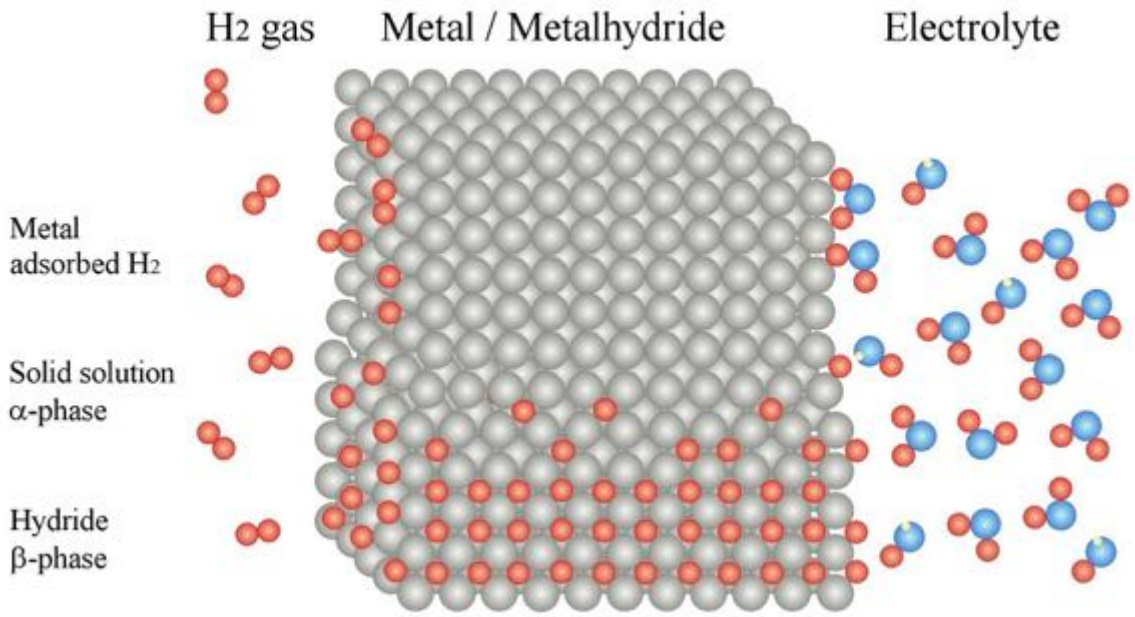
HYDRIDES

H_2 gas phase

alkaline electrolyte



1) Physisorption of H_2 molecules
2) Dissoziation (activation barrier)
3) Chemisorption of H-atoms
4) Diffusion of H-atoms
5) Intercalation

1) Physisorption of H_2O molecules
2) Electron transfer (desorption of OH^-)
3) Chemisorption of H-atoms
4) Diffusion of H-atoms
5) Intercalation

Hydrides

1. History of Hydrogen

2. Properties of Hydrogen
2.1. Size of Hydrogen molecule, atom and ions
2.2. States of Hydrogen
2.3. Compressed Hydrogen

3. Hydrogen phases

4. Physisorption of Hydrogen
4.1. BET Model
4.2. Area of a Monolayer of Adsorbed Gases
4.3. High Surface Area Materials
4.4. H2 vol. Density of High Surface Area A_{spec} Materials
4.5. High Surface Area Materials

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5.2. Metal Hydride
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5.5. Semi-empirical Model for the Stability
5.6. Hydrogen in the Metal
5.7. Lattice Gas Model
5.8. Thermodynamics of Hydrides

6.a) Hydrogen sorption film
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6.4. Van't Hoff Plot of Hydrides
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7. Interstitial Sites in Metal Hydrides
7.1. Hydrogen in and on Palladium (Pd)
7.2. Hydrogen in Palladium (Pd)
7.3. Hydrides of Intermetallic Compounds and Alloys
7.4. Hydride of LaNi5
7.5. Interstitial Sites in Laves Phases AB_2
7.6. Hydrides
7.7. No Correlation between Hydrogen Capacity and Stability
7.8. Metal Hydrides with Short H-H Separations
7.9. Body Centered Cubic (bcc) Solid Solution Alloys
7.10. Body Centred Cubic (bcc) Alloys

Hydrogen Storage

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8.1. Interstitial Sites for Hydrogen
8.2. Stability from Differential Scanning Calorimetry
8.3. Stability from BORN-HABER Cycle
8.4. Destabilisation of MgH_2
8.5. Hydrogen Absorption Kinetics in $LaNi_5$
8.6. Kinetics of Hydrogen Absorption

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9.2. Stability of Complex Hydrides
9.3. Comparison Metal Hydrides vs. Complex Hydrides
9.4. Development of the Gravimetric Hydrogen Density
9.5. Hydrogen Storage Materials
9.6. Hydrogen Storage Density

10. Applications

10.1. Metal Hydride Compressor
10.2. Pressure vs. Temperature
10.3.a) Metal Hydride Compressor Film
10.3.b) Metal Hydride Compressor Sequences
10.4. Energy Density
10.5. Hydrogen Storage in Mobility
10.6. Swiss Hydrogen Developments

11. Hydrogen Safety

11.1.a) Reaction of Metals with Water Film
11.1.b) Reaction of Metals with Water Film
11.2. Hindenburg Accident
11.3. Hindenburg Accident Investigation
11.4.a) Fuel Leak Simulation
11.4.b) Fuel Leak Simulation
11.5. Flammability & Explosion Limits
11.6. Properties of Fuels
11.7. Hydrogen Codes and Standard
11.8. Room & Materials
11.9. Fire Hazard & Protection
11.10. Fire Extinguisher & Protective Atmosphere
11.11. Storage & Transport
11.12. Health hazard of Metal Dust
11.13.a) Thermite on Ice Film
11.13.b) Thermite on Ice Sequence

1. History of Hydrogen

$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$ "Hydrogène"

Robert BOYLE
1670

Antoine LAVOISIER
1783

first H_2 balloon flight

Jacques Alexandre César CHARLES
1783

Metal hydride

Thomas GRAHAM
1868

liquid & solid H_2

James DEWAR
1889

Properties of H_2

H_2
T_c = 33 K
p_c = 13.3 bar

Zygmunt Florenty WRÓBLEWSKI
1885

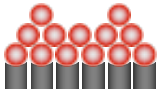
H_2 weather balloon

Leon Teisserenc DE BORT
1896

Zeppelin with H_2

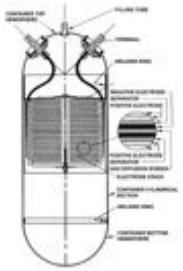
Graf Ferdinand VON ZEPPELIN
1900

Physisorption



Brunauer, Emmett, Teller
1938

Ni-Hydrogen Battery

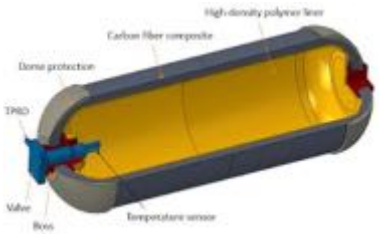


1971

Space Shuttle liq. H_2

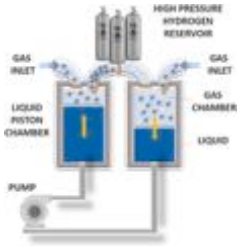
1981

Type IV H_2 tanks 700 bar



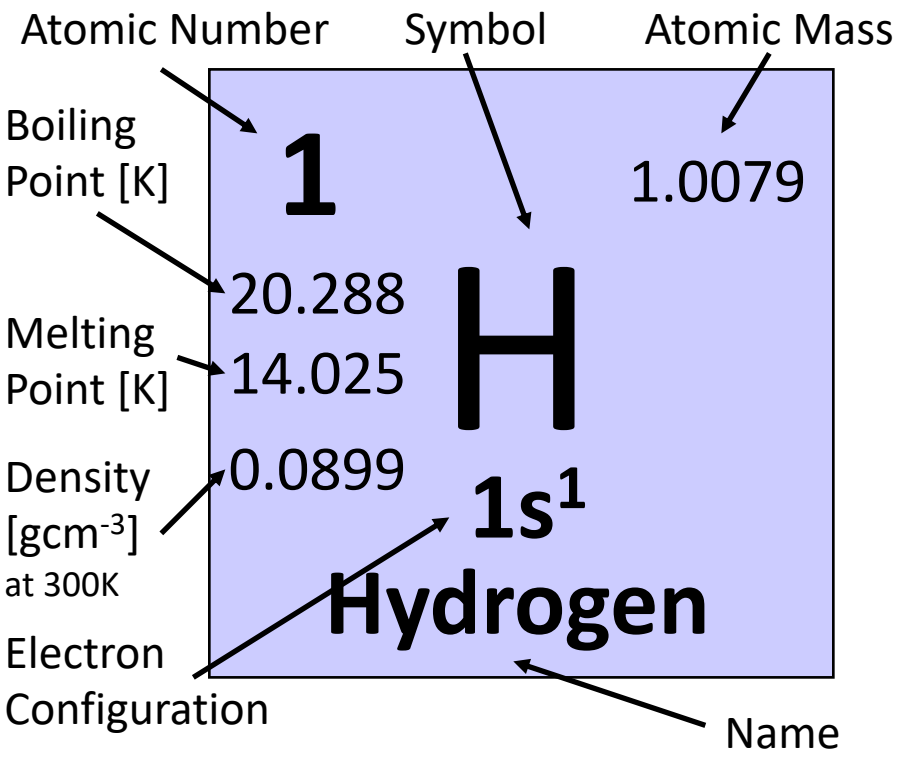
2001

Ionic liquid compressor

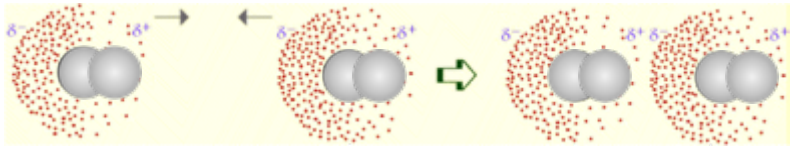


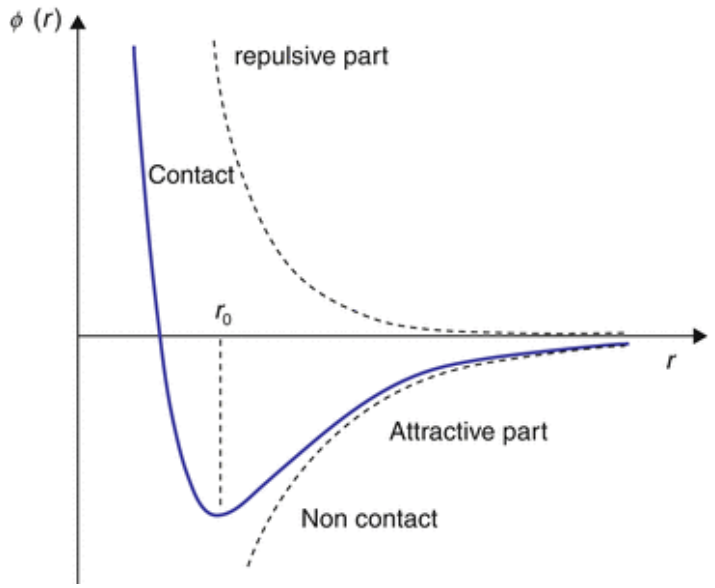
2005

2. Properties of Hydrogen

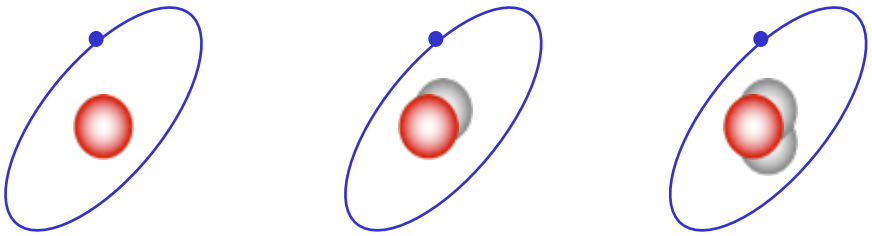


Van der Waals Forces





Isotopes



Hydrogen

Deuterium

$t_{1/2} = \infty$

Tritium

$t_{1/2}$ = 12.32y, β^-

kin. Gas Theory

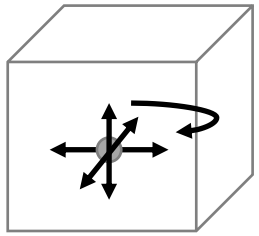
$$p = m\,n\left\langle v_x^2 \right\rangle$$

$$p = \frac{1}{3} m\,n\left\langle v^2 \right\rangle$$

$$p \cdot V = n \cdot R \cdot T$$

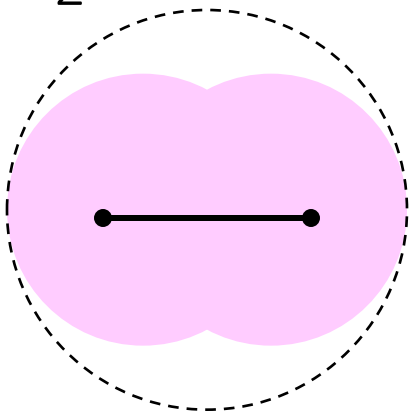
H_2

$$c = dQ/dT = 5/2 \cdot R$$



2.1. Size of Hydrogen molecule, atom and ions

H_2



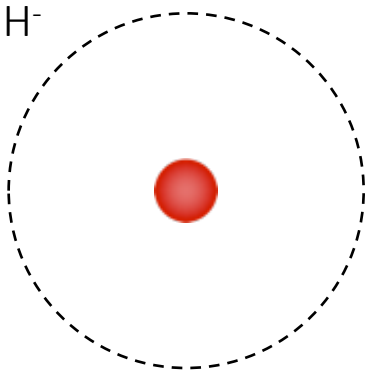
Van der Waals
$b(H_2) = 2.661 \cdot 10^{-5}$ $m^3 \cdot mol^{-1}$

$V(H_2) = 26.6$ $cm^3 \cdot mol^{-1}$
$r(H_2) = 2.34$ Å

Density of liquid
$r(H_2) = 70.8$ kg m^{-3}

$V(H_2) = 28.3$ $cm^3 \cdot mol^{-1}$
$r(H_2) = 2.38$ Å

H

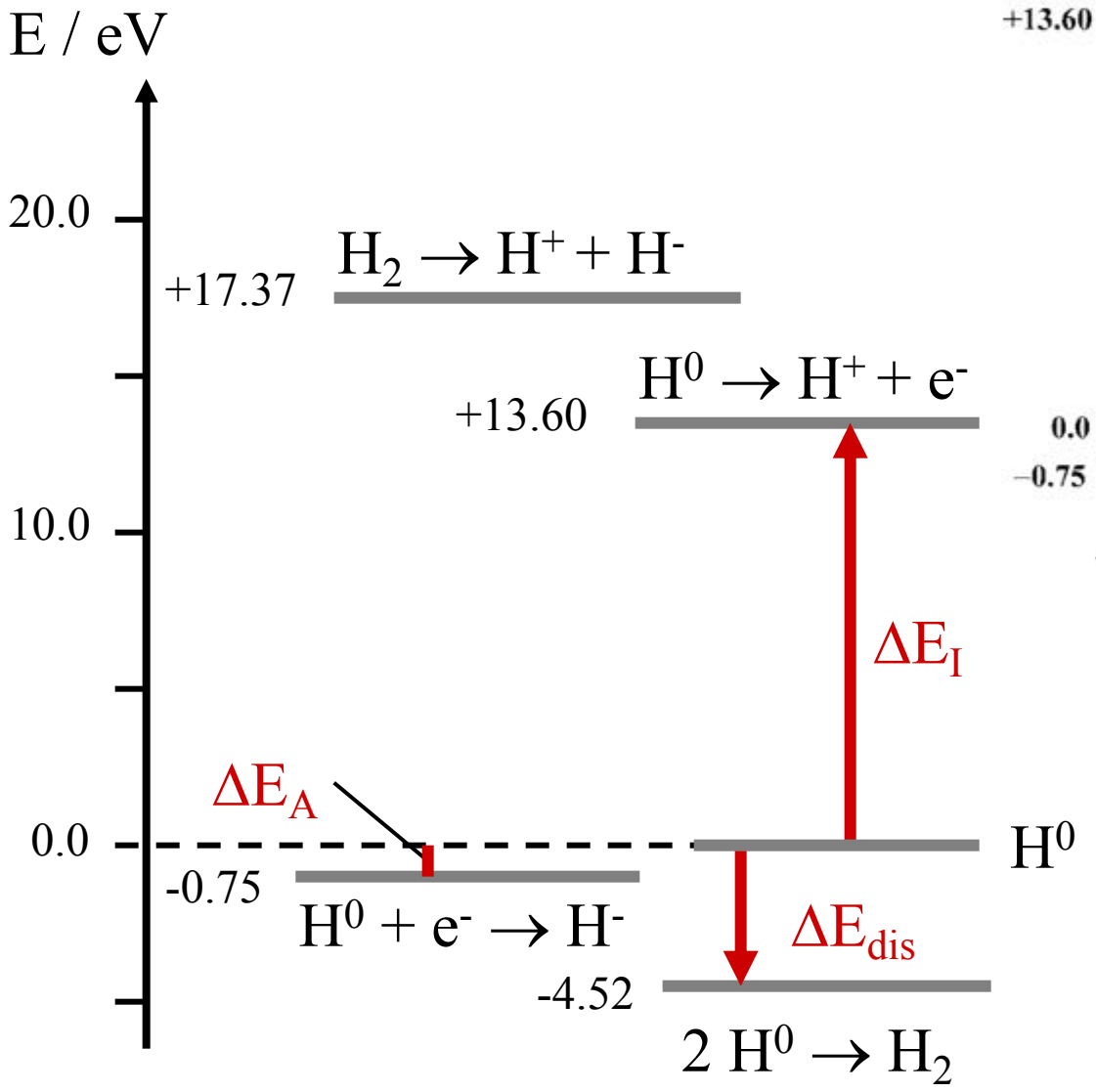


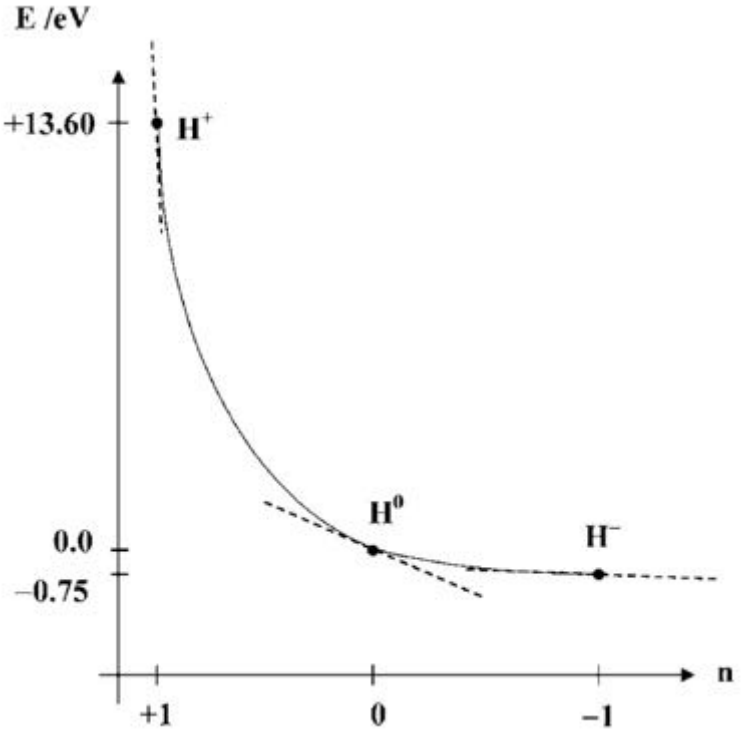
$r(H^0) = 0.37$ Å

$r(H^-) = 2.08$ Å

$r(H^+) = 10^{-5}$ Å

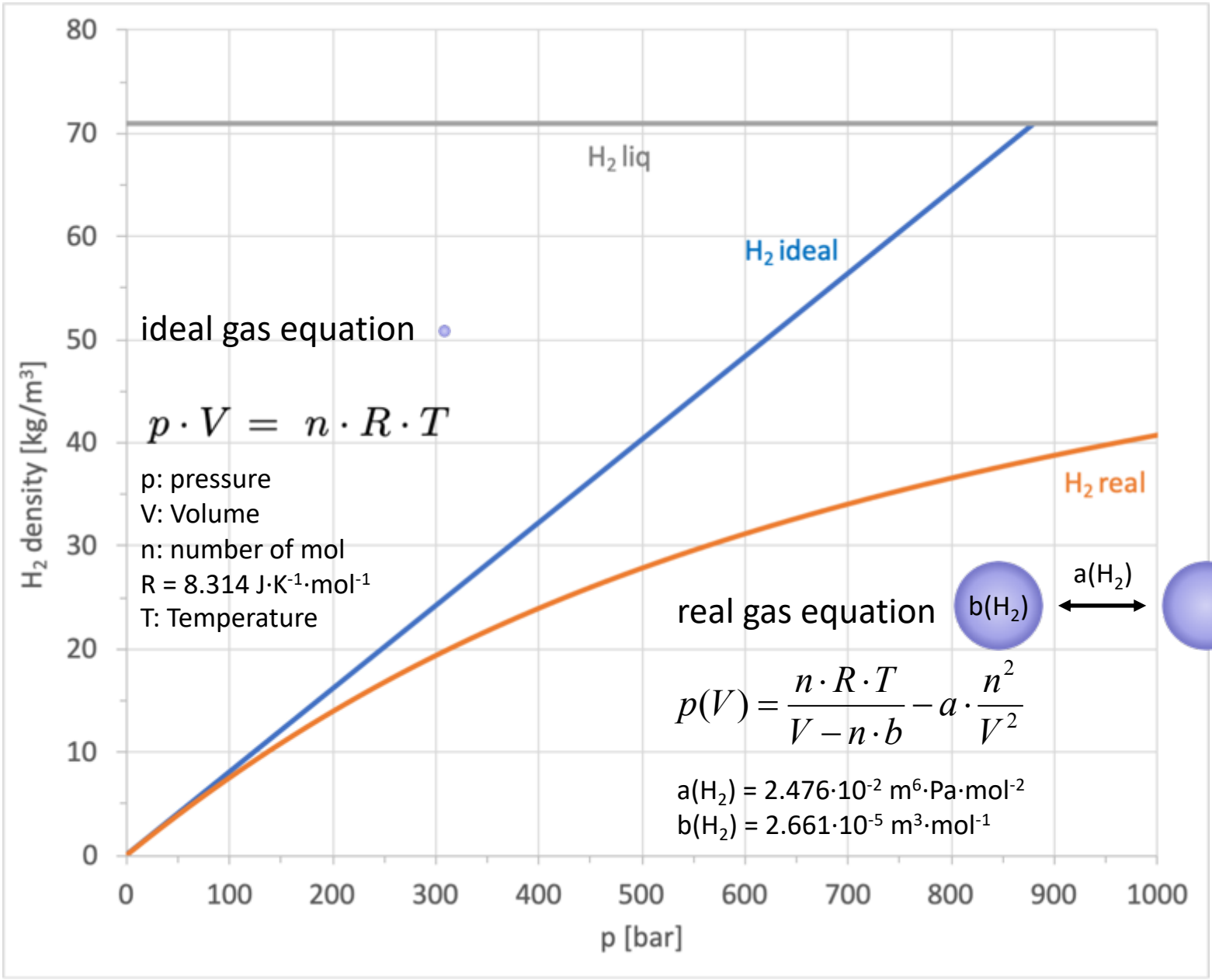
2.2. States of Hydrogen





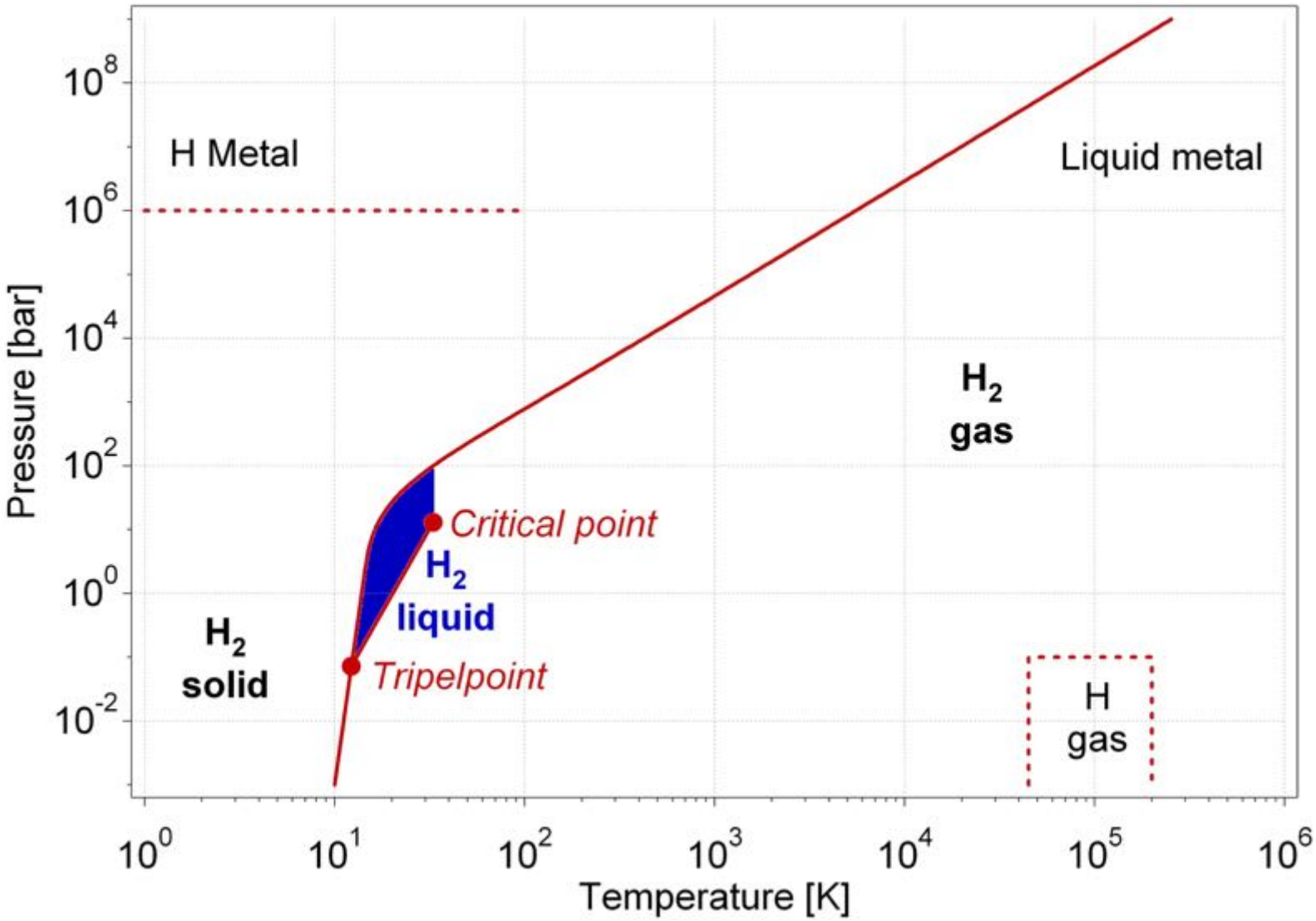
Ref.: Wojciech Grochala and Peter P. Edwards, “Thermal decomposition of the non-interstitial hydrides for the storage and production of hydrogen”, Chem. Rev. 104 (2004), pp. 1283-1315

2.3. Compressed Hydrogen



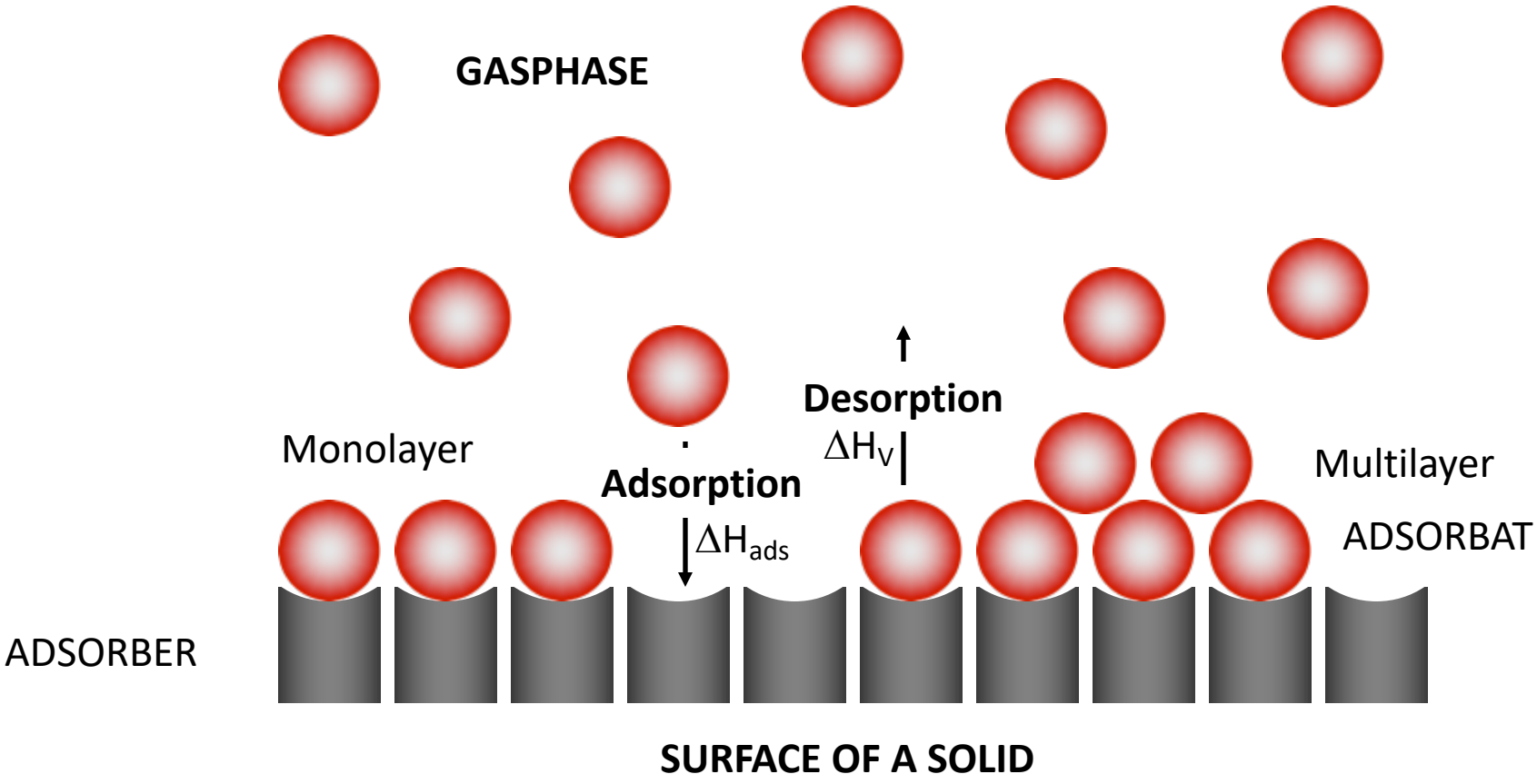
3. Hydrogen phases

Primitive Phase diagram



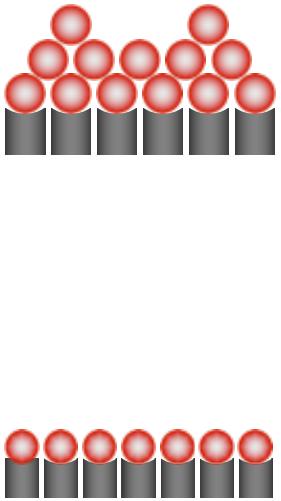
Ref: W. B. Leung, N. H. March and H. Motz, Physics Letters 56A (6) (1976), pp. 425-426

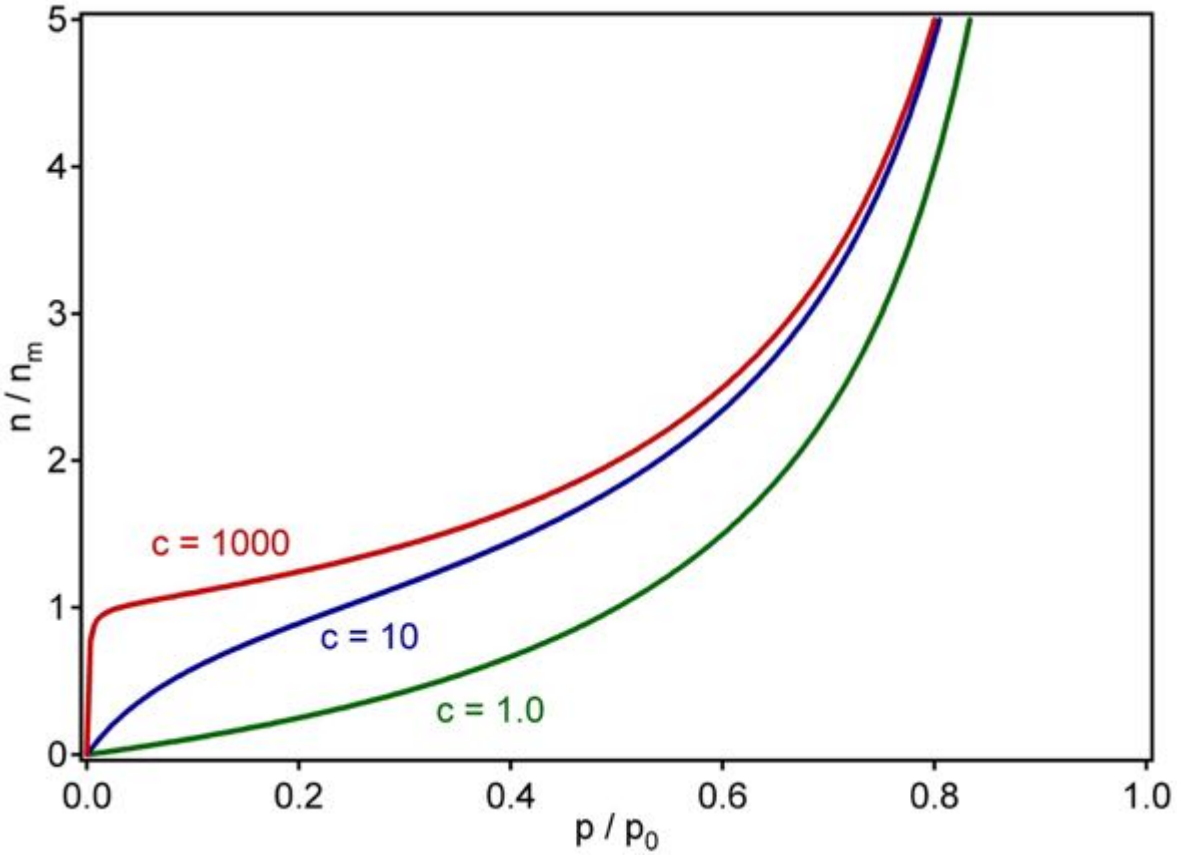
4. Physisorption of Hydrogen



Ref.: Stephen Brunauer, P. H. Emmett, Edward Teller: Adsorption of Gases in Multimolecular Layers. In: Journal of the American Chemical Society. Band 60, Nr. 2 (1938), pp. 309–319, doi:10.1021/ja01269a023

4.1. BET Model





$$c = e^{\frac{\Delta H_{ads} - \Delta H_V}{k \cdot T}}$$

$$\frac{n}{n_m} = \frac{c \cdot \beta}{(1-\beta)\cdot(1+(c-1)\cdot\beta)}$$

$$\beta = F \cdot \frac{k_a^0}{k_d^0} e^{\frac{\Delta H_V}{k \cdot T}} = \frac{p}{p_0}$$

linear form: $$\frac{1}{n[(p_0/p)-1]} = \frac{c-1}{n_m \cdot c} \cdot \left(\frac{p}{p_0}\right) + \frac{1}{n_m \cdot c}$$

$y = a \cdot x + b$

$n_m = (a+b)^{-1}$

$c = 1+a/b$

Ref.: Stephen Brunauer, P. H. Emmett, Edward Teller: Adsorption of Gases in Multimolecular Layers. In: Journal of the American Chemical Society. Band 60, Nr. 2 (1938), pp. 309–319, doi:10.1021/ja01269a023

4.2. Area of a monolayer of adsorbed gases

Gas	Density [g/cm^3]	VdWaals b [cm^3·mol^{-1}]	Mol mass [g·mol^{-1}]	Area [m^2·mol^{-1}]	d [Å]	d_{VdW} [Å]
H_2	0.082	26.61	2	71022	3.43	3.53
He	0.147	23.8	4	76397	3.56	3.40
N_2	0.808	38.7	28	89759	3.86	4.01
CO_2	1.562	42.67	44	78180	3.60	4.14
Ar	1.43	32.01	40	77747	3.59	3.76
H_2O	0.9998	30.49	18	58001	3.10	3.70

liquid (monolayer thickness):

$$d = \left(\frac{V_M}{N_A}\right)^{\frac{1}{3}} = \left(\frac{M}{\varrho \cdot N_A}\right)^{\frac{1}{3}}$$

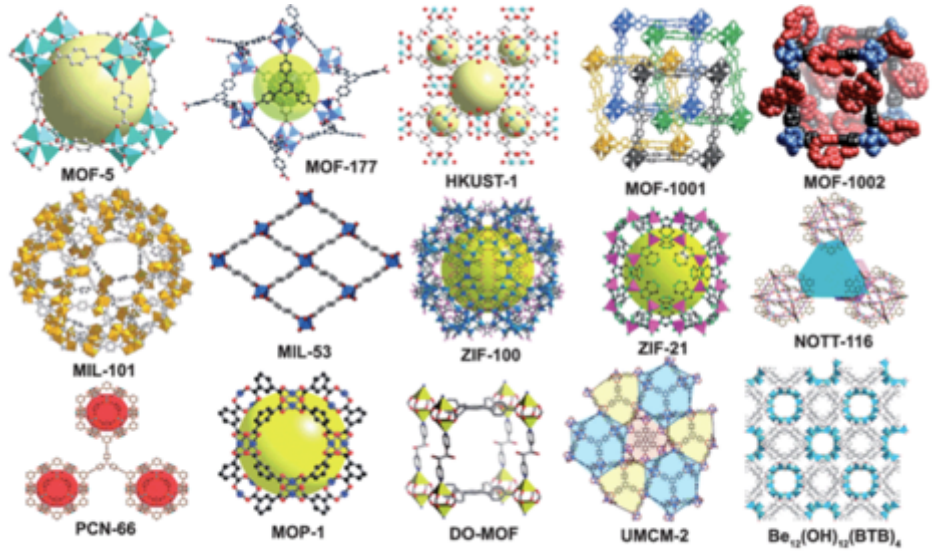
VdW Gas equation:

$$d = \left(\frac{b}{N_A}\right)^{\frac{1}{3}}$$

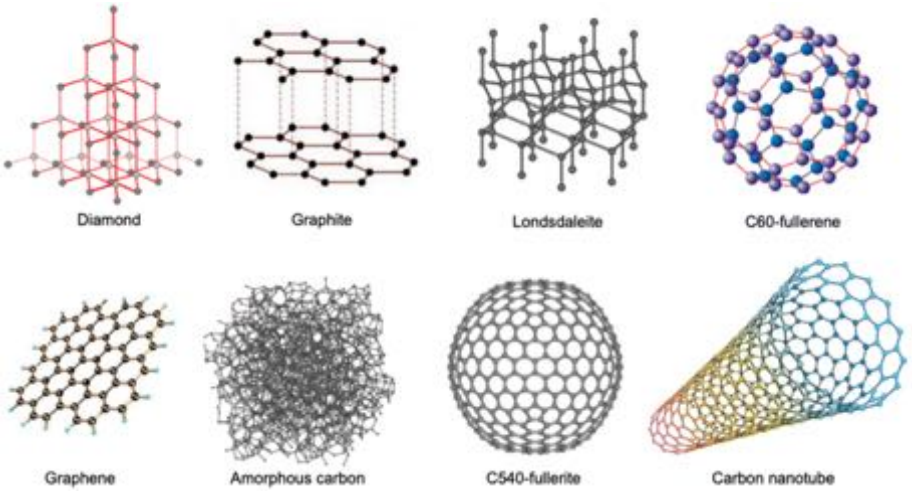
Monolayer area per mol:

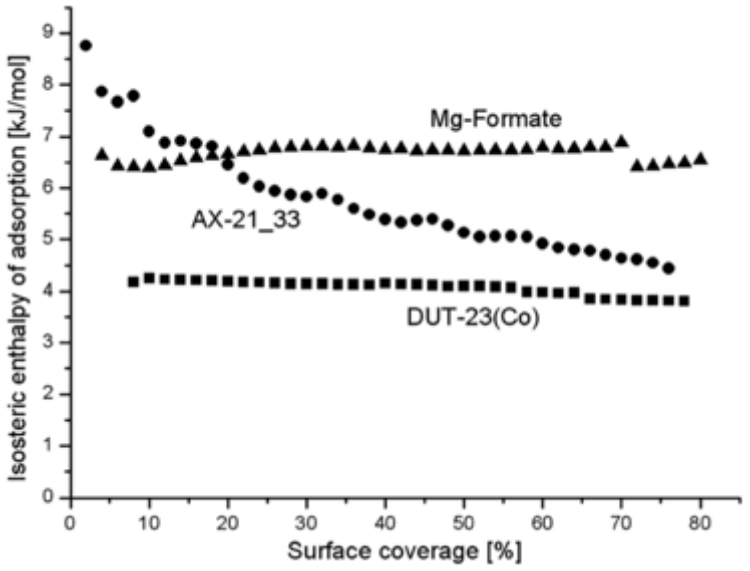
$$A = \frac{V_M}{N_A}\left(\frac{M}{\varrho \cdot N_A}\right)^{-\frac{1}{3}} = \left(\frac{M}{\varrho}\right)^{\frac{2}{3}}\left(\frac{1}{N_A}\right)^{-\frac{1}{3}}$$

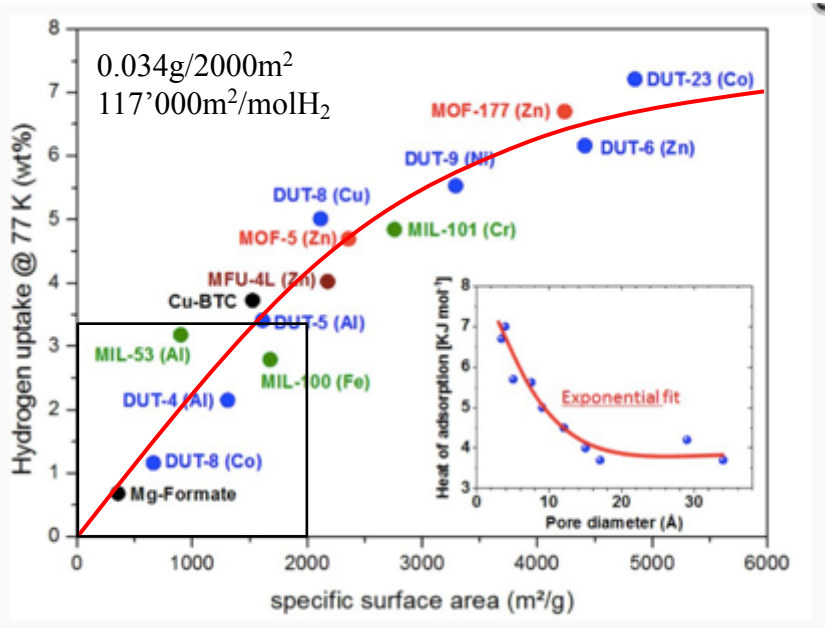
4.3. High Surface Area Materials



Zhonghua Xiang et al., *Energy Environ. Sci.* **3** (2010) 1469



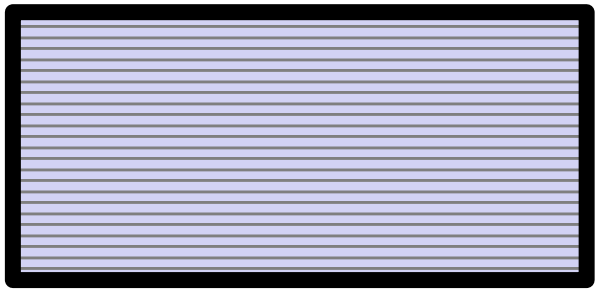




Ref.: Maurice Schlichtenmayer and Michael Hirscher, „Nanosponges for hydrogen storage“, J. Mater. Chem., 22 (2012), 10134.

4.4. H_2 vol. Density of High Surface Area A_{spec} Materials

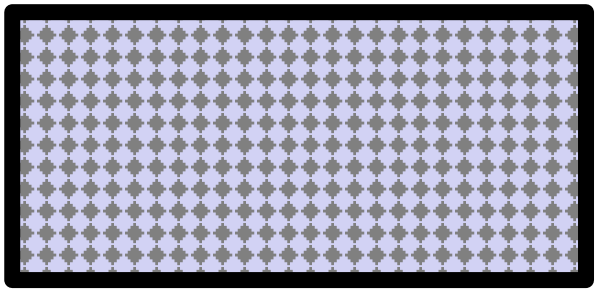
non porous material



Volume with n mol H_2 gas (real gas):

$$V = \frac{n \cdot R \cdot T}{p \cdot f_p(p,T)}$$

porous material



$$V = V_{H2} + V_M \qquad m_M = (V - V_{H2}) \cdot \varrho_M$$

$$V = V_M \qquad m_M = V \cdot \varrho_M$$

$$V_{H2} = (V - V_{H2}) \cdot \rho_M \cdot A_{spec} \cdot d_{ML} \cdot f_{ML}$$

$$V_{H2} = V \cdot \rho_M \cdot A_{spec} \cdot d_{ML} \cdot f_{ML}$$

$$A_{spec} = \left(\frac{V \cdot \rho_{H_2}}{n_{H2} \cdot M} - 1\right)^{-1} \frac{1}{\rho_M \cdot f_{ML} \cdot d_{ML}}$$

$$A_{spec} = \left(\frac{V \cdot \rho_{H_2}}{n_{H2} \cdot M}\right)^{-1} \frac{1}{\rho_M \cdot f_{ML} \cdot d_{ML}}$$

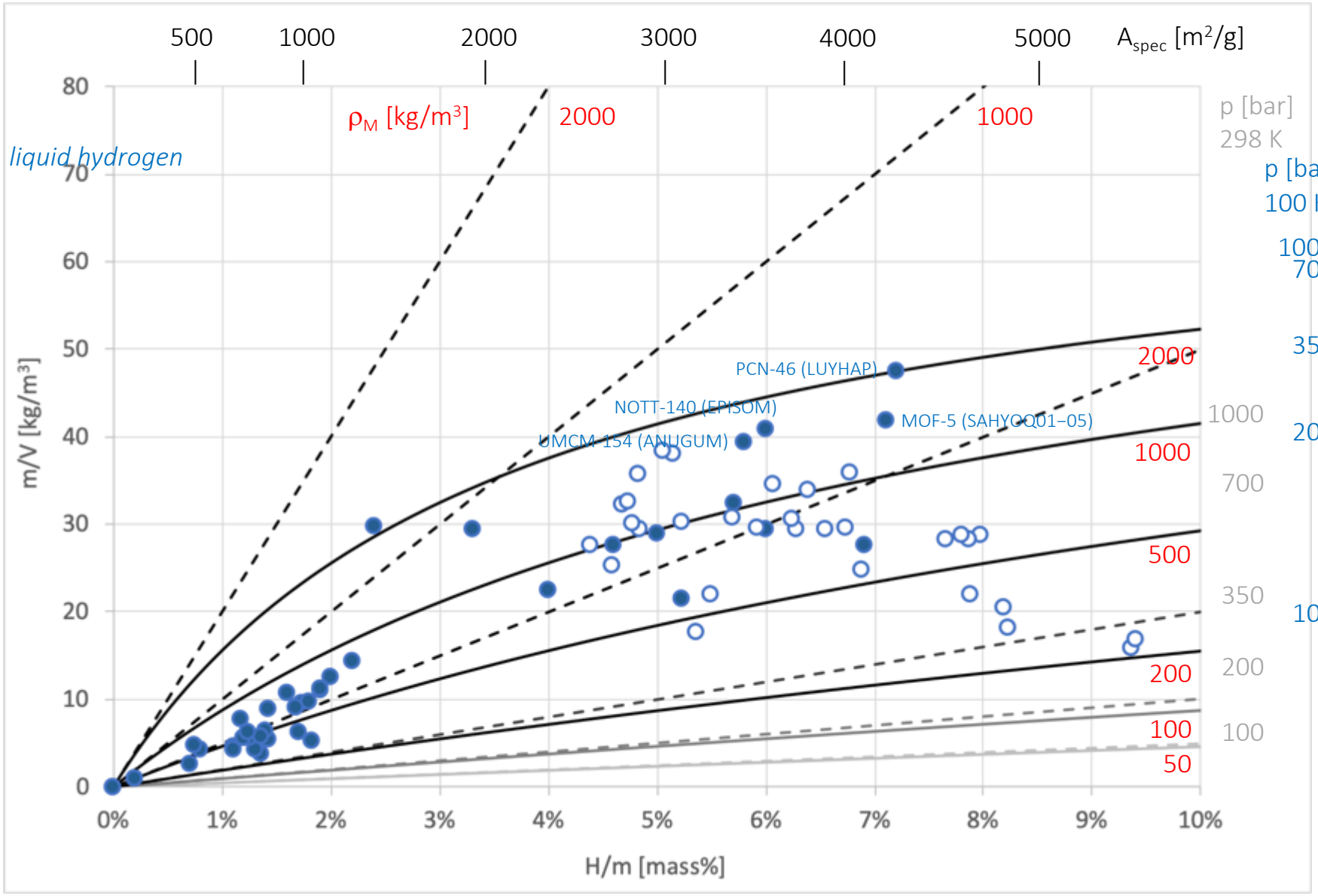
$$A_{spec} = \left(\frac{\rho_{H_2}}{M}\frac{R \cdot T}{f_p \cdot p} - 1\right)^{-1} \frac{1}{\rho_M \cdot f_{ML} \cdot d_{ML}}$$

$$A_{spec} = \frac{M}{\rho_{H_2}}\frac{f_p \cdot p}{R \cdot T}\frac{1}{\rho_M \cdot f_{ML} \cdot d_{ML}}$$

Specific surface area calculated from the material density for the same amount of hydrogen per volume as the volume filled with hydrogen gas.

4.5. High Surface Area Materials

$$m\% \cdot \frac{\rho_M}{M} = \frac{n_{H2}}{V} \qquad \frac{m\%}{d_{ML} \cdot \rho_{H_2} \cdot f_{ML}} = A_{spec}$$



5. Hydrides

1	2											13	14	15	16	17	18
H 2.20																	He
LiH 0.97	BeH_2 1.47											BH_3 2.01	CH_4 2.50	NH_3 3.07	H_20 3.50	HF 4.10	Ne
NaH 1.01	MgH_2 1.23	3	4	5	6	7	8	9	10	11	12	AlH_3 1.47	SiH_4 1.74	PH_3 2.06	H_2S 2.44	HCl 2.83	Ar
KH 0.91	CaH_2 1.04	ScH_2 1.20	TiH_2 1.32	VH VH_2 1.45	CrH (CrH_2) 1.56	Mn 1.60	Fe 1.64	Co 1.70	$NiH_{<1}$ 1.75	CuH 1.75	ZnH_2 1.66	(GaH_3) 1.82	GeH_4 2.02	AsH_3 2.20	H_2Se 2.48	HBr 2.74	Kr
RbH 0.89	SrH_2 0.99	YH_2 YH_3 1.11	ZrH_2 1.22	(NbH_2) 1.23	Mo 1.30	Tc 1.36	Ru 1.42	Rh 1.45	$PdH_{<1}$ 1.35	Ag 1.42	(CdH_2) 1.46	(InH_3) 1.49	SnH_4 1.72	SbH_3 1.82	H_2Tc 2.01	HI 2.21	Xe
CsH 0.86	BaH_2 0.97	LaH_2 LaH_3 1.08	HfH_2 1.23	TaH 1.33	W 1.40	Re 1.46	Os 1.52	Ir 1.55	Pt 1.44	(AuH_3) 1.42	(HgH_2) 1.44	(TlH_3) 1.44	PbH_4 1.55	BiH_3 1.67	H_2Po 1.76	HAt 1.90	Rn
Fr	Ra	AcH_2 1.00															

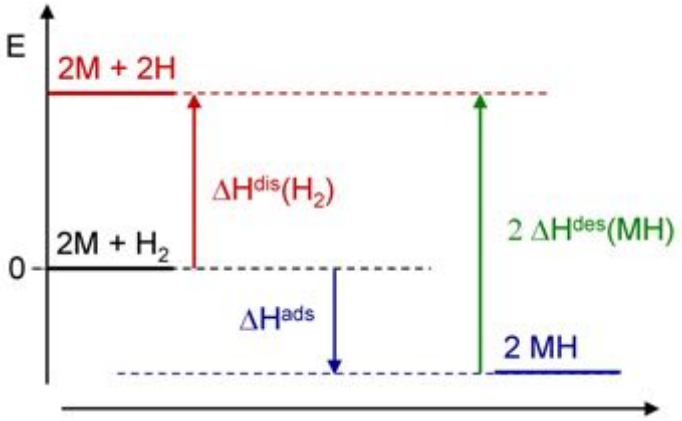
Allred-Rochow Electronegativity Ref: **Huheey, J.E. Inorganic Chemistry ; Harper & Row: New York, 1983**

Ionic hydrides
Covalent polymeric hydrides
Covalent hydrides
Metallic hydrides

Ref.: Gottfried Brendel, “Kapitel: Hydride”, Ullmanns Encyklopädie der technischen Chemie, 4. neubearbeitete und erweiterte Auflage, Band 13 (1977), pp. 109-133, Verlag Chemie Weinheim New York

CeH_3 1.06	PrH_2 PrH_3 1.07	NdH_2 NdH_3 1.07	Pm	SmH_2 SmH_3 1.07	EuH_2 1.01	GdH_2 GdH_3 1.11	TbH_2 TbH_3 1.10	DyH_2 DyH_3 1.10	HoH_2 HoH_3 1.10	ErH_2 ErH_3 1.11	TmH_2 TmH_3 1.11	(YbH_2) YbH_3 1.06	LuH_2 LuH_3 1.14
ThH_2 1.11	PaH_2 1.14	UH_3 1.22	NpH_2 NpH_3 1.22	PuH_2 PuH_3 1.22	AmH_2 AmH_3 1.2	Cm	Bk	Cf	Es	Fm	Md	No	Lr

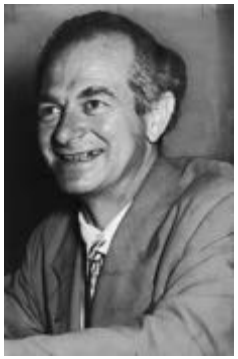
5.1. Binding energy M-H



Pauling electronegativity

1																	18
H																	He
2.20	2											13	14	15	16	17	
Li	Be											B	C	N	0	F	Ne
0.98	1.57											2.04	2.55	3.04	3.44	3.98	
Na	Mg											Al	Si	P	S	Cl	Ar
0.93	1.31	3	4	5	6	7	8	9	10	11	12	1.61	1.90	2.19	2.58	3.16	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.82	1.00	1.36	1.54	1.63	1.66	1.55	1.83	1.88	1.91	1.90	1.65	1.81	2.01	2.18	2.55	2.96	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Tc	I	Xe
0.82	0.95	1.22	1.33	1.60	1.16	1.19	1.22	1.28	1.20	1.93	1.69	1.78	1.96	2.05	2.10	2.66	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0.79	0.89	1.10	1.30	1.50	2.36	1.90	1.22	1.20	1.28	1.54	2.00	1.54	2.33	2.02	2.00	2.20	
Fr	Ra	Ac															
0.70	0.90	1.10															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1.12	1.13	1.14	1.13	1.17	1.20	1.20	1.20	1.22	1.23	1.24	1.25	1.10	1.24
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
1.30	1.50	1.38	1.36	1.28	1.30	1.30	1.30	1.30	1.30	1.30	1.30	1.30	



Linus Carl Pauling
* 28. 2. 1901; † 19. 8. 1994
1954 Nobelprize for chemistry
1962 Nobelprize for peace

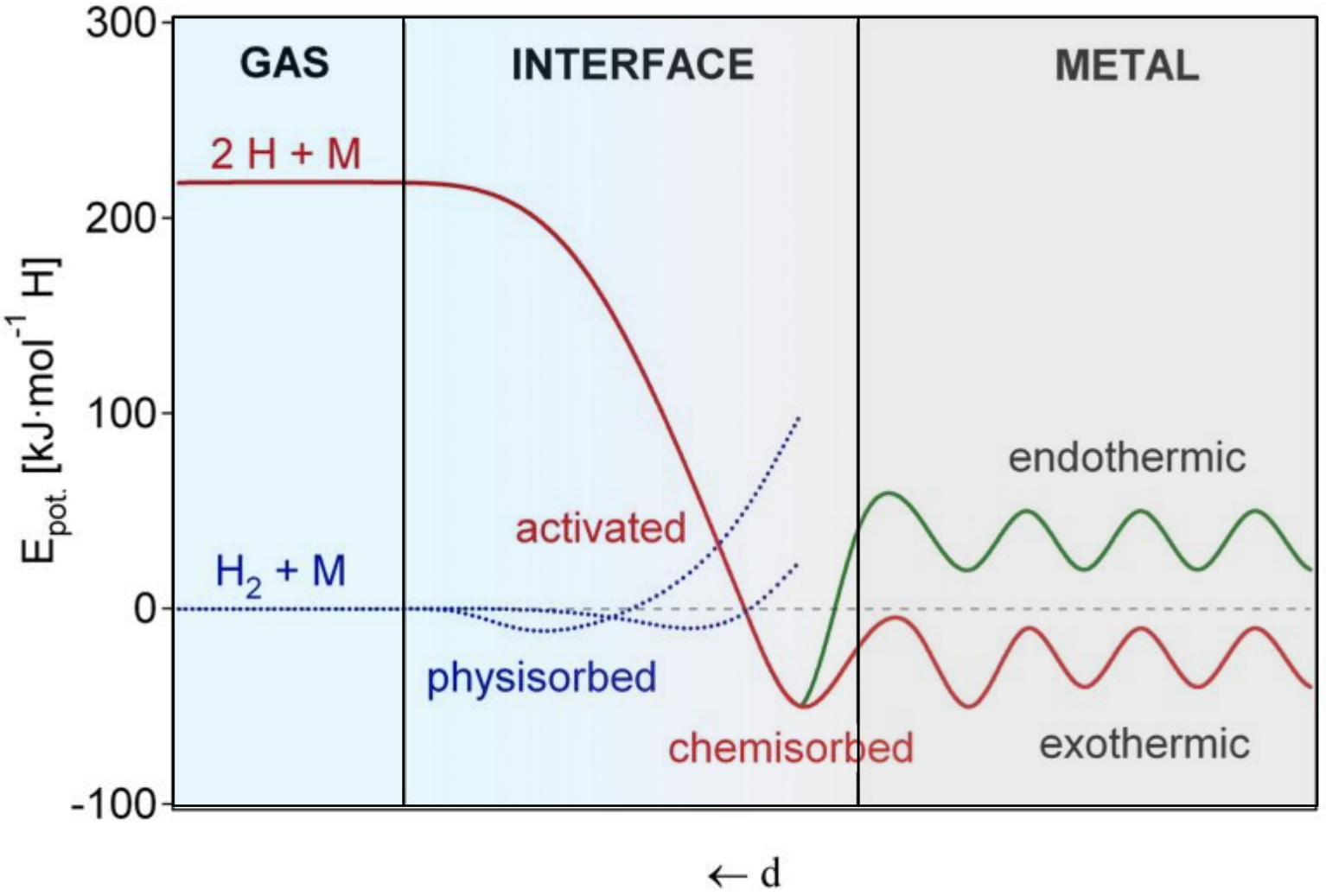
Pauling: $$\Delta H_{MH}^{dis}\left[kJ\cdot mol^{-1}\right]=\tfrac{1}{2}\cdot\left(\Delta H_{MM}^{dis}+\Delta H_{HH}^{dis}\right)+97\cdot\left(X_M-X_H\right)^2$$

Absorption Energy: $$\Delta H^{ads}\left[kJ\cdot mol^{-1}\right]=\Delta H_{MM}^{dis}+194\cdot\left(X_M-X_H\right)^2$$

Ref.: Linus Pauling, “THE PRINCIPLES DETERMINING THE STRUCTURE OF COMPLEX IONIC CRYSTALS“, Journal of the American Chemical Society, 1929 - pubs.acs.org

5.2. Metal Hydride

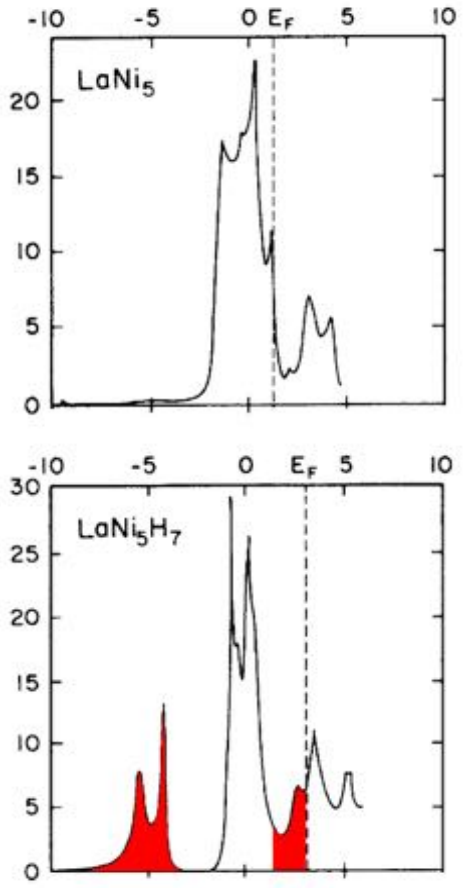
Lennard-Jones Potential



Ref.: J. E. Lennard-Jones, Trans. Faraday Soc. 28 (1932), pp. 333.
L. Schlapbach, Chapter 1, L. Schlapbach (Ed.) in Intermetallic Compounds I, Springer Series Topics in Applied Physics, Vol. 63, Springer–Verlag, 1988, p. 10.

5.3. Electronic structure

Bandstructure of $LaNi_5$ and $LaNi_5H_7$



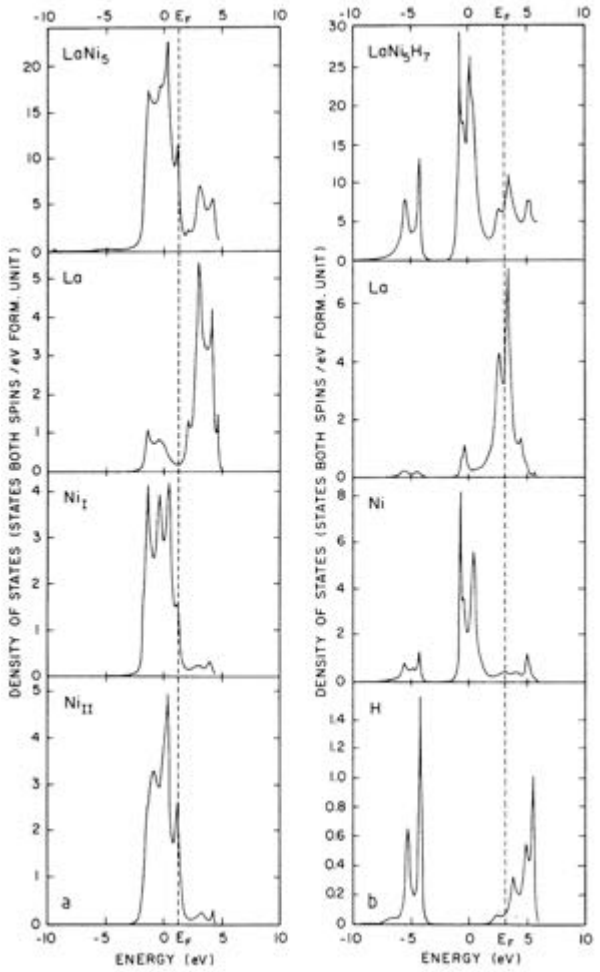
1) Lattice expansion reduces the band-width.

2) Attractive potential of the proton affects the metal states and leads to the metal-hydrogen band 5 to 8 eV below E_F.

3) The H-H interaction results in new features in the lower part of the density of states for systems with more than one H atom per unit cell.

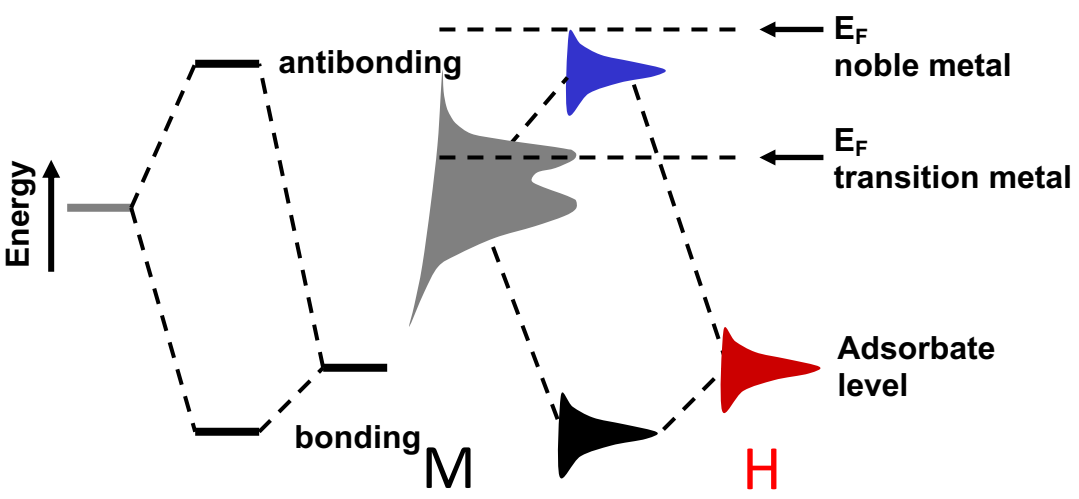
4) An upwards shift of E_F results from the balance between the additional electrons brought in by hydrogen and the number of new states below E_F.

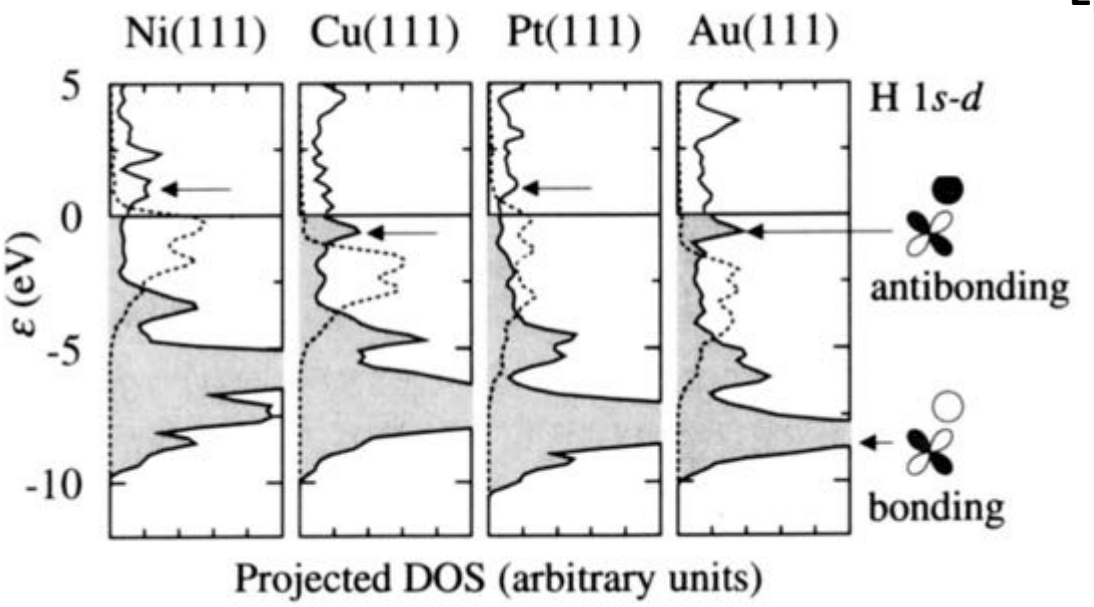
The balance between the 'exothermic' lowering of occupied states and the 'endothermic' upwards shift of E_F determines the stability of the metalhydride.

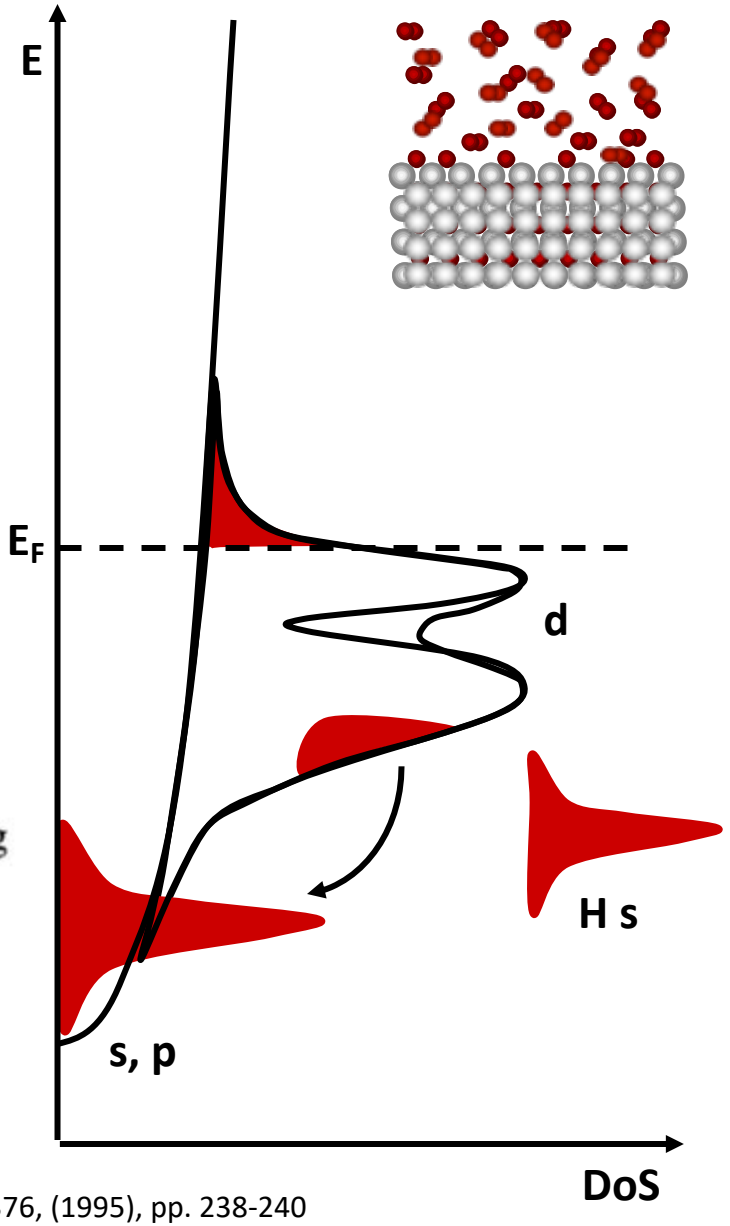


Ref.: L. Schlapbach, F. Meli, and A. Züttel, Chap. 21: "Intermetallic Hydrides and their Applications" in Intermetallic Compounds: Vol. 2, Practice, J. H. Westbrook and R. L. Fleischer (1994) John Wiley & Sons Ltd.

5.4. Binding of Hydrogen







Ref.: Hammer B; Norskov J K, "Why Gold is the Noblest of all the Metals", Nature 376, (1995), pp. 238-240

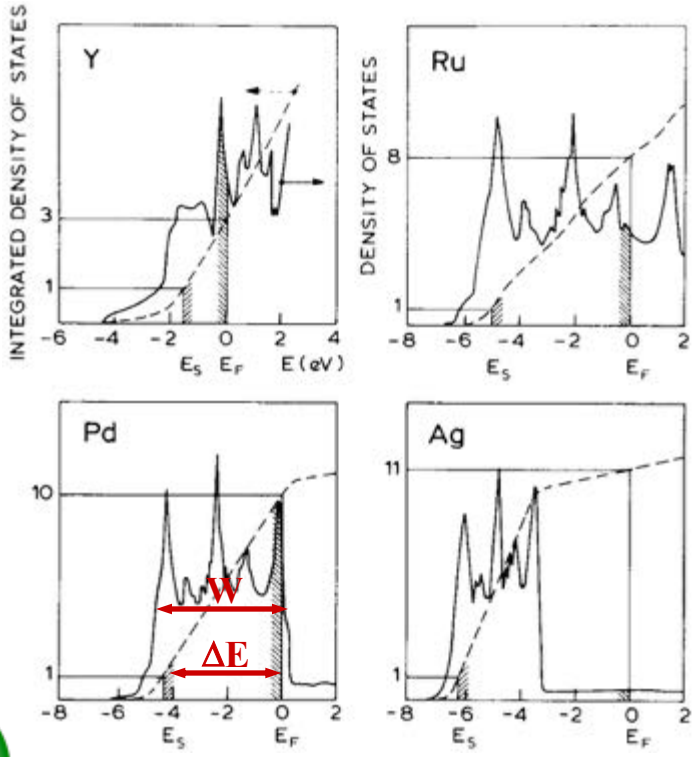
5.5. Semi-empirical Model for the Stability

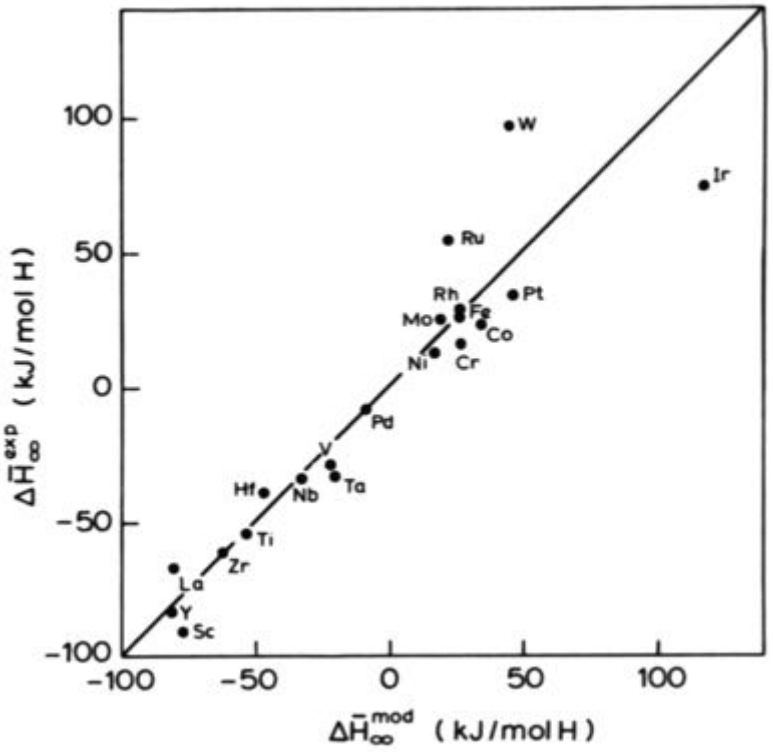
The Local Band-Structure Model

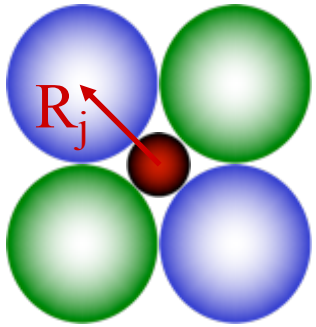
$$\Delta\bar{H}_{\infty} = a \cdot \Delta E \cdot \sqrt{W} \cdot \sum_j R_j^{-4} + b$$

a = 18.6 kJ·mol^{-1}HÅ^{4}eV$^{-3/2}$

b = -90 kJ·mol^{-1}H



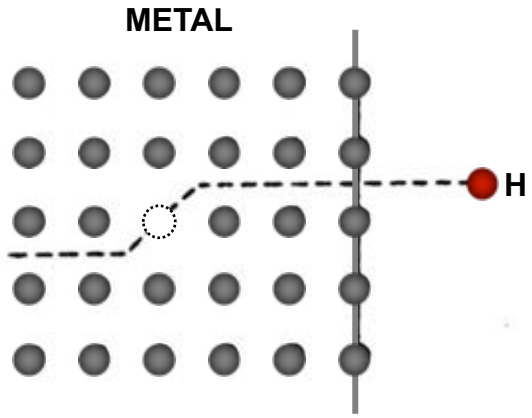


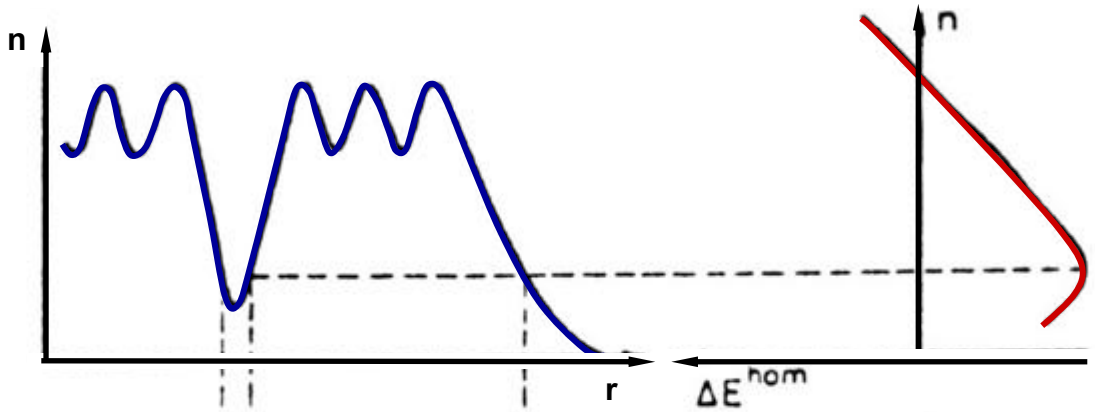


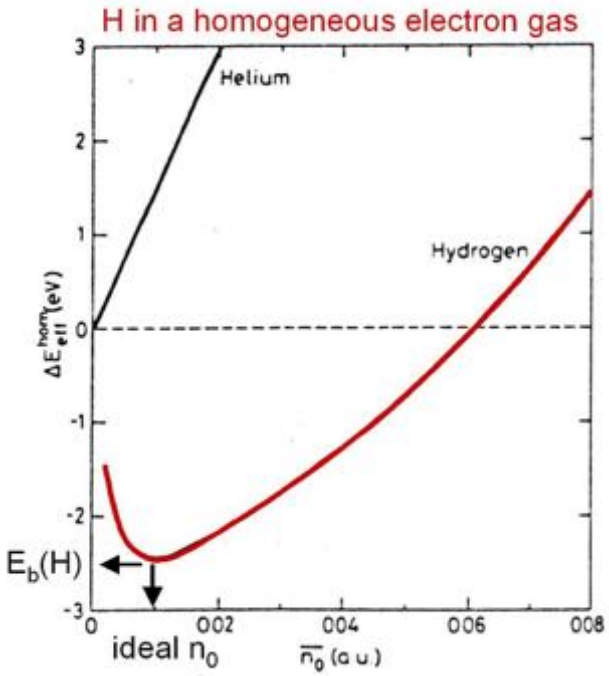
Ref.: R. Griessen, Phys. Rev. B 38 (1988), pp.3690-3698 and V.L. Moruzzi, J. F. Janak, A.R. Williams, „Calculated Electronic Properties of Metals“, Pergamon, New York (1978)

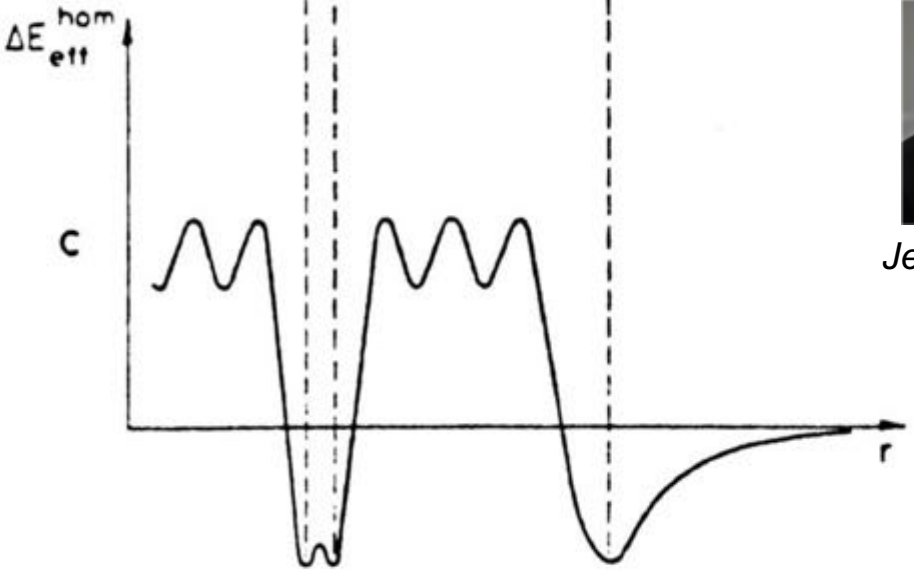
5.6. Hydrogen in the Metal

Effective Medium Theory







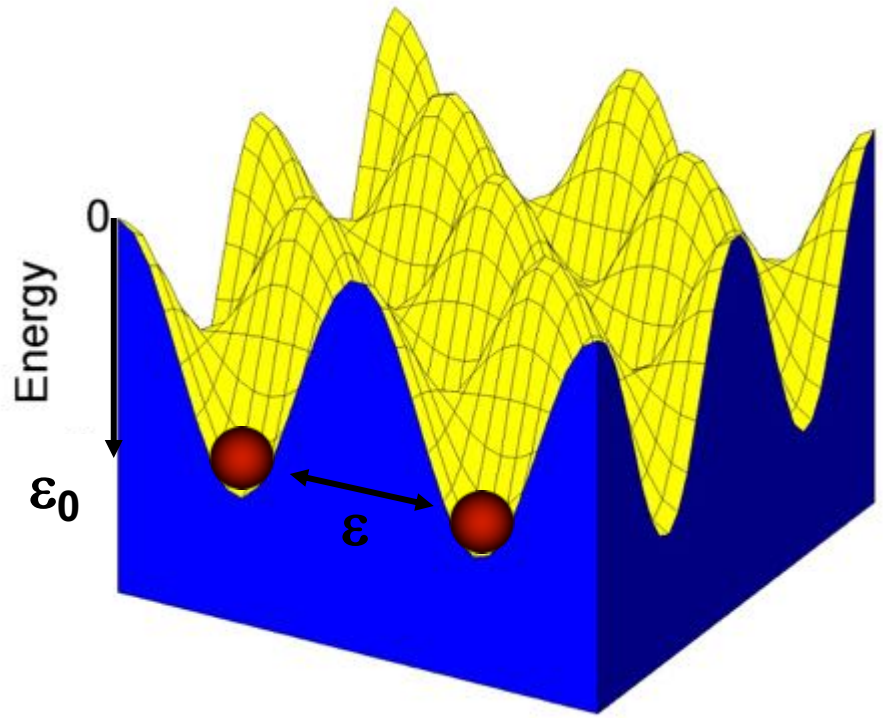


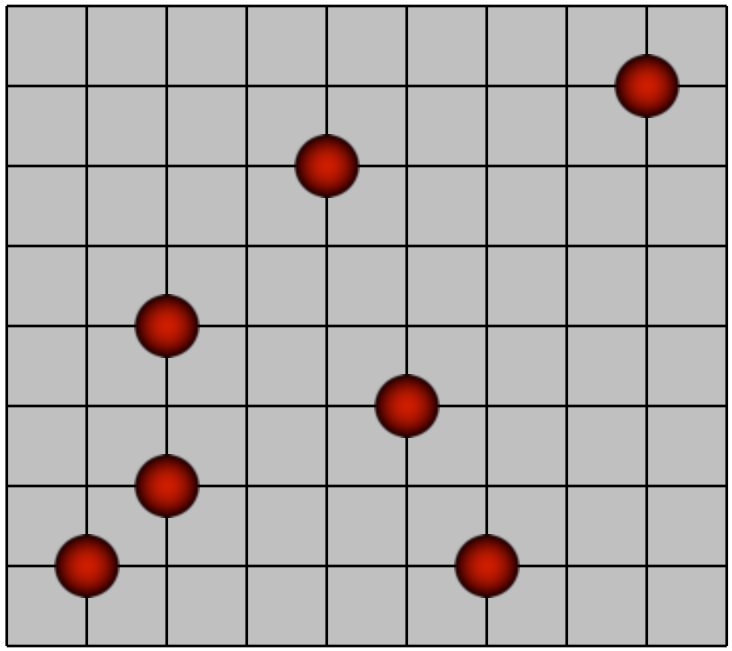
Jens Norskov

Ref.: P. Nordlander, J. K. Norskov, and F. Besenbacher, J. Phys. F. Metal Phys. 16:9 (1986), pp. 1161-1171. J.K. Norskov and F. Besenbacher, J. of the Less-Common Metals 130 (1987), pp. 475-490

5.7. Lattice Gas Model

$$E = N_H \varepsilon_o + N_{HH} \varepsilon$$





The free energy $F = U - T \cdot S$ is

$$F = -kT \ln \sum \exp\left[-\frac{N_H \varepsilon_o + N_{HH} \varepsilon}{kT} \right]$$

N	: total number of sites
N_H	: number of H
ε_0	: H binding energy
N_{HH}	: number of nearest neighbour H-pairs
ε	: H-H pair interaction energy

Ref. Ronald Griessen, VU Amsterdam, NL
Hemmes H, Salomons E, Griessen R, Sänger P, Driessen A., Phys Rev B Condens Matter. (1989);39(15):10606-10613.

5.8. Thermodynamics of Hydrides

Ronald Griessen

$$\underbrace{\tfrac{1}{2}\cdot k\cdot T\cdot \ln\frac{p}{p_0(T)}}_{\Delta G} = \underbrace{\varepsilon_0 + \varepsilon\cdot n\cdot c_H - \tfrac{1}{2}\varepsilon_b}_{\Delta H} + \underbrace{T\cdot k\cdot \ln\frac{c_H}{1-c_H}}_{\Delta S}$$

Ref. Ronald Griessen, VU Amsterdam, NL

Solubility (Sieverts)

$$\frac{1}{2}\cdot k\cdot T\cdot \ln\frac{p}{p_0(T)} \cong k\cdot T\cdot \ln c_H$$

$$p \to 0 \qquad c_H \to 0$$

Plateau (Maxwell)

$$k\cdot T\cdot \ln\frac{p_{dis}}{p_0(T)} = 2\cdot\varepsilon_0 + \varepsilon\cdot n - \varepsilon_b$$

Coexistence curve

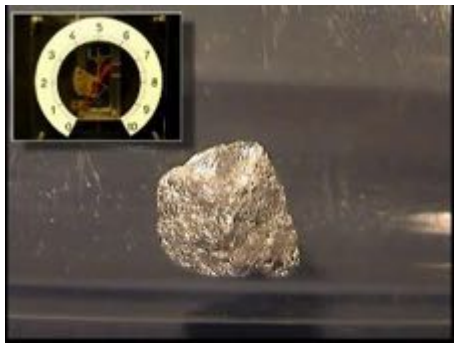
$$k\cdot T\cdot \ln\frac{c_i}{1-c_i} + \varepsilon\cdot n\cdot(c_i - \tfrac{1}{2}) = 0$$

6.a) Hydrogen sorption film

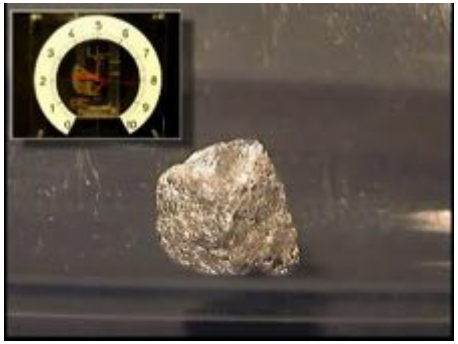
Ph. Mauron, M. Bielmann, Empa, Switzerland

6.b) Hydrogen Sorption Sequences

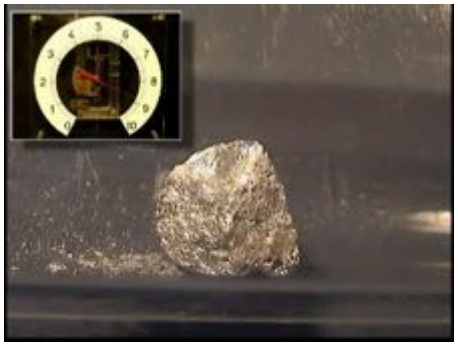
$ZrMn_{1.5}$



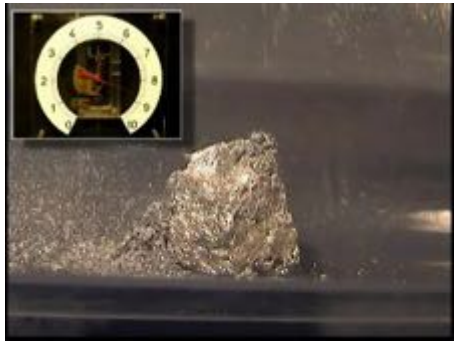
0 sec (vacuum)



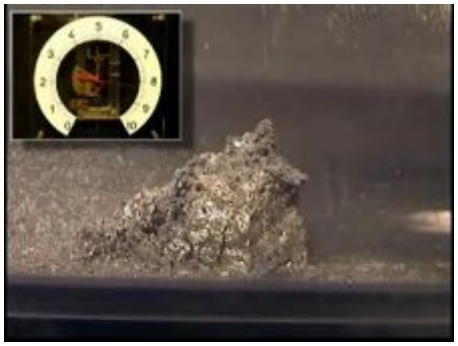
5 sec (8 bar H_2)



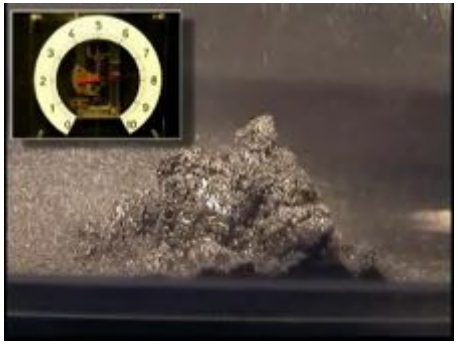
8 sec (8 bar H_2)



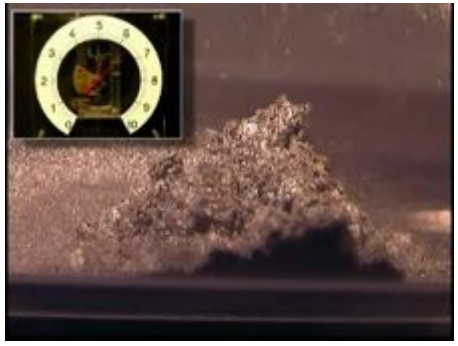
15 sec (8 bar H_2)



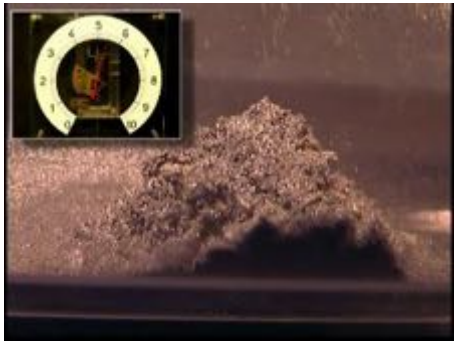
20 sec (7.5 bar H_2)



30 sec (7 bar H_2)

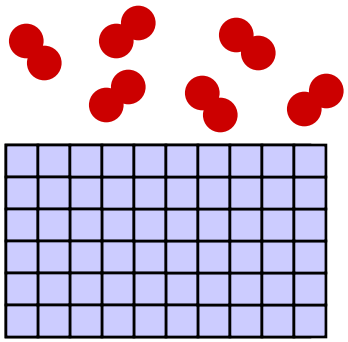


45 sec (6 bar H_2)



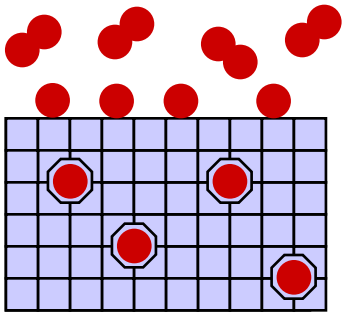
60 sec (5 bar H_2)

6.1. Hydride Phases



Hydrogen gas

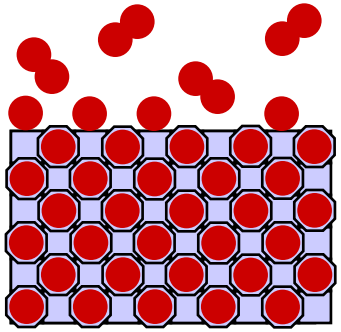
Metal



α-Phase: Solid Solution

MH_x $(0 < x < 0.1)$

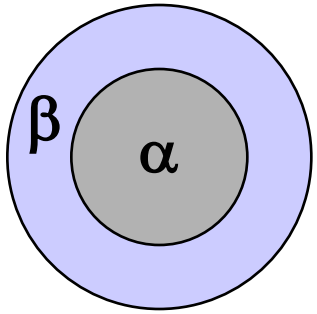
H ⟷ H $\Delta V/V = k \cdot c_H$



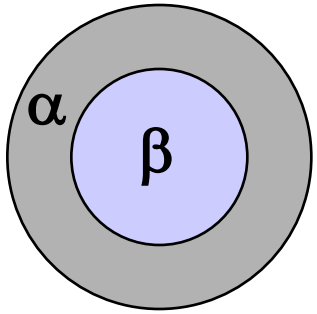
β-Phase: Hydride Phase

MH_x $x = \{1, 2, 3, \ldots\}$

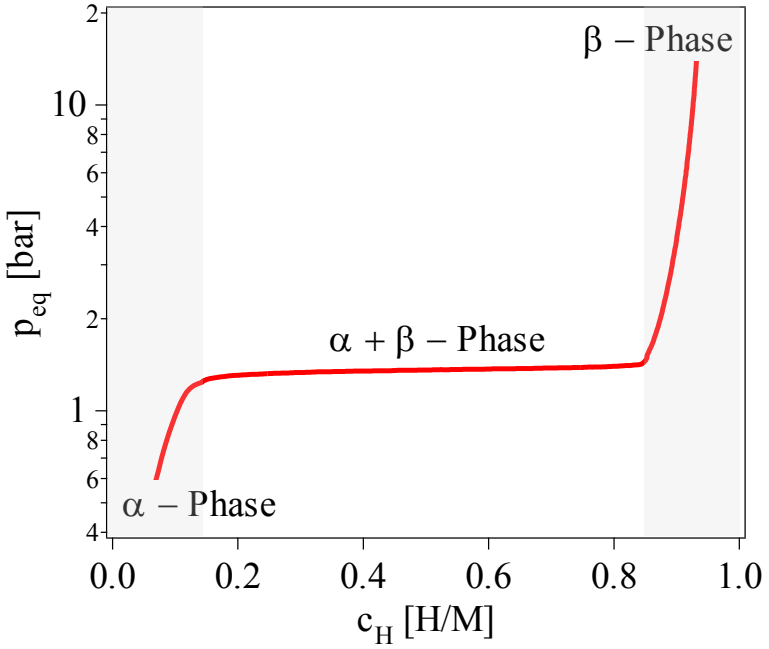
H ⟷ H



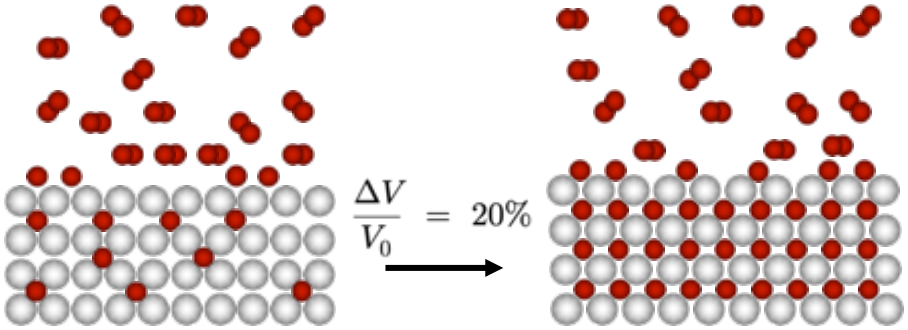
Absorption

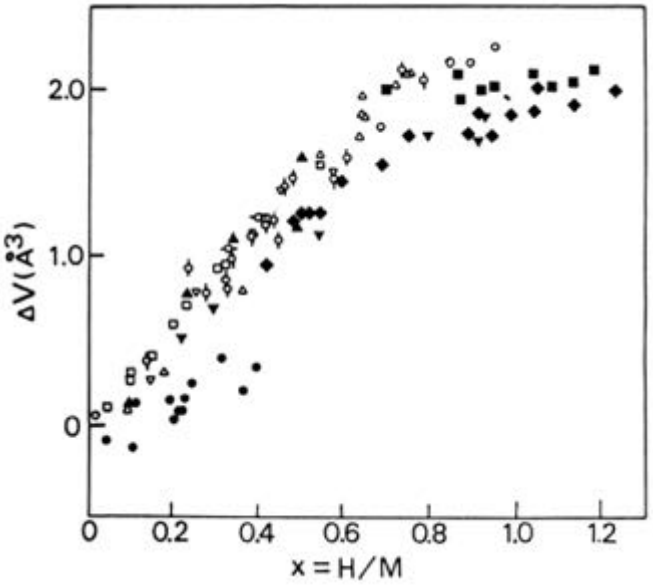


Desorption



6.2. Volume Expansion & Heat Transfer





Max. filling level:

$$V - \Delta V = V\left(1 - \frac{1}{\frac{V_0}{\Delta V} + 1}\right)$$

$LaNi_5 + 3H_2 \rightleftarrows LaNi_5H_6$

$$ln\left(\frac{p}{p_0}\right) = -\frac{\Delta H^0}{R \cdot T} + \frac{\Delta S^0}{R}$$

at $p = p_0$

$$\Delta H^0(T) = T \cdot \Delta S^0(T)$$

$$S^0(H_2) = 130\ J \cdot K^{-1} \cdot mol^{-1}$$

$$LaNi_5 + 3H_2 \xrightarrow{\Delta H^0 \nearrow} LaNi_5H_6$$

$$LaNi_5H_6 \xrightarrow{\Delta H^0 \swarrow} LaNi_5 + 3H_2$$

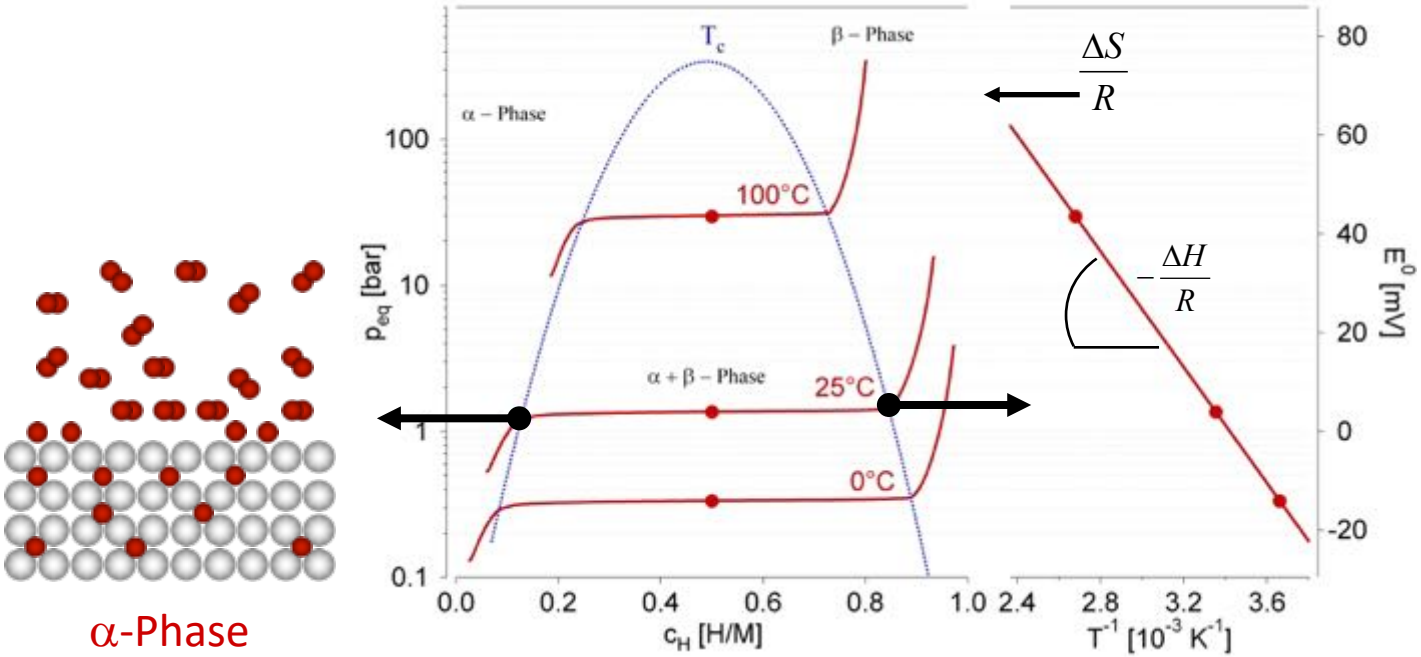
ΔH^0 = 38 kJ·mol^{-1}H$_2$ at 20°C

$$\frac{\Delta H^0}{\Delta Q_{HHV}} = T \cdot \frac{130 J \cdot K^{-1} \cdot mol^{-1}}{283.7 kJ \cdot mol^{-1}}$$

Q_{HHV} = 283.7 kJ·mol^{-1}H$_2$ at 20°C

$\Delta H^0/Q_{HHV}$ = 13%

6.3. Metal to Hydride Phase Transition



α-Phase
Solid Solution

α+β-Phase

β-Phase
Hydride Phase

$$\frac{1}{2}\ln\left(\frac{p}{p_0}\right) = k \cdot T \cdot \ln(c_H)$$

$$\ln\left(\frac{p}{p_0}\right) = -\frac{\Delta H^0}{R \cdot T} + \frac{\Delta S^0}{R}$$

$$\frac{1}{2}\ln\left(\frac{p}{p_0}\right) = k \cdot T \cdot \ln(c_H)$$

Van't Hoff equation

MH_x $(0 < x < 0.1)$

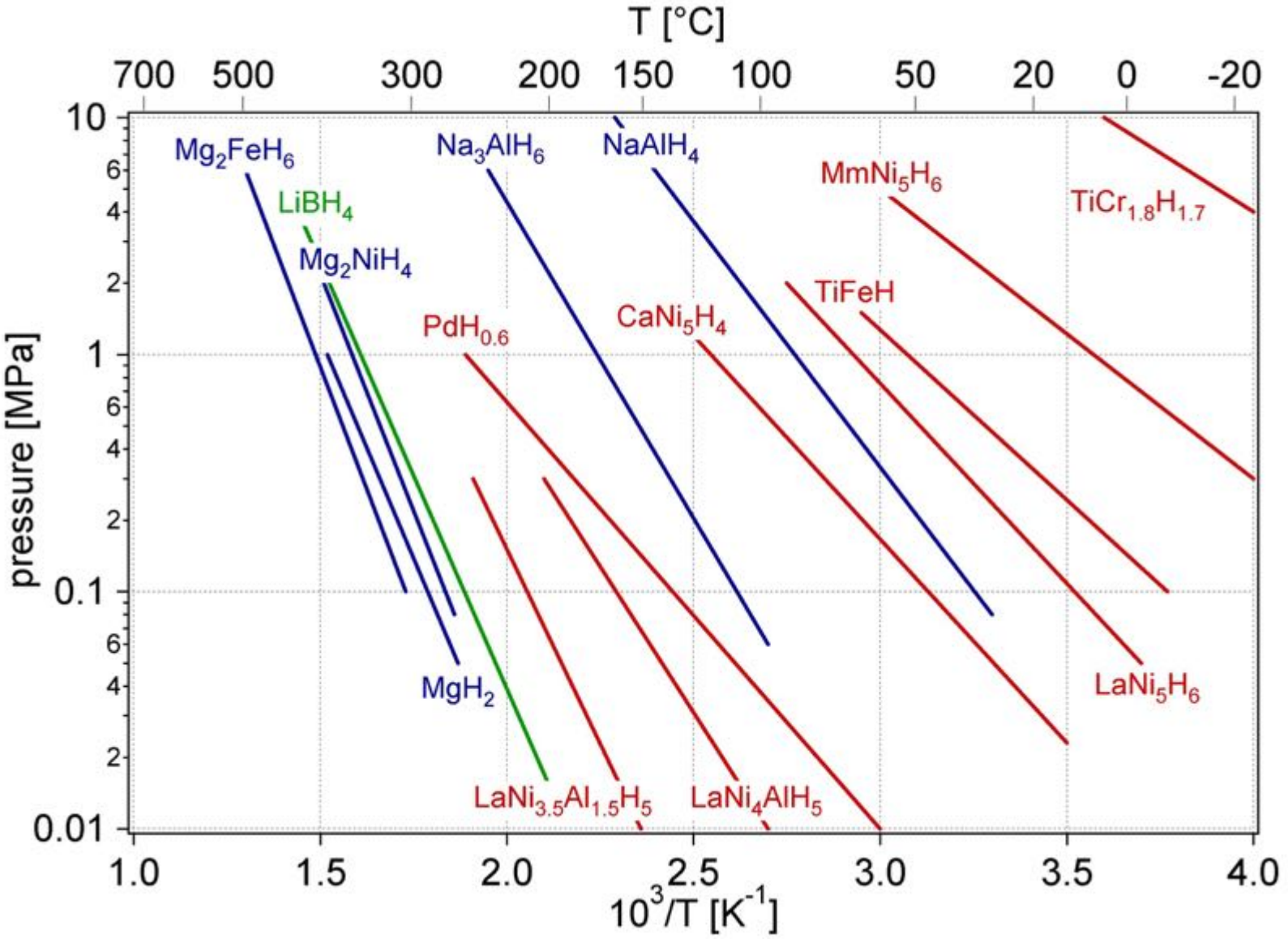
~~H ⟷ H~~, $\Delta V/V = k \cdot c_H$

MH_x $x = \{1, 2, 3, \ldots\}$

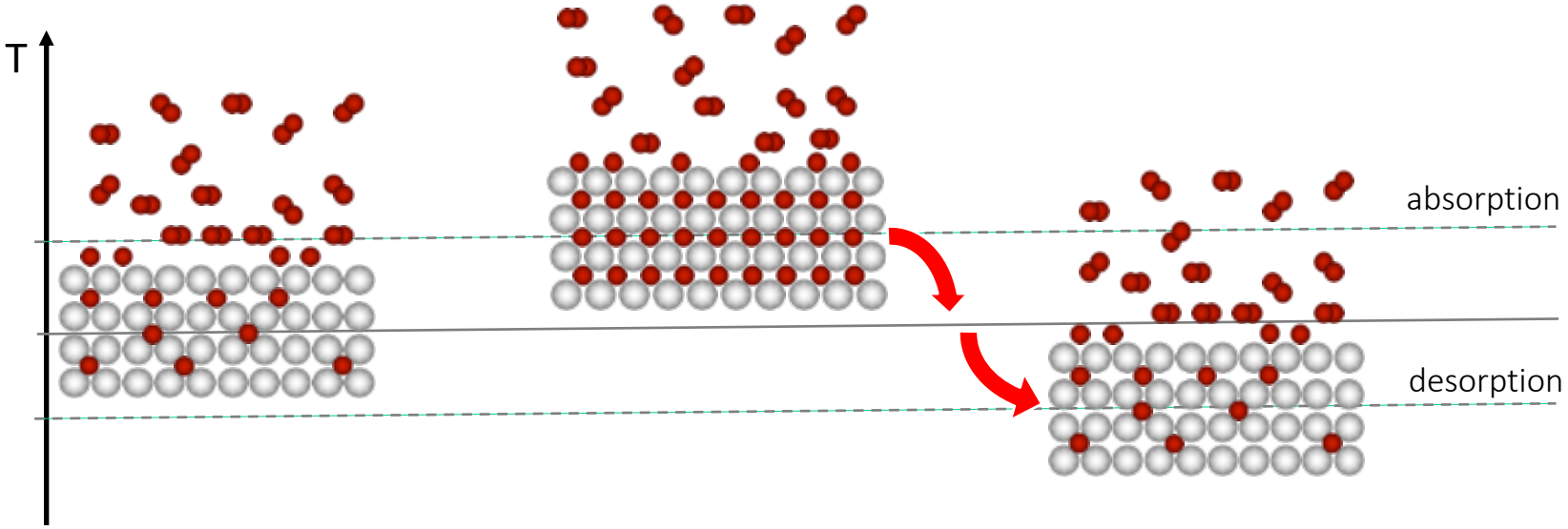
H ⟷ H

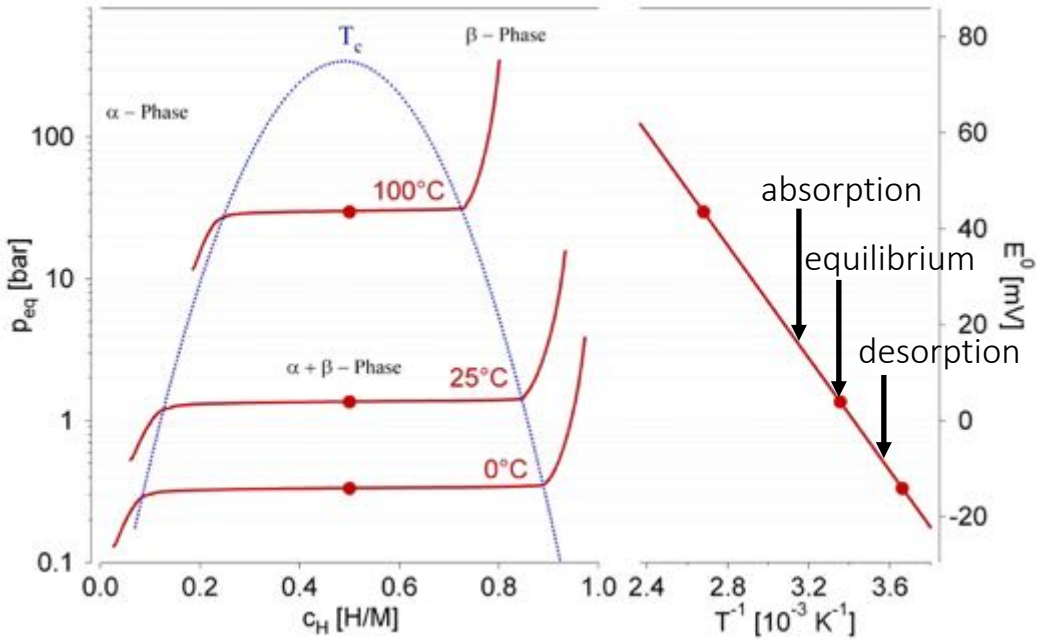
6.4. Van't Hoff Plot of Hydrides

$$\ln\left(\frac{p}{p_0}\right) = -\frac{\Delta H^0}{R \cdot T} + \frac{\Delta S^0}{R}$$



6.5. Sorption Hysteresis

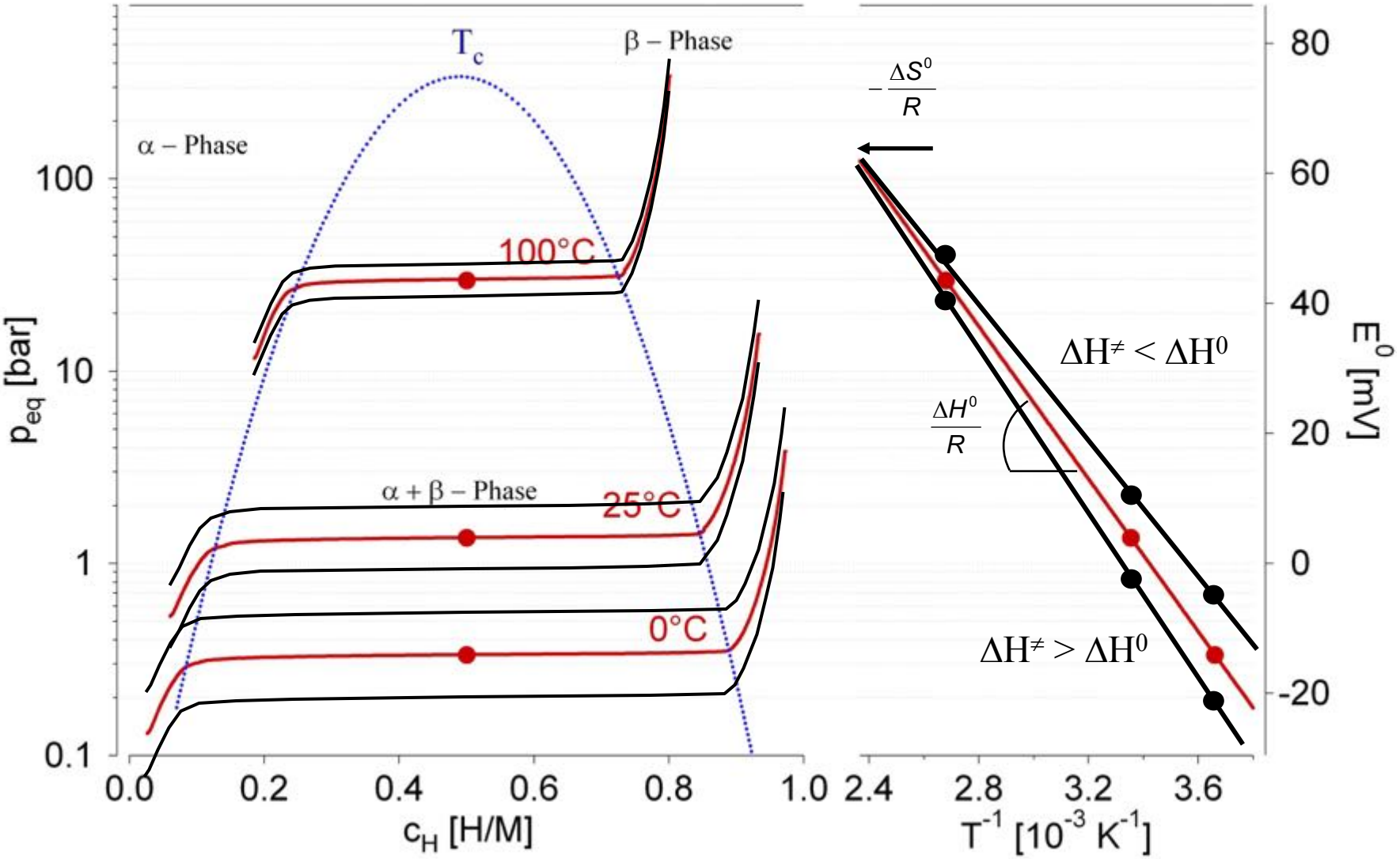




$$ln\left(\frac{p}{p_0}\right) = -\frac{\Delta H^0}{R \cdot T} + \frac{\Delta S^0}{R}$$

6.6 Hysteresis in the Van't Hoff plot

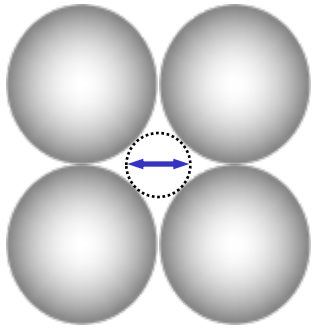
$$ln\left(\frac{p}{p_0}\right) = -\frac{\Delta H^0}{R \cdot T} + \frac{\Delta S^0}{R}$$



6.7. Occupation of Interstitial Sites

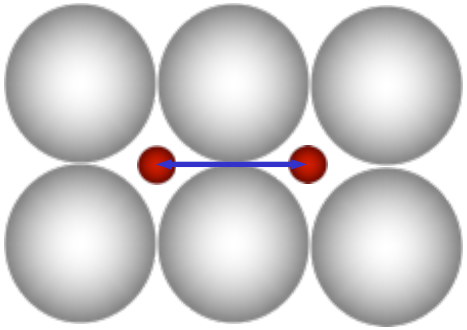
1) Size of interstitial site:

r > 0.37 Å



Westlake criterion

Ref.: D. G. Westlake, J. Less-Common Metals **91** (1983), pp.275-292



2) Distance between hydrogen atoms:

d > 2.1 Å

Ref.: A. C. Switendick, Z. Phys. Chem. N.F. 117 (1979), pp. 89

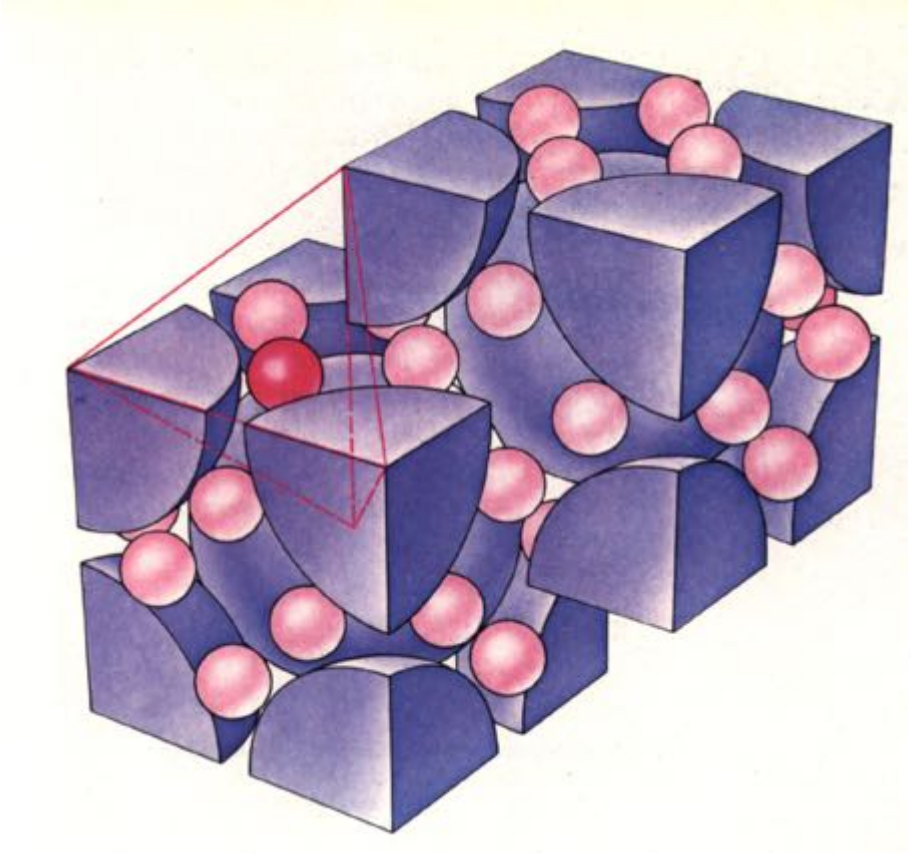
$\rho_V < 245$ kg m^{-3}

Number of hydrogen atoms:

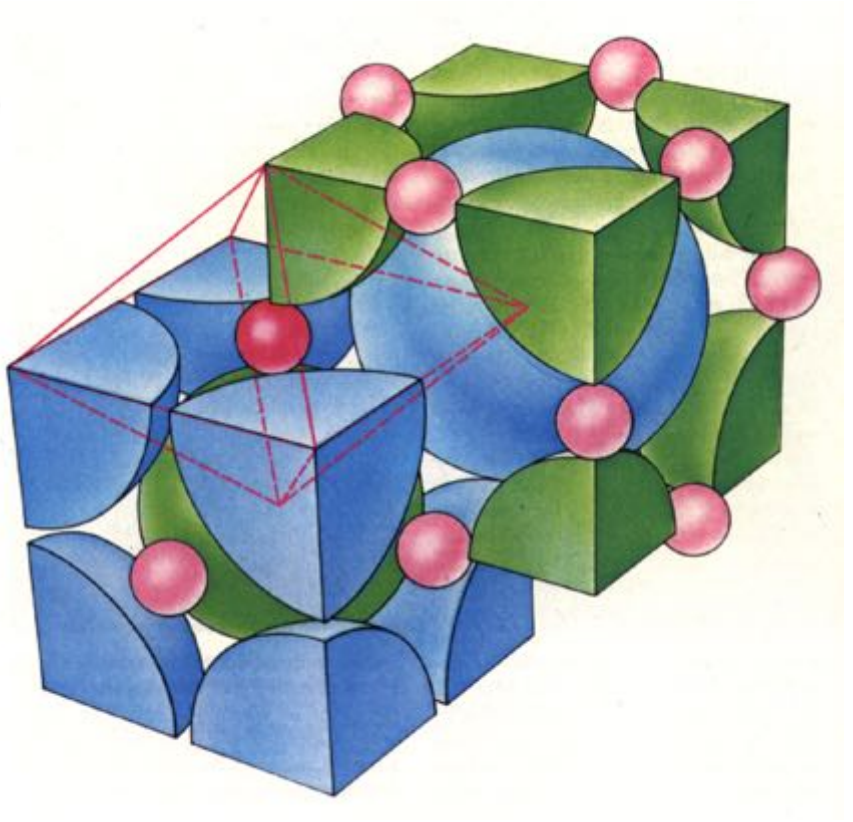
Number of interstitial sites for which 1) and 2) applies.

7. Interstitial Sites in Metal Hydrides

HYDROGEN ON TETRAHEDRAL SITES



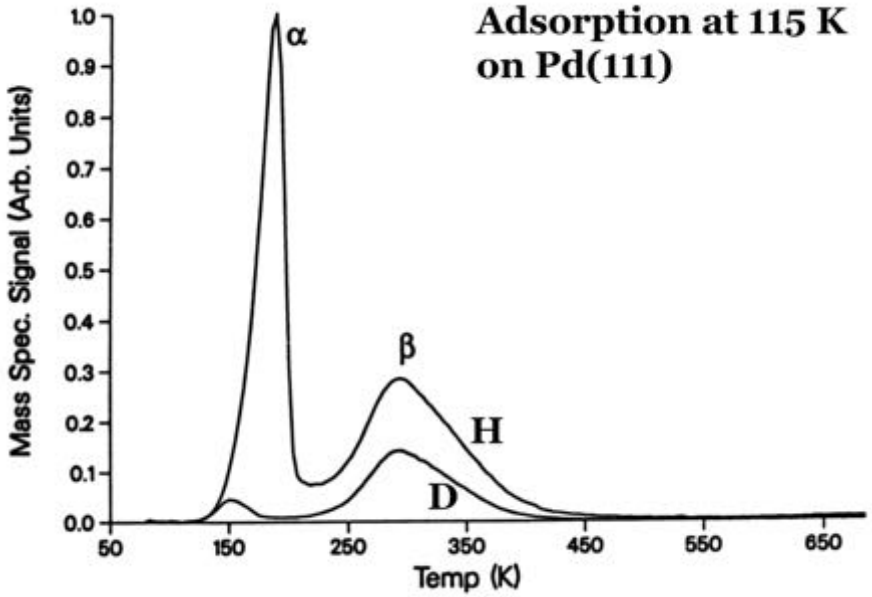
HYDROGEN ON OCTAHEDRAL SITES



Ref: J. J. Reilly, G. D. Sandrock, “Metallhydride als Wasserstoff-Speicher”, Spektrum der Wissenschaften (April 1980), pp. 53-59

7.1. Hydrogen in and on Palladium (Pd)

THERMO DESORPTION SPECTROSCOPY



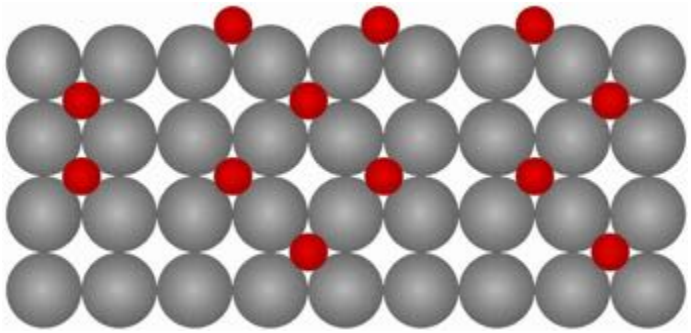
α: chemisorbed hydrogen at the surface
β: interstitial hydrogen

Ref.: G. E. Godowski, R. H. Stulen, T. E. Felter, J. Vac. Sci. Technology A5 (1987), pp. 1103

After exposing Pd(111) at 115 K to equal doses of H_2 and D_2 a much stronger desorption of a-H than a-D is observed apparently due to faster H than D absorption into a-states.

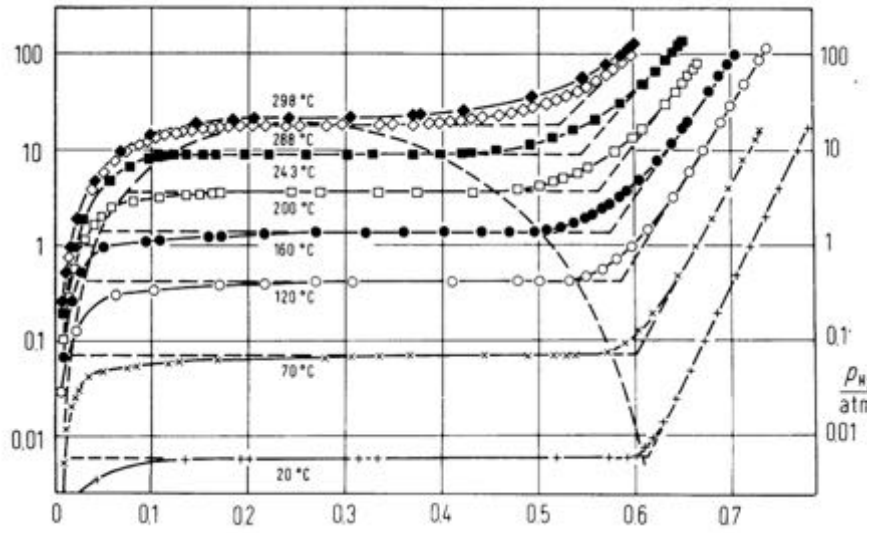
α

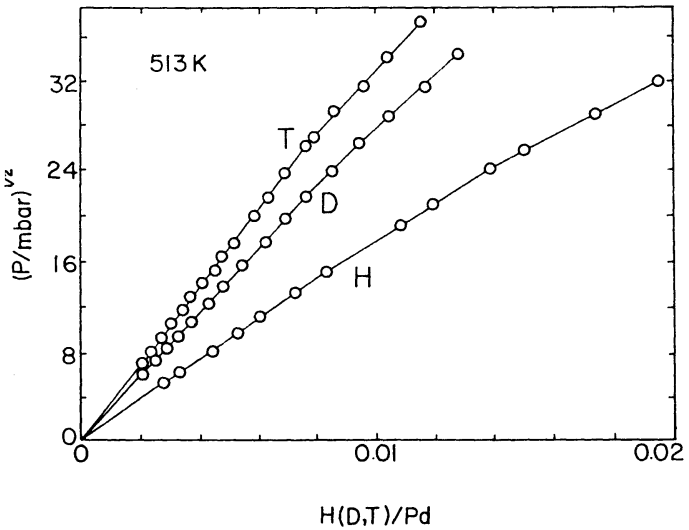
β

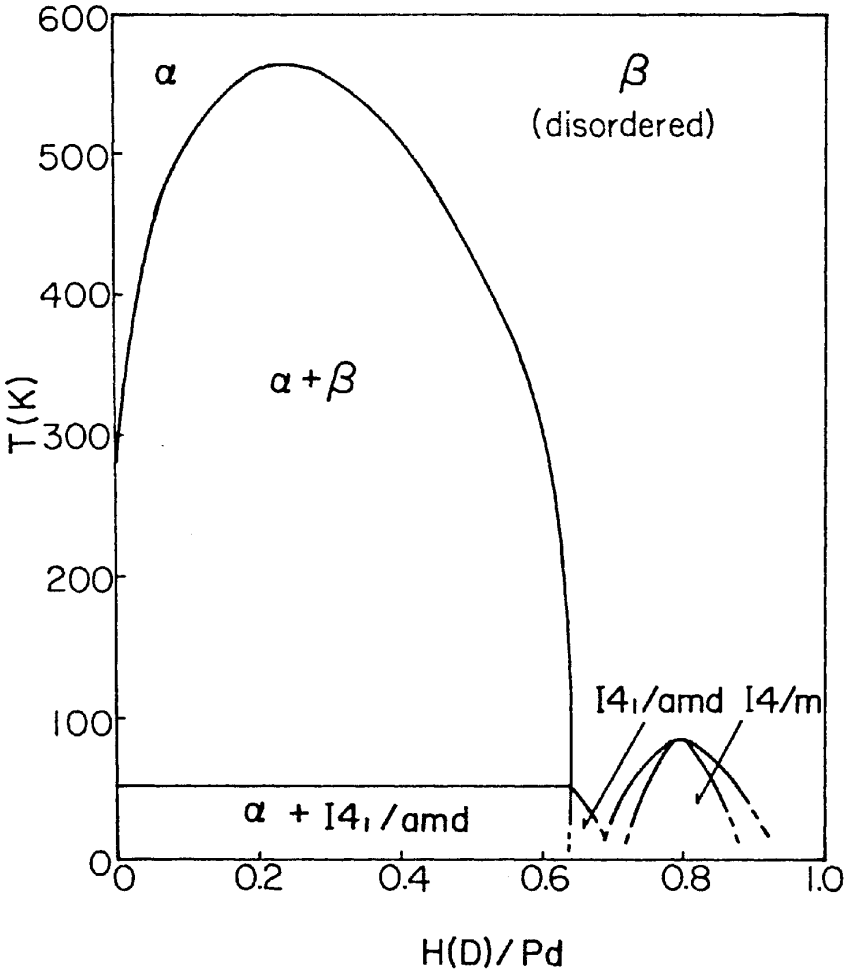


Only minor HD desorption was observed. Apparently the gas which was dosed second bypassed the chemi-sorption state.

7.2. Hydrogen in Palladium (Pd)

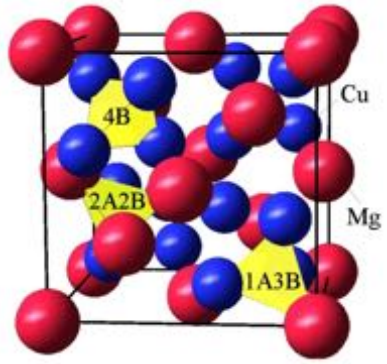


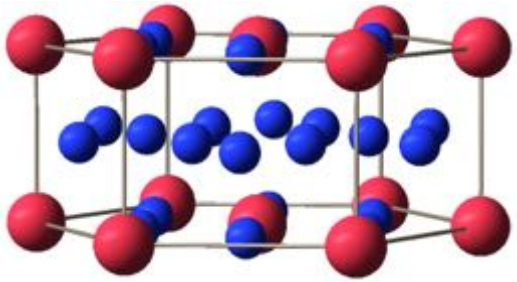




Ref: E. Wicke, H. Brodowsky, in: G. Alefeld, J. Völk (Eds.), Hydrogen in Metals II, Springer Verlag, Berlin, 1978, p. 73.

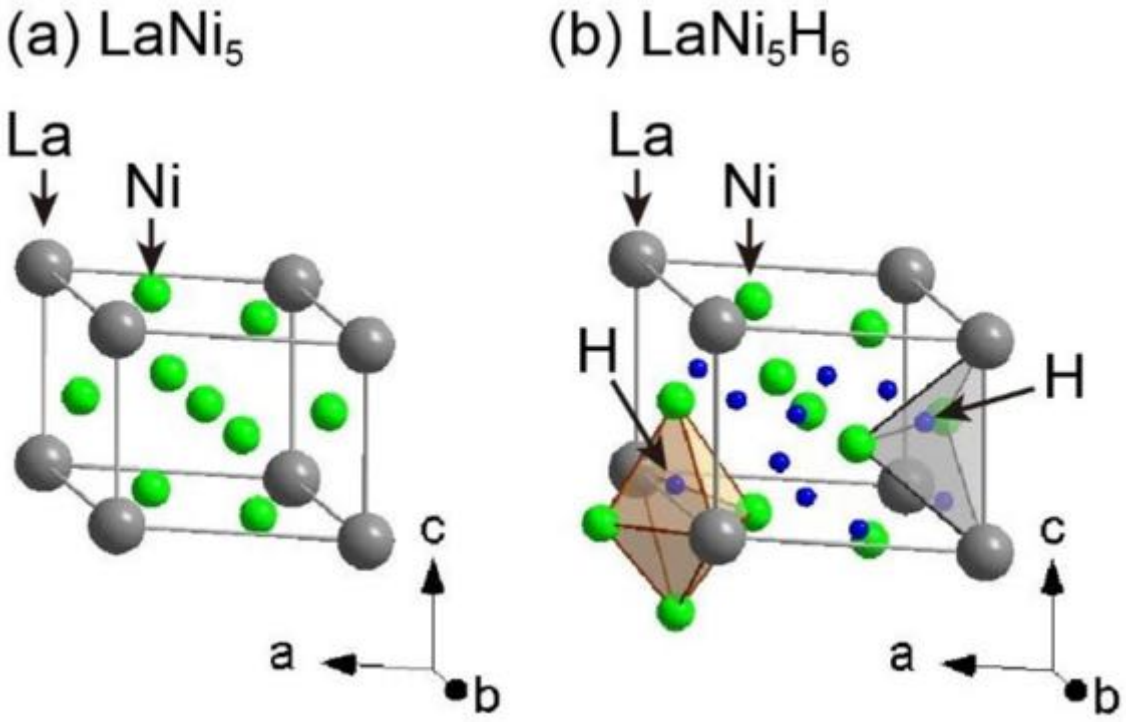
7.3. Hydrides of Intermetallic Compounds and Alloys





Intermetallic compound	Prototype	Structure
AB_5	$LaNi_5$	Haucke phases, hexagonal
AB_2	ZrV_2, $ZrMn_2$, $TiMn_2$	Laves phase, hexagonal or cubic
AB_3	$CeNi_3$, YFe_3	hexagonal, $PuNi_3$-typ
A_2B_7	Y_2Ni_7, Th_2Fe_7	hexagonal, Ce_2Ni_7-typ
A_6B_{23}	Y_6Fe_{23}	cubic, Th_6Mn_{23}-typ
AB	TiFe, ZrNi	cubic, CsCl- or CrB-typ
A_2B	Mg_2Ni, Ti_2Ni	cubic, $MoSi_2$- or Ti_2Ni-typ

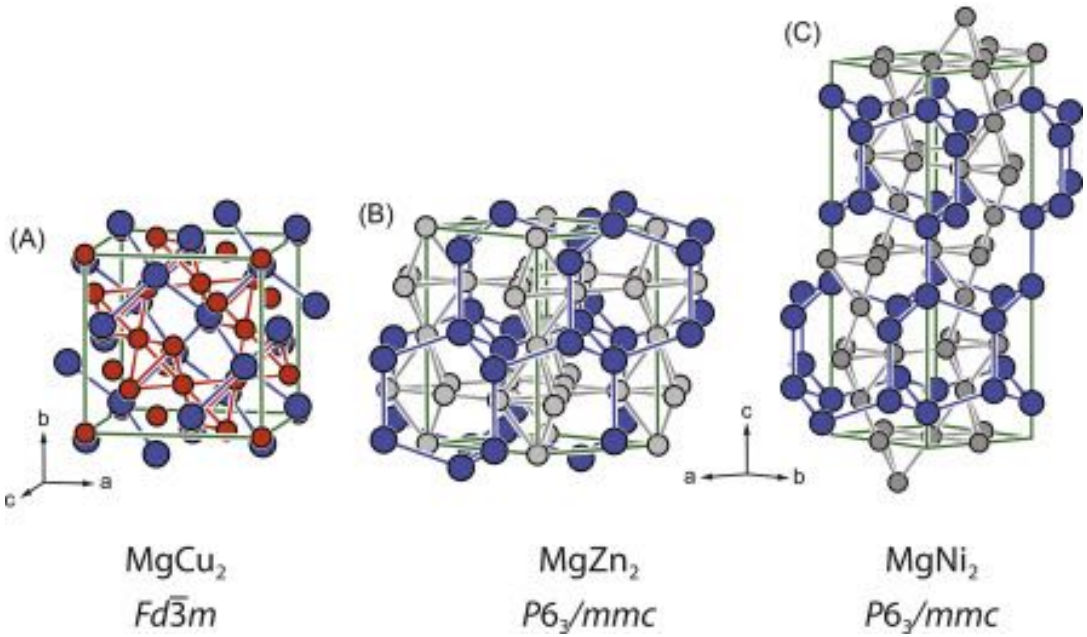
7.4. Hydride of $LaNi_5$

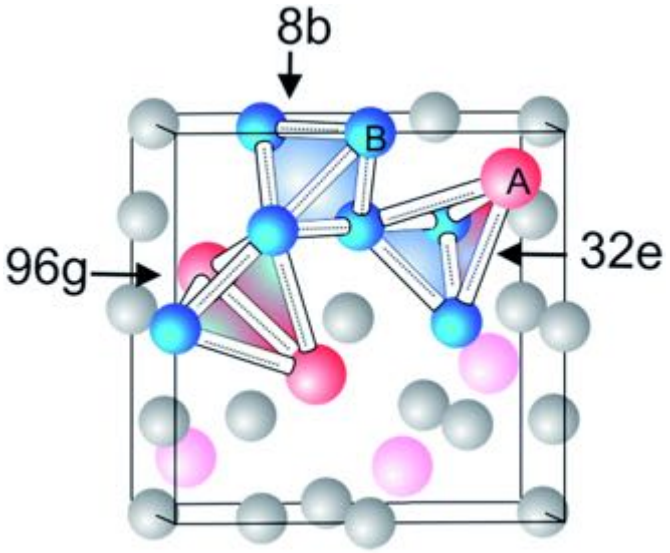


Crystal structures of (a) $LaNi_5$ with a = 5.013 Å and c = 3.987 Å in the space group P6/mmm (No. 191), and (b) $LaNi_5H_6$ with a = 5.410 Å and c = 4.293 Å in the space group P31m (No. 157). Gray, green, and blue spheres indicate La, Ni, and H atoms, respectively. The brown octahedron and gray tetrahedron denote H atomic sites at 3c and 6d, respectively.

Ref: Sato, Toyoto, Hiroyuki Saitoh, Reina Utsumi, Junya Ito, Yuki Nakahira, Kazuki Obana, Shigeyuki Takagi, and Shin-ichi Orimo. 2023. "Hydrogen Absorption Reactions of Hydrogen Storage Alloy LaNi5 under High Pressure" Molecules 28, no. 3: 1256. https://doi.org/10.3390/molecules28031256

7.5. Interstitial Sites in Laves Phases AB_2





Laves phases are intermetallic compounds that have a stoichiometry of AB_2 and are formed when the atomic size ratio is between 1.05 and 1.67. There are three classes of Laves phases, namely, cubic $MgCu_2$ (C15), hexagonal $MgZn_2$ (C14), and hexagonal $MgNi_2$ (C36). In these compounds, the A atoms take up ordered positions as in diamond, hexagonal diamond or related structure while the B atoms take up tetrahedral positions around A atoms. In case the atomic size ratio of A and B atoms is around 1.225, they form topologically tetrahedral close-packed structures with overall packing density of 0.71.

Cubic C15 Laves phase unit cell, with indicated 96g (A_2B_2), 32e (AB_3), and 8b (B_4) tetrahedral interstitials. Some atoms are omitted for clarity.

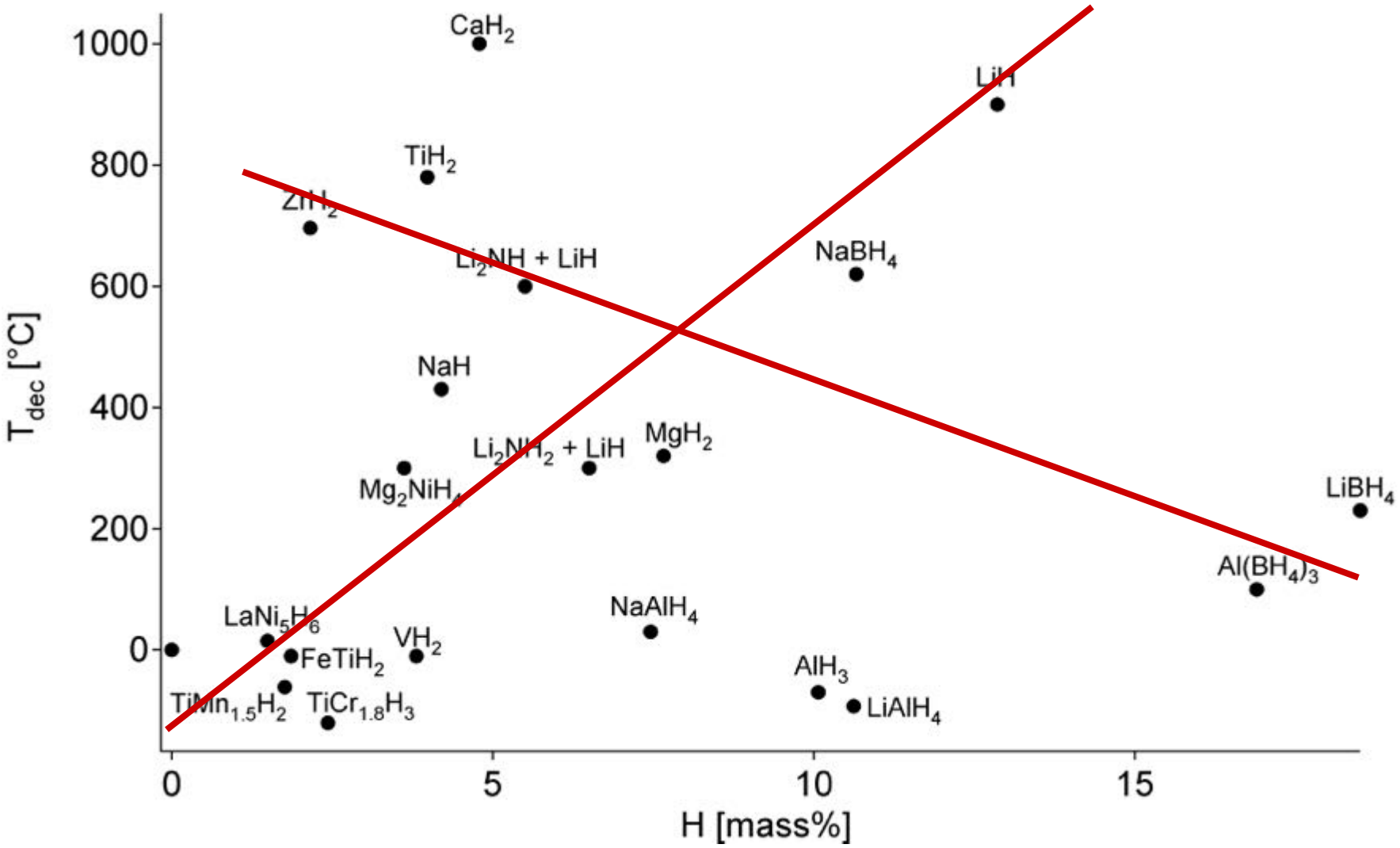
Ref: Jana Radaković, Katarina Batalović, Ivan Mađarević and Jelena Belošević-Čavor, „Interstitial hydrogen in Laves phases – local electronic structure modifications from first-principles“, RSC Adv., 2014,4, 54769-54774

7.6. Hydrides

$$T_{dec} = \frac{\Delta H^0_{dec}(H_2)}{S^0(H_2)}$$

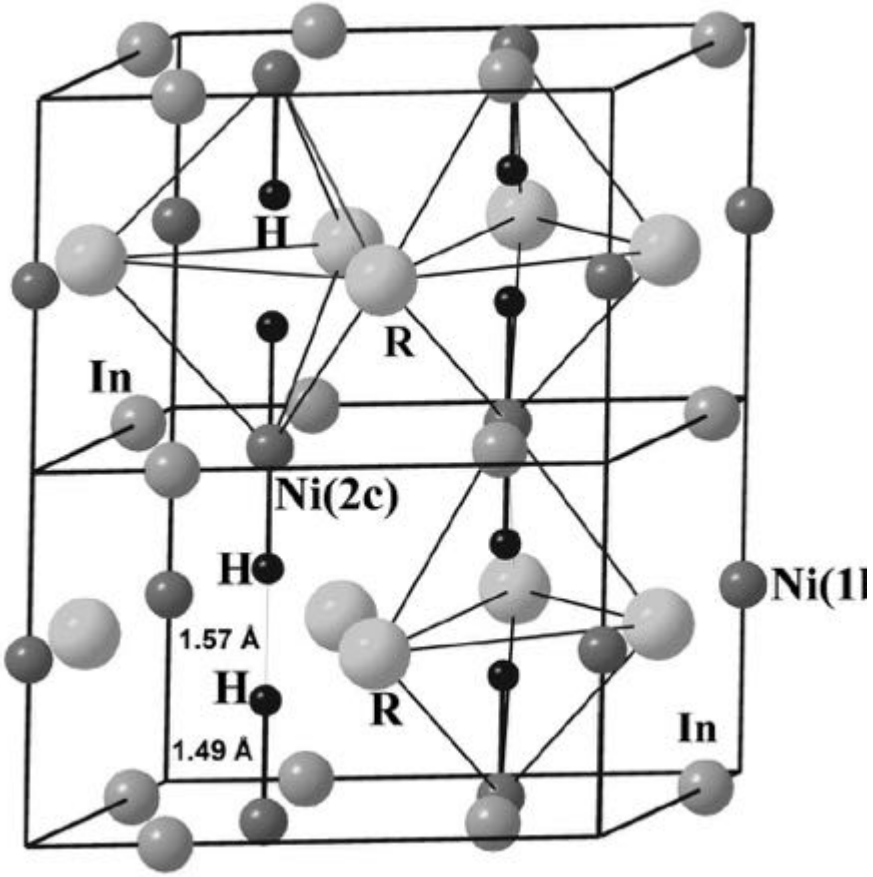
Material	H_2 [mass%]	T_{dec} [° C] 1 bar
$LaNi_5H_6$	1.49	15
$TiMn_{1.5}H_{2.5}$	1.76	-61
$FeTiH_2$	1.86	-10
ZrH_2	2.16	696
$TiCr_{1.8}H_{3.5}$	2.43	-120
Mg_2NiH_4	3.62	300
VH_2	3.81	-10,
TiH_2	3.98	780
NaH	4.20	430
CaH_2	4.79	1000
Li_2NH + LiH	5.50	600
$LiNH_2$ + LiH	6.50	300
$NaAlH_4$	7.46	30, 120
MgH_2	7.66	320
AlH_3	10.07	<RT
$LiAlH_4$	10.62	-93
$NaBH_4$	10.66	620
LiH	12.86	900
$Al(BH_4)_3$	16.90	<100
NH_3	17.75	-32
$LiBH_4$	18.51	230

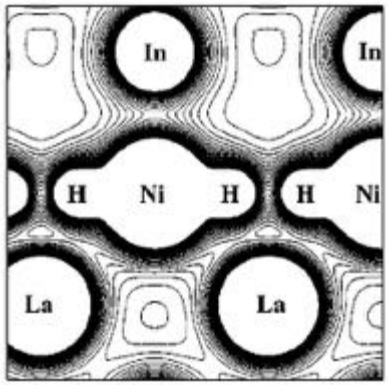
7.7. No Correlation between Hydrogen Capacity and Stability

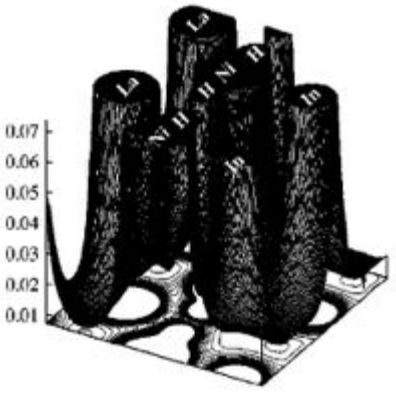


7.8. Metal Hydrides with Short H-H Separations

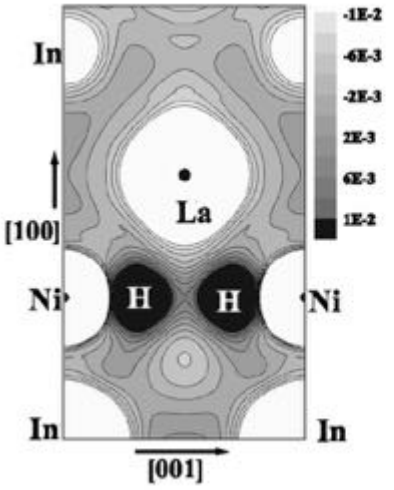
$RTInH_{1.333}$ (R = La, Ce, Pr, or Nd; T = Ni, Pd, or Pt)



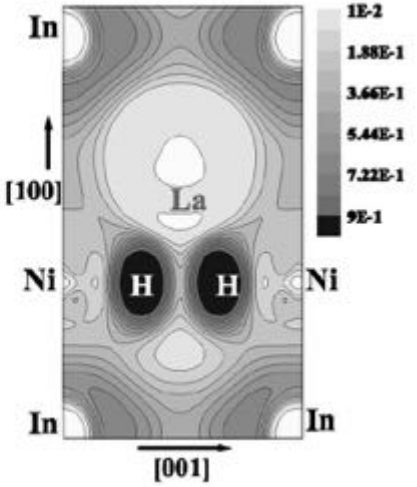




charge transfer



electron density

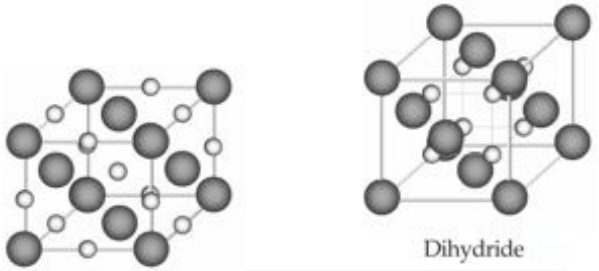


Ref.: P. Vajeeston, P. Ravindran, R. Vidya, A. Kjekshus, H. Fjellva, and V. A. Yartys, "Short hydrogen-hydrogen separation in $RNiInH_{1.333}$ „R=La, Ce, Nd…", Phys. Rev. B 67 (2003), 014101

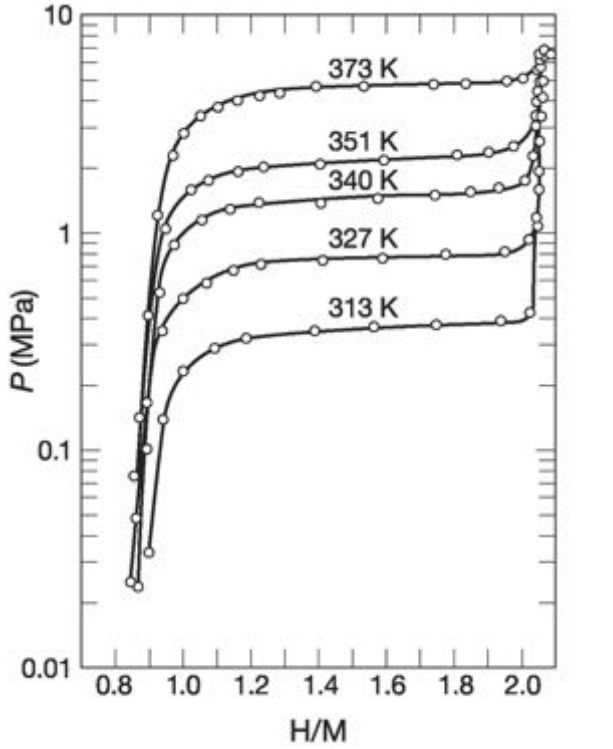
7.9. Body Centered Cubic (bcc) Solid Solution Alloys

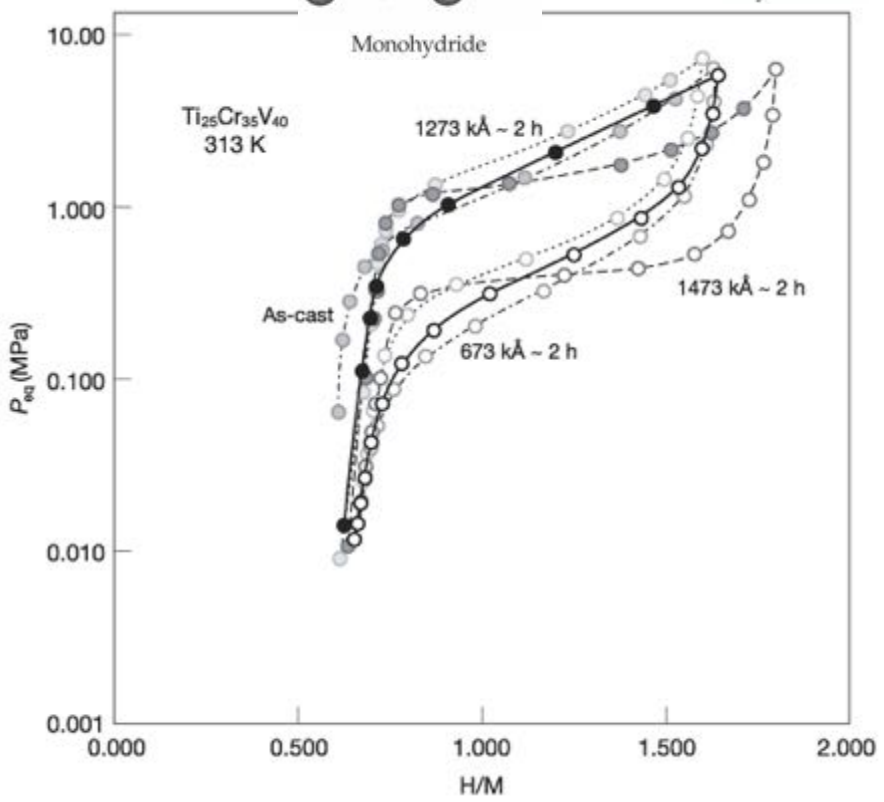
BCC Alloys: Ti-V-Mn, Ti-V-Cr, Ti-V-Cr-Mn, and Ti-Cr-(Mo, Ru)

Structure	fcc & hcp		bcc	
Site	O	T	O	T
Number	1	2	3	6
Size	0.414	0.255	0.155	0.291



V ⟶ VH ⟶ VH_2

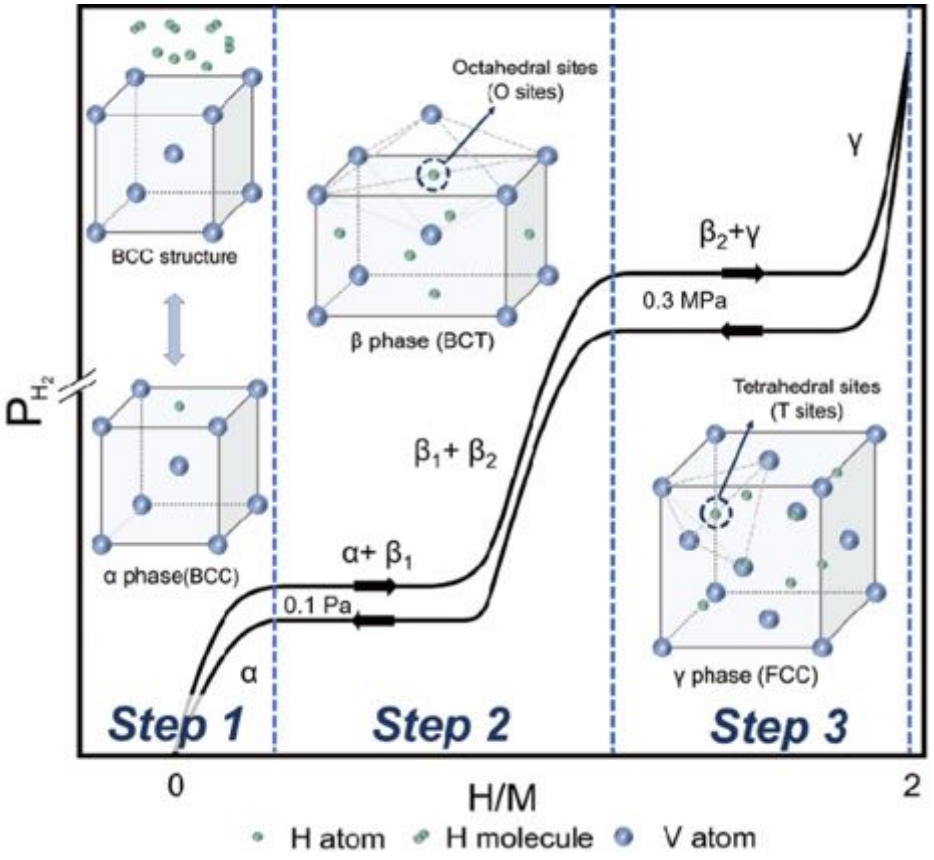




Ref.: E. Akiba and M. Okada, "Metallic Hydrides III: Body-Centered-Cubic Solid-Solution Alloys", MRS BULLETIN/SEPTEMBER 2002 699-703

7.10. Body Centred Cubic (bcc) Alloys

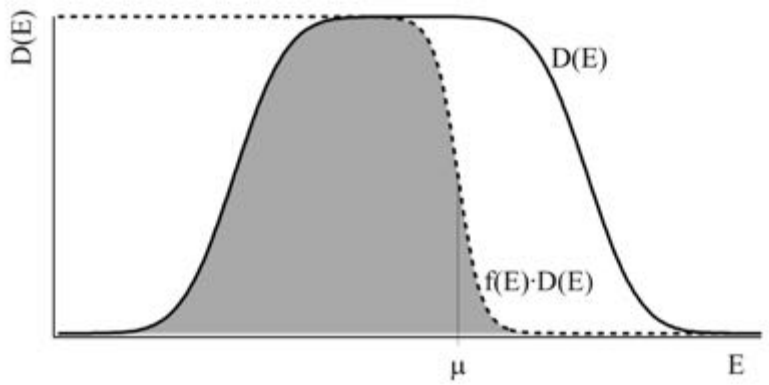
Vanadium (V)-based alloys attract wide attention, owing to the total hydrogen storage capacity of 3.8 wt% and reversible capacity above 2.0 wt% at ambient conditions, surpassing the AB_5-, AB_2- and AB-type hydrogen storage alloys. However, several challenges, such as insufficient capacity, cyclic stability and high raw material costs, hinder the practical applications of V-based alloys.

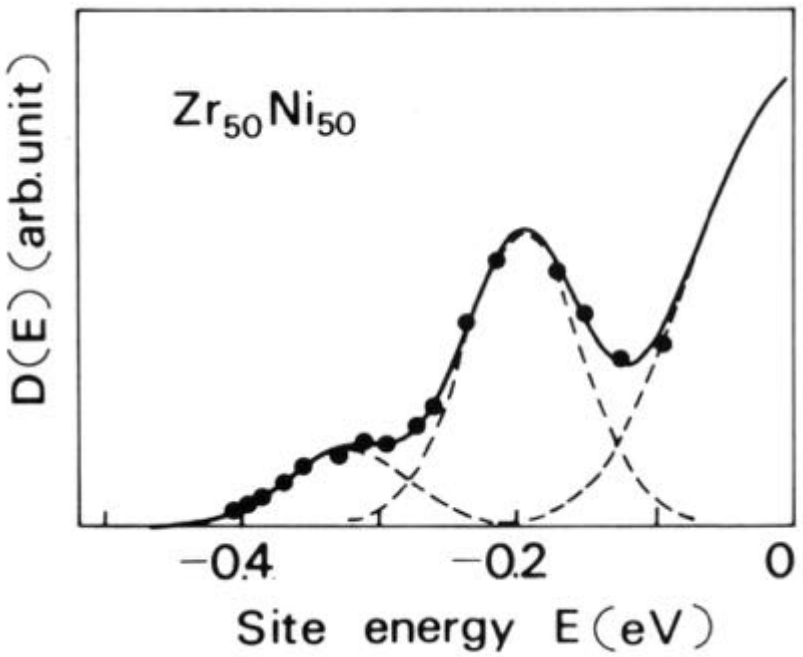


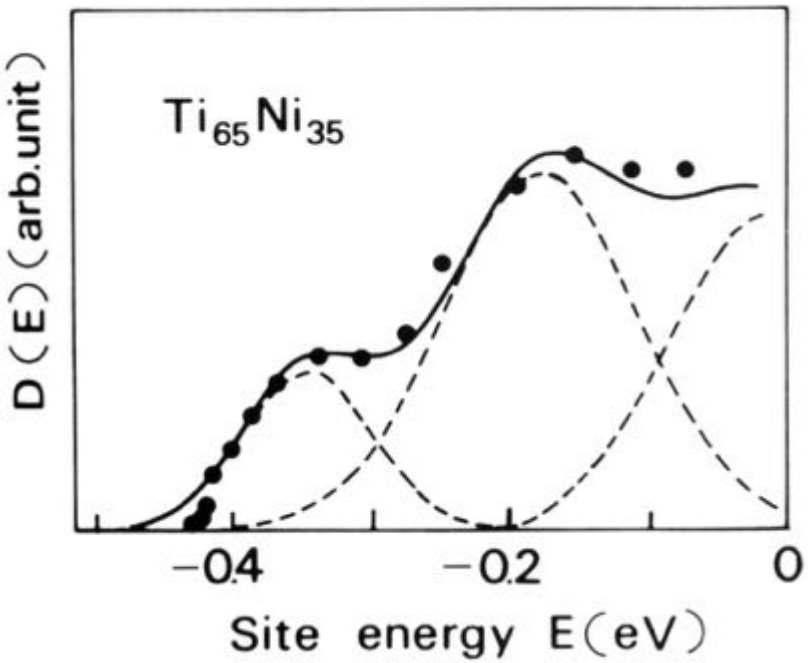
Compositions	Absorption (wt%)	Desorption (wt%)
$Ti_{0.16}Zr_{0.05}Cr_{0.22}V_{0.57}$	3.55	2.14
V–7.4Zr–7.4Ti–7.4Ni	2	1.6
$TiCr_{1.5}V_{0.3}$	3.49	2.05
$V_{0.68}Ti_{0.2}Cr_{0.12}$	3.6	1.5
Ti–Cr–(5–7%)V	3	2.2
Ti–20V–10Cr–30Mn	2.4 / 1.32	1.6
Ti–24V–10Cr–26Mn	3.25/ 2.08	2.61
Ti–28V–10Cr–22Mn	3.9 / 2.51	3.41
Ti–32V–10Cr–18Mn	3.98 / 2.45	3.62
$Ti_{26.7}Cr_{33.3}V_{40}$	3.46	1 / 1.6 /1.8
$(Ti_{0.267}Cr_{0.333}V_{0.40})_{93}Fe_7$	2.9	1.6 /1.65 / 1.7
$(Ti_{0.267}Cr_{0.333}V_{0.40})_{93}Fe_7Ce_{0.4}$	3.3	2 / 2.05 / 2.12
$(Ti_{0.267}Cr_{0.333}V_{0.40})_{93}Fe_7Ce_{1.1}$	3.4	2.05 / 2.15 / 2.16
$(Ti_{0.267}Cr_{0.333}V_{0.40})_{93}Fe_7Ce_{2.0}$	3.24	1.9 / 2 / 2.04
$TiMn_{0.9}V_{1.1}$	3.2	0.5
$TiMn_{0.9}(FeV)_{1.1}$	1.8	1
$TiMn_{1.1}V_{0.9}$	1.8	0.8
$TiMn_{1.1}(FeV)_{0.9}$	1.6	1.1

Ref.: Han-Yang Kong, Qing-Feng Xie, Chao-Ling Wu, Yao Wang, Yun-Gui Chen, Hai-Wen Li & Yi-Gang Yan, “Vanadium-based alloy for hydrogen storage: a review,” Rare Met., Volume 43 (2024), pages 6201–6232.

8. Investigation of Hydrides: Interstitial Sites for Hydrogen





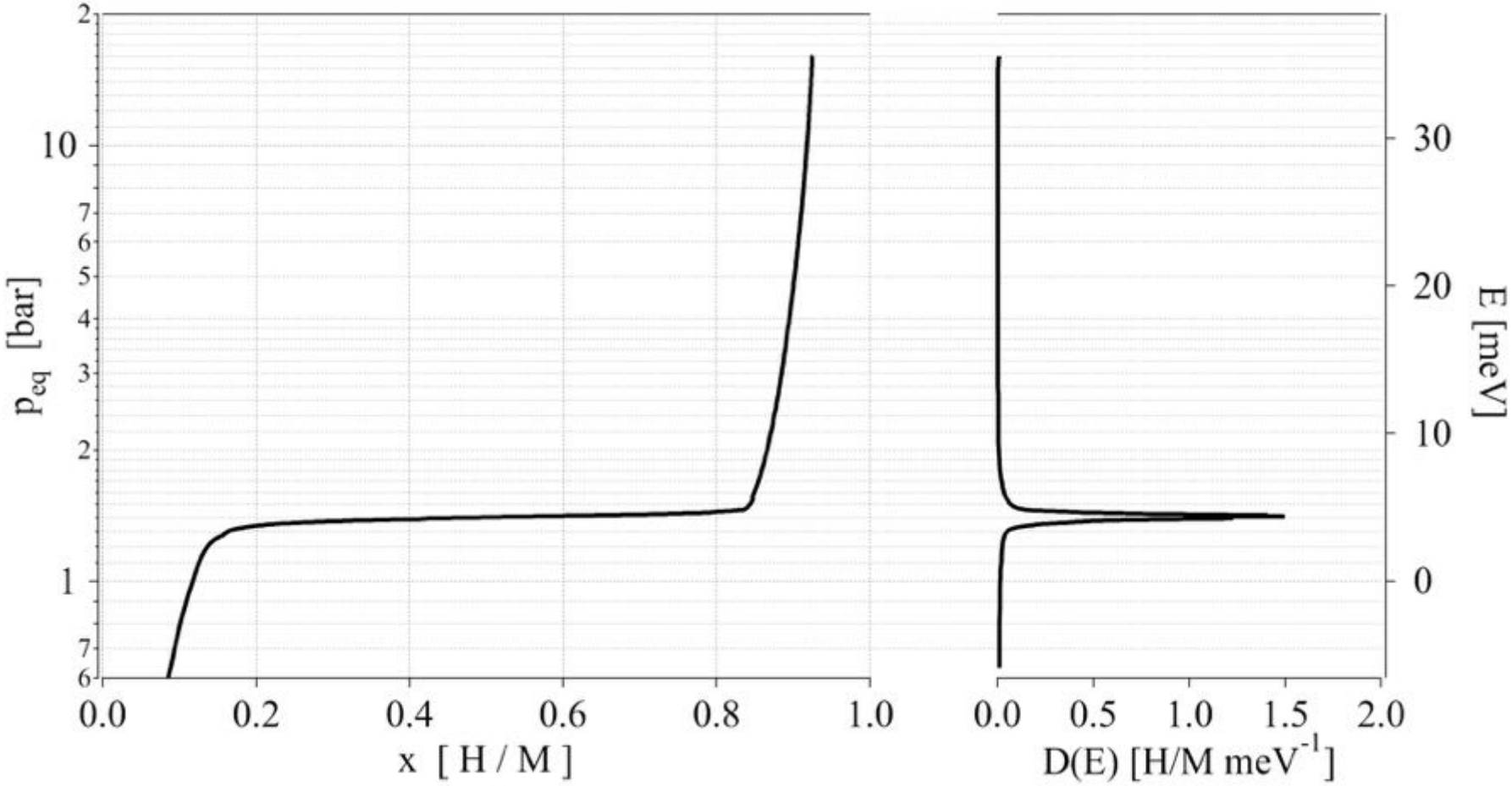


Ref.: I. Bakonyi, F. Mehner, A. Rapp, A. Cziraki, E. Toth-Kadar, V. Skumryev, R. Reisser, H. Kronmüller and R. Kirchheim , Zeitschrift für Metallkunde (1993)

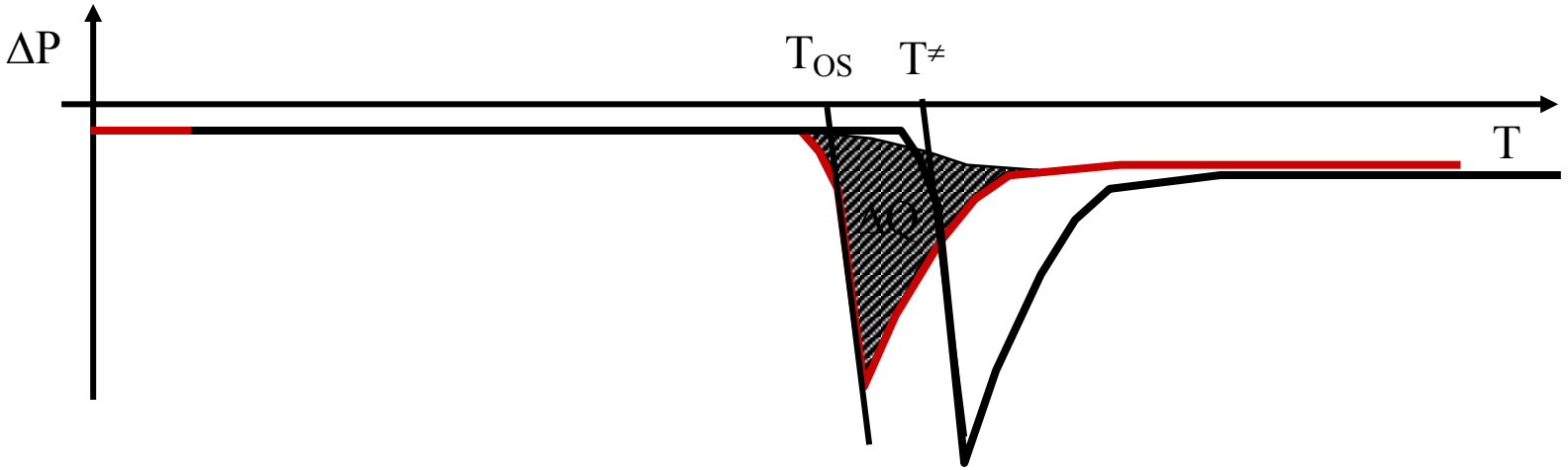
8.1. Interstitial Sites for Hydrogen

$$E = R \cdot T \cdot ln(p/p_0)$$

$$\frac{dx}{dE} = D(E)$$



8.2. Stability from Differential Scanning Calorimetry



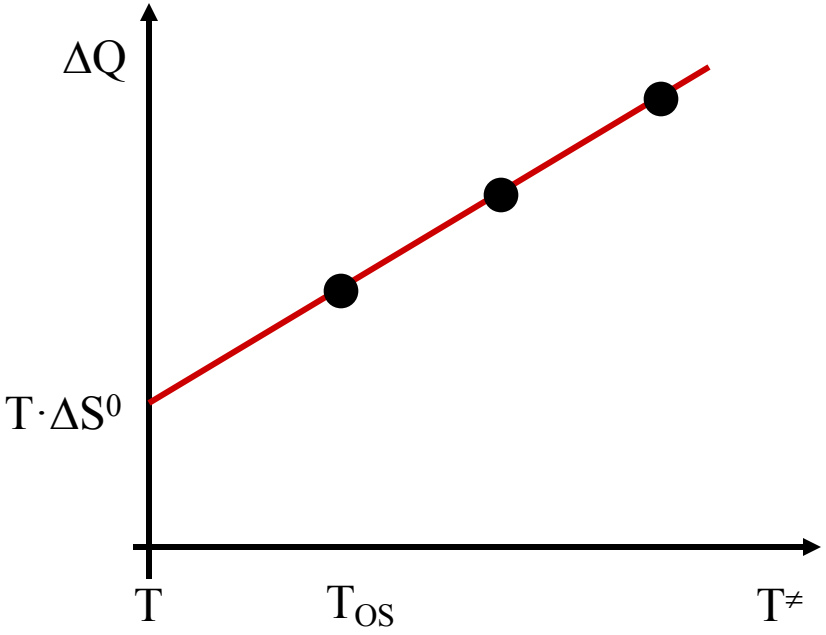
$$\Delta G^0 = R \cdot T \cdot \ln\left(\frac{p}{p_0}\right) = \Delta H^0 - T \cdot \Delta S^0$$

for $p = p_0$

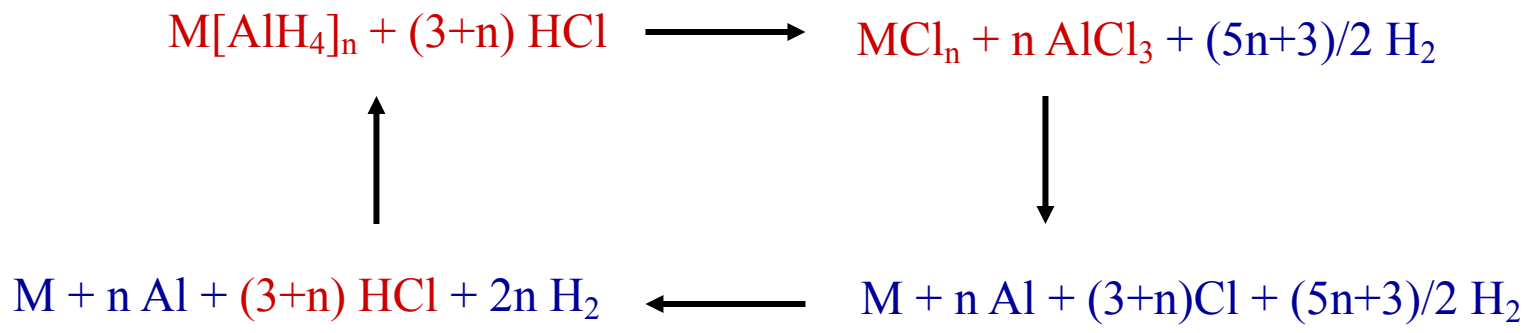
$$\Delta H^0 = T \cdot \Delta S^0 = \Delta Q$$

$$\Delta H^{\neq} = T^{\neq} \cdot \Delta S^0 = \Delta Q^{\neq}$$

$$\Delta H^{\neq}_{des} \geq \Delta H^0 \geq \Delta H^{\neq}_{abs}$$



8.3. Stability from BORN-HABER Cycle



$$\Delta H^0 = T \cdot \Delta S^0 = \Delta Q$$

Table VIII. Heats and Free Energies of Formation at 25° C.

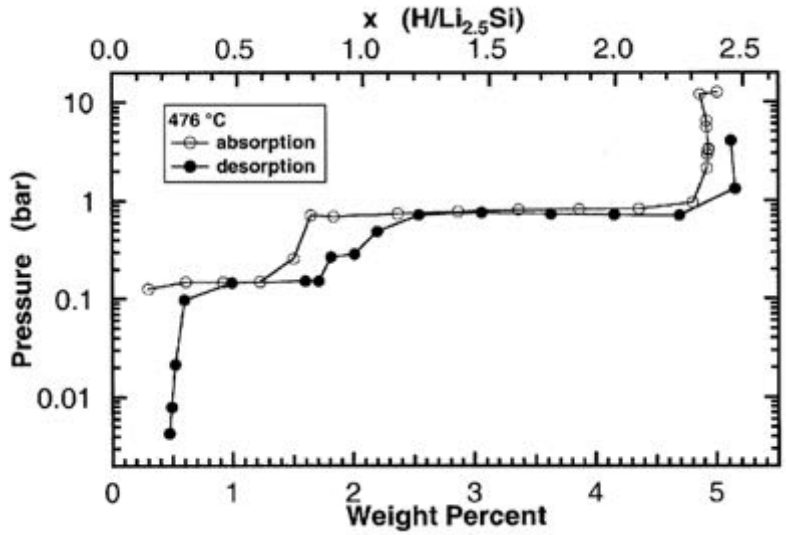
Crystalline Compound	$-\Delta H_f^0$, Kcal./Mole	$-\Delta F_f^0$, Kcal./Mole	$-298.15\ \Delta S_f^0$, Kcal./Mole	S^0 (25° C.)
LiH	21.67[a]	16.8	4.9	5.9[b]
NaH	13.49[a]	8.6	4.9[c]	11.4
KH	13.82[a]	8.9	4.9[c]	14.5
CsH	11.92[d]	7.0	4.9[c]	19.3
$LiAlH_4$	28.5[d,e]	12.9	15.6[f]	23.5
$NaAlH_4$	27.0[d]	11.6	15.4[f]	29.6
$KAlH_4$	39.8[d]	23.8	16.0[f]	30.8
$CsAlH_4$	39.4[d]	23.5	15.9[g]	36.0
$LiBH_4$	46.37[e]	30.75	15.62[i]	18.13[b]
$NaBH_4$	45.63[e]	30.19	15.44	24.21[b]
KBH_4	54.70[h]	38.70	16.00	25.48[i]

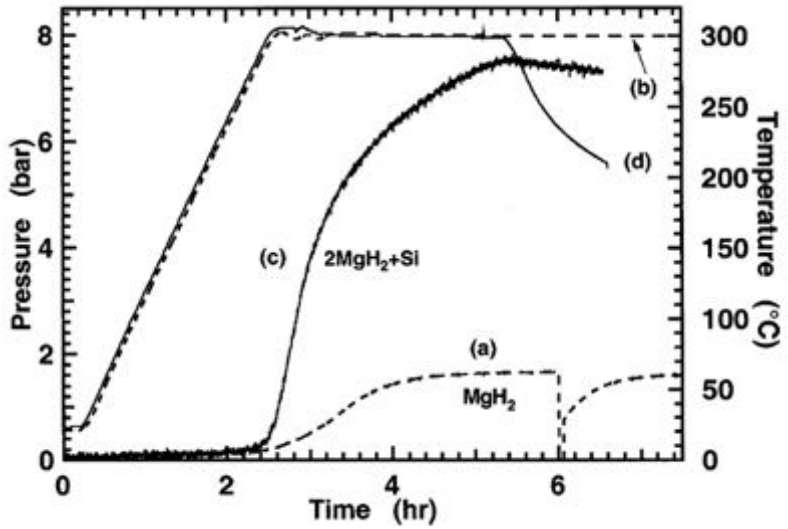
Ref.: Smith and Bass, "Heats and free energy of formation of alkali aluminum hydrides", J. Chem. Eng. Data 8:3 (1963), pp. 342-347

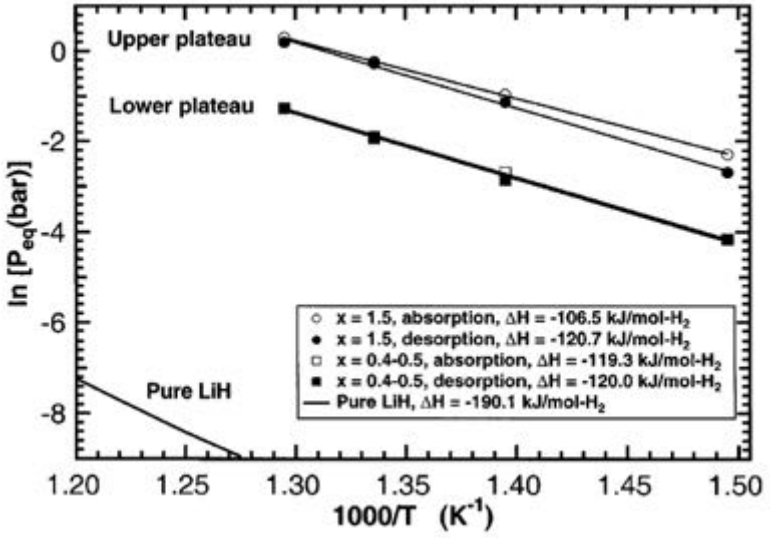
8.4. Destabilisation of MgH_2

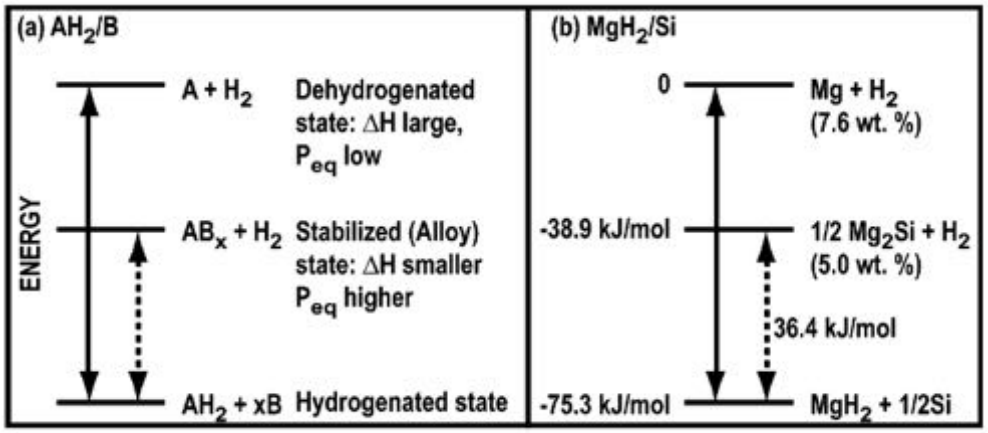
$2.5\ LiH + Si \rightarrow Li_{2.5}Si + 1.25H_2$

$2\ MgH_2 + Si \rightarrow Mg_2Si + 2H_2$



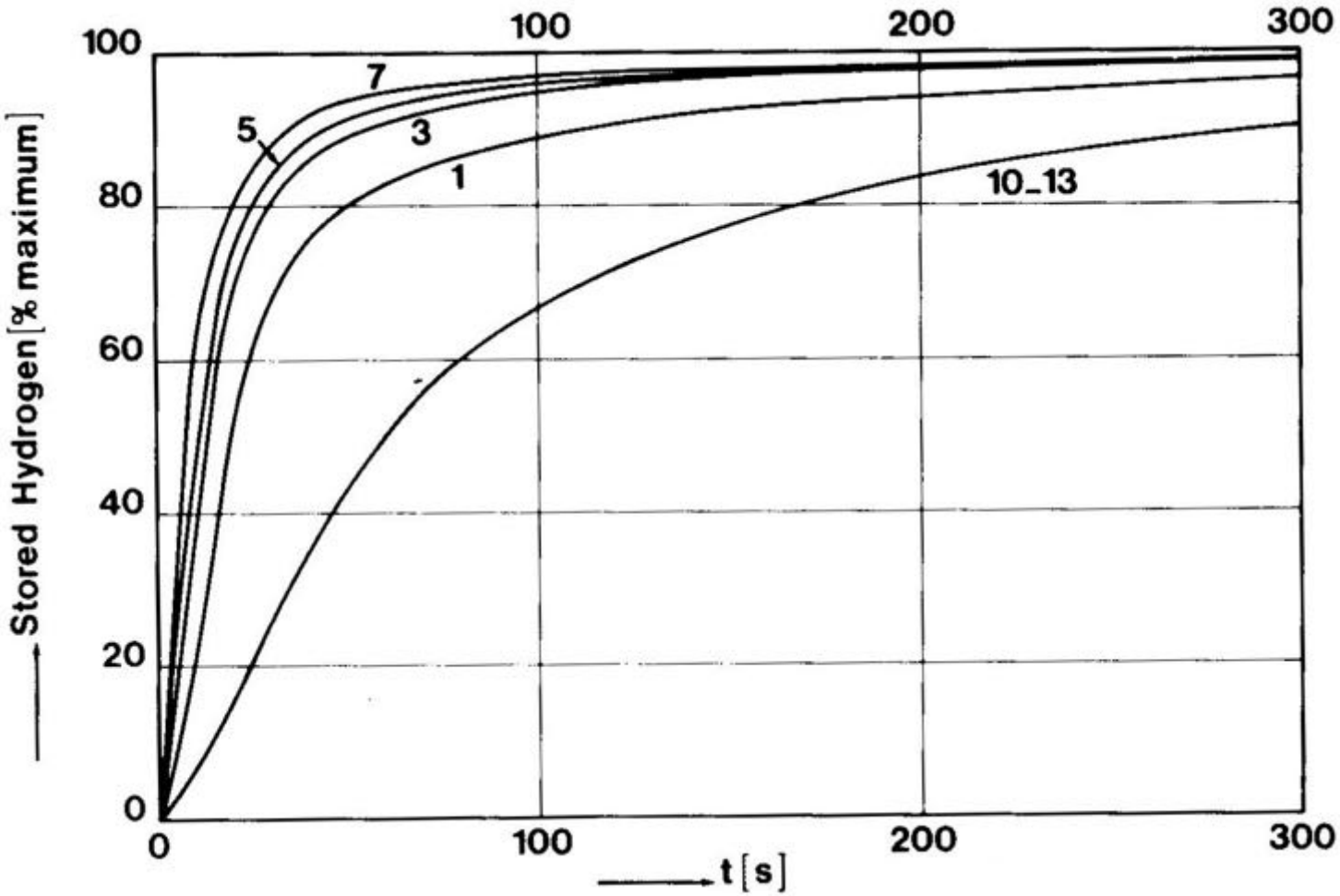






Ref.: J. J. Vajo, F. Mertens, C. C. Ahn, R. C. Bowman Jr, B. Fultz, J. Phys. Chem. B 108 (2004), 13977-13983

8.5. Hydrogen Absorption Kinetics in $LaNi_5$



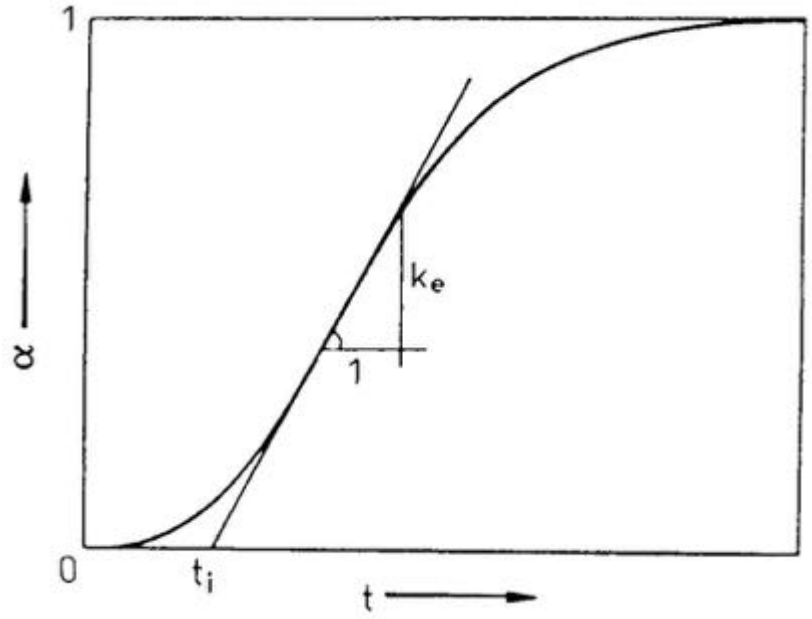
Ref.: A. Percheron-Guegan, J.-M.Welter,Chapter 2, L. Schlapbach (Ed.) in Intermetallic Compounds I, Springer Series Topics in Applied Physics, Vol. 63, Springer–Verlag, 1988, p. 36.

A. Züttel, V Güther, A Otto,M Bärtsch, R Kötz, D Chartouni, Ch Nützenadel, L Schlapbach , "About the mechanism and the rate limiting step of the metalhydride electrode reaction ", Journal of Alloys and Compounds 293-295 (1999), pp. 663-669

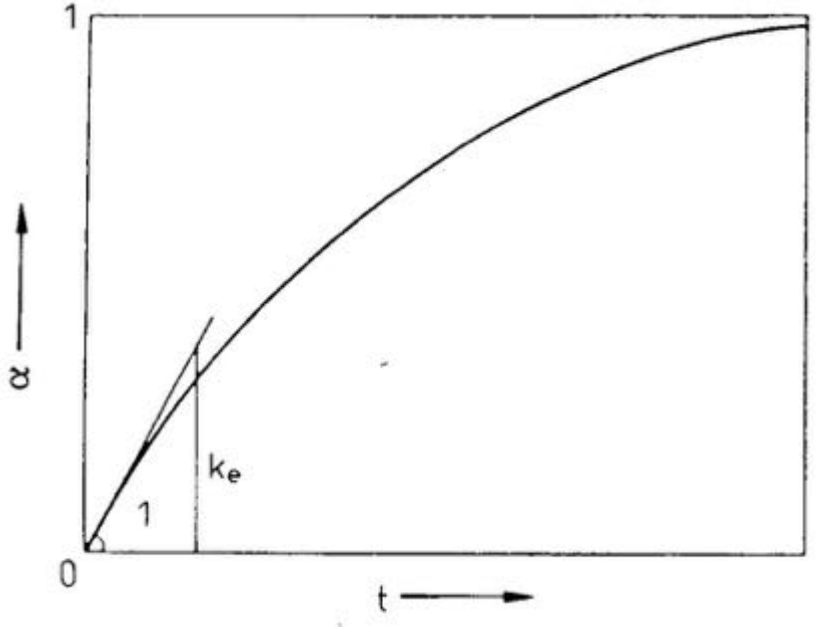
8.6. Kinetics of Hydrogen Absorption

$$x(\beta) = 1 - e^{-k \cdot t^n}$$

nucleation and growth



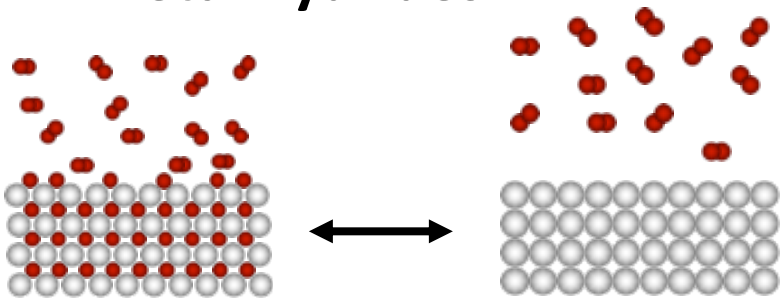
diffusion limited



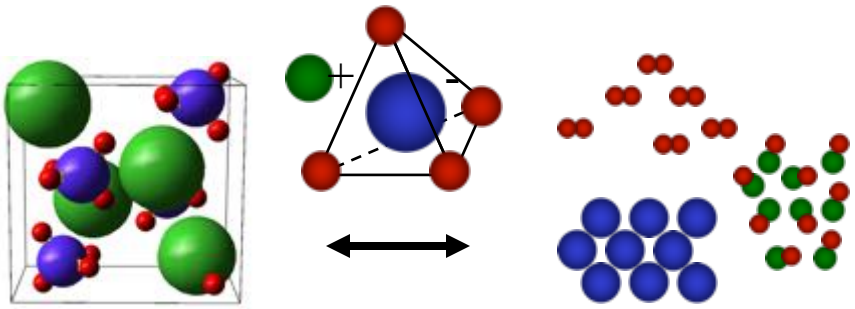
Ref.: B. V. Erofeyev, “A Generalized Equation of Chemical Kinetics and its Application in Reactions Involving Solids.”, Comptes Rendus Acad. Sci. URSS, 52, 511-514 (1946) (in English) (Doklady) Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS Volume LII, No. 6 (1946).

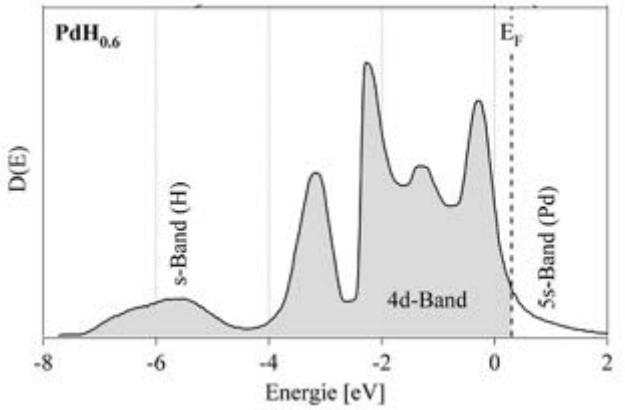
9. Metal- and Complex Hydrides

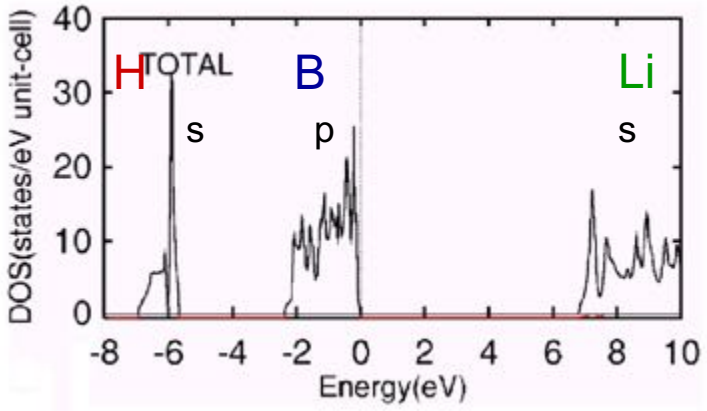
metal hydrides



complex hydrides







Ref. K. Miwa, N. Ohba, S. Towata, Y. Nakamori, S. Orimo, Phys. Rev. B 69 (2004), 245120

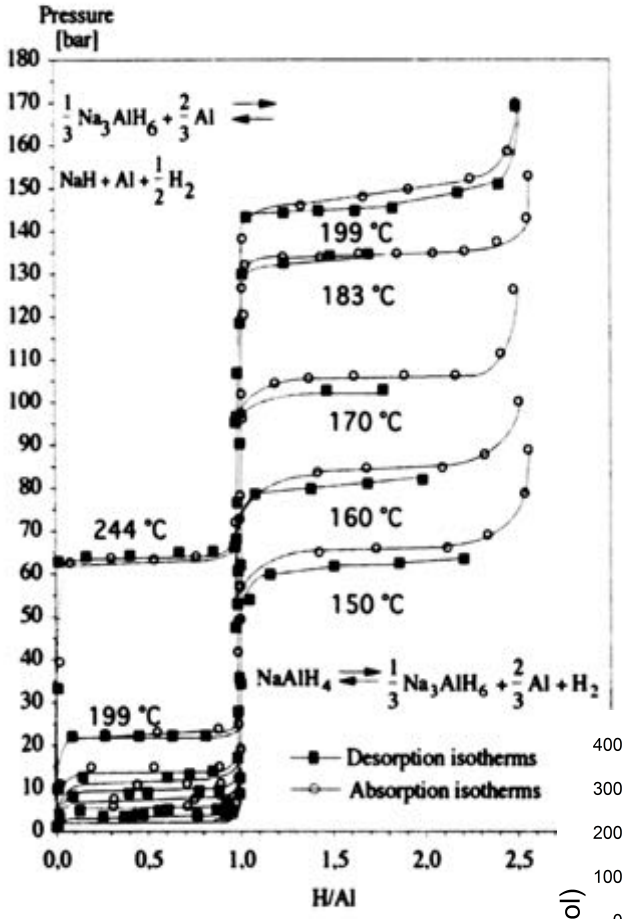
$$x\ MH_{2/x} \rightarrow x\ M + H_2$$

$$ln\left(\frac{p}{p_0}\right) = -\frac{\Delta H^0}{R}\cdot\frac{1}{T} + \frac{\Delta S^0}{R}$$

$$^2/_3\ ABH_4 \rightarrow {}^2/_3\ AH + {}^2/_3\ B + H_2$$

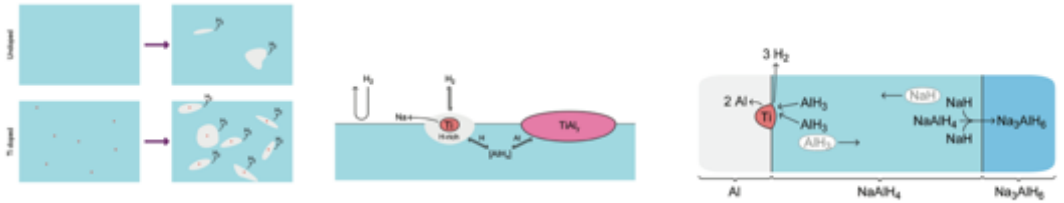
$$T_{dec}(p = p_0) = \frac{\Delta H^0}{\Delta S^0}$$

9.1. Catalysis of Complex Hydrides



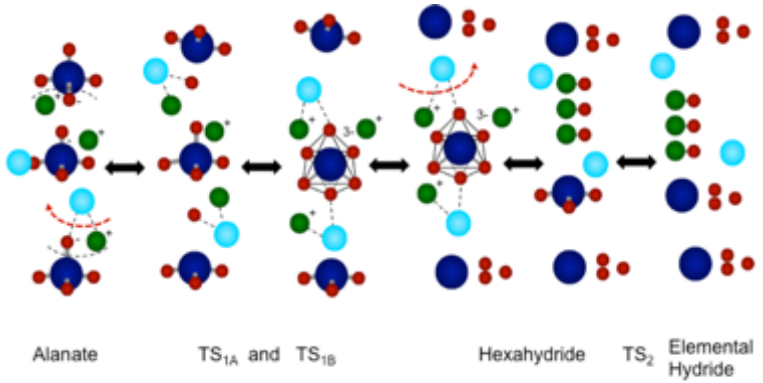
Ref.: B. Bogdanovic, M. Schwickardi, "Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials", Journal of Alloys and Compounds 253 (1997), 1-9.

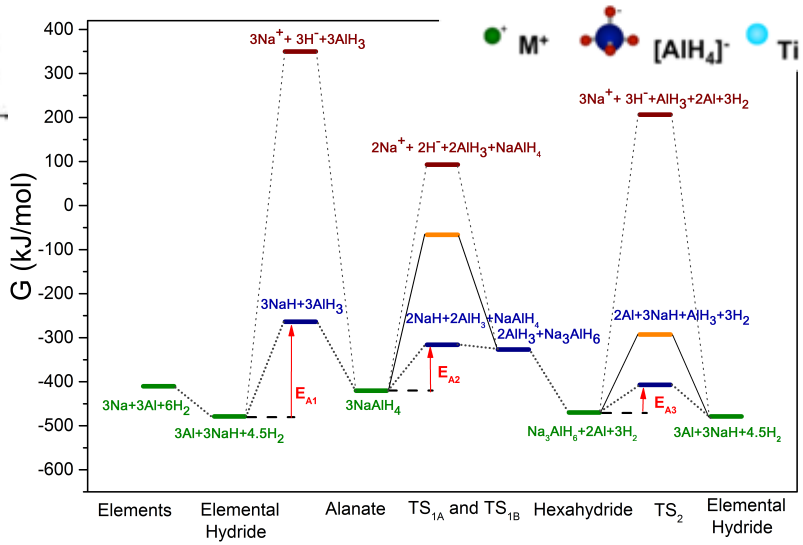
Nucleation/Phase Growth **Surface process** **Diffusion of AlH_3, Al and NaH**



Ref.: T.J. Frankcombe, „Proposed Mechanisms for the Catalytic Activity of Ti in $NaAlH_4$", Chem. Rev. 112 (2012), pp. 2164 - 2178

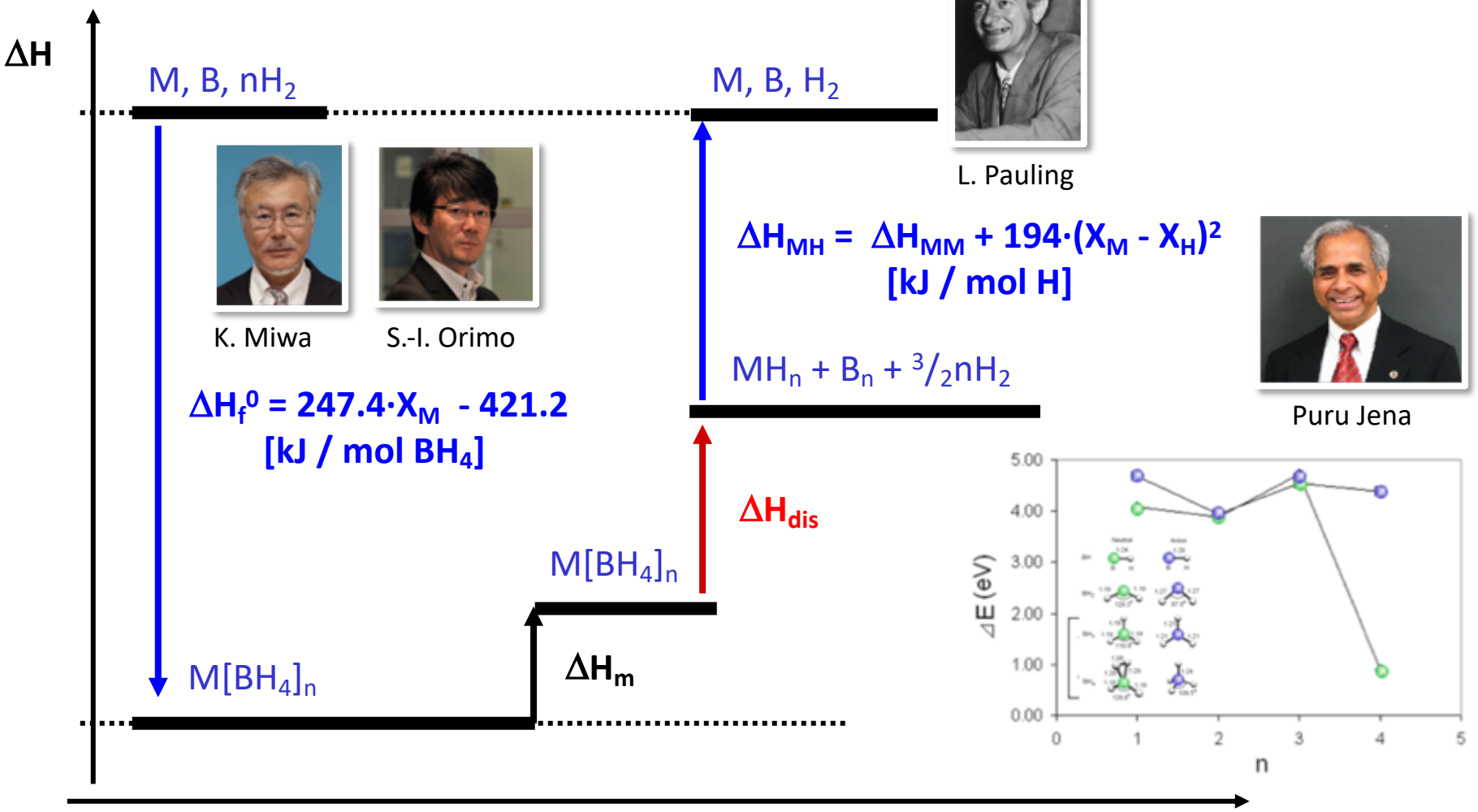
Boris BOGDANOVIC 1997





Ref.: Z. Ö. Kocabas Atakli, E. Callini, S. Kato, P.Mauron, S. Orimo, A. Züttel, "Catalyzed Hydrogen Sorption Mechanism in Alkali Alanates", Phys. Chem. Chem. Phys. 17:32 (2015), p. 20932-20940.

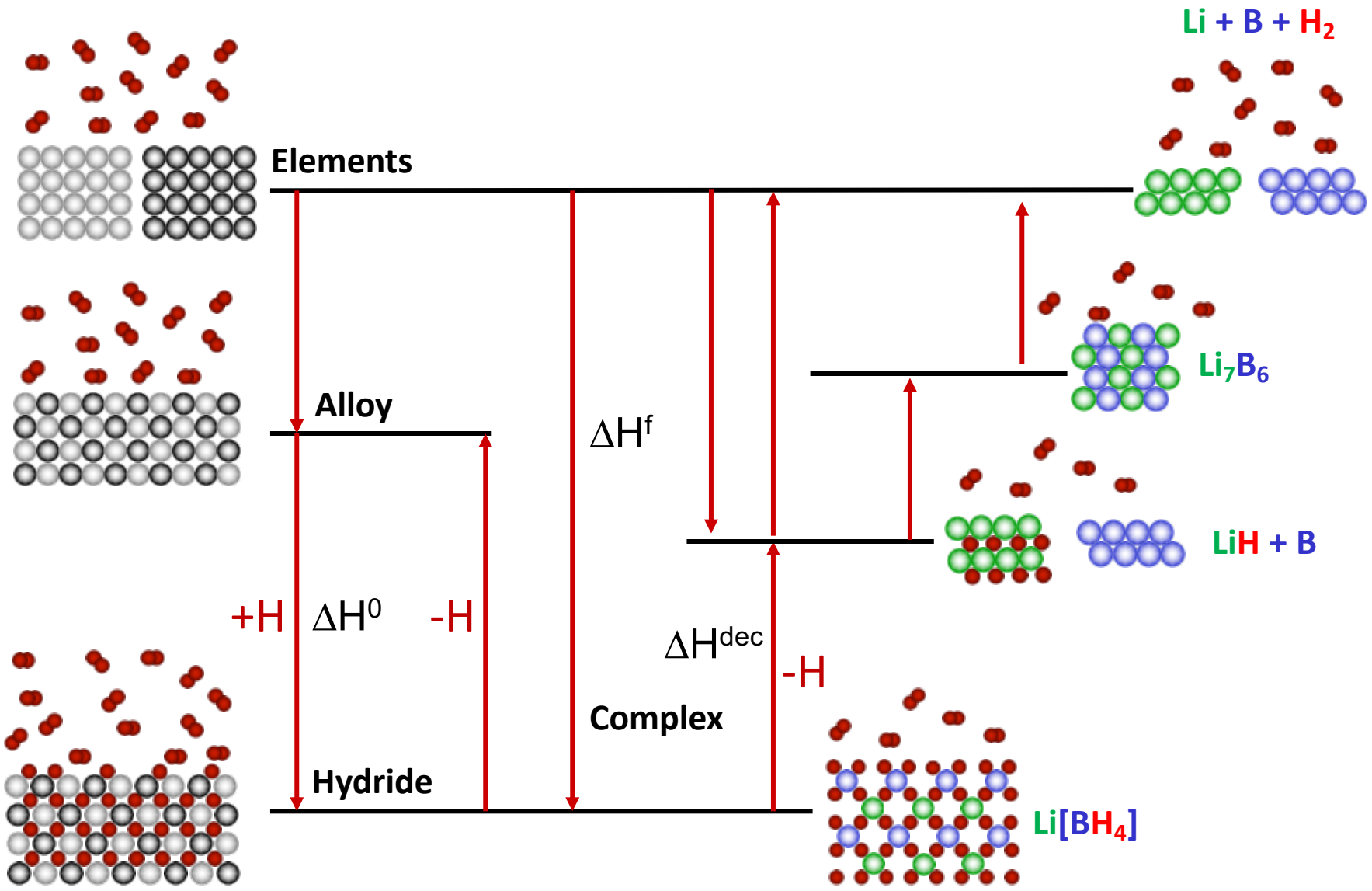
9.2. Stability of Complex Hydrides



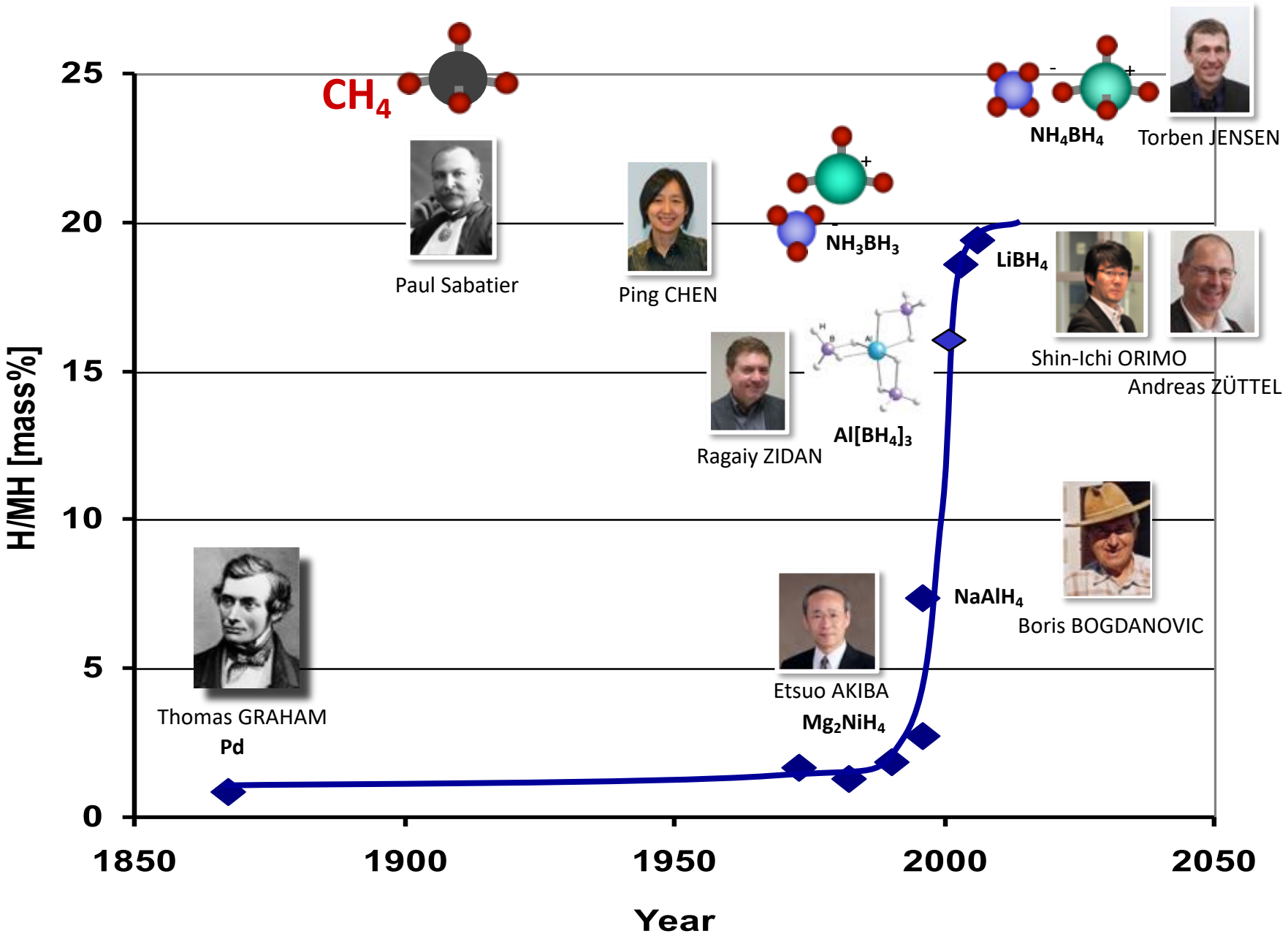
$$\Delta H_{dis} = \Delta H_f^0 - \Delta H_{MH} - \Delta H_m$$

Ref.: Y. Nakamori, K. Miwa, A. Ninomiya, H. Li, N. Ohba, S.-I. Towata, A. Züttel, and Shin-ichi Orimo, Physical Review B 74, 045126 (2006); Linus Pauling, "THE PRINCIPLES DETERMINING THE STRUCTURE OF COMPLEX IONIC CRYSTALS", Journal of the American Chemical Society, 1929 - pubs.acs.org

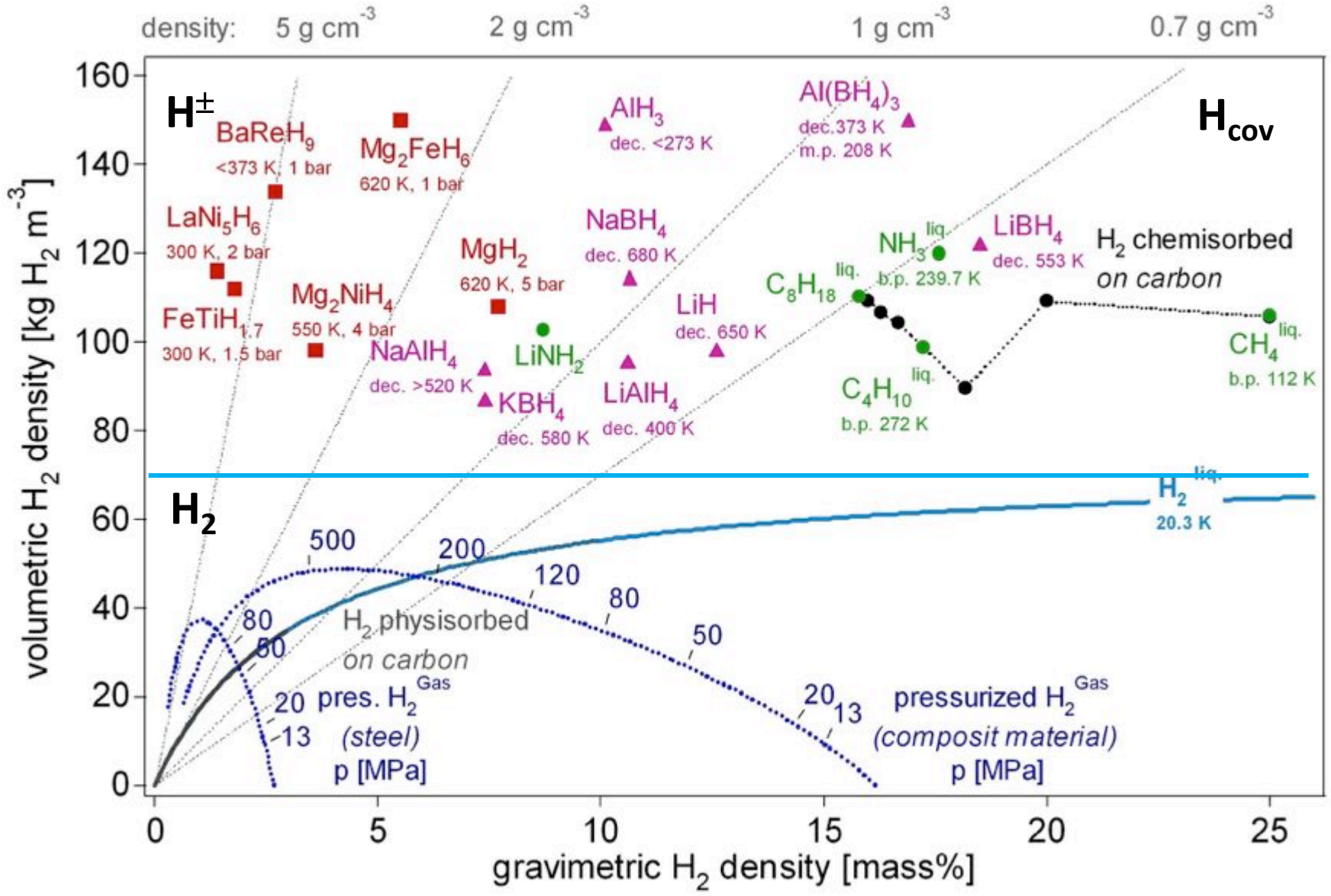
9.3. Comparison Metal Hydrides vs. Complex Hydrides



9.4. Development of the Gravimetric Hydrogen Density

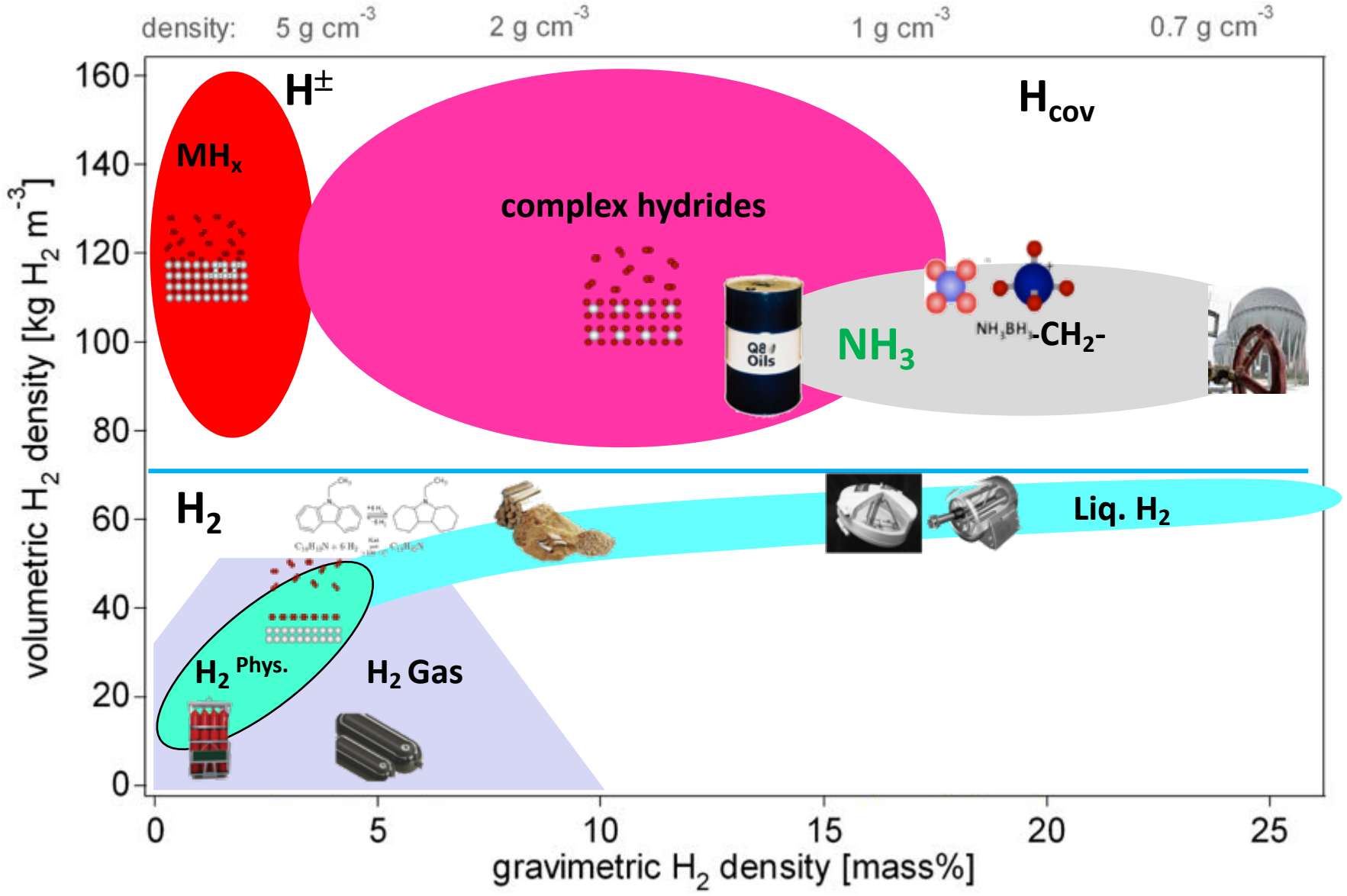


9.5. Hydrogen Storage Materials



Ref: A. Züttel, "Materials for hydrogen storage", materialstoday, Septemper (2003), pp. 18-27

9.6. Hydrogen Storage Density



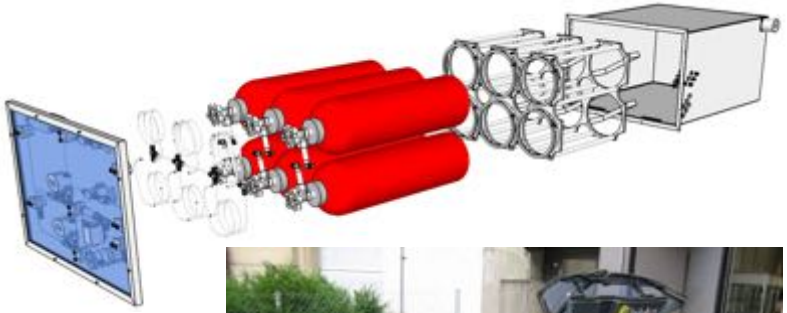
Ref: A. Züttel, "Materials for hydrogen storage", materialstoday, Septemper (2003), pp. 18-27

10. Applications

IC snowmobil, MH storage
5 kg H_2, 1.0 mass%

MHStorage, 2 kg H_2,
50l, 250 kg, 80 kWh

FC canal boat, MH storage
2.5 kg H_2, 1.0 mass%

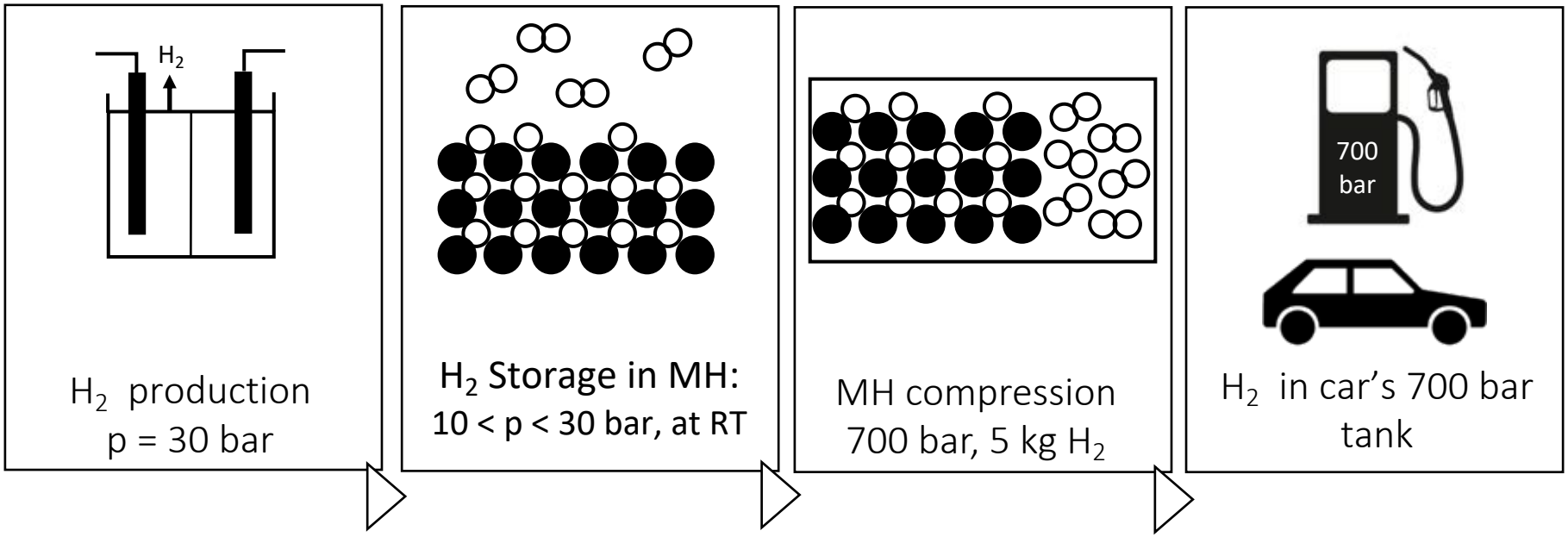


SELF

FC vehicle MH storage
0.5 kg H_2, 1.2 mass%

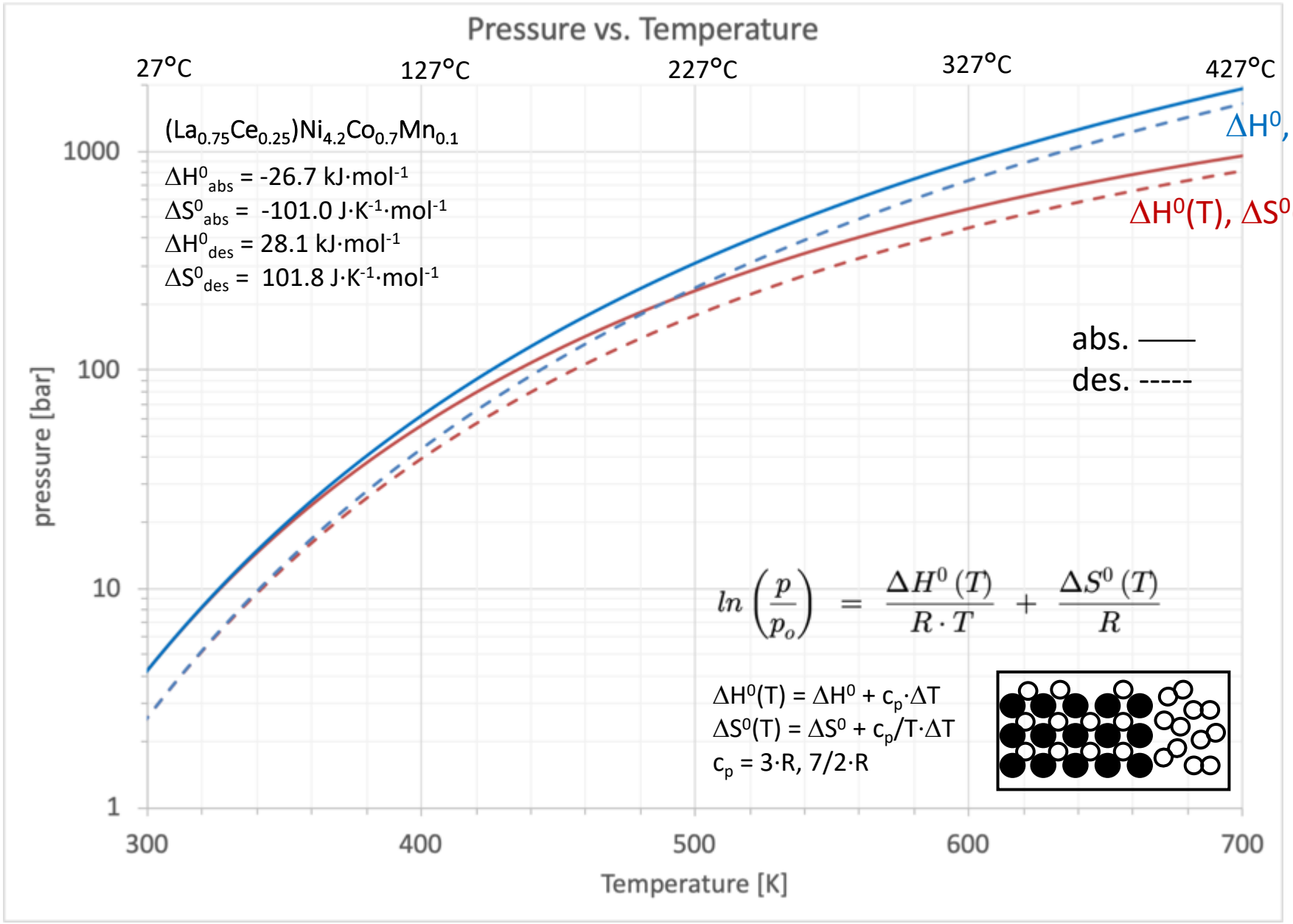
MH Storage, 0.5 kg H_2,
30 kg, 20 kWh

10.1. Metal Hydride Compressor



www.grz-technologies.com

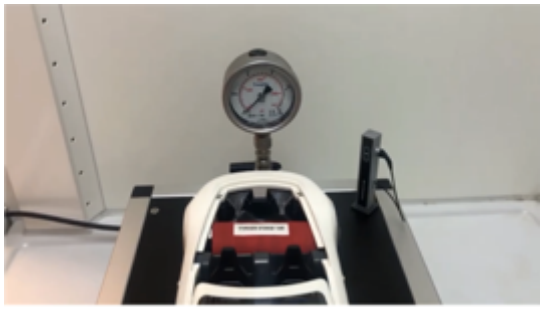
10.2. Pressure vs. Temperature



10.3.a) Metal Hydride Compressor Film

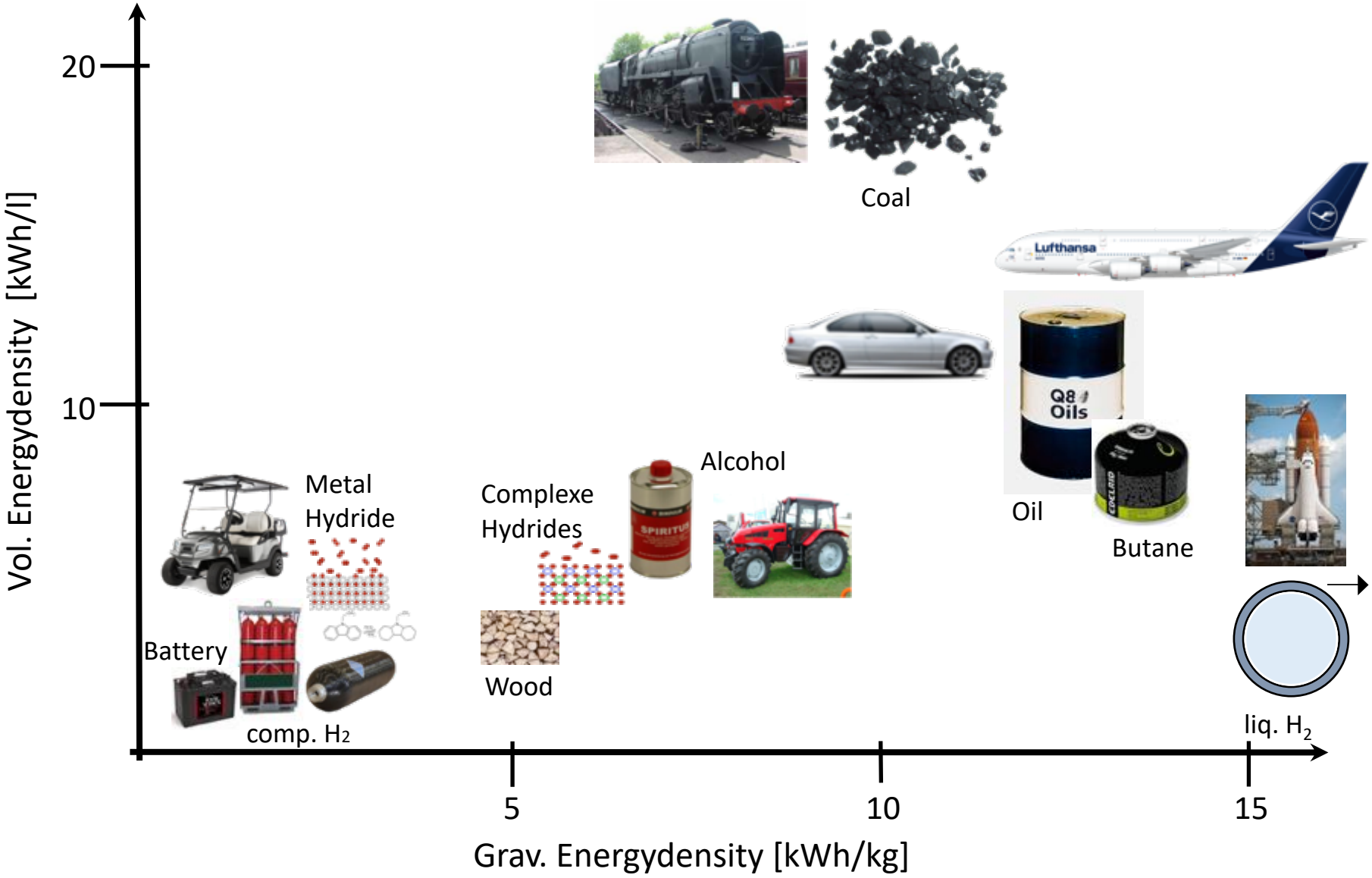
Dr. Heena YANG, EPFL

10.3.b) Metal Hydride Compressor Sequences



Dr. Heena YANG, EPFL

10.4. Energy Density



10.5. Hydrogen Storage in Mobility

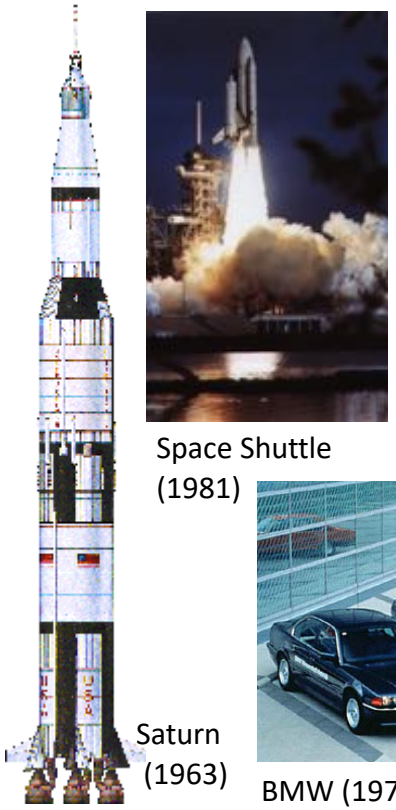
Francois Isaac de Rivaz (1813)

Hindenburg (1937)

Karl Kordesch: Austin A40 (1966)

Tupolev 155 (1988)

Hy.move (2009)



Saturn (1963)

Space Shuttle (1981)

Necar 1 (1994)

NuBus, 250kW (2002)

Necar 4 (2002)

Hyundai Nexo hydrogen car FCEV (2018)

BMW (1978)

Ratrac (2004)

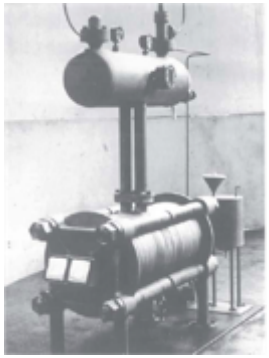
Toyota Mirai (2014)

Coradia iLint (2018)

10.6. Swiss Hydrogen Developments

First H_2 ICE 1807
Francois Isaac de Rivaz

Hydroelectric plant Gampel 1898



Ewald Zdansky 1949

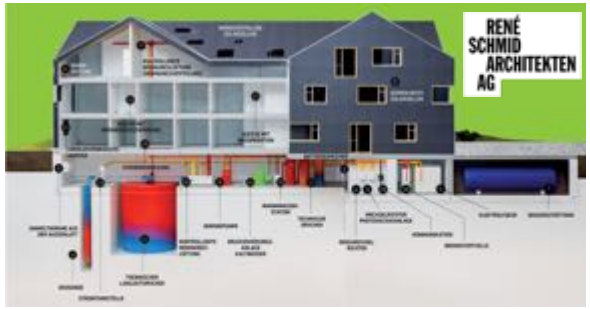
Alkaline Electrolyzer 4MW, 1980
Giovanola, Lurgi, IHT

PV, Electrolysis, Car, Stove
Markus Friedli 1991

Hydrogen Storage 1997 2001
in Monthey

Ratrac MH & ICE 2004

H_2 FC Street sweeper
Hy.move 2009



Energy self sufficient house 2016

PEM Fuel cell 2017

Hyundai H_2 trucks 2020

DASH MH-FC Storage
System 2021

11. Hydrogen Safety

LZ 129 “HINDENBURG” 1937

Space Shuttle “Challenger” USA, 28.1.1986

Tank explosion *Muskingum River Power Plant’s* , USA, 8.1. 2007

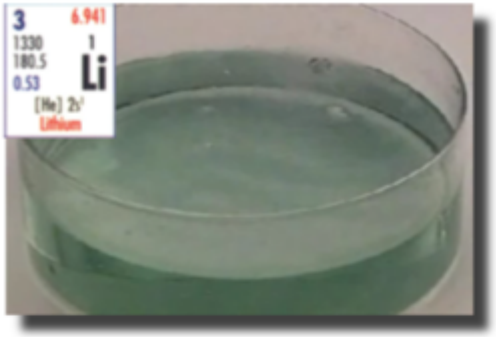
Nuclear power station in Fukushima , Japan, 12. 3. 2011

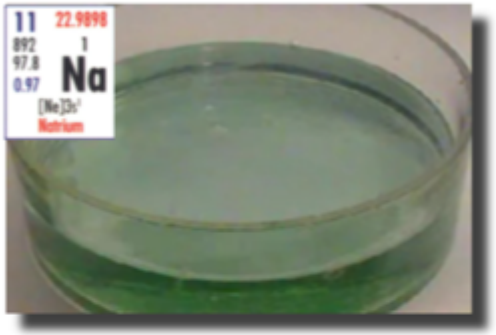
Hydrogen explosion in fueling station, Norway 5. 7. 2019

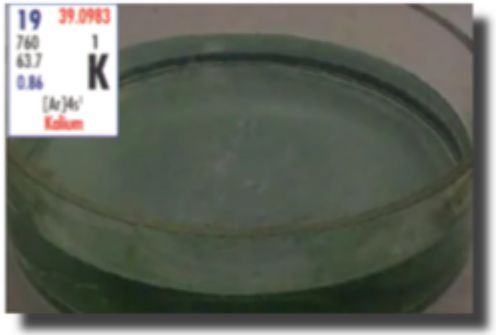
Tank explosion in Gangwon Technopark, South Korea 24. 5. 2019

11.1.a) Reaction of Metals with Water Film

11.1.b) Reaction of Metals with Water Film







11.2. Hindenburg Accident

LZ 129 “HINDENBURG”

New York / Lakehurst, May 6th 1937, 6 pm

Accident:

While the airship was landing she has got on fire about 80 meters above ground level and crashed.

Fatalities:

13 of 36 passengers,

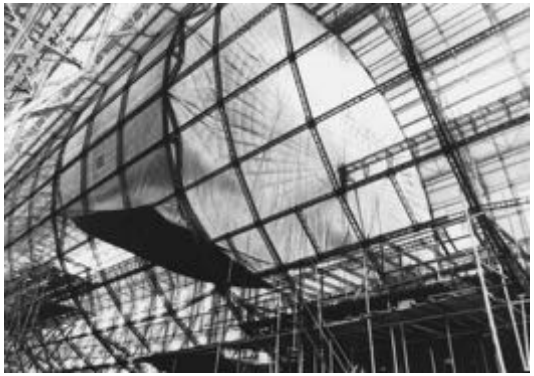
22 of 60 crew members

1 member of 228 ground staff holding the ship.

Ref.: Addison Bain, Wm. D. Van Vorst, "The Hindenburg tragedy revisited: the fatal flaw found", Int. Journal of Hydrogen Energy 24 (1999), pp. 399-403

11.3. Hindenburg Accident Investigation

New investigation: The inflammable skin of the Hindenburg was ignited by an electric discharge arc between the electrostatic charged skin and the grounded metallic frame.



Ref.: Addison Bain, Wm. D. Van Vorst, "The Hindenburg tragedy revisited: the fatal flaw found", Int. Journal of Hydrogen Energy 24 (1999), pp. 399-403

11.4.a) Fuel Leak Simulation

Ignition t = 3 s

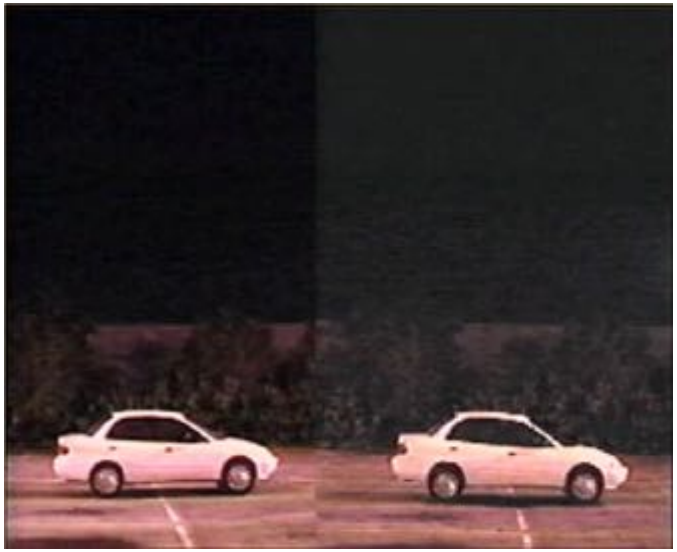
t = 60 s

t = 90 s

Ref.: Michael R. Swain, University of Miami, Coral Cables, FL 33124, USA

11.4.b) Fuel Leak Simulation

Before ignition t = 0 s



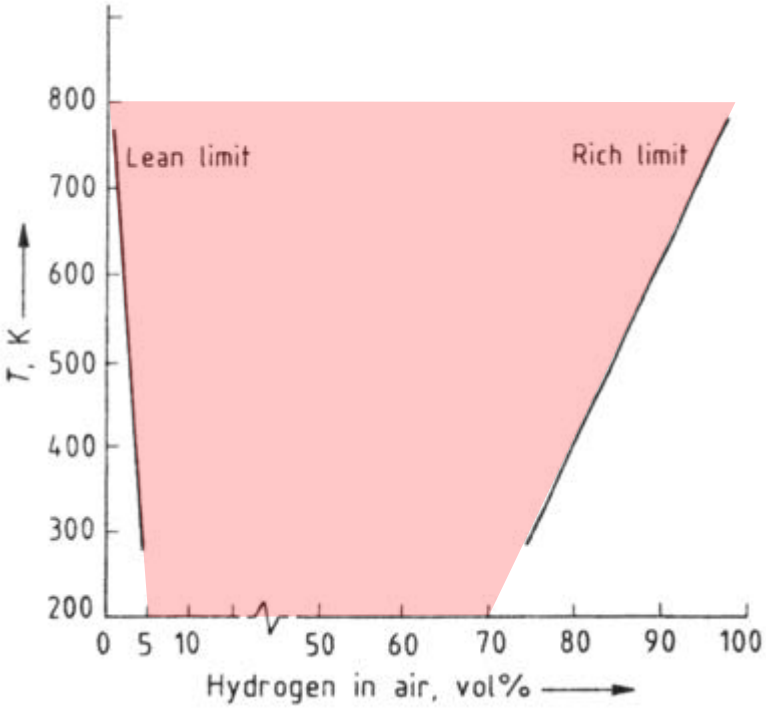
Ignition t = 3 s

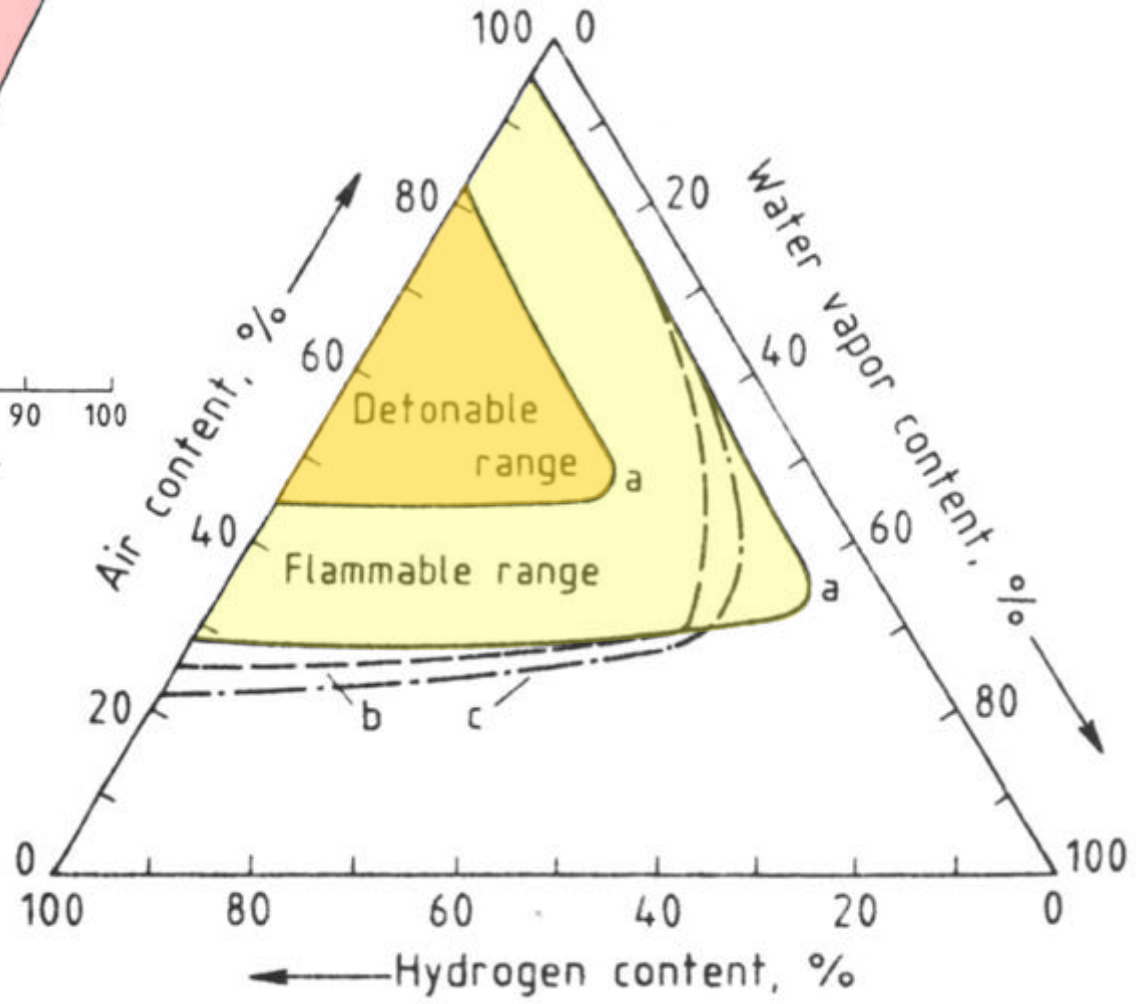
t = 60 s

t = 90 s

Ref.: Michael R. Swain, University of Miami, Coral Cables, FL 33124, USA

11.5. Flammability & Explosion Limits

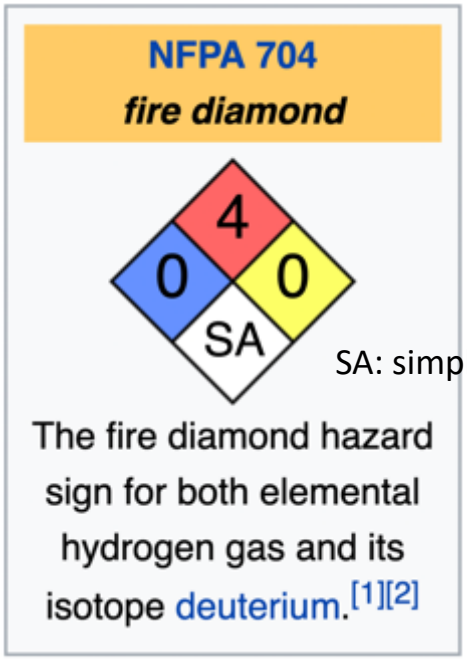




11.6. Properties of Fuels

Properties		Hydrogen (H_2)	Methane (CH_4)	Gasoline ($-CH_2-$)
lower heating value	[kWh $\cdot kg^{-1}$]	33.33	13.9	12.4
self ignition temperature	[° C]	585	540	228-501
flame temperature	[° C]	2045	1875	2200
ignition limits in air	[Vol%]	4 - 75	5.3 - 15	1.0 - 7.6
minimal ignition energy	[mWs]	0.02	0.29	0.24
flame propagation in air	[m $\cdot s^{-1}$]	2.65	0.4	0.4
detonation limits	[Vol%]	13 - 65	6.3 - 13.5	1.1 - 3.3
detonation velocity	[km $\cdot s^{-1}$]	1.48 - 2.15	1.39 - 1.64	1.4 - 1.7
explosion energy	[kg TNT $\cdot m^{-3}$]	2.02	7.03	44.22
diffusion coefficient in air	[$cm^2 \cdot s^{-1}$]	0.61	0.16	0.05

11.7. Hydrogen Codes and Standard



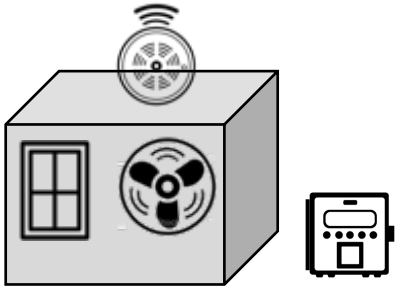
SA: simple asphyxiant gas

HySafe Initial Guidance for Using Hydrogen in Confined Spaces.
http://www.hysafe.org/download/1710/HYSAFE_D113_version_1.1.pdf

AIAA G-095-2004, Guide to Safety of Hydrogen and Hydrogen Systems" . AIAA.
https://arc.aiaa.org/doi/10.2514/4.105197.001

Gregory, Frederick D. (February 12, 1997). "Safety Standard for Hydrogen and Hydrogen Systems". NASA.
https://www.energy.gov/sites/prod/files/2014/03/f11/871916.pdf

11.8. Room & Materials



Experiments with hydrogen should only be carried out in well-ventilated rooms. Minimum security requirements are an open window and a hydrogen detector on the ceiling of the room.
U: https://h2tools.org/bestpractices/laboratory-design

The following material selection criteria should be observed for the construction of hydrogen reactors:
At room temperature: Most **elastomers** are inert to hydrogen. Hydrogen is not corrosive, so all common **non-reactive metals** can be used at low pressure. At high pressures, the hydrogen can embrittle metals, especially cold-formed ferritic steel. At high temperatures: To avoid embrittlement and carbon segregation at the grain boundaries, **austenitic stainless steel (AISI 316 or 304) and above 300°C (AISI 316L and 304L)** should be used. **Aluminum, silicon carbide and silicon nitride** are also suitable.

At low temperatures, materials that remain sufficiently ductile should be used. Austenitic stainless steel of the quality **AISI 304 and 304L as well as aluminum and aluminum alloys** meet this requirement. **Teflon® (PTFE, polytetrafluoroethylene) and Kel-F®** are also suitable.

11.9. Fire Hazard & Protection

The thermodynamic properties of hydrogen in the temperature range of 100K and 1000K and up to a pressure of 1 Mbar have been determined by Hemmes et al. published (H. Hemmes, A. Driessen, R. Griessen, Physica 139B, 140B (1986), pp. 116.)

The alkali and alkaline earth hydrides as well as the complex hydrides of the boron group are extremely reactive, moisture-sensitive substances that have a strong alkaline reaction (only $NaBH_4$ and KBH_4 are quite resistant to hydrolysis). When applied to the skin or inhaled as dust, they are extremely corrosive. The eyes and the mucous membranes of the respiratory organs are particularly at risk. Compared to this corrosive effect, the certain toxicity of lithium hardly plays a role in individual cases.

When handling the hydrides LiH, CaH_2 $NaBH_4$, $LiAlH_4$, protective goggles, a dust mask, hard hat with face mask, rubber gloves and, if necessary, special protective clothing should be worn. If hydride gets on the skin, rinse it off immediately with plenty of running water and wash it off with a little diluted acetic acid. If the eyes are affected, you should first rinse them thoroughly with water and then with 1.2% boric acid solution, then consult your doctor immediately.

11.10. Fire Extinguisher & Protective Atmosphere

The potentially greatest source of danger when handling hydrides is their **high content of hydrogen**.
In the case of **hydrolysis-sensitive hydrides**, this is released in a violent reaction by the ingress of water. This can suddenly create dangerously high pressure in the closed vessel.
In air, **oxyhydrogen gas** mixtures are formed which can lead to explosions. Some hydrides are as a powder **self-igniting** in moist air and represent a potential ignition source for explosive hydrogen (solvent vapor) air mixtures.
Safety measures: **strict exclusion of water** (use of inert heating and cooling media in the equipment), all operations carried out in a pure **inert gas (N_2, Ar) atmosphere**, explosion protection of all electrical installations, prevention of static charges, sufficient ventilation of the work area and equipment of the reaction vessel with safety valves, blow-off line and flame arrester.
Dry powder extinguishers (preferably based on NaCl), asbestos blankets and breathing apparatus must be available for fire fighting; dry powder showers as self-rescuers should be nearby.

Under no circumstances may **water, carbon dioxide or carbon tetrachloride** extinguishers be used for fire fighting.

11.11. Storage & Transport

The hydrides described can be stored indefinitely if air and moisture are excluded. As they are dangerous working materials, special safety regulations must be observed when they are stored and transported.

The alkali and alkaline earth hydrides as well as the complex boron and aluminum hydrides are goods of hazard class Ie / 2b, titanium and zirconium hydride goods of class II / 6e. When transporting hydrides, according to the transport regulations, the net content of the individual packs must not exceed the following sizes:
50 kg for NaH in oil, $NaBH_4$ and KBH_4;
40 kg for NaH powder;
10 kg for LiH, MgH_2, CaH_2, $LiBH_4$, $LiAlH_4$ and the substituted MBH_4 and $MAlH_4$.

Sending the hydrides by post is not permitted.

Ref.:

[1] R. Kühn, K. Birett, „Merkblätter Gefährlicher Arbeitsstoffe“, Verlag Moderne Industrie, Dummer & Co., München 1974
[2] G. Hommel, „Handbuch der gefährlichen Güter“, Springer, Berlin 1973/74.

11.12. Health hazard of Metal Dust

Metals and metal compounds (e.g. oxides depending on solubility) can be toxic and cancerogenic. Working concentration limits are listed for which no health risks are expected for 8h daily working time over the whole life. The technical target concentration for Beryllium, Cadmium Chrome, Cobalt, Nickel, Platinum, Tungsten, Tin was replaced in 2005 by acceptance (4:10'000, low risk) or tolerance (4:1'000, high risk) concentration (add cancer:worker after 40 years e.g. smoking 108:1'000).

Metal	composition	health hazard	dust <10 µm	dust <100 µm
Nickel	metal	cancerogenic (lung)	6 $\mu g \cdot m^{-3}$	30 µg·m-3
	-oxide	cancerogenic (skin, lung)	6 $\mu g \cdot m^{-3}$	
Cobalt	metal	cancerogenic (lung)	5 $\mu g \cdot m^{-3}$	
	-oxide	cancerogenic (skin, lung)	0.5 $\mu g \cdot m^{-3}$	

Ref.: [1] Carsten Schleh, Berufsgenossenschaft Holz und Metall, Presentation: https://www.vdri.de/fileadmin/uploads/seminardaten/2018_02_09_Nürnberg_Fachinformation.pdf

11.13.a) Thermite on Ice Film

11.13.b) Thermite on Ice Sequence