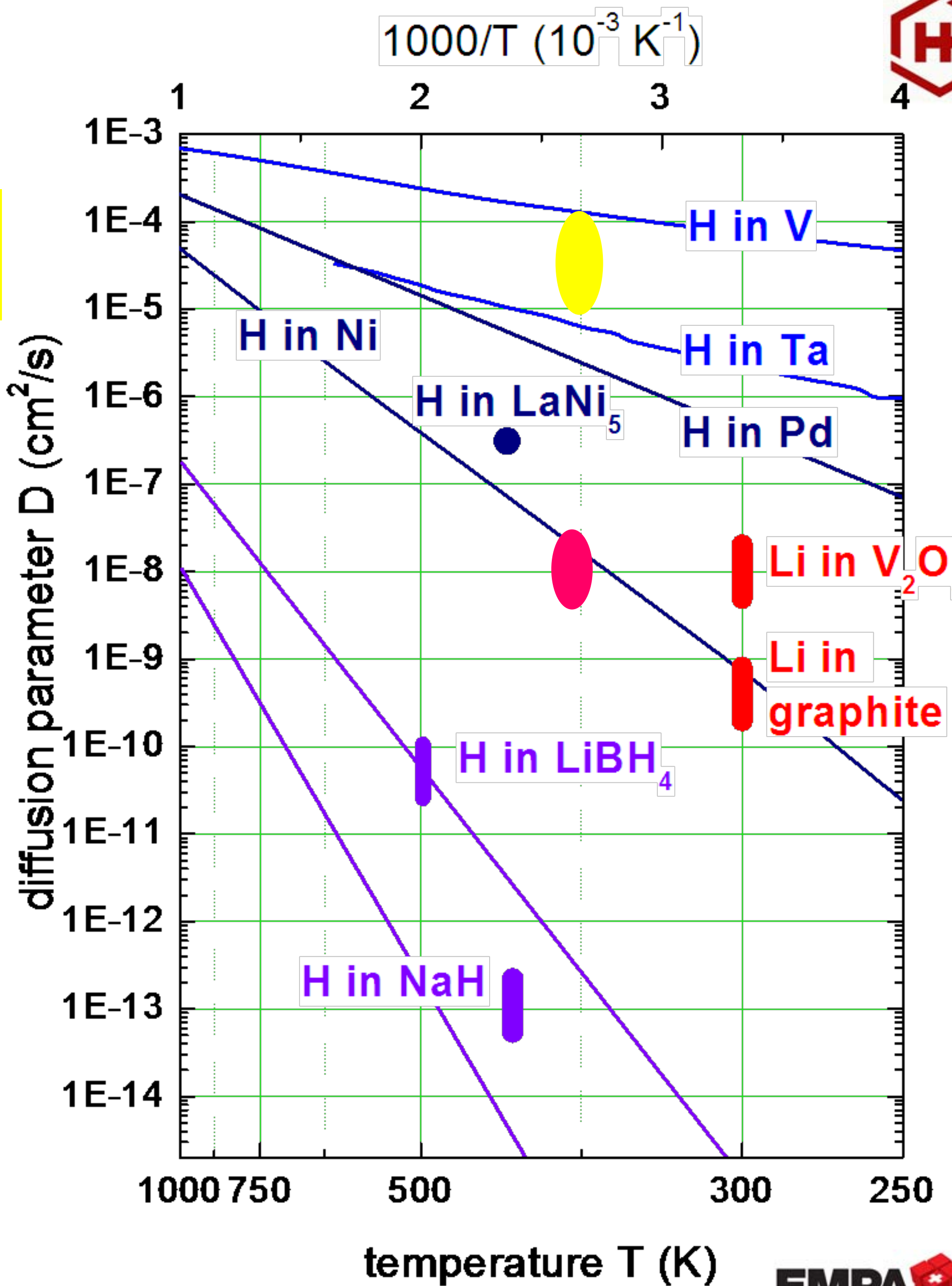
water in pasta:
1 mm in 5 min

Li in $LiBH_4$

H in NiMH batteries
~ 10 μm in min

Li in Li-ion batteries
~ μm in min

H in complex hydrides
~ μm in days



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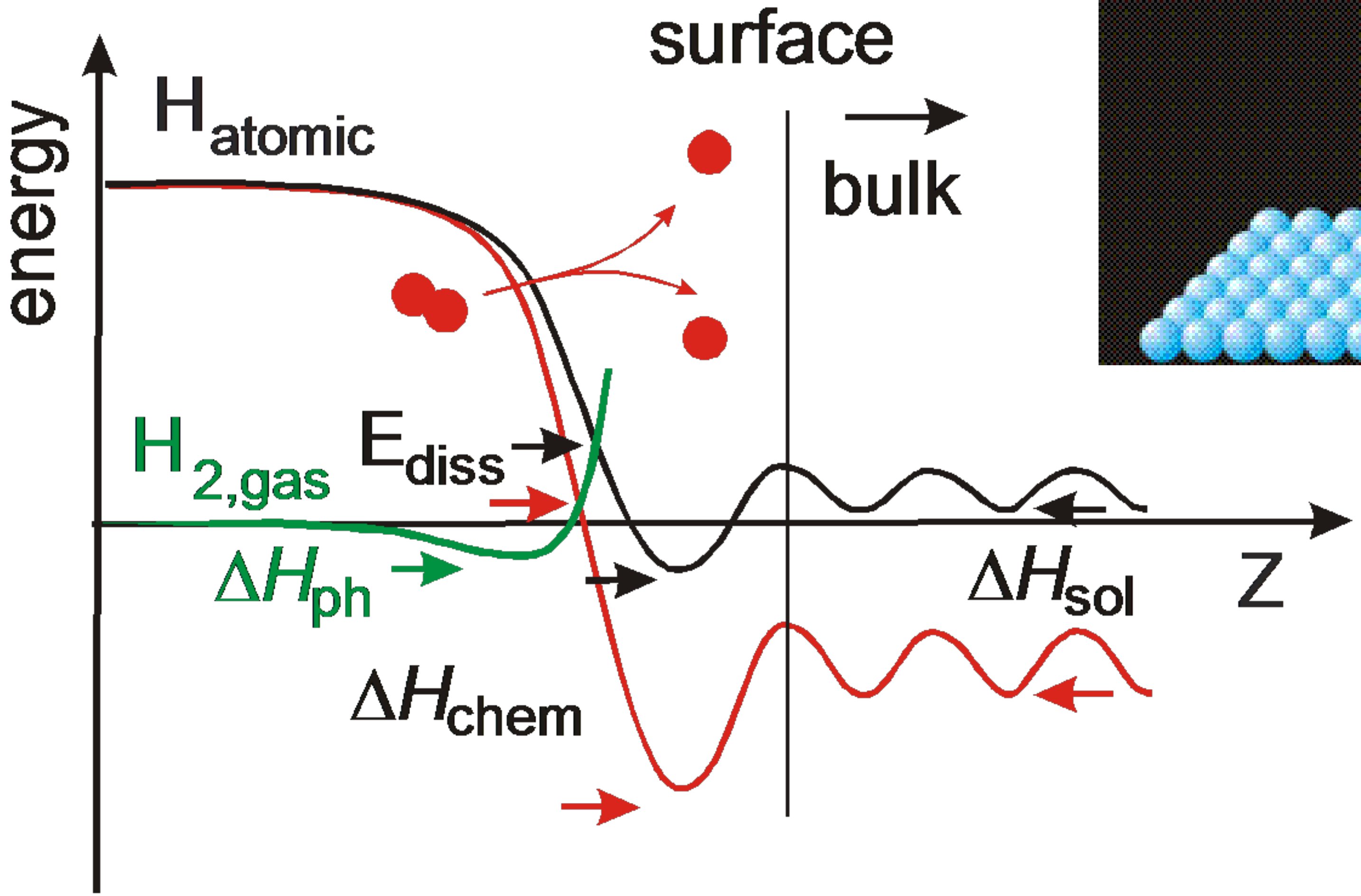
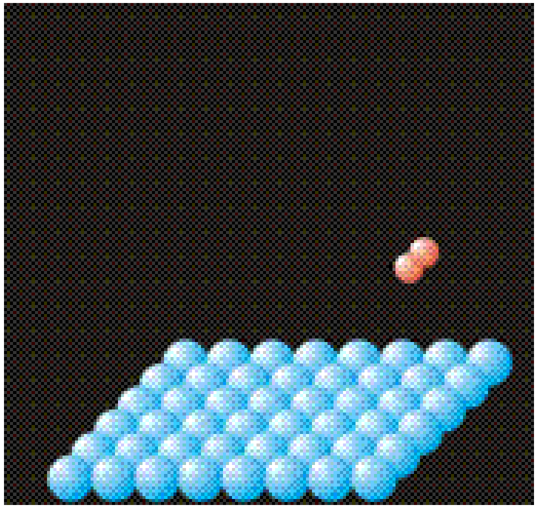
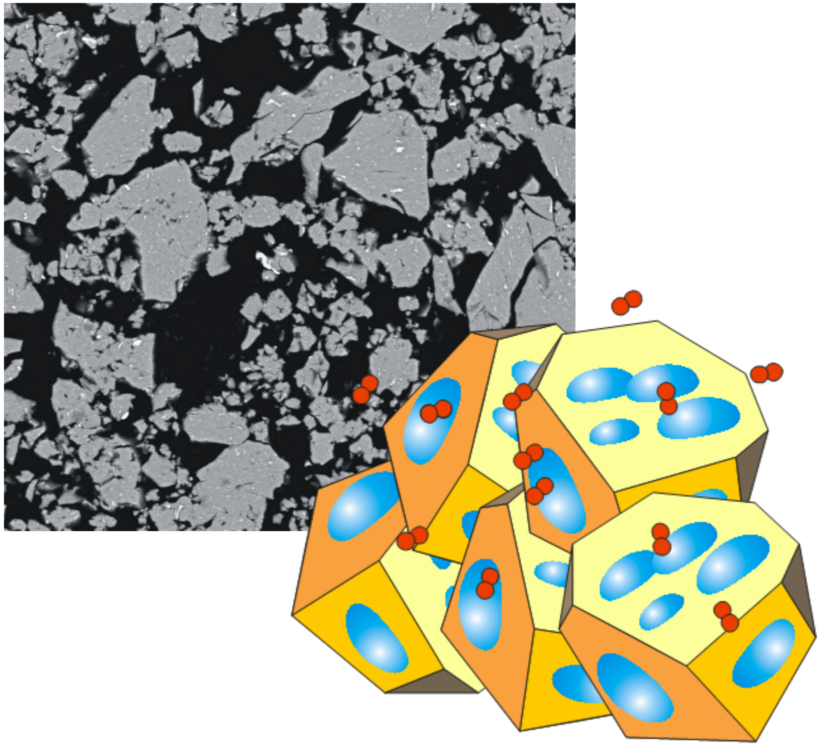
Surface mechanisms

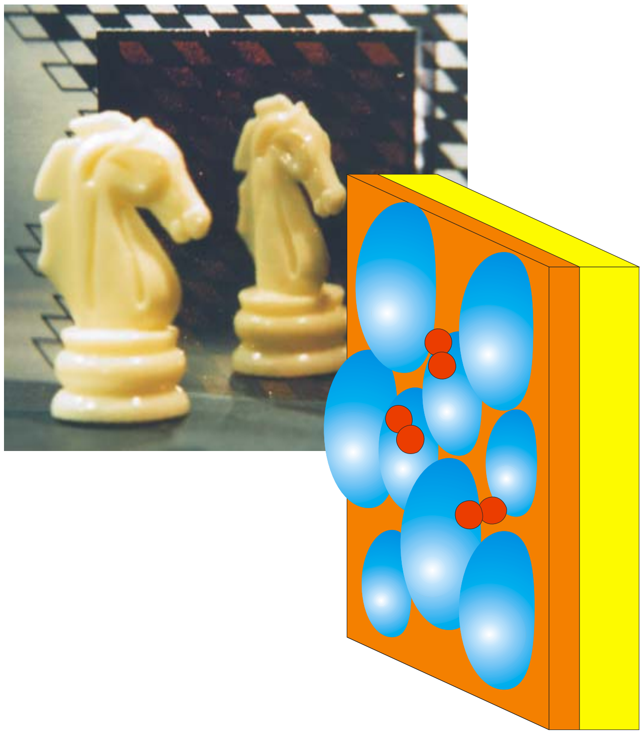




A. Borgschulte et al. Journal of Catalysis **239** (2006) 263–271

Depicting reality: Thin metal hydride films



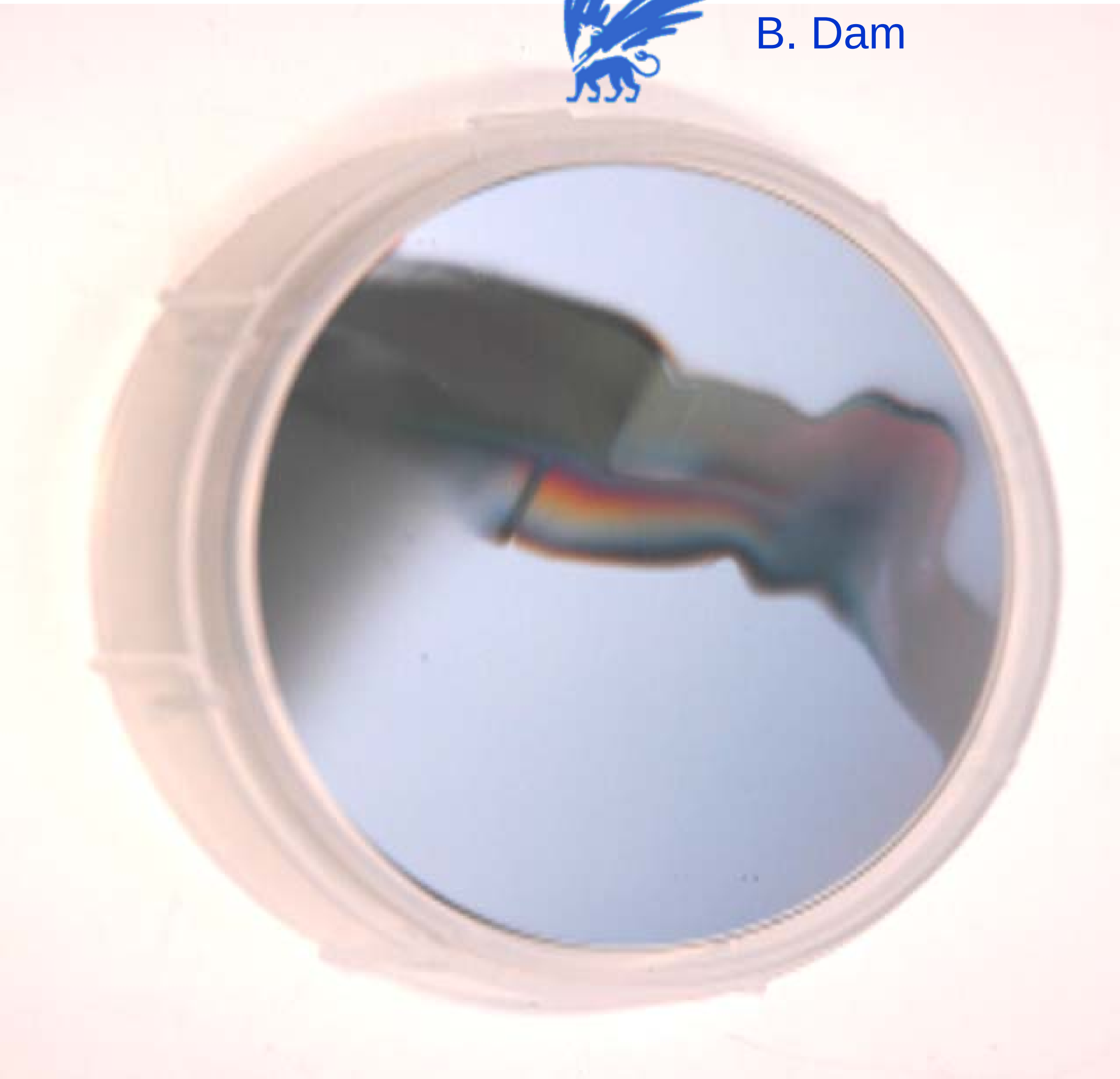


- **Switch. Mirrors: Pd-clusters, Y-oxide, YH_x**
- **$LaNi_5$: Ni-clusters, La-oxide, $LaNi_5H_x$**
- **MgH_2: Surface (additive), MgH_2, MgH_0**

A. Borgschulte et al., PRB 78, 094106 (2008)

Hydrogen in materials changes optical properties

R. Griessen/
B. Dam



- Measurements of hydrogen content in **thin films**
- Determination of thermodynamics and kinetics
- Thin film setup for testing models

Huiberts et al. Nature **380** (1996) 231;

Gremaud et al. Adv. Mat. **19** (2007) 281.

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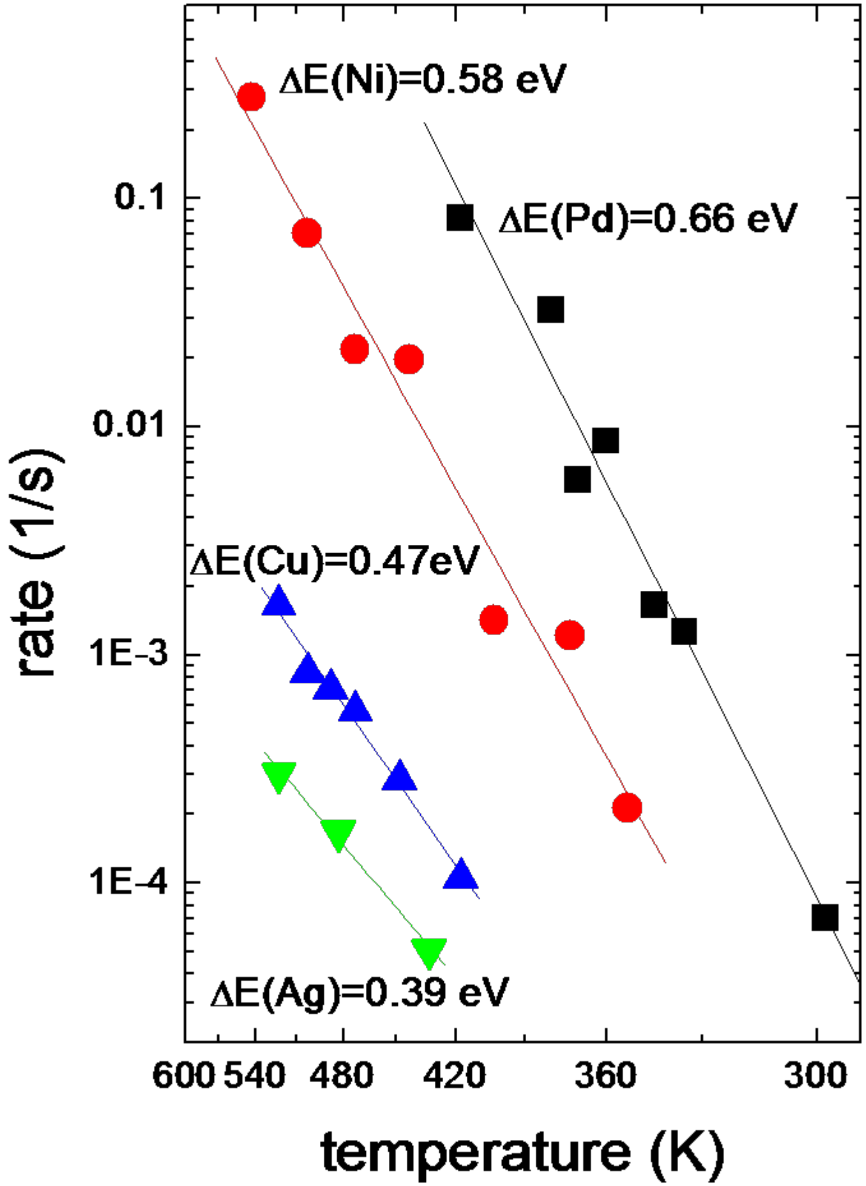
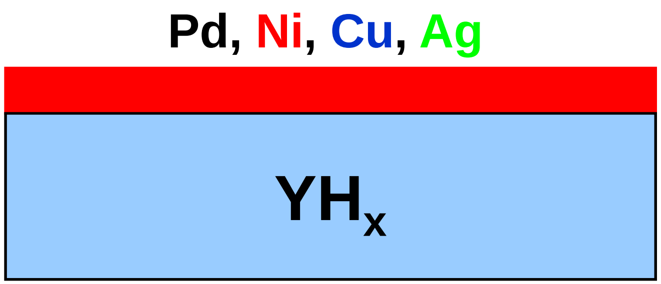
Temperature dependence of H-uptake in yttrium catalyzed by noble metal coatings



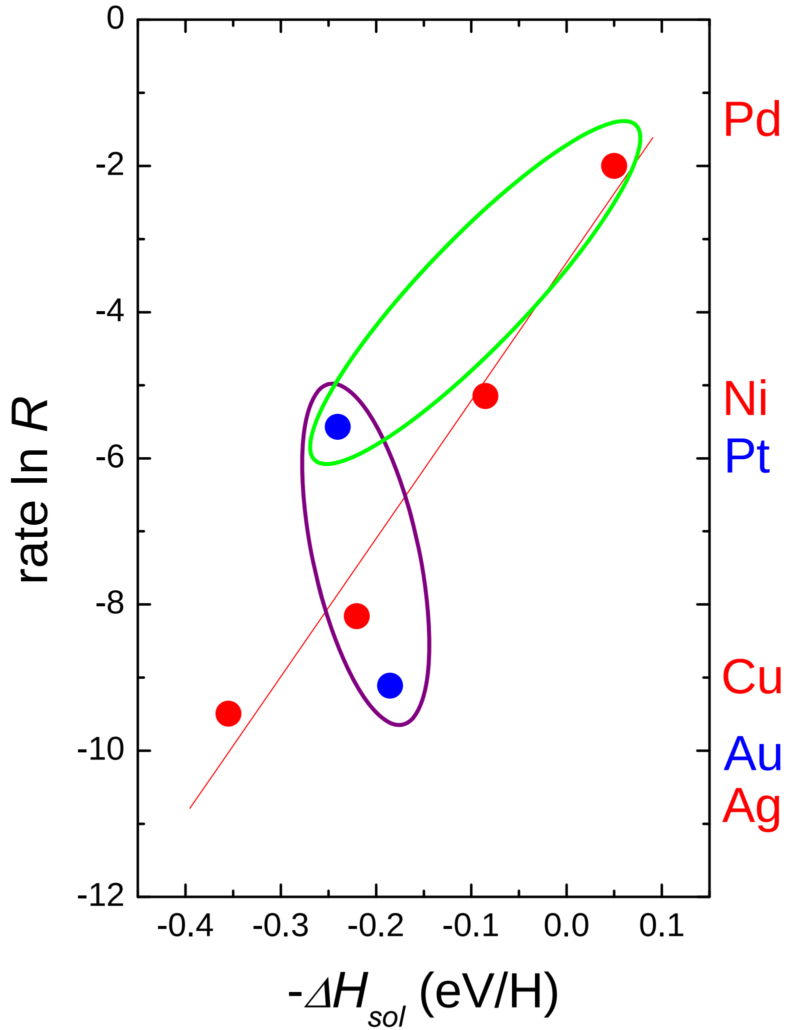


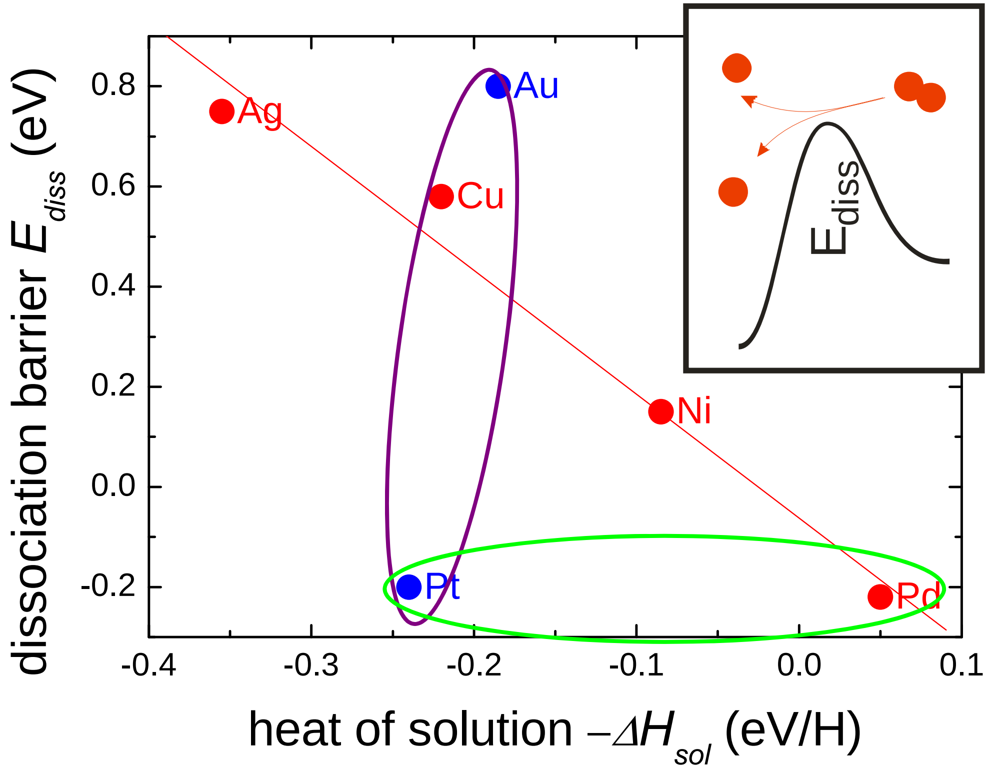
The higher the activation energy

The higher the rate?

A. Borgschulte et al. J. Catal. **239** (2006) 263–271

What cluster material is the best?
The catalytic effect of noble metals on yttrium





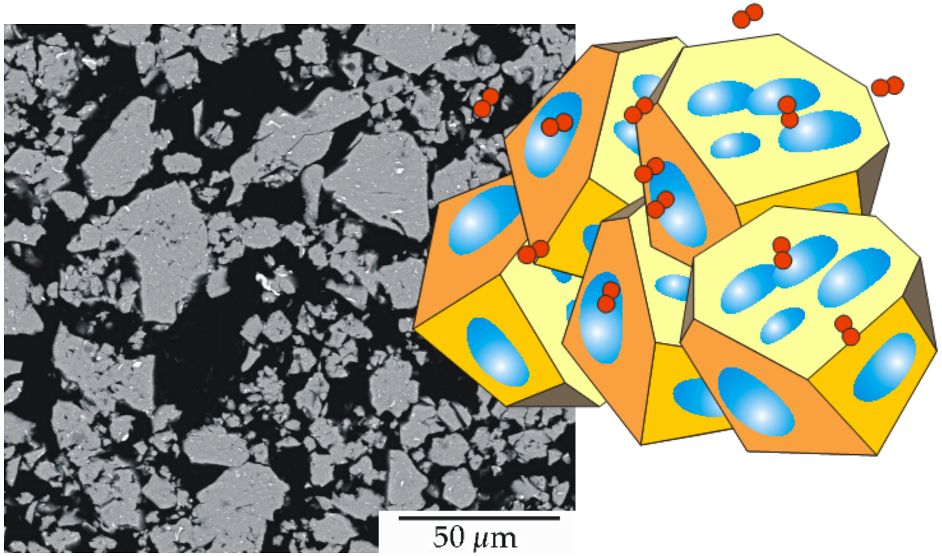
high rate =

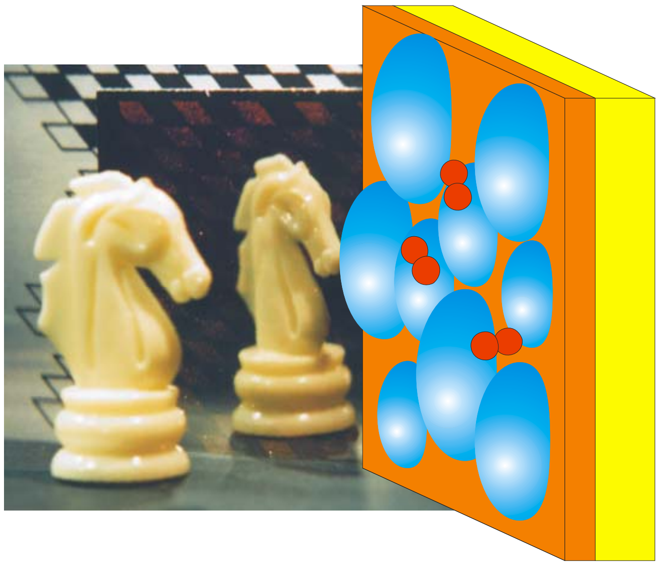
small dissociation barrier

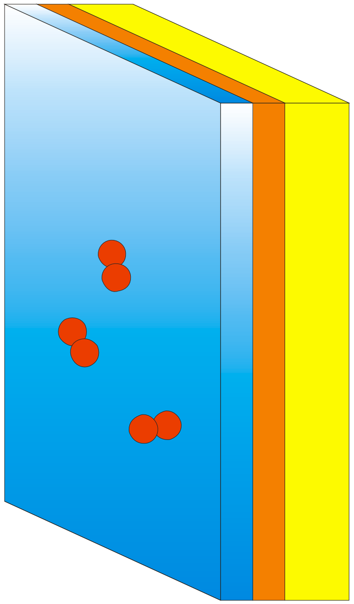
+ high negative heat of solution

A. Borgschulte et al. Journal of Catalysis **239** (2006) 263–271

Depicting reality: The two layers model



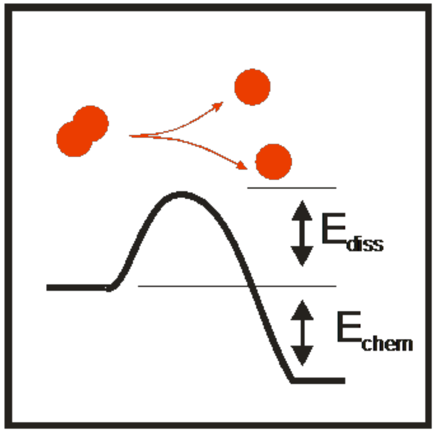




- **Constant plateau pressure:**
  $p(x_{ae} \ldots x_{ba}) = p_{pl} \sim const., \; p_{pl} \neq f(t)$
- **One dissociation step**
- **One diffusion step**

A. Borgschulte et al., PRB 78, 094106 (2008)

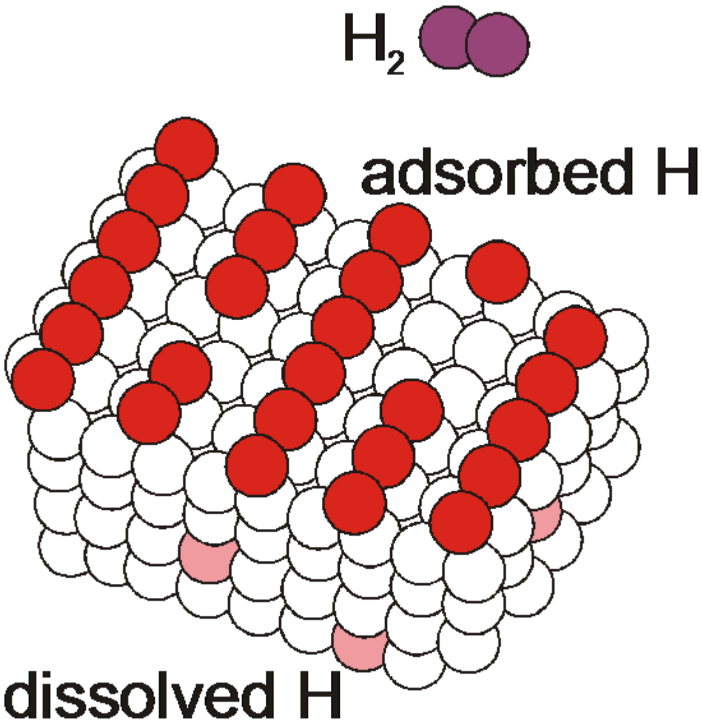
SURFACE



Dissociation

H- coverage

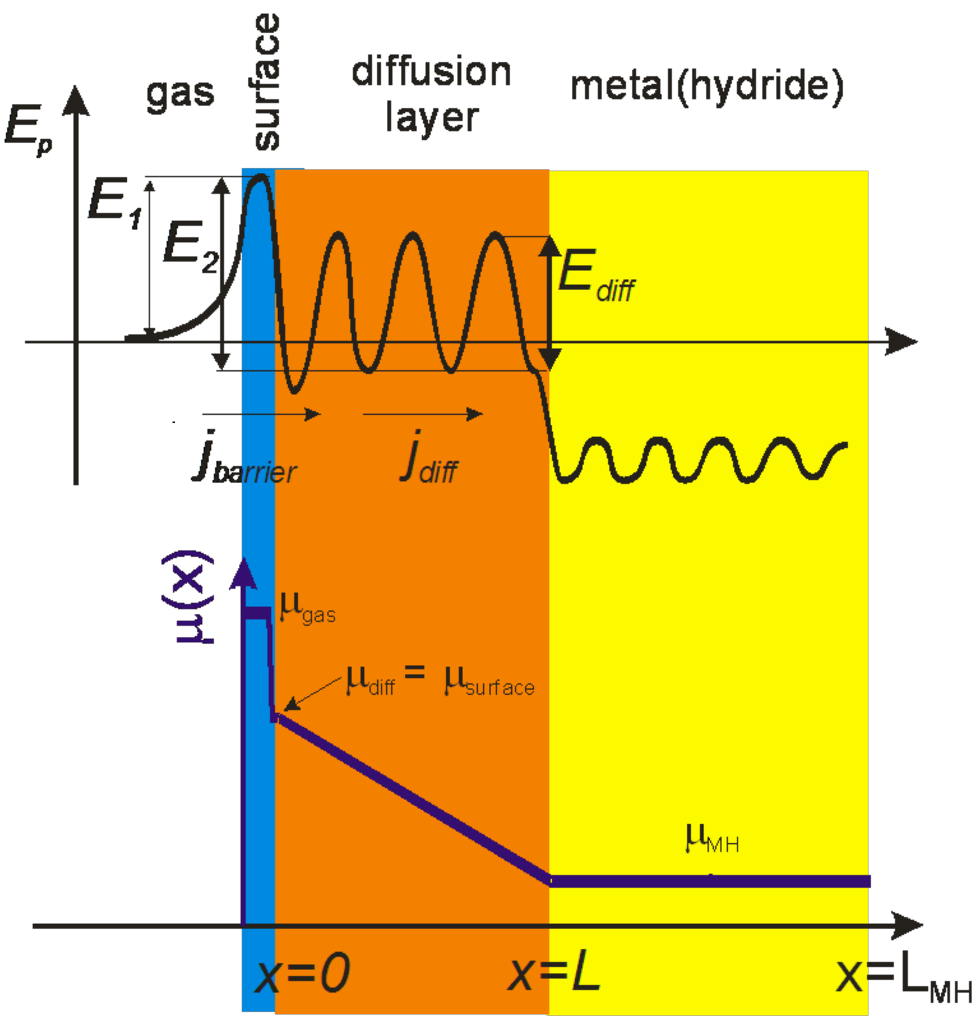
$$j_{diss} = a p_{H_2} \cdot e^{-E_{diss}/kT} \cdot \left(1-\theta_H\right)^2 - b \cdot e^{-\left(E_{diss}+E_{chem}\right)/kT}\theta_H^2$$

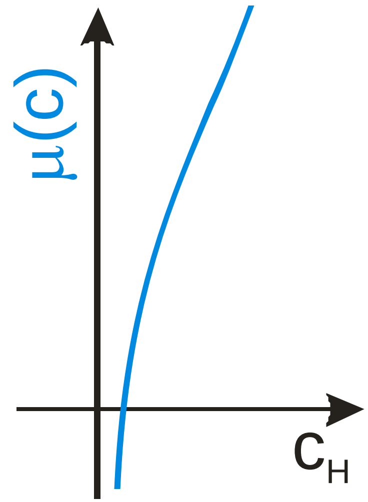


The chemical potential **at the surface** is equal to that **under the surface:**

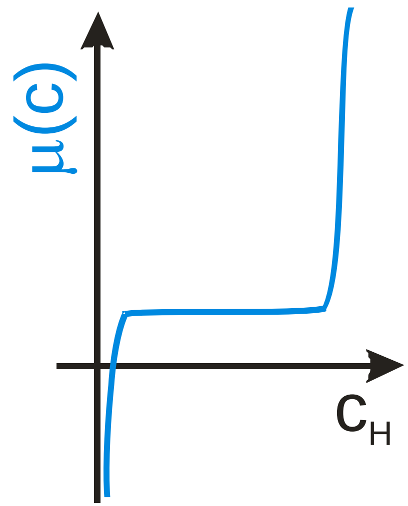
$$\frac{\theta_H}{1-\theta_H}e^{-\Delta G_{surf}/kT} = \frac{c_H}{1-c_H}e^{-\Delta G_{bulk}/kT}$$

Diffusion through material





Model potential
In the diffusion
layer



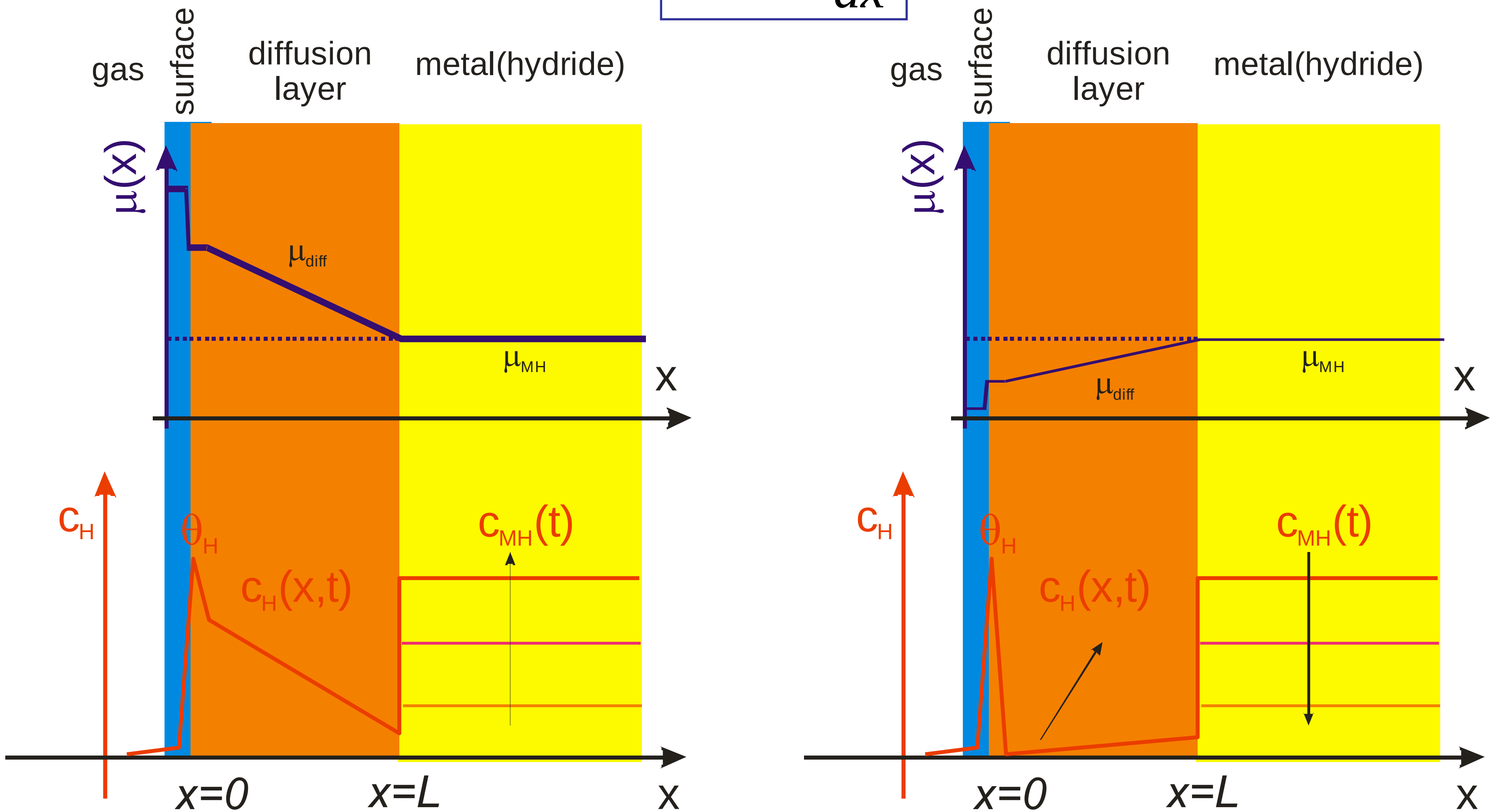
Model potential
in the hydride
layer

Chemical Potential in NON-EQUILIBRIUM

Chemical potential of hydrogen gas .... Chemical potential in metal hydride

Rate is defined by

$$j = -L\frac{d\mu}{dx}$$



Analytical solution and approximation

$$R \propto \frac{D}{L}\left[\frac{-\frac{D}{L}+\sqrt{\left(\frac{D}{L}\right)^2+4B\left(\frac{\alpha D}{L}\sqrt{p_{pl}}+Ap\right)}}{2B}-\alpha\sqrt{p_{pl}}\right]$$

If $Ap_{H_2} >> \frac{D}{L}$ **i.e. low diffusion, the rate is**

Diffusion-limited $R \propto \frac{D}{L}\left[\sqrt{\frac{A}{B}}\cdot\sqrt{p}-\alpha\sqrt{p_{pl}}\right]$

If $Ap_{H_2} << \frac{D}{L}$ **i.e. high diffusion, the rate is**

Dissociation-limited $R \propto A\left(p-p_{pl}\right)$

Compare to M. Pasturel, et al., Chem. Mater. 19, 624 (2007).

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Pressure dependence

rate-limiting step conditions	simplified kinetics	activation energy
dissociation $p >> p_{pl}$	$R = Ap$	E_1
dissociation $p \simeq p_{pl}$	$R = A(p - p_{pl})$	$E_1 + \frac{p_{pl}}{p - p_{pl}} 2\Delta H_{MH}$
diffusion $p >> p_{pl}$,	$R = \frac{D}{L}\sqrt{\frac{A}{B}\cdot p} = \frac{D}{L}\alpha \cdot \sqrt{p}$	$\Delta H_{sol} + E_{diff}$
diffusion $p \simeq p_{pl}$	$R = \frac{D}{L} \cdot \alpha \left[\sqrt{p} - \sqrt{p_{pl}}\right]$	$\Delta H_{sol} + E_{diff} + \frac{\sqrt{p_{pl}}}{\sqrt{p} - \sqrt{p_{pl}}} \Delta H_{MH}$
diffusion $p_{pl} >> p \simeq 0$,	$R = -\frac{D}{L}\sqrt{\frac{A}{B}}\sqrt{p_{pl}} = \frac{D}{L}\alpha \cdot \sqrt{p_{pl}}$	$\Delta H_{sol} + E_{diff} - \Delta H_{MH}$
recombination $p_{pl} >> p \simeq 0$	$R = -Ap_{pl}$	$E_1 - 2\Delta H_{MH}$

A. Borgschulte et al., PRB 78, 094106 (2008)

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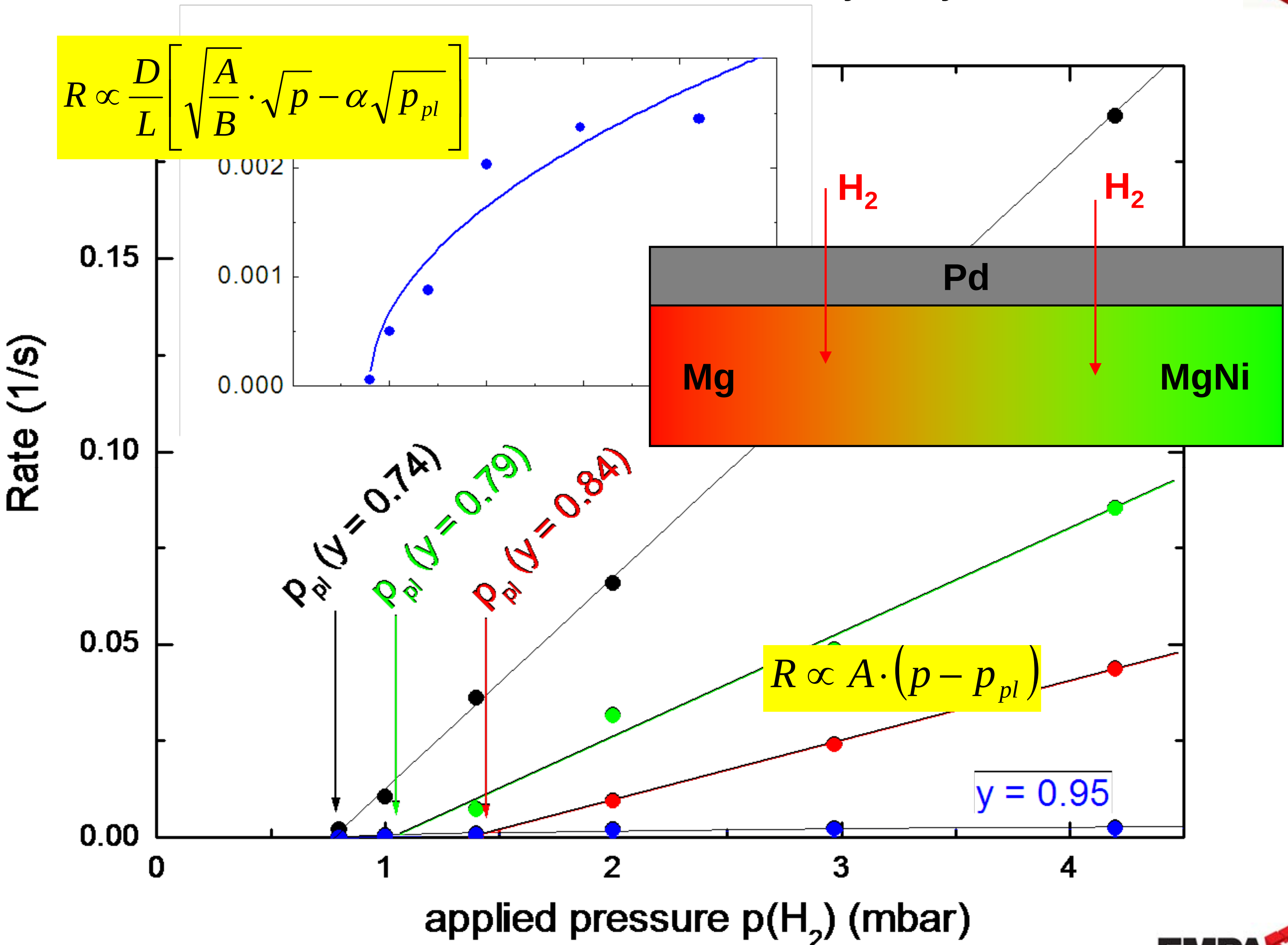
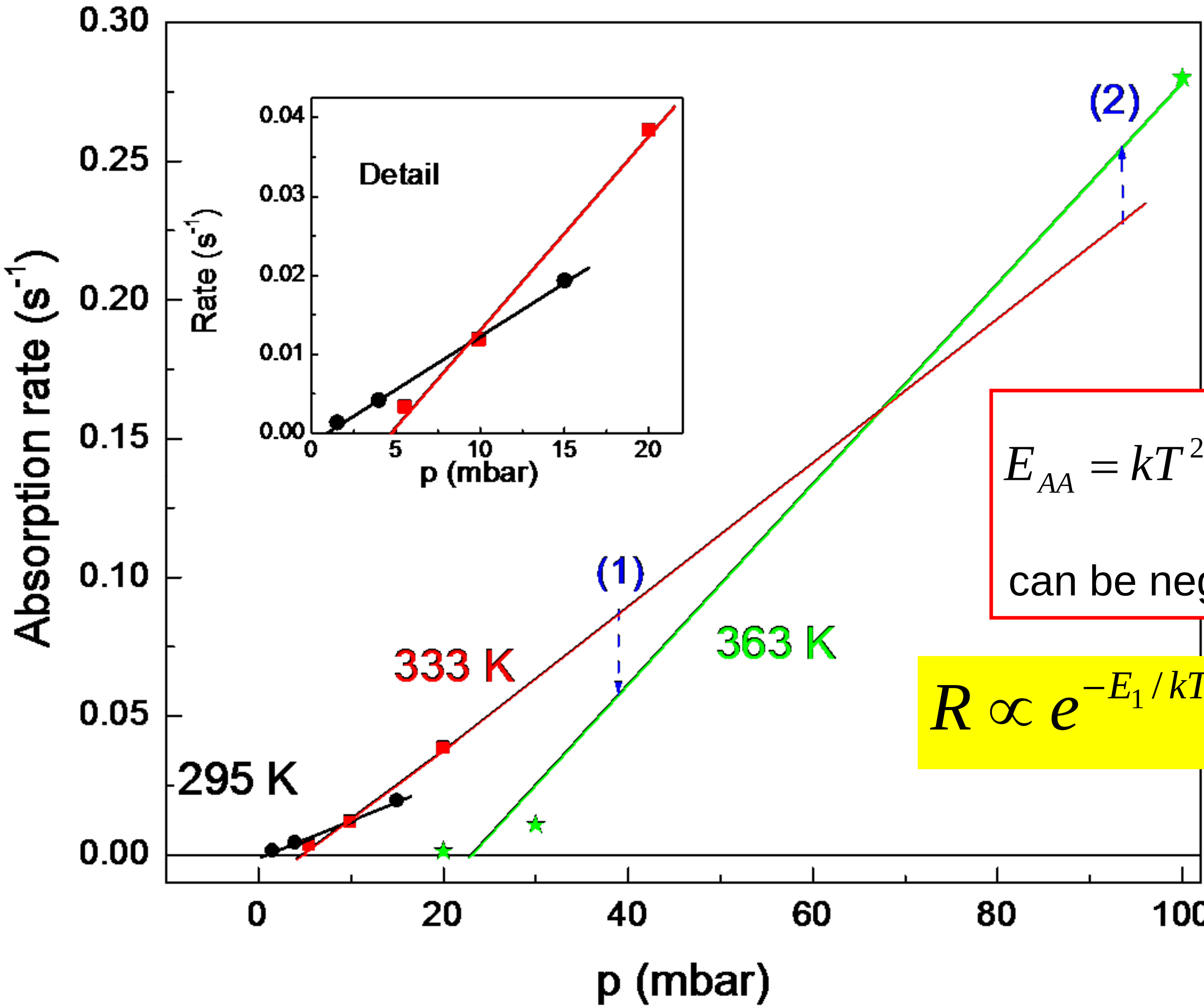
Pressure dependence of Pd-capped Mg_yNi_{1-y} thin films



A. Borgschulte et al., PRB 78, 094106 (2008)

Hydrogen absorption of Pd-capped Mg_2Ni thin films: pressure dependence



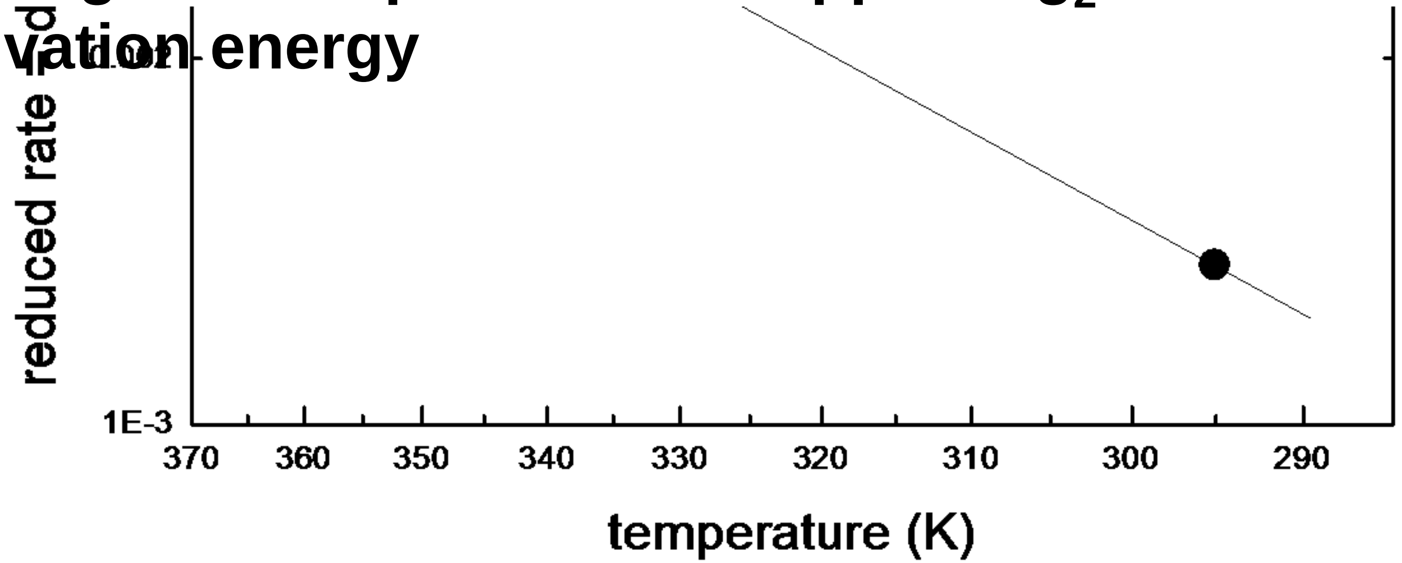
$$E_{AA} = kT^2 \frac{\partial \ln R}{\partial T}$$

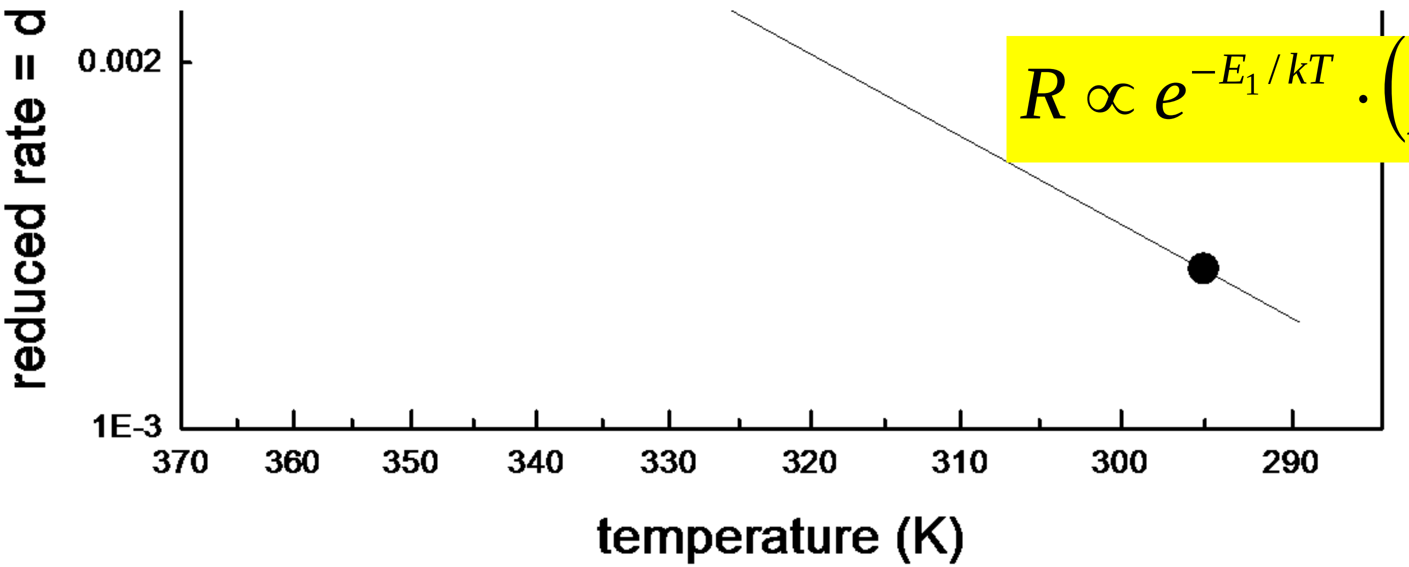
can be negative!

$$R \propto e^{-E_1/kT} \cdot \left(p - p_{pl}\right)$$

A. Borgschulte et al., PRB 78, 094106 (2008)

Hydrogen absorption of Pd-capped Mg_2Ni thin films: activation energy

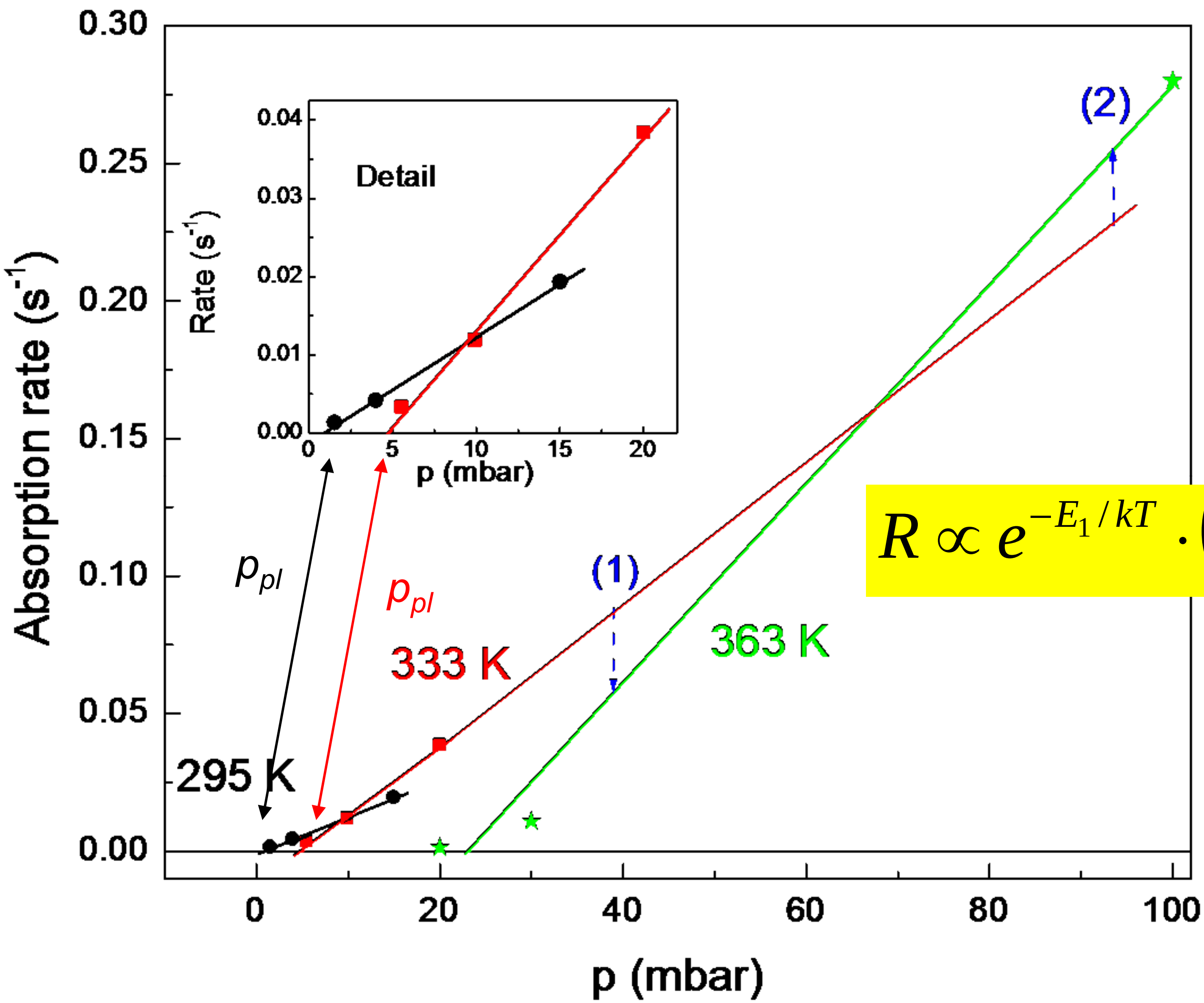




$$R \propto e^{-E_1/kT} \cdot \left(p - p_{pl}\right)$$

A. Borgschulte et al., PRB 78, 094106 (2008)

Hydrogen absorption of Pd-capped Mg_2Ni thin films: pressure dependence



$$R \propto e^{-E_1/kT} \cdot (p - p_{pl})$$

A. Borgschulte et al., PRB 78, 094106 (2008)

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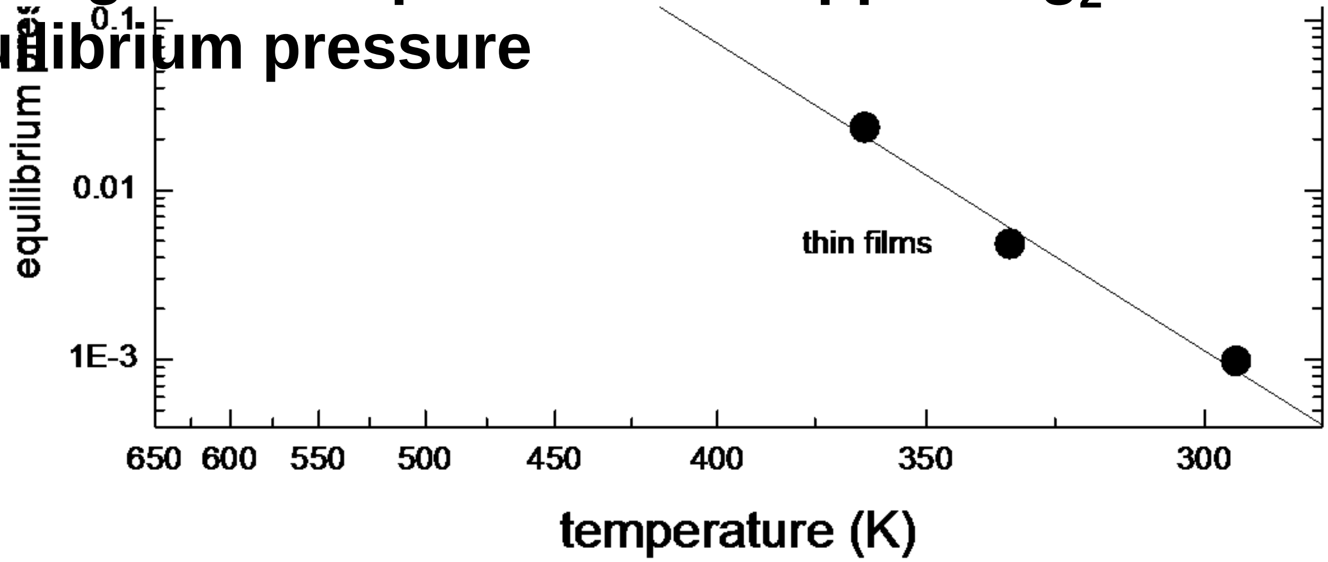
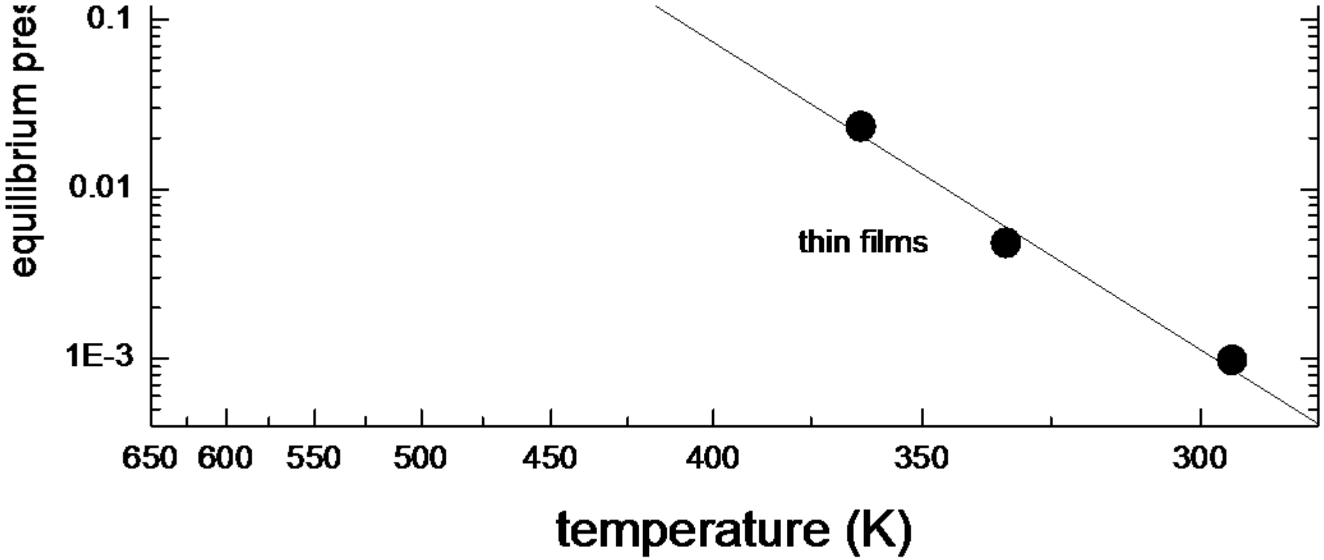
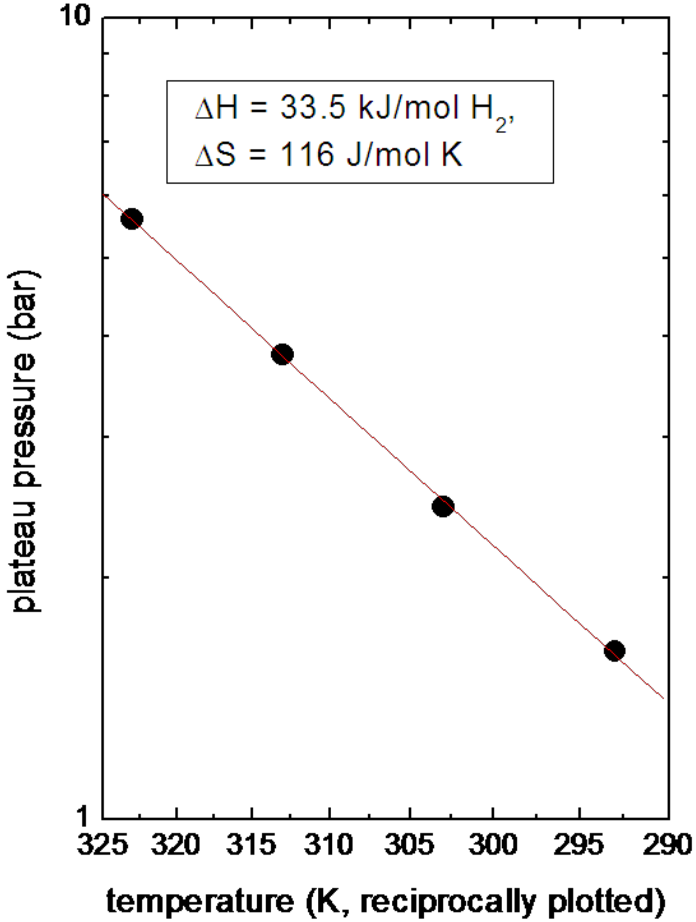
Hydrogen absorption of Pd-capped Mg_2Ni thin films: equilibrium pressure

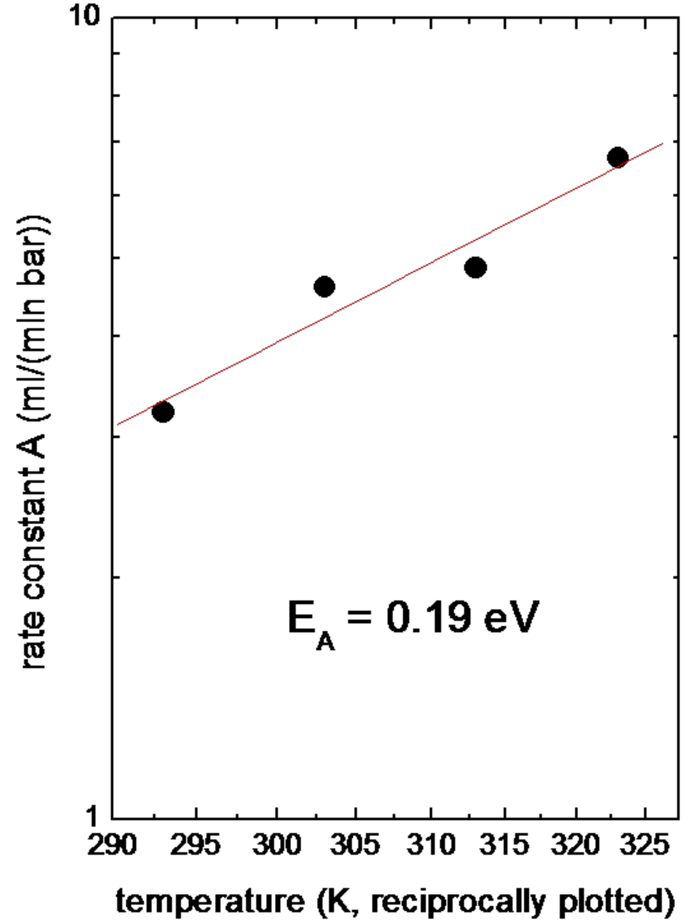




A. Borgschulte et al., PRB 78, 094106 (2008)

Stability and Kinetics of $LaNi_5H_x$

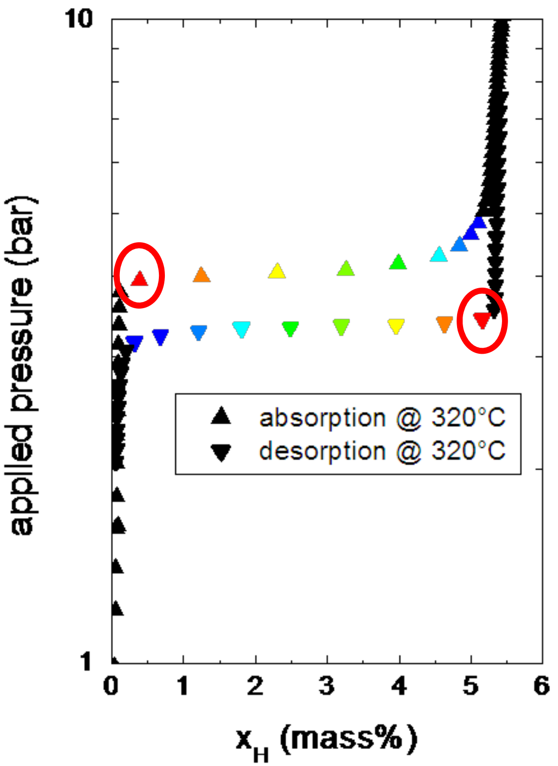




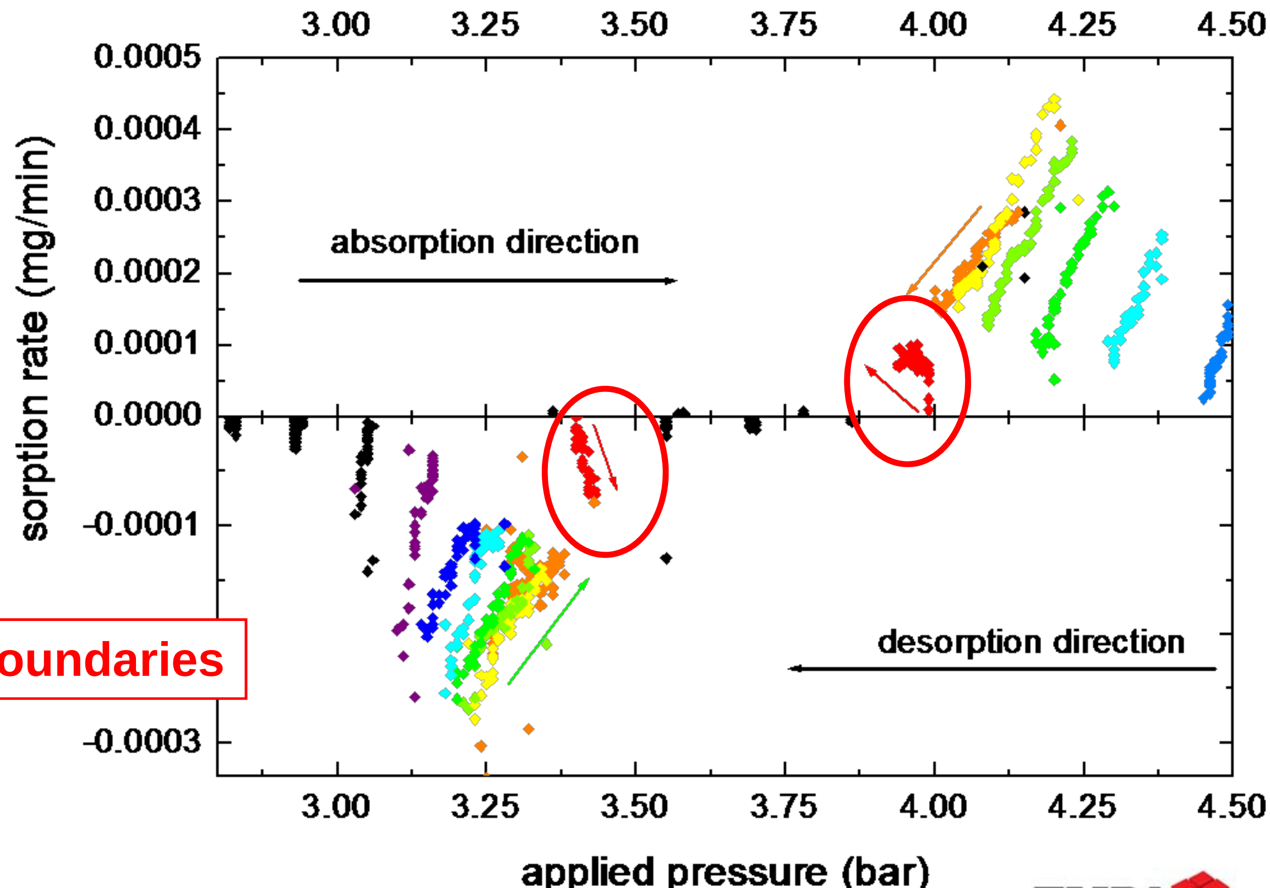
Literature values:

ΔH = -32 kJ/mol H_2: H.H. van Mal, Phips Res. Repts. Suppl. 1 (1976);
ΔH = -32.1 kJ/mol H_2: W.N. Hubbard et al., J. Chem. Thermodynam. 15 (1983) 785;
ΔH = -34.8 kJ/mol H_2: J.J. Murray, M.L. Post, J.B. Taylor, J. Less-Common Met. 80 (1998) 81.
E_A = 0.19…0.5 eV (several original Refs., see A. Andreasen et al., J. Phys. Chem. B 109, 3340 (2005)

Sorption kinetics in MgH_2



$$R = f(p, x_H, t)$$



nucleation @ plateau boundaries

SUMMARY

- The knowledge of the **hydrogen sorption mechanism** is mandatory
  - To extrapolate equilibrium values
  - To gain information on kinetics, i.e. barrier heights etc.

- **Analysis of kinetic curves**
  - Qualitatively: nucleation, diffusion, dissociation
  - Quantitatively: Two-step model

Thank you for interest!

First Conference Announcement

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The International Association for Hydrogen Energy (IAHE)

Organized by: EnergieAgentur.NRW

In cooperation with:

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DWV Deutscher Wasserstoff- und Brennstoffzellen-Verband

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