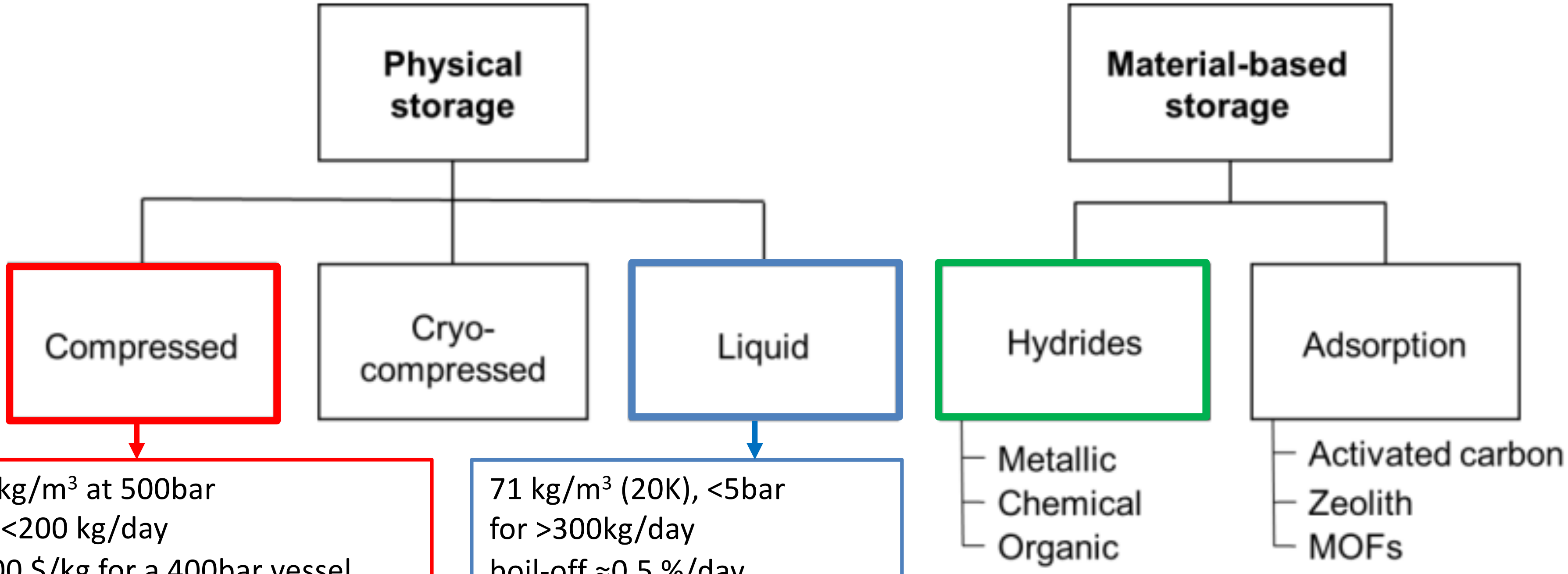
H_2 storage methods

- as compressed H_2 gas (=> 1000bar)
- as liquid H_2 (1bar)
  - optional: further cryocompression of liq H_2
- as physically adsorbed H_2-layer on high surface area materials
  - sorption increases at low T
- as H in hydrides
  - solid solution ---- > hydride H (interstitial H up to intermetallic compound)
  - complex hydrides (e.g. $NaBH_4$)
- as H in other chemical compound
  - LHOC (liquid hydrogen organic carrier)
  - NH_3 etc.

H_2 storage overview

(figure: Leonardo Gant)



33 kg/m^3 at 500bar
for <200 kg/day
1000 $/kg for a 400bar vessel
energy cost = 5-15% of LHV
40ft container: 1 t H_2, cost 0.9 M$

mature

71 kg/m^3 (20K), <5bar
for >300kg/day
boil-off ≈0.5 %/day
energy cost = 30% of LHV
LH_2 costs 10% more than CH_2

mature

6-8wt%
LOHC : 9 kg/m^3 at 1bar
Hydrides : 40 kg/m^3

under dvpmt

H_2 vs. hydrocarbons: properties

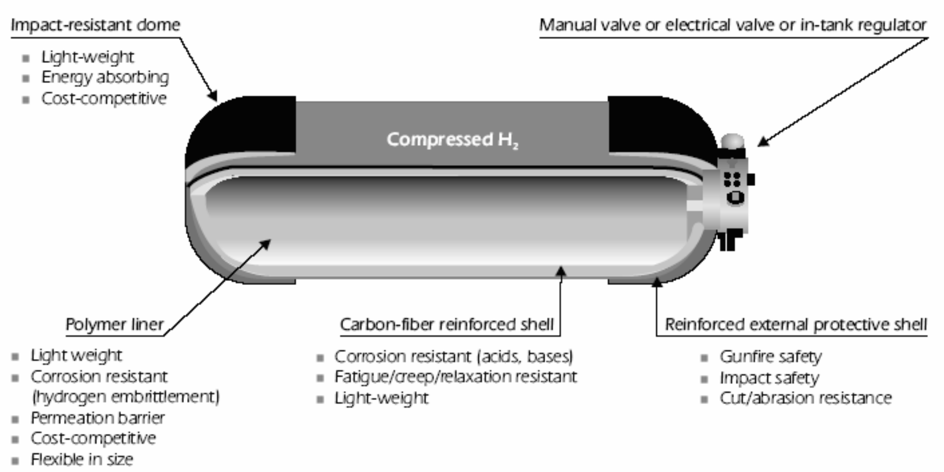
lowest **volumetric** density

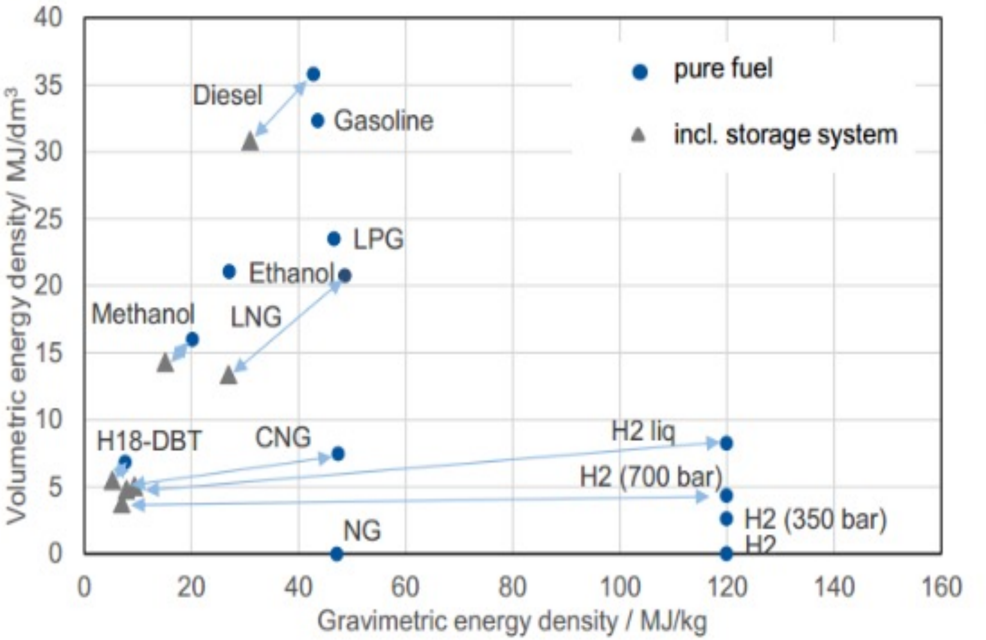
	H_2	Natural gas (CH_4)	Gasoline
Boiling point	-252.7 °C	-160°C	40-200°C
Melting point	-259 °C	-182°C	-40°C
Gas density	**0.089 kg/m³**	0.707 kg /m³	4 kg /m³
Liquid density	0.071 kg/L	0.41-0.5 kg/L	0.72-0.78 kg/L
Lower HV	120.2 MJ/kg 8.6 MJ/L as liquid	47 MJ/kg 21 MJ/L as liquid	42 MJ/kg
Higher HV	**142 MJ/kg** 12.7 MJ/m³ 10.1 MJ/L as liquid	53 MJ/kg, 40 MJ/m³ 24 MJ/L as liquid	46 MJ/kg 36 MJ/L
Autoignition	585°C	632°C	220°C
Flammability in air	4-75%	5-15%	1-7.6%
Flame temperature	2045°C	1875°C	2200°C

highest **gravimetric** density

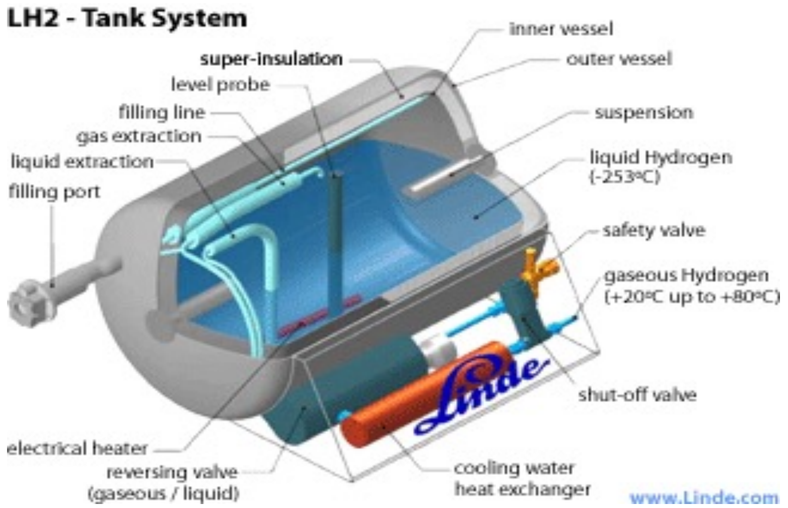
H_2 storage : compressed gas, and liquid

1. CH_2
2. LH_2
3. Pipelines
4. Other methods





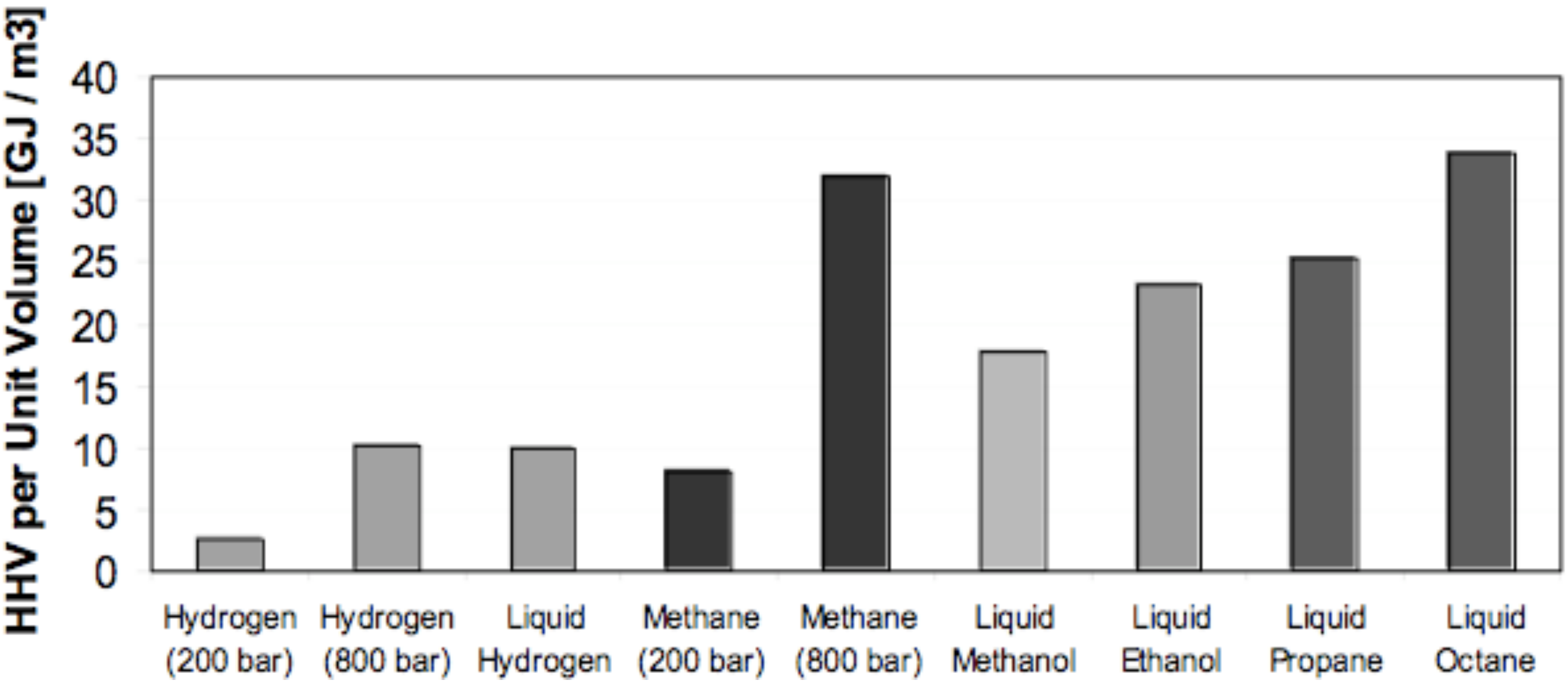
loss 0.1 – 3% / day



fuel density (kg^{-1}) alone is high;
not when adding storage medium weigth

(figures: Leonardo Gant)

HHV by volume



U. Bossel, H_2-economy

Review of hydrogen compression technologies

G. Sdanghi, G. Maranzana, A. Celzard, V. Fierro, "Review of the current technologies and performances of hydrogen compression for stationary and automotive applications", Renewable and Sustainable Energy Reviews 102 (2019), pp. 150 – 170

@1 atm

highest gravimetric density:	140	MJ/**kg**	(496.0 moles)
lowest volumetric density:	0.011	MJ/**L**	(1/22.4th of a mole = 0.0446 mole)

H_2 compression technologies overview

- Mechanical: **volume flow** for H_2 is confined by a displacement device
  1. reciprocating piston
  2. diaphragm
  3. linear (magnetic)
  4. ionic liquid
- Non-mechanical : specifically designed for H_2 application
  1. cryogenic
  2. electrochemical (**mass flow**)
  3. adsorption (thermal)
  4. metal-hydride (thermal)

In terms of H_2-economy (‘pack, distribute, store, deliver’), the cheapest solution today is:
H_2-gas compression + truck-delivery (for small stations); in carbon-/glass fiber storage tanks to reduce weight:
best values 1-2wt% @250 bar (steel), to 6wt% @700 bar (composite), and 30g H_2/L
(still below the US-DOE targets of 40 g/L and 5.5wt%)

Mechanical compression

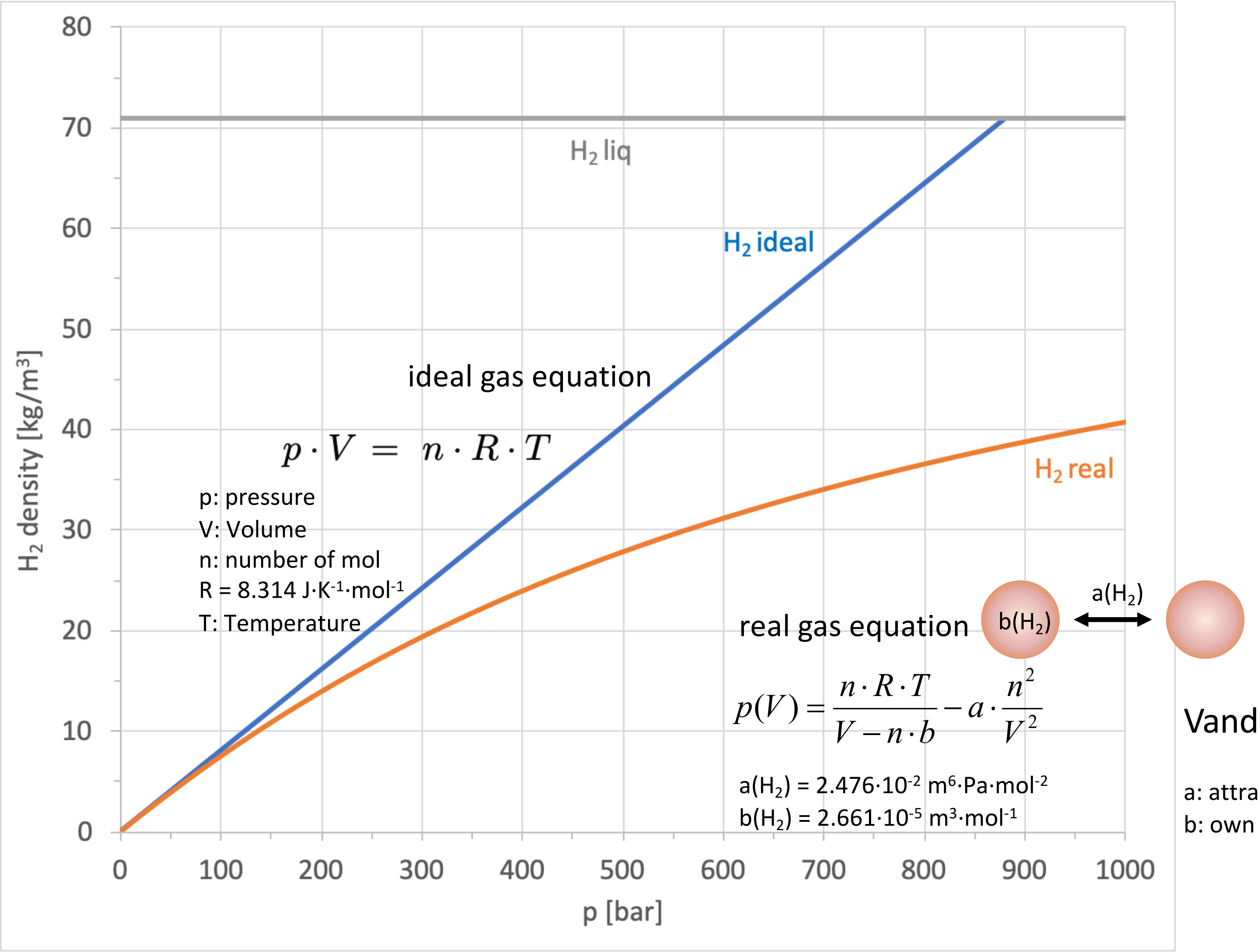
1. Reciprocating
2. Diaphragm
3. Linear
4. Ionic liquid

Due to low volumetric density of H_2, mechanical compression efficiency is intrinsically low. Up to 1/3 of the stored gas energy is used in compression work.

Pressurized H_2

1 bar = 2 g / 22.4 L = 90 g /m^3
ideal gas: 1000 bar = 90 kg/m^3

(water : 1000kg/m^3 !)



ideal gas equation

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

p: pressure
V: Volume
n: number of mol
R = 8.314 J·K^{-1}·mol^{-1}
T: Temperature

real gas equation

$$p(V) = \frac{n \cdot R \cdot T}{V - n \cdot b} - a \cdot \frac{n^2}{V^2}$$

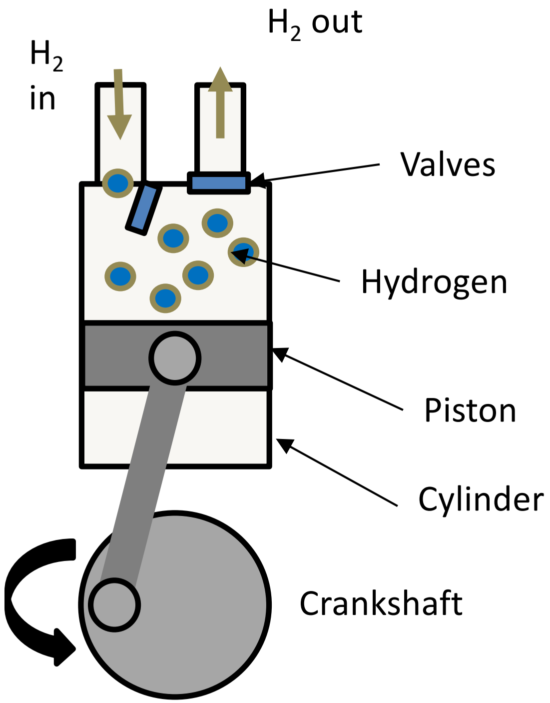
a(H$_2$) = 2.476·10^{-2} m^6·Pa·mol^{-2}
b(H$_2$) = 2.661·10^{-5} m^3·mol^{-1}

VanderWaals gas

a: attraction term btw molecules
b: own volume of the molecules

slide from Prof A Züttel, EPFL

1. Reciprocating piston compression



- Periodically compresses and expands the hydrogen through mechanical moving parts
- The work is generated by a thermal or electrical motor

slide from T Macherel, EPFL

Reciprocating piston

Advantages

- Mature
- Good for >30 bar; up to 1000 bar
- Good for multi-stage compression, on-site HRS where H_2 is generated at 6 bar
- Good for moderate flow. Large range of capacities (up to several thousands of Nm^3/h, as high as 890 kg/h at 250 bar, 11 MW, and 430 kg/h at 850 bar, 300 Nm^3/h at 1000 bar)

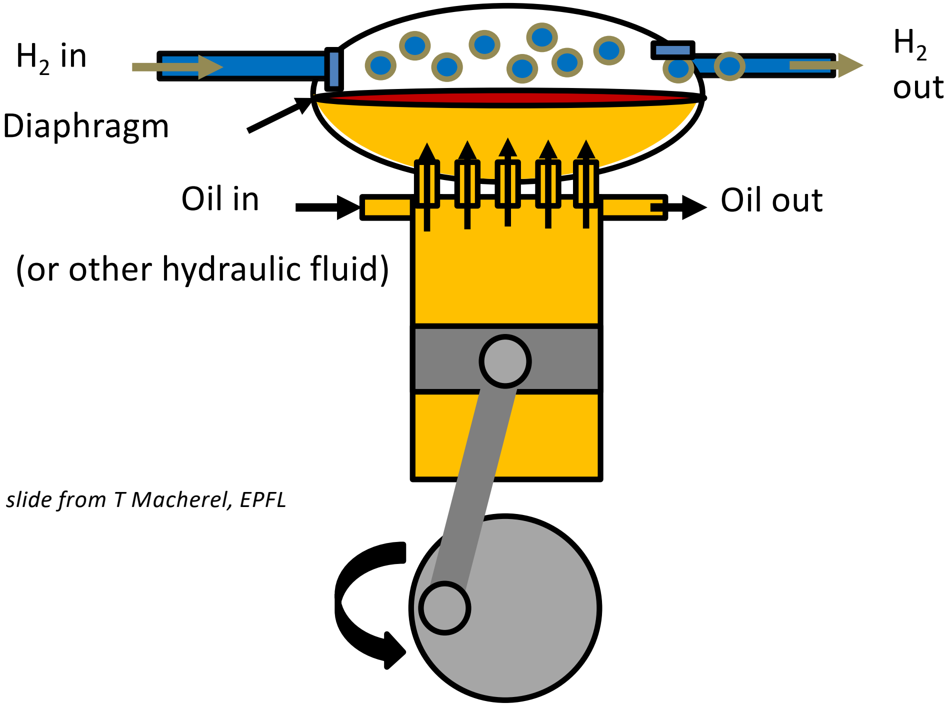
Limitations

- Not good for highest flow rates: limited by cylinder dimensions and cycle speed.
- Embrittlement of materials (must be selected): (cast) iron or steel with liner coating for wall protection and servicing
- pressure fluctuations
- Multiple moving mechanical parts → noise, vibration and maintenance (cost)
- Risk of hydrogen leakage (use of piston rings) and (lubricating oil) contamination
- difficult heat management (piston cooling not efficient) =>limited efficiency

Applications

- Catalytic reformers
– H_2 plants
– Compressed gas storage
– HRS
– FCEV tanks
– Moving gas between vessels

2. Diaphragm compressor



H_2 in

Diaphragm

Oil in

(or other hydraulic fluid)

H_2 out

Oil out

slide from T Macherel, EPFL

Picture by Olivier Thomann

Diaphragm compressor

Advantages

- Mature
- High throughput, low power consumption, low cooling requirement (easier to cool the oil circuit)
- Up to 950 bar
- Good range of capacities (up to several 100 Nm^3/h; 400-600 Nm^3/h at 280bar; 50-280 Nm^3/h at 510bar). High volumetric efficiency.
- Low risk of hydrogen leakage and contamination. High purity H_2 since piston and H_2 are isolated.

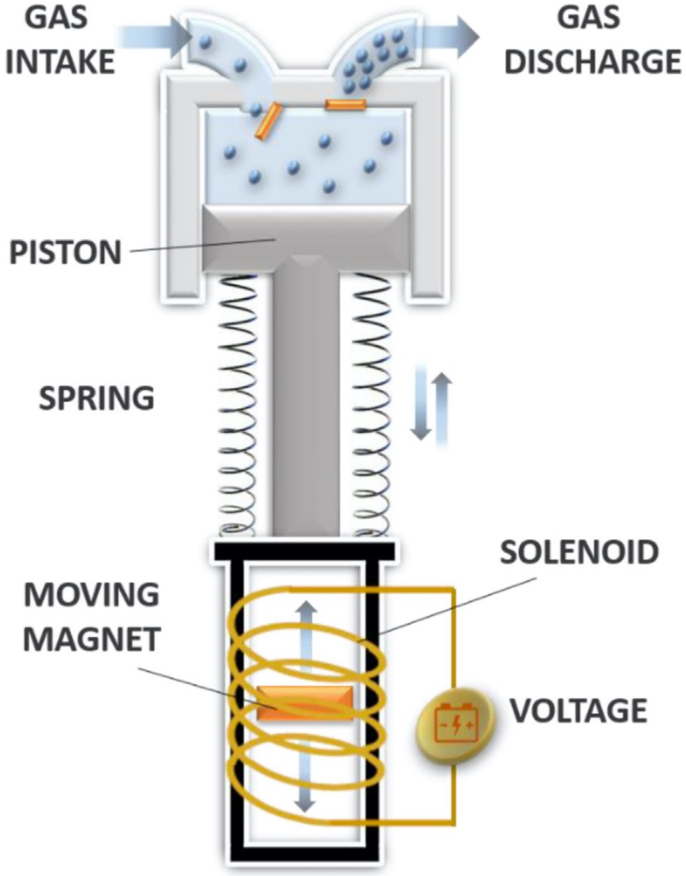
(High purity is crucial since H_2 leakage affecting the mechanical compressors are the primary risk in HRS.)

Limitations

- Intermittent compression (fluctuating)
- Moving mechanical parts→ noise, vibration and maintenance
- Rather for lower flows. For microscale: electrostatic principle (diaphragm is moved by piezo)
- Fragility of the diaphragm which is the key component (mechanical stress, corrosion resistance, CrNi-steel, Cu-Be-alloys) → maintenance

Applications
- HRS
- FCEV filling

3. Linear compressor



- Piston connected to **linear motor** with spring, absence of rod-crank system (less moving parts => cost saving)
- used in cryogenic applications (Stirling), and cooling of electronics
- Linear motor: usually magnetic (moving coil or moving magnet)
- High efficiency (73%), low vibration, low noise, long life, very reliable
- Piston and cilinder separated by gas bearing: high purity (no oil), no friction, silent
- Challenge is positioning control of the piston (effects of V, T)

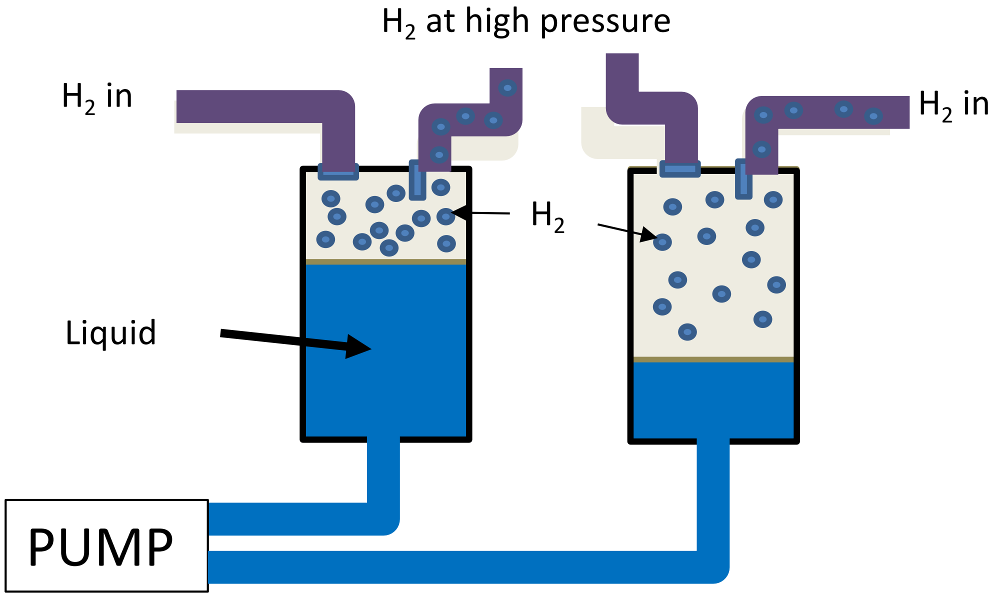
Fig. from G. Sdanghi, G. Maranzana, A. Celzard, V. Fierro, "Review of the current technologies and performances of hydrogen T compression for stationary and automotive applications", Renewable and Sustainable Energy Reviews 102 (2019), pp. 150 – 170

4. Liquid compressors

- Use of liquids to directly compress gas without mechanical sliding seals: quasi-isothermal => high efficiency (83%)

- Liquid column piston driven by a pump. Used for compressed air storage @200-300 bar.
- Liquid rotary compressors. For saturated gases (with high liquid content). Low efficiency (50%).
- **Ionic liquid** (low melting point salts). Specifically developed for H_2.

Ionic liquid compressor



slide from T Macherel, EPFL

- The ‘piston’ is an ionic liquid instead of a solid part
- The liquid is connected to a pump that periodically compresses the gas in a cylinder while emptying the other
- Liquid : high thermal and chemical stability, very low volatility, very good lubricating behaviour (oil-free), very low solubility of most gases, good coolant => high compression ratio and high volumetric efficiency
- Efficiency 65-83%

Ionic liquid compressor

Advantages

- Up to 1000 bar. 8-30 kg/h at 450-900 bar, 100-700 Nm^3/h
- good heat management
- less mechanical moving parts
- low energy consumption, long service life, low material costs, low noise

Limitations

- only one company (Linde, D)
- available only for high capacities (more than 300 Nm^3/h)
- corrosion of components due to the ionic liquid => maintenance cost (316L steel is well suited)
- leakage of the ionic liquid

Application

- HRS

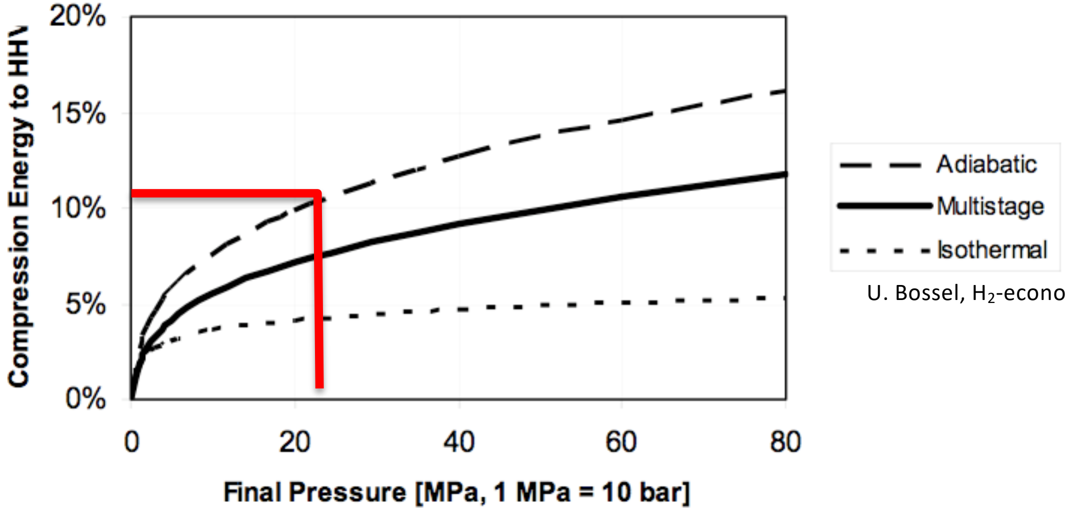
Compression work

- ideal isothermal work_{id} (J/kg) = $p_0 V_0 \ln(p_1/p_0)$
- adiabatic $\text{work}_{ad} = (\gamma/\gamma-1)\, p_0 V_0 \left((p_1/p_0)^{(\gamma-1)/\gamma}-1\right)$

  V_o initial volume(m^3/kg) (11.11 m^3/kg for H_2, 1.39 m^3/kg for CH_4)

  p_0 initial pressure, p_1 final pressure, $\gamma = C_p/C_v$ (1.41 for H_2, 1.31 for CH_4)

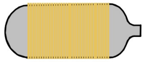
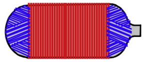
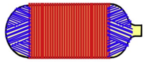
- @200 bar (W_{ad}): for CH_4 2 MJ/kg, for H_2 **14 MJ/kg** (10% HHV)



U. Bossel, H_2-economy

Compressed storage tanks

CRFP: carbon-fiber reinforced polymer

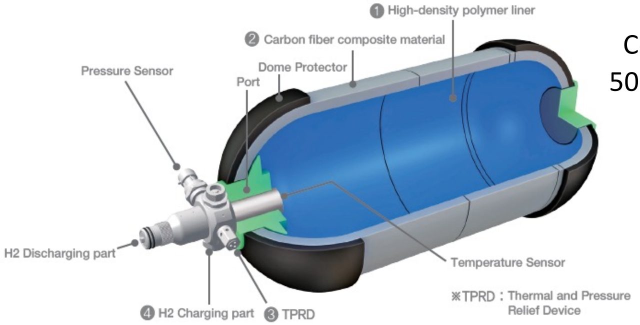
	V1	V2	V3	V4
composition	 **All Metal**	 **Metal Liner** **+** **GFRP layer** **(hoop lap)**	 **Metal Liner** **+** **CFRP layer** **(full lap)**	 **Plastic Liner** **+** **CFRP layer** **(full lap)**

Aluminum
10 bar, 1L

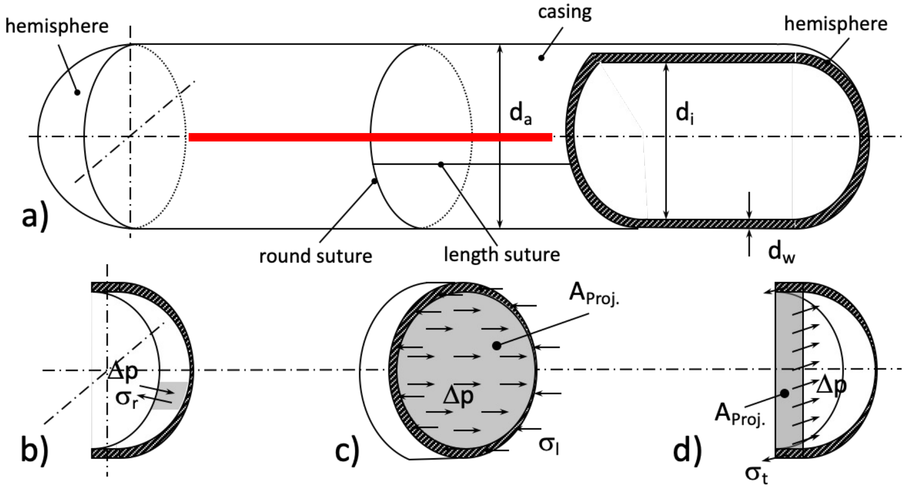
Steel
30 bar

0.9kg H_2

Steel, Type 1
200 bar, 50L, 70kg



Composite, Type 4
500 bar, 300L, 270kg



Tensile breaking strength σ_v
(which affects storage tank material choice):

$$\sigma_v = \sigma_{\max} - \sigma_{\min}$$

$\Rightarrow$ storage tank minimal wall thickness d_w :
(which will affect its weight)

$$d_w = \frac{\Delta p \cdot d_i}{2 \cdot \sigma_v + \Delta p}$$

$$d_w = \frac{\Delta p \cdot d_a}{2 \cdot \sigma_v \cdot f_1 + \Delta p} + f_2$$

Wilhelm Matek, Dieter Muhs, Herbert Wittel and Manfred Becker, “Roloff/Matek Maschinenelemente”, Viewegs Fachbücher der Technik (1994), 690 pages, ISBN: 3-528-74028-0

slide from Prof A Züttel, EPFL

Joule-Thomson effect /coefficient

isenthalpic expansion/compression:

$$\boxed{\mu_{J-T} = \left(\frac{dT}{dP}\right)_{\boldsymbol{H}} = -\frac{(\alpha T - 1)V}{C_P}}$$

α : expansion coefficient at const. P

C_P : heat capacity at const. P

$\boxed{\mu_{J-T} > 0}$

positive J-T-coefficient

@ low P:
the gas cools upon expansion

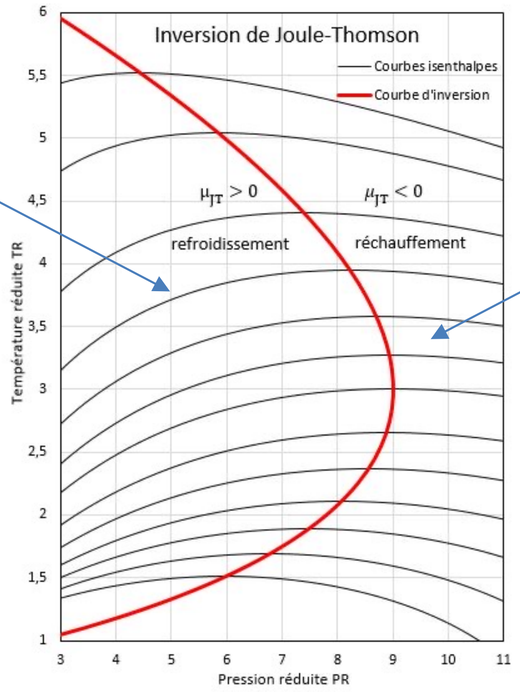
μ_{J-T} = 0 for an ideal gas
no T-change during J-T-expansion

$\boxed{\mu_{J-T} < 0}$

negative J-T-coefficient

@ high P:
the gas heats upon expansion

(expansion accelerates the molecules,
$h_{total} = h_{static} + c^2/2$,
friction heating dominates the expansion cooling)



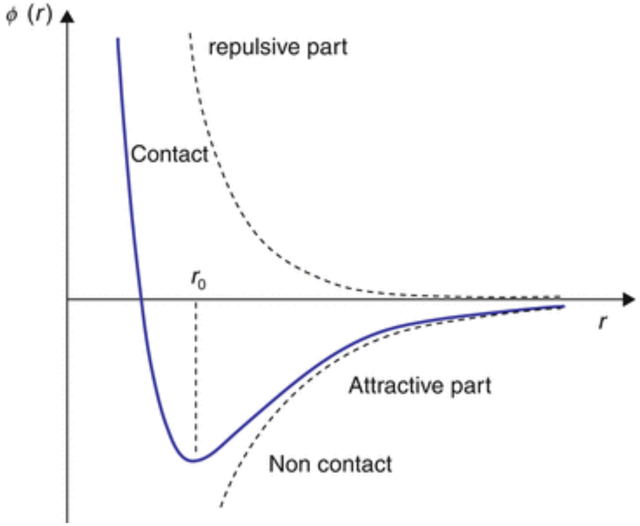
The gas can therefore be cooled (and eventually liquified), only

- by expansion if $\mu_{J-T} > 0$
- by compression if $\mu_{J-T} < 0$

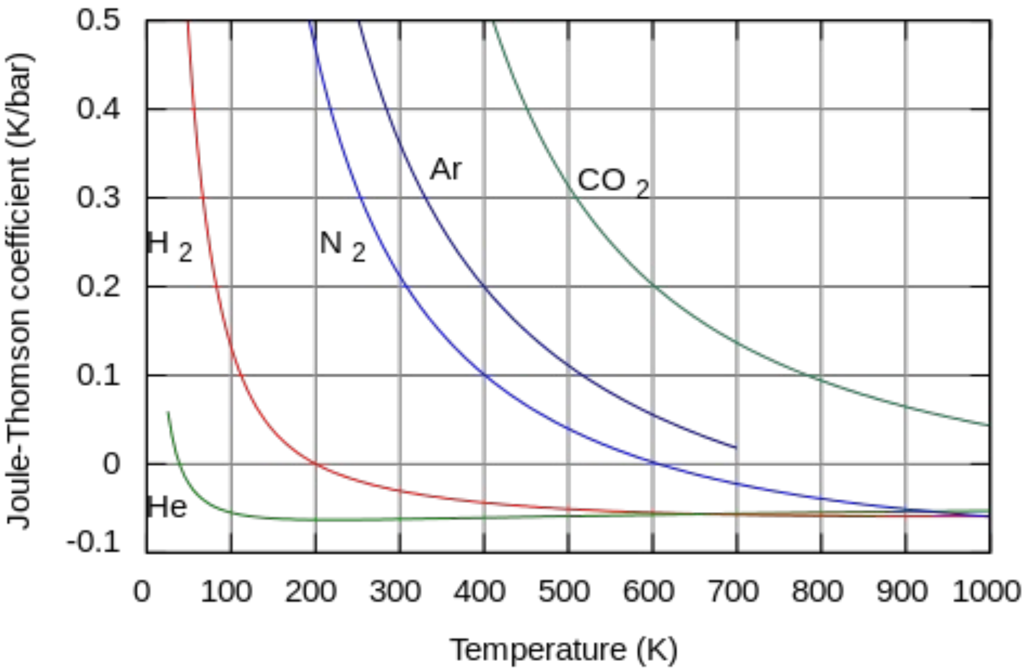
=> for H_2-filling, cooling is needed !

Joule-Thomson Effect

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial p}\right)_H$$



Van der Waals



$$\mu_{\mathrm{JT}} = \frac{1}{C_p} \cdot \left(\frac{2a}{RT} - b\right) \qquad T_{\mathrm{inv}} = \frac{2a}{Rb}$$

$a(H_2) = 2.476 \cdot 10^{-2}$ $m^6 \cdot Pa \cdot mol^{-2}$
$b(H_2) = 2.661 \cdot 10^{-5}$ $m^3 \cdot mol^{-1}$
$R = 8.314$ $J \cdot K^{-1} \cdot mol^{-1}$

$\Rightarrow T_{\mathrm{inv}} = 200K$

At ambient T, H_2 must be cooled for filling (expansion), and heated when compressing.
At cryo-conditions (e.g. 77K and lower), it is the opposite.

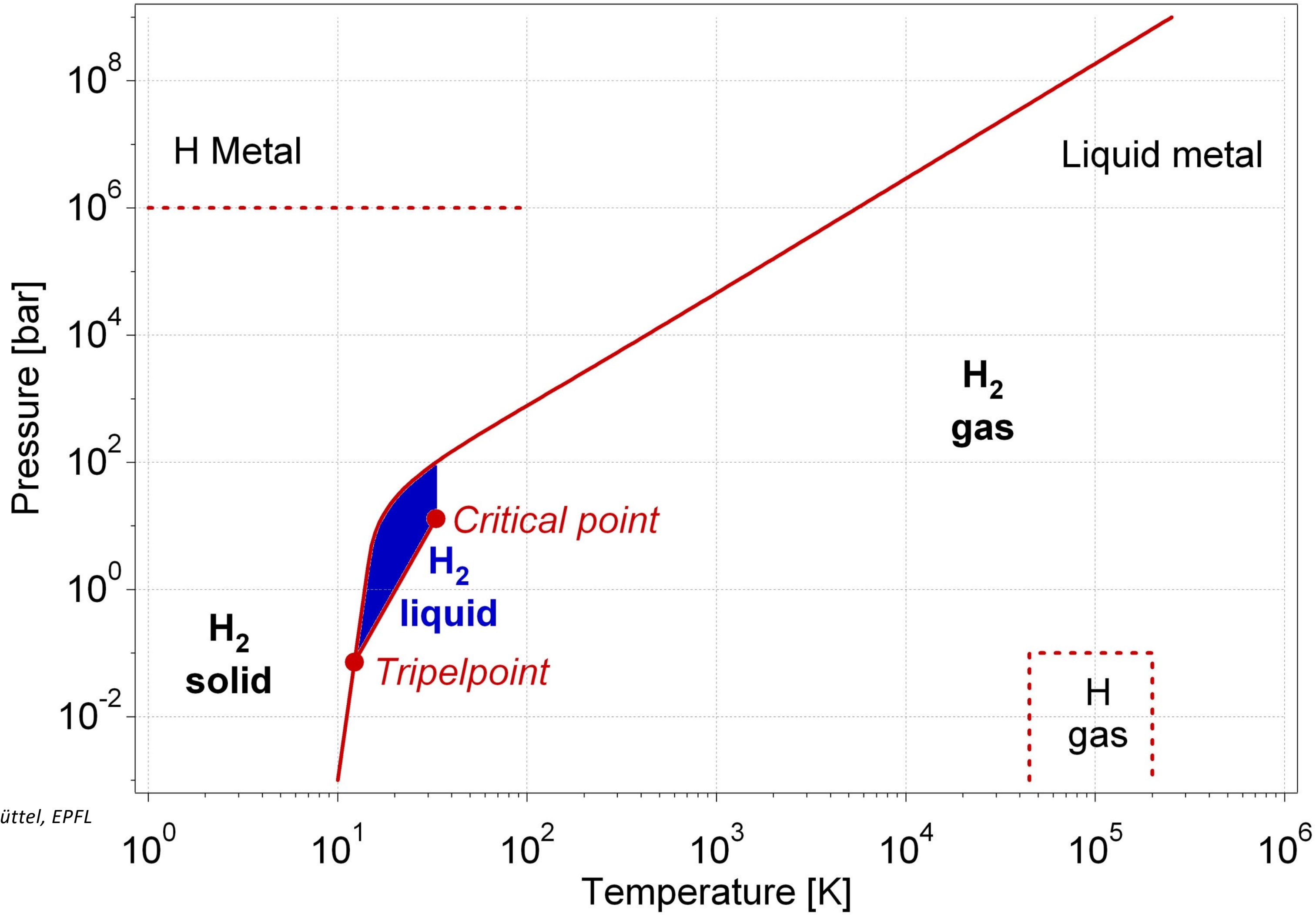
slide from Prof A Züttel, EPFL

Non-mechanical compressors

- Cryogenic compression of liquefied H_2
- Electrochemical compression
- Thermally driven:
  - Adsorption of H_2 on high surface materials
  - Metal-hydride

Liquid Hydrogen

Primitive Phase diagram



slide from Prof A Züttel, EPFL

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

Liquefaction work

As Carnot cycle with a heat sink at 300 K, the ideal work of liquefaction is W_L = 13 MJ kg^{-1} (3.6 kWh kg^{-1}) for LH_2

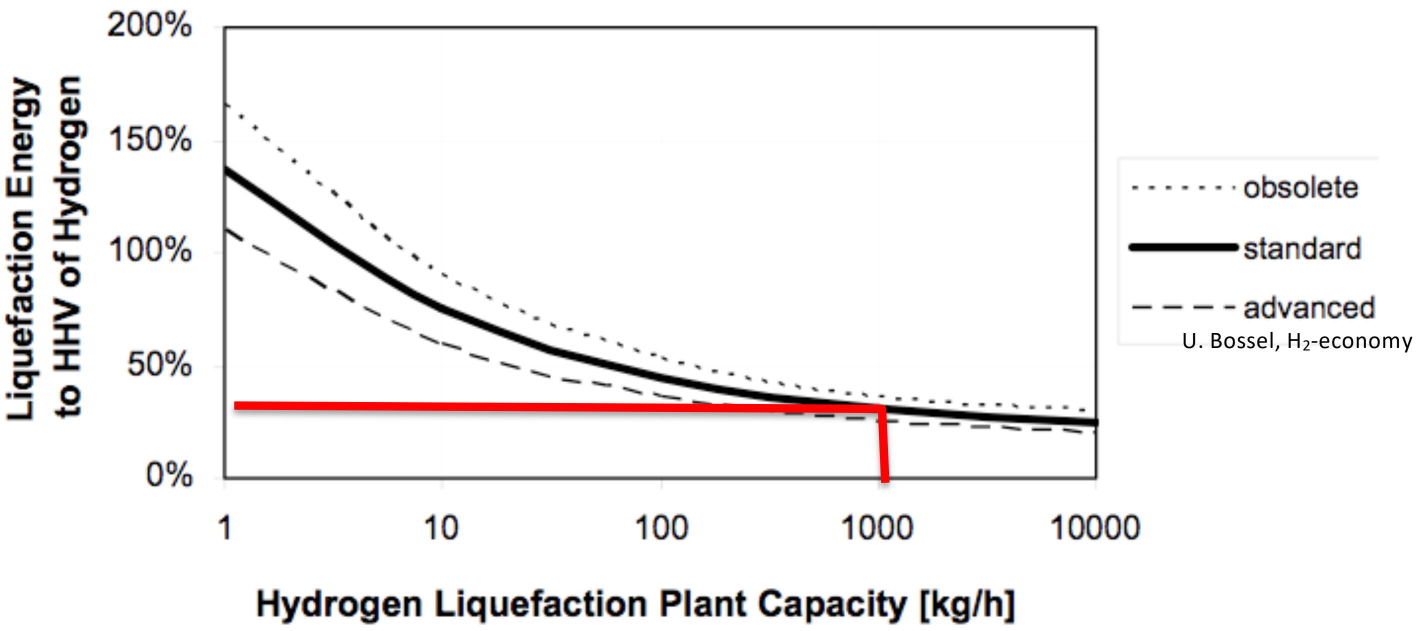
300K

$$W_{\mathrm{L}} = \Delta H \frac{(T_{\mathrm{a}} - T_{\mathrm{e}})}{T_{\mathrm{e}}}$$

225 kJ/kg
+703 kJ/kg

20K

298 K → 20 K	MJ need per kg liquid H_2	Reference
theoretical requirement	13 (10% of HHV)	Carnot
usual scale	54	182 kg / h, Linde plant (D)
large scale	36	2000 kg / h, USA
ultimate scale	30-25	12000 kg/h, study case

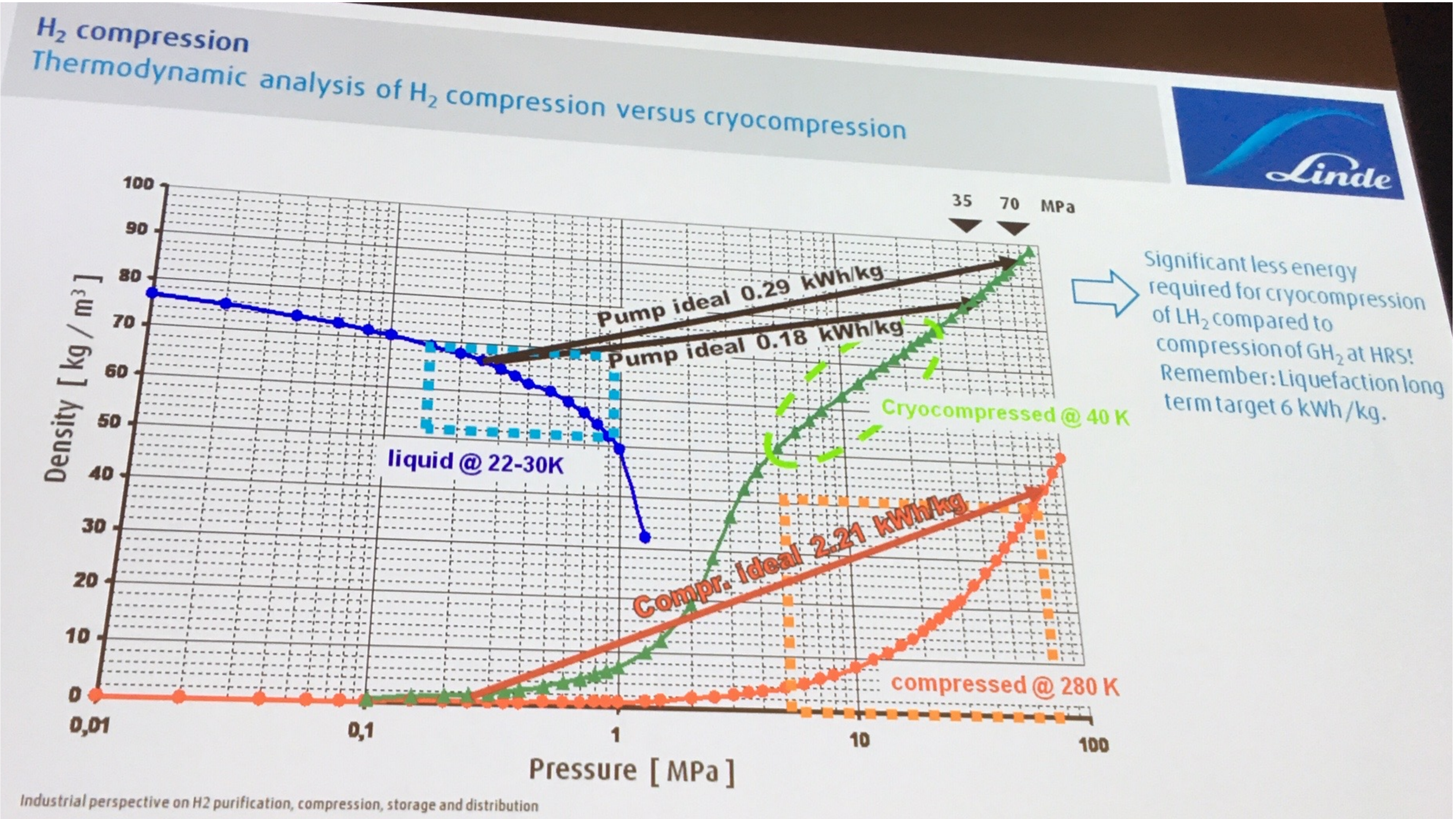


U. Bossel, H_2-economy

Cryogenic compression

- Combines liquefaction and then compression (of liq H_2) with the benefits and challenges of both high P at low T
- Interest: higher volumetric energy density of H_2 at low T => less compression work needed (only 1% of LHV). Twice the volumetric efficiency of mechanical compressors.
- But low T is a challenge (thermal insulation, vacuum stability). Only 30% (LHV) of the energy is stored due to the prior liquefaction energy requirement (=10-13 kWh/kg).
- 850 bar, 100 kg/h, 80g/L, 1000 Nm^3/h
- Vessel: outer steel tank, inner carbon-coated metal tank, intermediate vacuum space filled with metallized plastic. (Al-alloy vessel can reach 9 wt% H_2 stored)
- Compared to liq. H_2 stored at 1 bar, cryo-compressed liq. H_2 has lower evaporation loss and less head space, allowing more fuel storage (2-3x). E.g. 100L tank 750 bar has 4 kg H_2 @RT = only 150 bar at 77K.
- Toyota Prius. BMW.

Cryocompression (Linde AG)



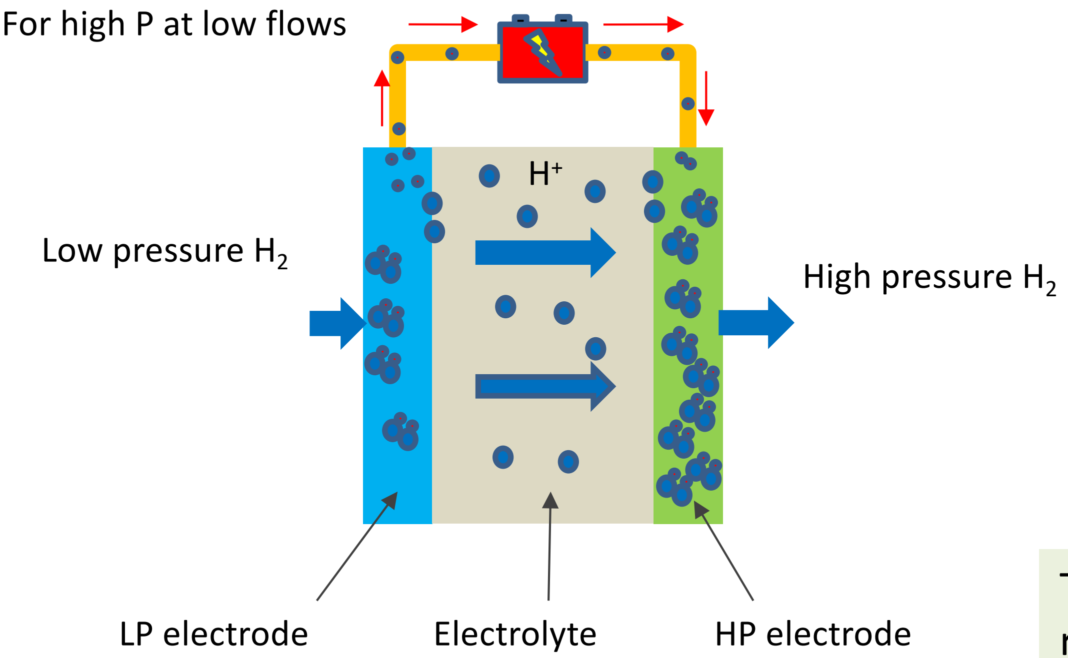
H_2 compression

Thermodynamic analysis of H_2 compression versus cryocompression

Significant less energy required for cryocompression of LH_2 compared to compression of GH_2 at HRS!
Remember: Liquefaction long term target 6 kWh/kg.

Industrial perspective on H2 purification, compression, storage and distribution

Electrochemical 'pump'



At LP electrode:

$$H_2(LP) \rightarrow H^+ + 2e^-$$

At HP electrode:

$$H^+ + 2e^- \rightarrow H_2(HP)$$

Minimum voltage:

$$E_{rev} = \underbrace{\frac{RT}{zF}}_{13\text{mV}} \ln\left(\frac{P_{HP}}{P_{LP}}\right)$$

Theoretically only 84 mV needed to raise from 1 to 700 bar. (ln(700)=6.55)
However, ohmic drop and overpotentials increase the voltage.
Achieved: 140mV for 50 bar @0.2A/cm^2
=> 0.3 kWh/Nm^3 v. low consumption

slide from T Macherel, EPFL

Electrochemical pump

Advantages

- up to 1300 bar (usually 200-350 bar), with multi-stack
- acts as a purification device
- continuous compression, vibration-free
- High efficiency (up to 90% at 1A/cm^2 and low applied voltage, but down to 60% due to overvoltages). Practically isothermal! E.g. 2 kWh/kg H_2 for EC-compression vs 7 kWh/kg H_2 for mech. compression

Limitations

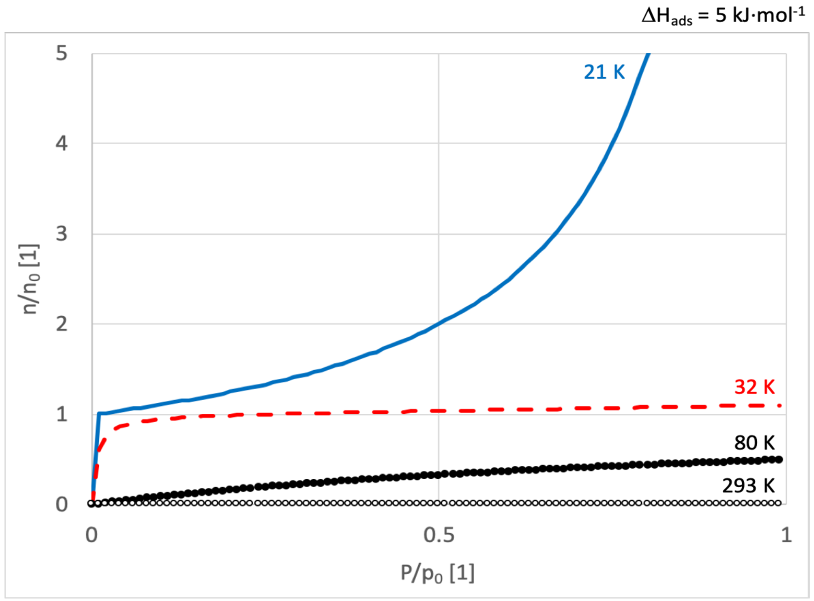
- Limited capacity (usually few Nm^3/h)
- Back diffusion of H_2 through membrane at high pressure ratio: highest single stage 170 bar, multi-stack up to 850 bar

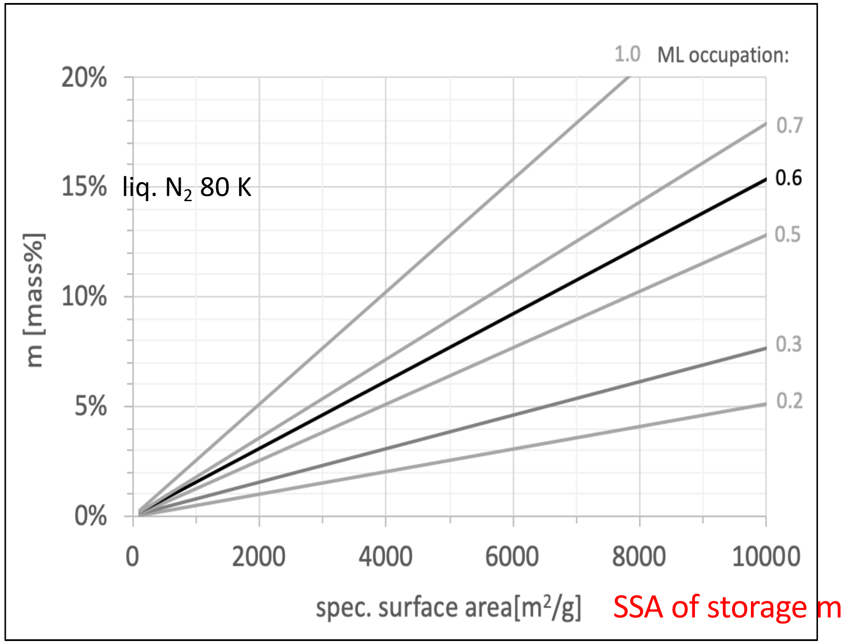
Adsorption compressors

- Cf. absorption heat pump principle
- Tank filled with **very high surface area material** that can reversibly physisorb H_2 at low T (Van der Waals monolayer, 0.01-0.1eV, surface process). Then the tank is closed and heated to desorb H_2 that fills the available tank gas volume => raise in P.
- thermally-driven like metal-hydride (MH) compressor, whereas MH is a volume process involving chemical bonding
- **Sorbent materials**: activated C (AC), MOFs, C-nanotubes, zeolites (much lower weight than MH!)
- Adsorption is exothermal and thus enhanced at low T (77K rather than 300K, where thermal motion energy 0.025 eV is of the same order as the Van der Waals forces).
- MOF 6000 m^2/g achieves 10 wt% H_2 at 77 K and 56 bar
- AC 2600m^2/g reached 6.4 wt% at 77K and 40 bar (theor limit is 6.8 wt%). At RT, the storage is only 1.6 wt% (700 bar).

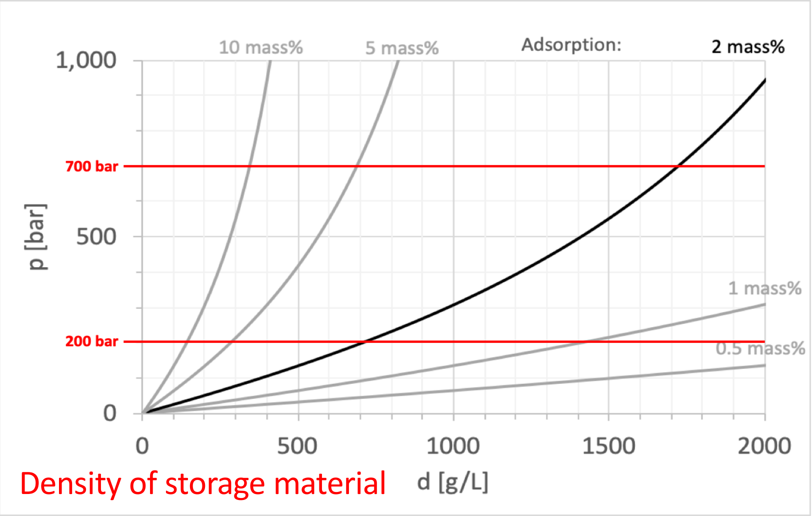
Hydrogen Physisorption

The lower the temperature, the more H_2 can be adsorbed

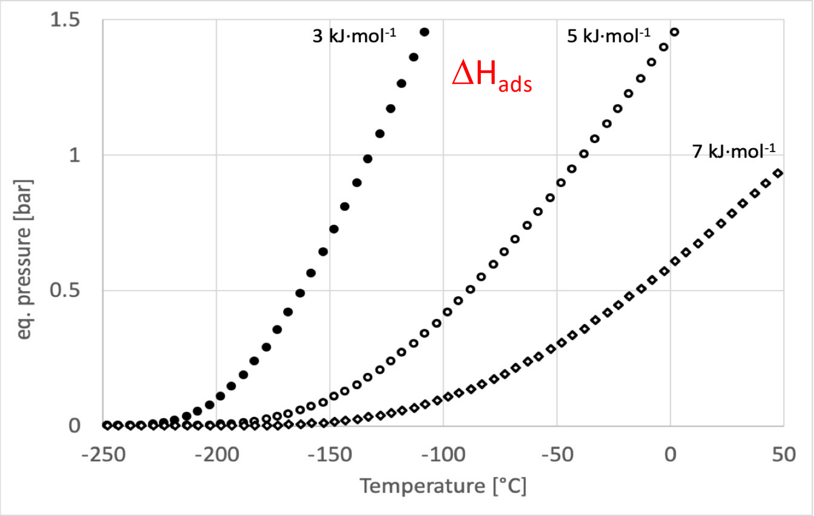




SSA of storage material



Density of storage material



ΔH_{ads}

slide from Prof A Züttel, EPFL

Adsorption compression

Advantages

- Low pressures to store a given amount of H_2 (safety)
- Low weight

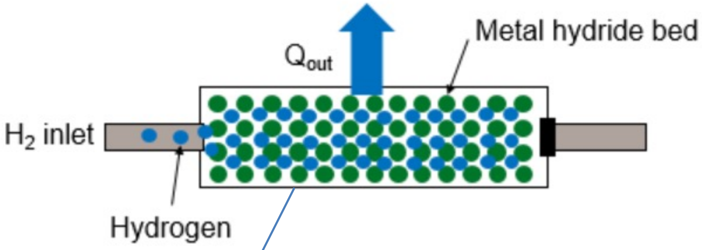
Limitations

- Complicated thermal management (heating/cooling at low T). Thermal gradients in beds (low material conductivity) => low efficiency (like MH)
- Limited capacity (<100 Nm^3/h), 100-350 bar

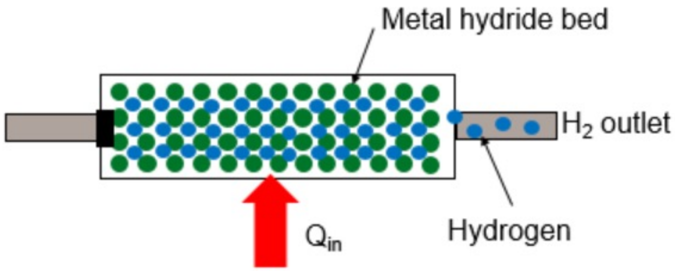
Metal hydride compression

$$M_{(s)} + \frac{x}{2} H_{2(g)} \underset{des}{\overset{abs}{\leftrightarrow}} MH_x + Q$$

Hydride heats up during absorption
=> needs heat removal



Steel tank.
Tubular for easy heat/mass transfer



Heat supply increases the storage pressure

slide from T Macherel, EPFL

Hydride Materials

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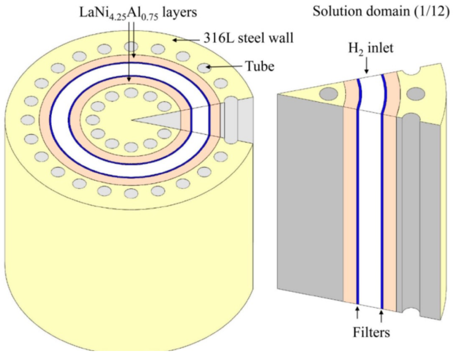
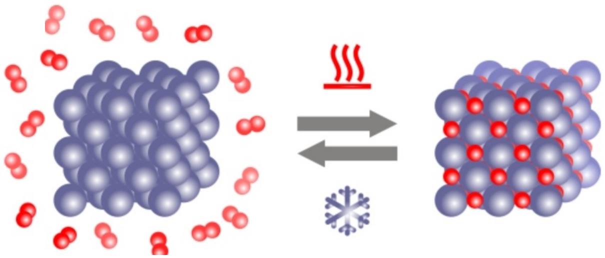
Mg alloy as flakes for H₂ storage





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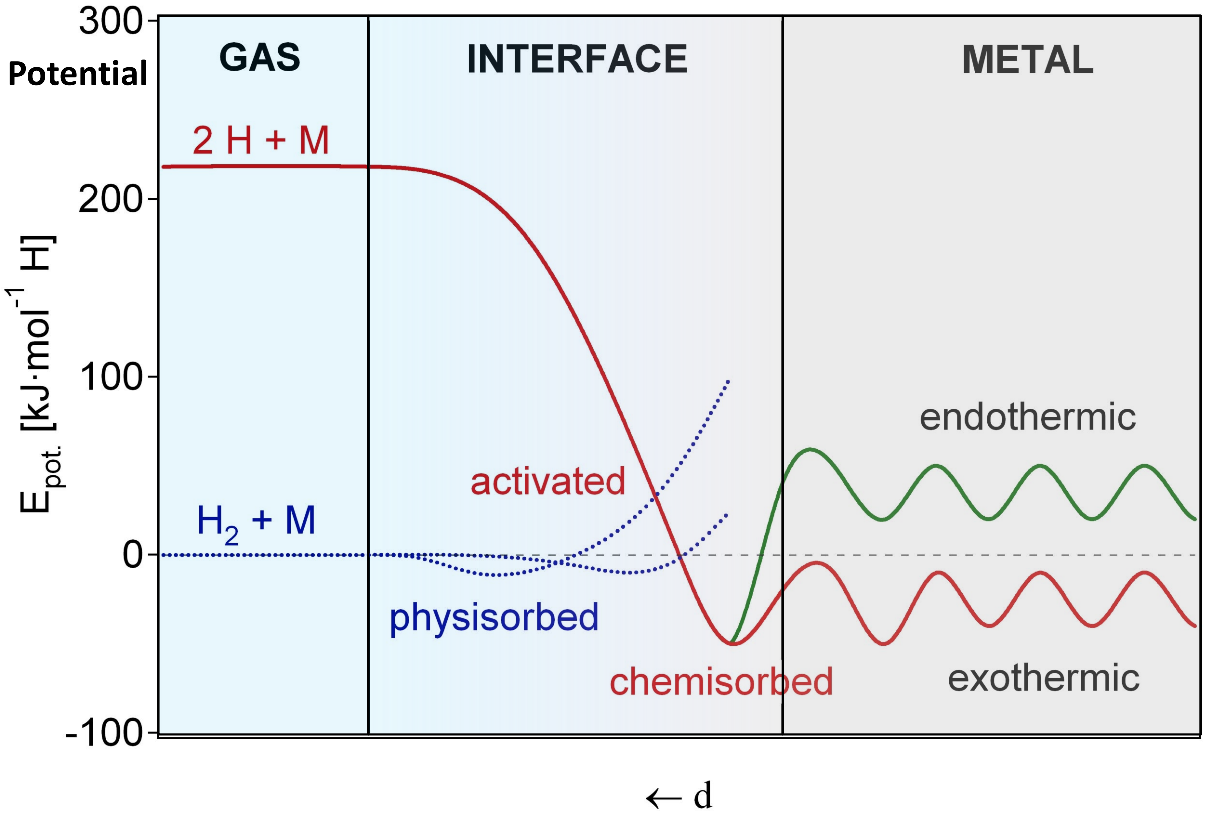
Hydrogenation-Dehydrogenation (schematic)

Metal Hydrides (MH)

Lennard-Jones Potential



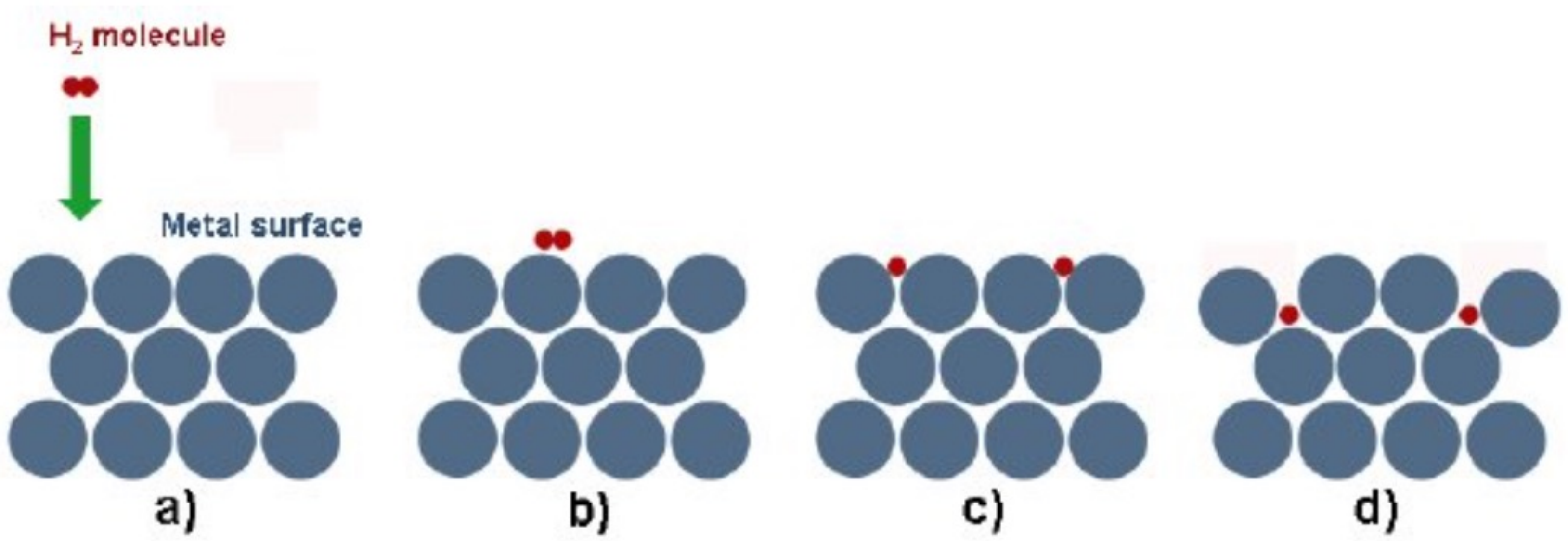
Chemisorption: **volume process**, chemical reaction btw H_2 and 'sorbent'. Usually heavier materials, hence lower H_2 wt% storage

Physisorption: **surface process** ⇒ high SSA needed. With low density sorbent materials like carbon, higher H_2 wt% can be achieved

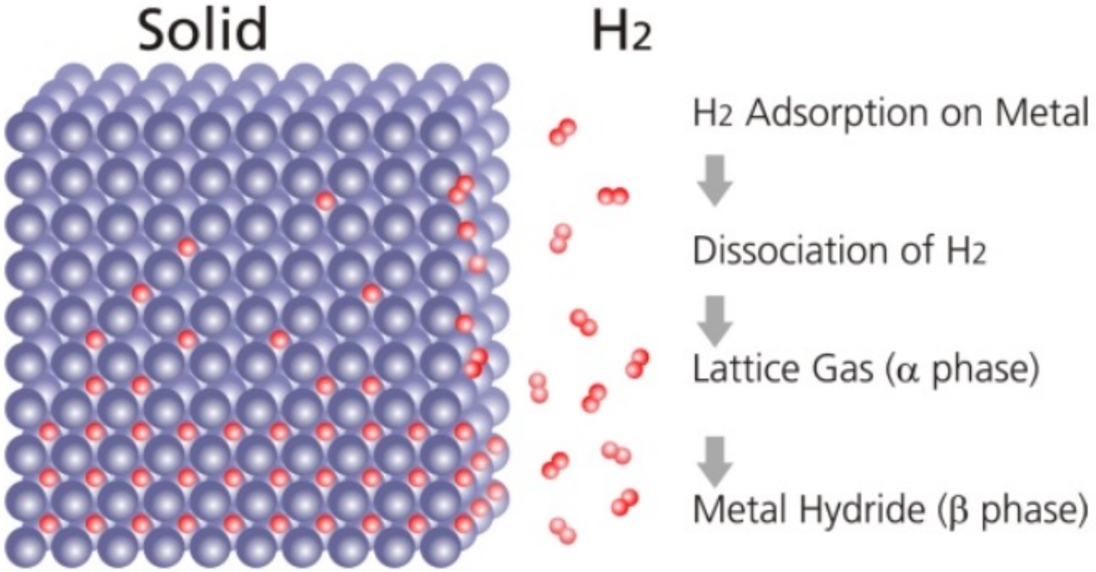
J. E. Lennard-Jones, Trans. Faraday Soc. 28 (1932), pp. 333.
L. Schlapbach, Chapter 1, L. Schlapbach (Ed.) in Intermetallic Compounds I, Springer Series Topics in Applied Physics, Vol. 63, Springer–Verlag, 1988, p. 10.

slide from Prof A Züttel, EPFL

Absorption of H_2 with the metal to form a solid solution

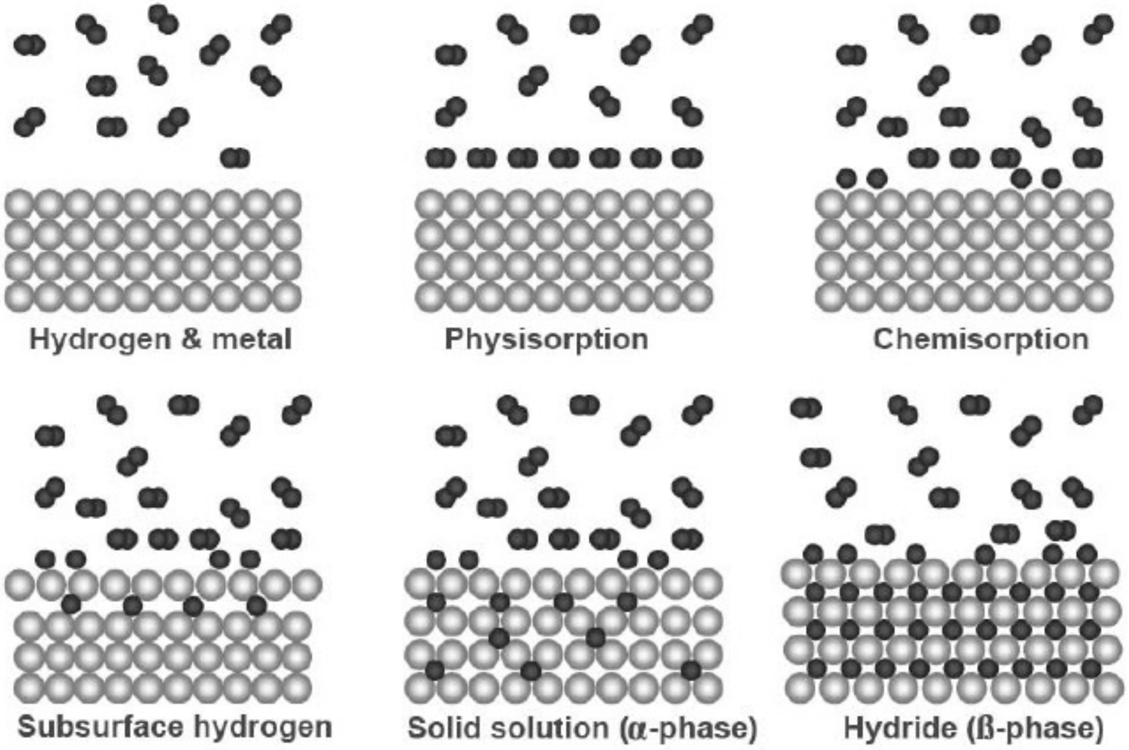


The basic hydride formation process

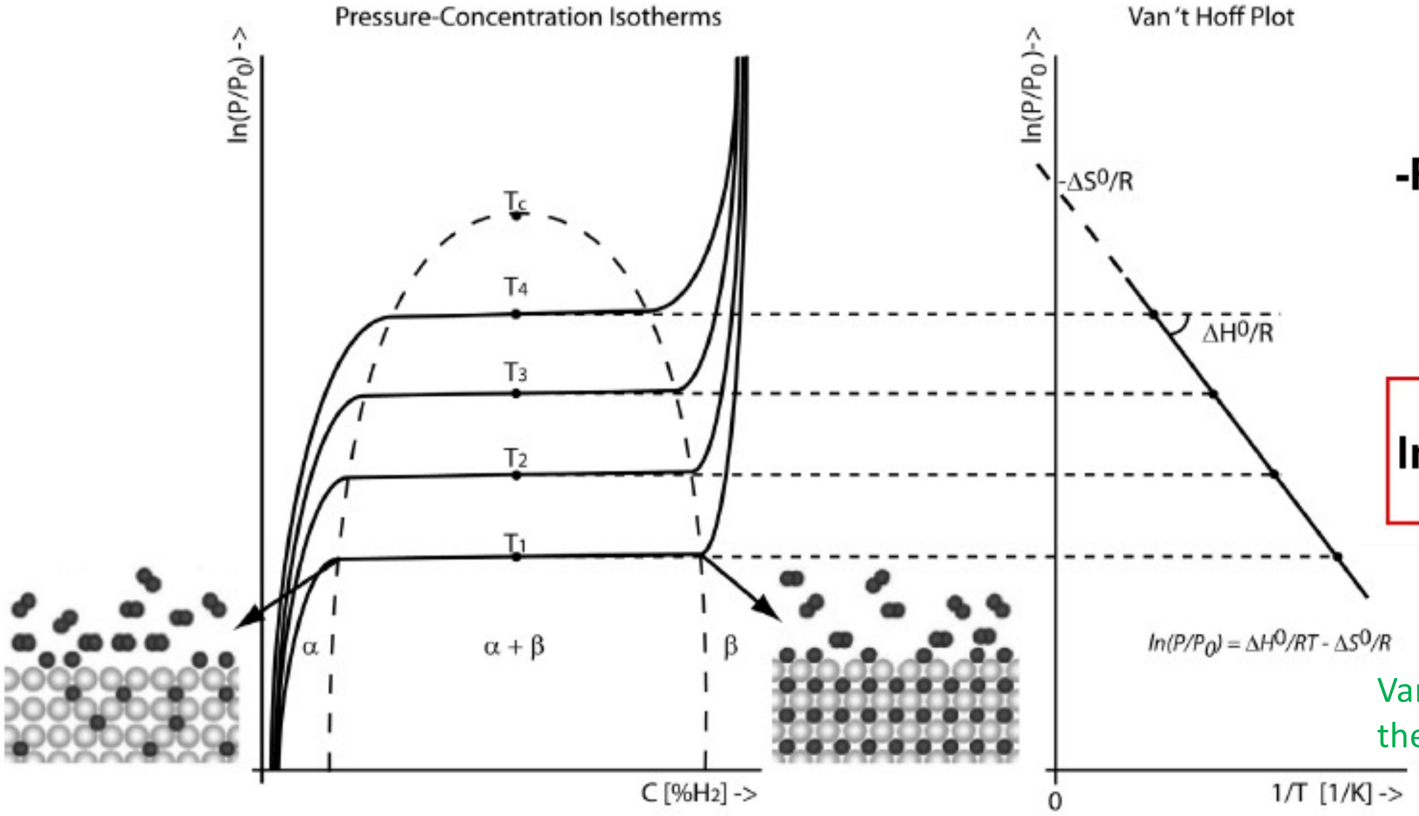


H_2 sorption into the solid lattice forming the dilute α and then fully filled β metal hydride phase

α and β metal hydride phases



Pressure – Concentration – Temperature isotherm (PCT) plot



The Van't Hoff Equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^o = -RT\ln(K)$$

$$-RT\ln(K) = \Delta H^o - T\Delta S^o$$

$$\ln(K) = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

$$\boxed{\ln(K) = -\left(\frac{\Delta H^o}{R}\right)\left(\frac{1}{T}\right) + \frac{\Delta S^o}{R}}$$

Van't Hoff plot to determine ΔH^0 for the H_2 absorption to form the β phase

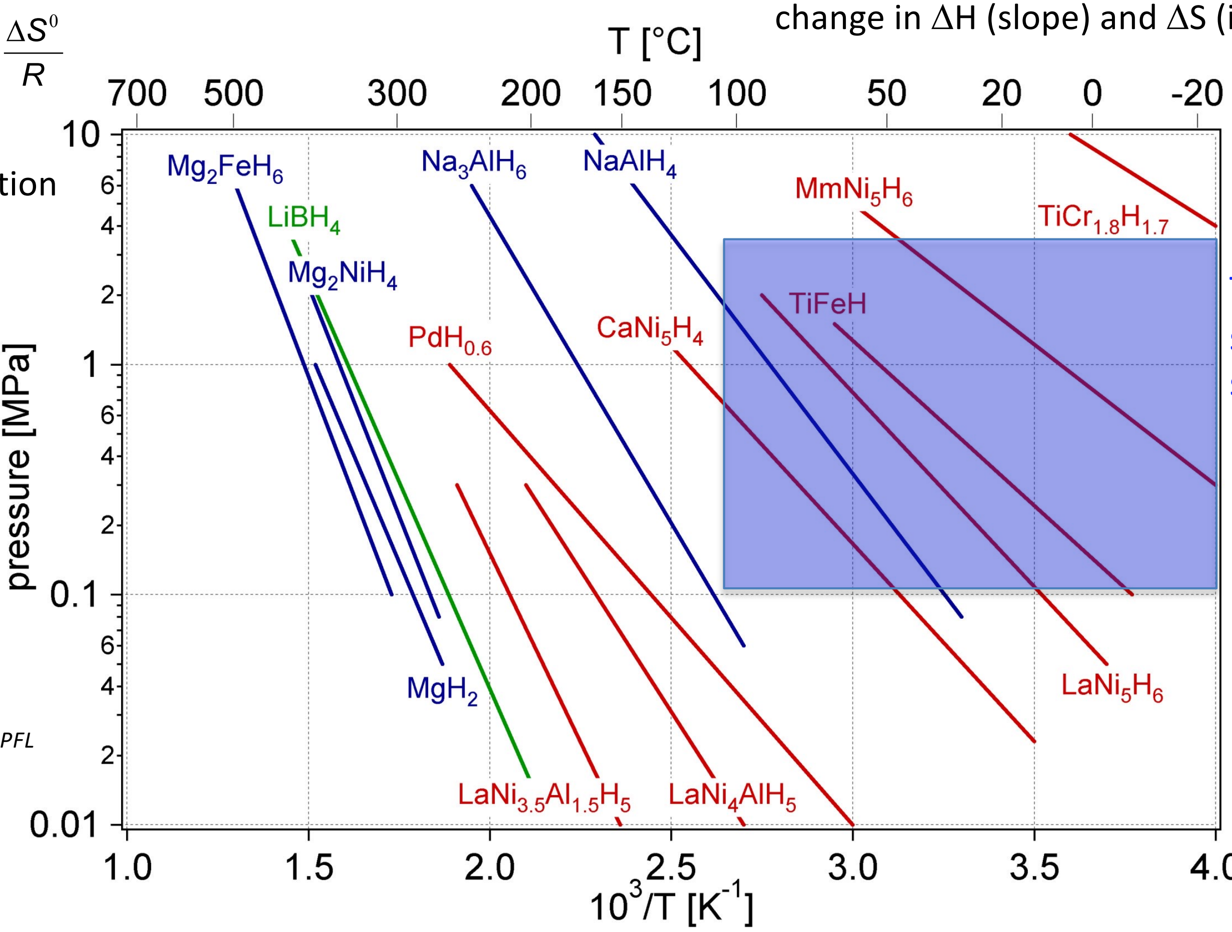
PCT plot summarizes the property of hydrogen concentration (C) in an equilibrium state when an HM alloy is exposed to various hydrogen pressures (P) while maintaining a certain alloy temperature (T).

Hydrides van’t Hoff plot

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

van’t Hoff plot: K_{eq} variation vs 1/T to explore change in ΔH (slope) and ΔS (intercept) of a reaction

Desorption reaction (endothermal)



Target for stationary ambient system

neg. slope = endothermal

the steeper, the bigger ΔH_{abs} (≈ ΔH_{des}). Therefore, at higher T, somewhat less H is adsorbed

slide from Prof A Züttel, EPFL

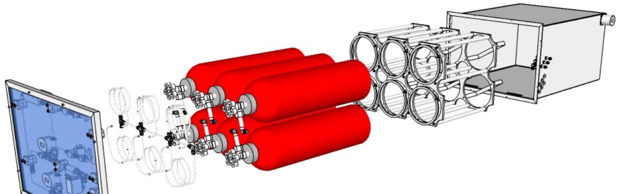
Hydride storage applications

Battery : 300 Wh/kg = 30kWh/100kg

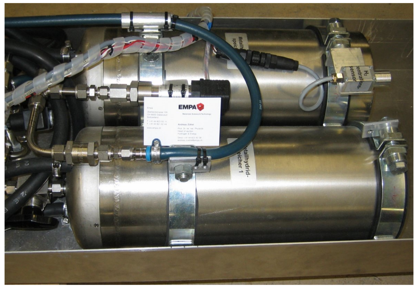
IC snowmobil, MH storage
5 kg H_2, 1.0 mass%

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

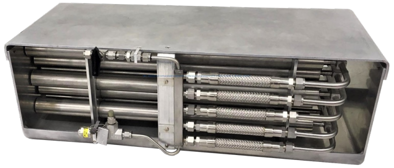
FC canal boat, MH storage
2.5 kg H_2, 1.0 mass%



SELF



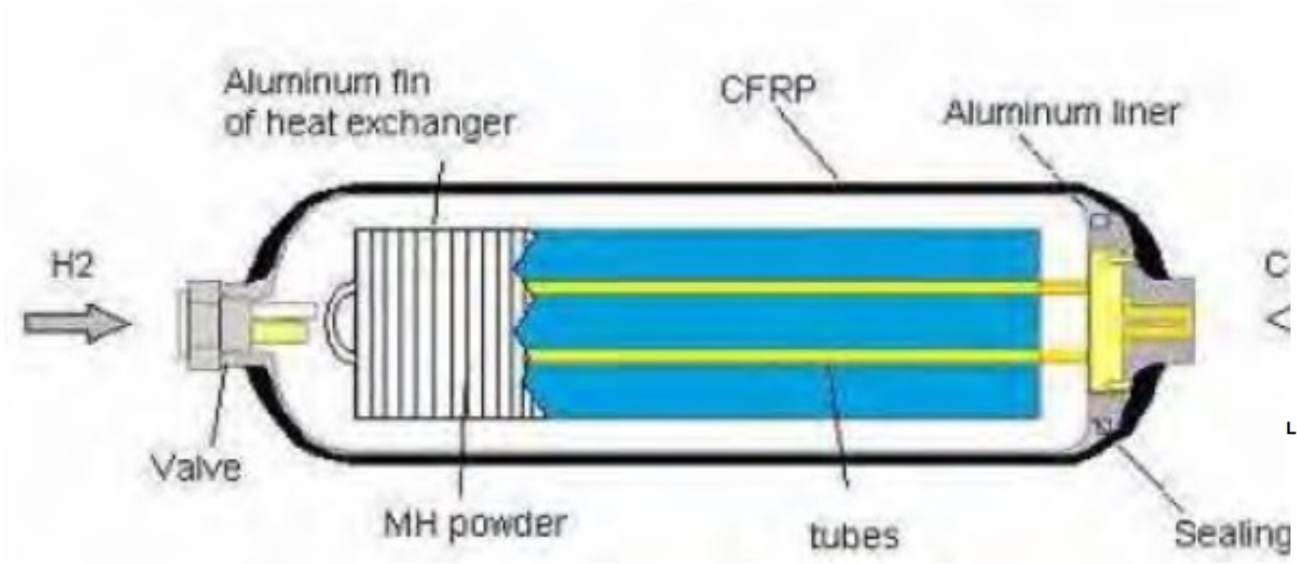
FC vehicle MH storage
0.5 kg H_2, 1.2 mass%



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

slide from Prof A Züttel, EPFL

Metal hydride storage container with cooling



Laboratoire d'Analyse et Modélisation de Systèmes pour l'Aide à la Décision
CNRS UMR 7024

Compared to conventional pressure vessels, metal hydride storage systems have a more than 10 times higher energy density by volume at pressures of 30 to 50 bars

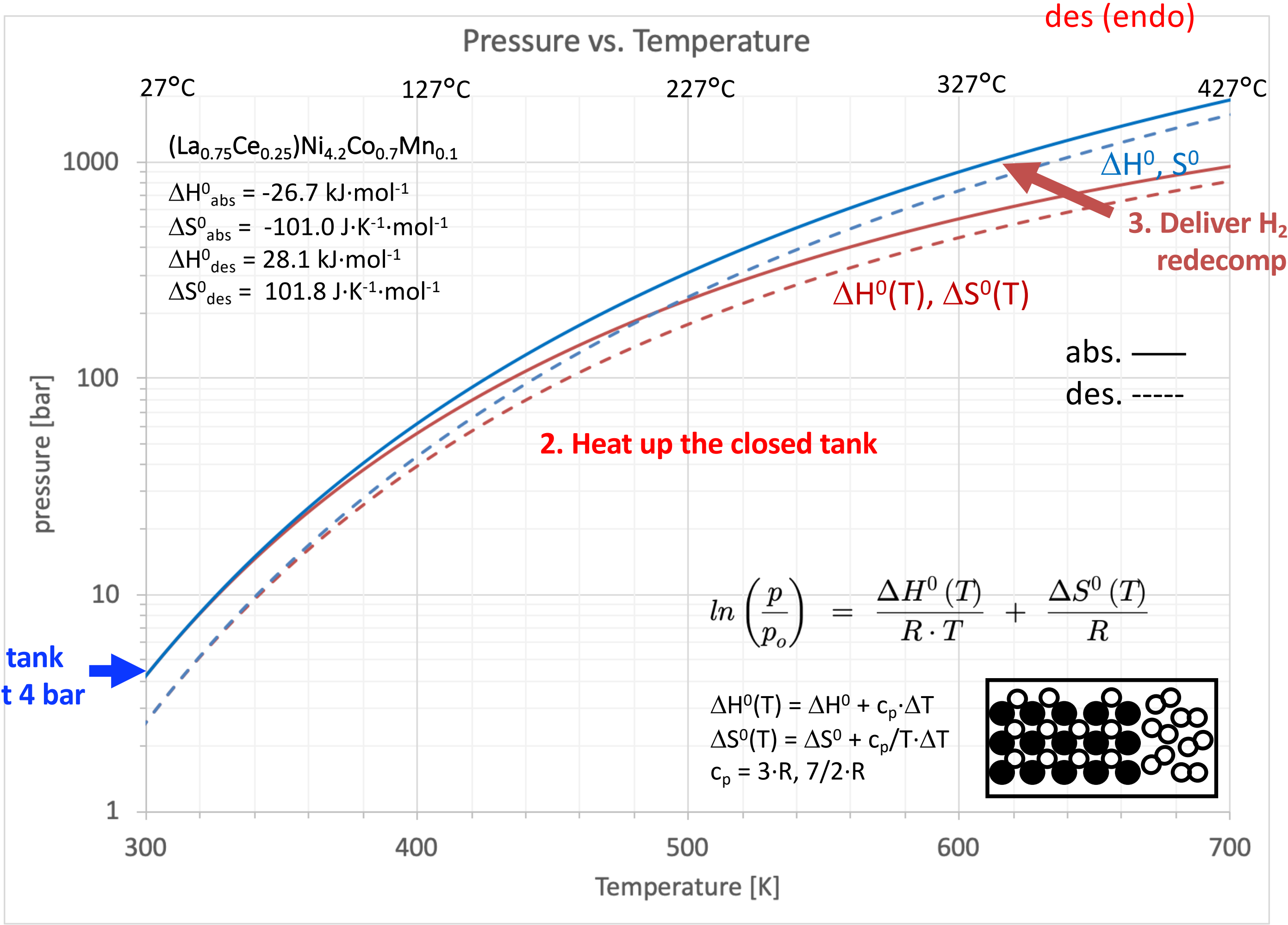
www.grz-technologies.com

Metal Hydride Compression

abs (exo)

$LaNi_5 + 3H_2 \rightleftarrows LaNi_5H_6$

des (endo)



$(La_{0.75}Ce_{0.25})Ni_{4.2}Co_{0.7}Mn_{0.1}$

$\Delta H^0_{abs} = -26.7\ kJ \cdot mol^{-1}$

$\Delta S^0_{abs} = -101.0\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta H^0_{des} = 28.1\ kJ \cdot mol^{-1}$

$\Delta S^0_{des} = 101.8\ J \cdot K^{-1} \cdot mol^{-1}$

1. fill the hydride tank with H_2 at 300K at 4 bar

2. Heat up the closed tank

3. Deliver H_2 at high P via the redecomposed hydride

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

$\Delta H^0(T) = \Delta H^0 + c_p \cdot \Delta T$

$\Delta S^0(T) = \Delta S^0 + c_p/T \cdot \Delta T$

$c_p = 3 \cdot R,\ 7/2 \cdot R$

slide from Prof A Züttel, EPFL

Metal-Hydride compression: procedure

- Absorption starts at low T and continues until the equilibrium pressure P_{eq} (where both MHα-solution and β-hydride phase coexist), is equal to the supply pressure. P_{eq} is evaluated from Pressure-composition isotherms (P-c) specific to the hydride-forming material.
- Once P_{eq} is reached, heat is supplied to decompose the metal β-hydride and so desorb H_2, delivered at a desired discharge pressure (3-10 times the supply pressure, depending on T-level), to reach a new P-c equilibrium.
- In essence, H_2 compression is the result of the sequential cooling and heating of the MH and controlled almost entirely by **heat** transfer (by natural or forced air convection, water- or oil-cooling).
- Multi-stage compression possible when selecting the successive hydride materials accordingly. $LaNi_5$ (<100 bar 1 stage, 700 bar 2-stage). $MnTi_2$ (700 bar), TiFe.

Metal hydride compression

Advantages

- Absence of moving parts→ no wear, noise or vibration, low maintenance cost (1000 €/year vs 8000 €/year for mech. compressors)
- Compact design (400 L/1000 kg vs 6000 L/ 3600 kg for a mechanical compressor). High volumetric efficiency (93%)
- up to 700 bar; often 100-200 bar
- Thermally driven compressor, using waste or solar heat instead of electricity. (uses only 0.5 kWe vs 20 kWe for a comparable mechanical compressor). Smart is to recover electrolyser heat to drive a downstream MH-compressor at the electrolyser outlet.
- Safe; high purity H_2

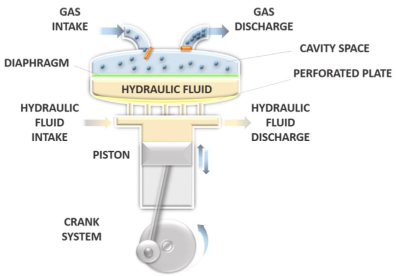
Limitations

- Low capacities (< 10 Nm^3/h)
- Poor efficiency (10kWh/kg), when expressed as compression work vs heat input (max 25% and usually <10%), due to poor heat transfer with the MH.
- Repeated cycles can pulverise the MH alloys

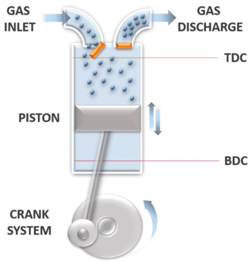
Applications

- Small scale
- FCEV
- HRS
- industry

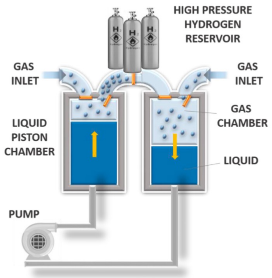
H_2 compression comparison



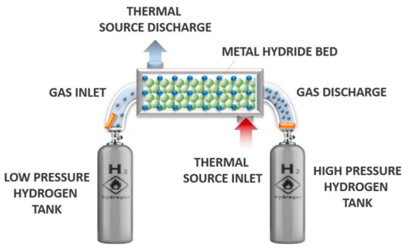
Diaphragm Compressors
10 bar, 1L



Piston Compressors
30 bar



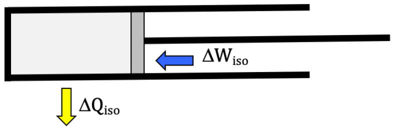
Ionic liquid
200 bar, 50L, 70kg



Metal hydride
500 bar, 300L, 270kg

Isothermal compression

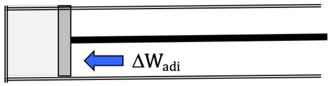
T = const. → $\Delta Q = -\Delta W$



$$\Delta W = n \cdot R \cdot T \cdot ln\left(\frac{p_2}{p_1}\right)$$

Adiabatic compression

$\Delta Q = 0 \rightarrow \Delta U = \Delta W$



$$\Delta W \;=\; -n \cdot c_V \cdot (T_2 - T_1)$$

$$\frac{p_1}{p_2} = \left(\frac{T_1}{T_2}\right)^{\frac{c_V}{R}+1}$$

Thermal compression

$$\Delta Q_S = m \cdot c_V \cdot (T_2 - T_1)$$

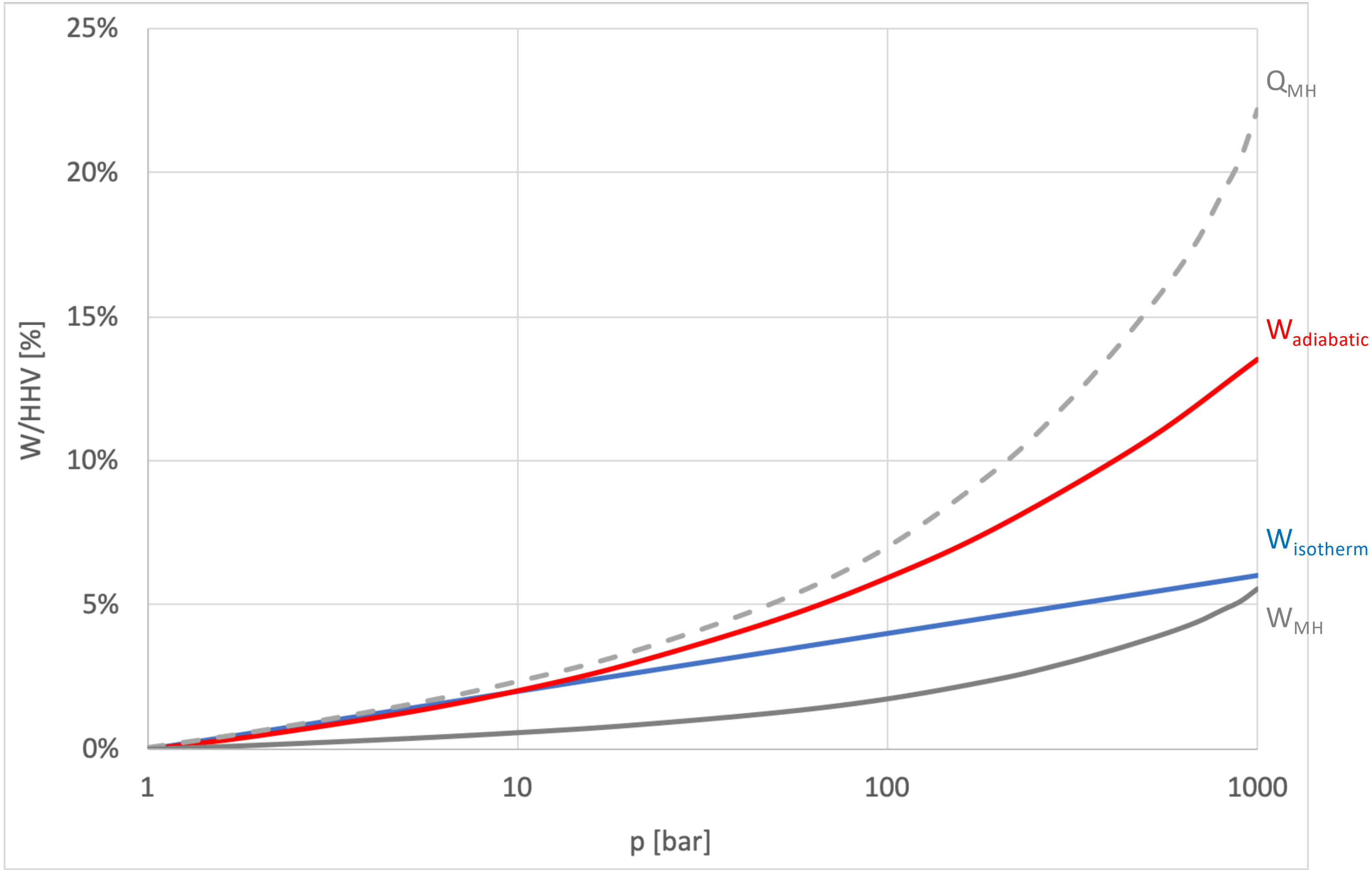
$$ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta H(T)}{R \cdot T} - \frac{\Delta S}{R}$$

$$\Delta Q_L = \Delta H(T)$$

G. Sdanghi, G. Maranzana, A. Celzard, V. Fierro, "Review of the current technologies and performances of hydrogen T compression for stationary and automotive applications", Renewable and Sustainable Energy Reviews 102 (2019), pp. 150 – 170

slide from Prof A Züttel, EPFL

Hydrogen Compression Energy (Q: heat and W: work)



slide from Prof A Züttel, EPFL

H_2 compression overview (Linde AG)

	Piston	Membrane	Screw	Electro-chemical	Metal-hydride	Ionic compressor	Turbo-compressor
Scale Nm^3/h	10 - 115000	1 - 4000	200 - 100000	5 - 280	1 - 12	750	>1000
Max P (bar)	1300	3000	55	950	250	1000	<50
TRL (H_2)	9	9	commercial	7	5-6	8	low
Advant.	availability	availability no contamination	availability low maintenance	no moving parts low OPEX	thermal no contamin. no mov. parts	efficiency no contamination	availability low mainten. high vol. flow
Disadvant.	contamination maintenance	lim. suction maintenance	contamination H2 backflow	low vol. flow R&D	low vol. flow R&D	maintenance	Δp depends on mol weight

Linde AG presentation EFCF July 2019: Industrial perspective on H_2 purification, compression, storage and distribution

Overall compression technologies comparison: depends on application

Type of compressors		Capacity and pressure range	Availability of the market	Contamination And leaks	Efficiency [%]	Price of the market [€] *	Weight and volume	Type of flow	Noise/vibration /pressure fluctuations
Mechanical	Reciprocating piston	🟩	🟩	🟥	🟨 50-80	🟩 20k-80k	🟥	🟥 Intermittent	🟥
	Diaphragm	🟩	🟩	🟨	🟨 50-80	🟩 30k-75k	🟥	🟥 Intermittent	🟨
	Ionic liquid	🟥	🟥	🟨	🟩 70	No data	No data	🟥 Intermittent	🟨
Non-mechanical	Metal hydride	🟨	🟥	🟩	🟥 < 10	No data	🟩	🟥 Intermittent	🟨
	Electrochemical	🟩	🟨	🟩	🟩 80-90	🟥 >180k	🟩	🟩 Continuous	🟩

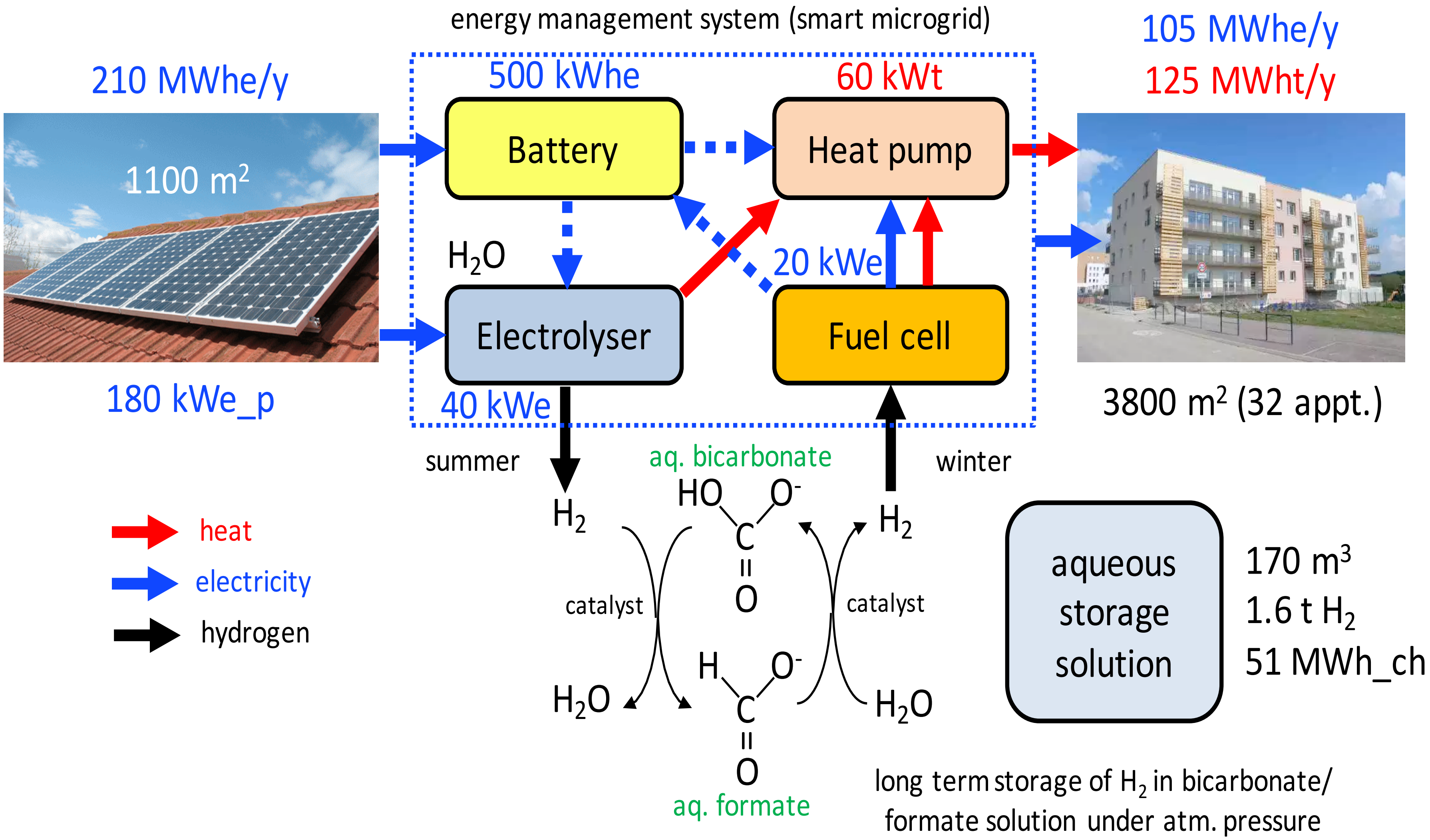
* For 1.5 Nm^3/h, 0 bar(g) inlet and 15-20 bar(g) outlet pressure

slide from T Macherel, EPFL

Chemical H-storage

- Formic acid or formate
- NH_3
- LOHC (liquid organic hydrogen carriers)
- …

Seasonal H_2 storage example with formate cycle ($HCOO^-$)



energy management system (smart microgrid)

210 MWhe/y

1100 m^2

180 kWe_p

500 kWhe

Battery

60 kWt

Heat pump

105 MWhe/y

125 MWht/y

3800 m^2 (32 appt.)

H_2O

Electrolyser

40 kWe

20 kWe

Fuel cell

summer

winter

aq. bicarbonate

H_2

catalyst

H_2O

aq. formate

heat

electricity

hydrogen

aqueous storage solution

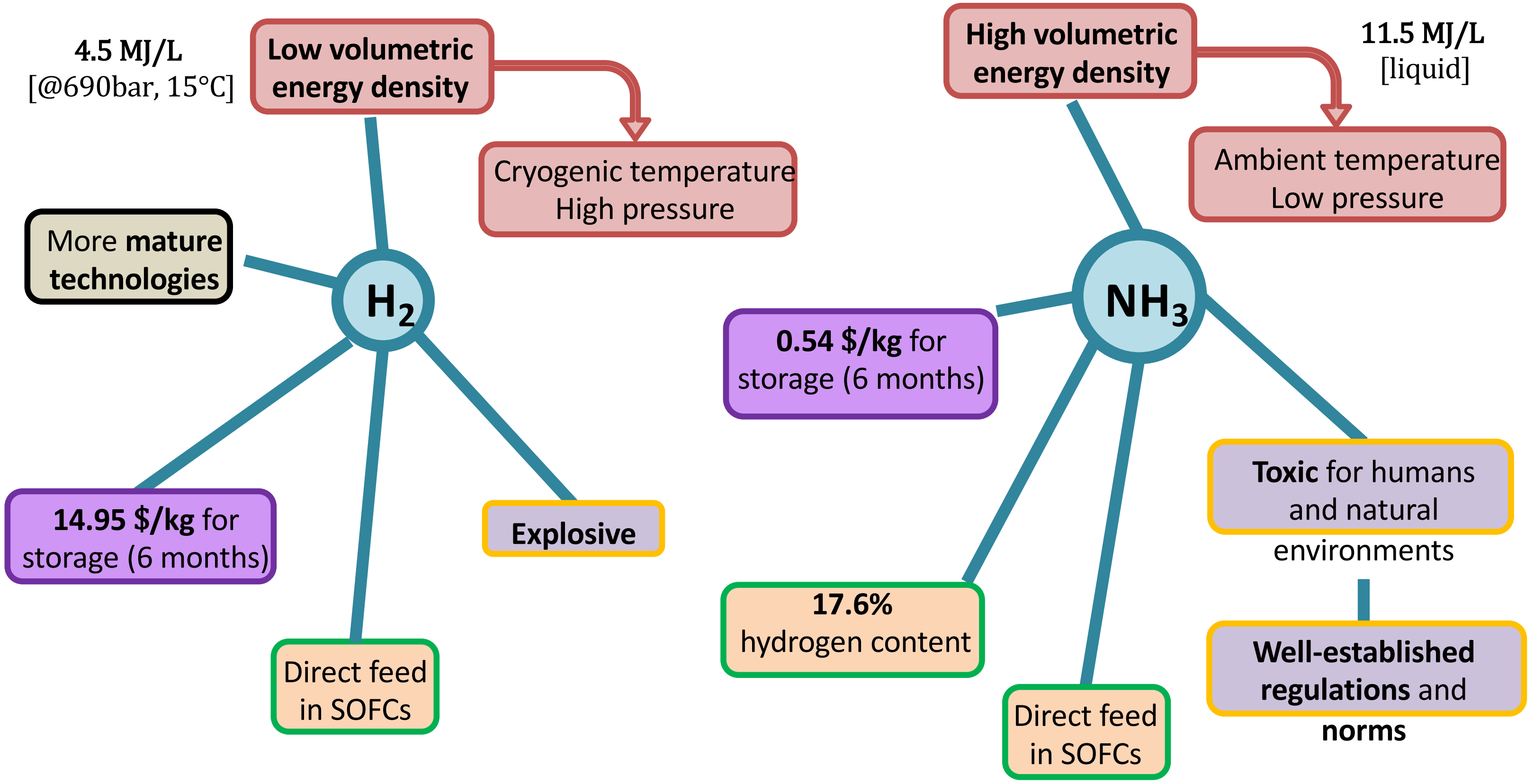
170 m^3

1.6 t H_2

51 MWh_ch

long term storage of H_2 in bicarbonate/ formate solution under atm. pressure

Ammonia as H_2 energy vector



H_2

4.5 MJ/L
[@690bar, 15°C]

Low volumetric energy density

Cryogenic temperature
High pressure

More **mature technologies**

14.95 $/kg for storage (6 months)

Direct feed in SOFCs

Explosive

NH_3

High volumetric energy density

11.5 MJ/L
[liquid]

Ambient temperature
Low pressure

0.54 $/kg for storage (6 months)

17.6%
hydrogen content

Direct feed in SOFCs

Toxic for humans and natural environments

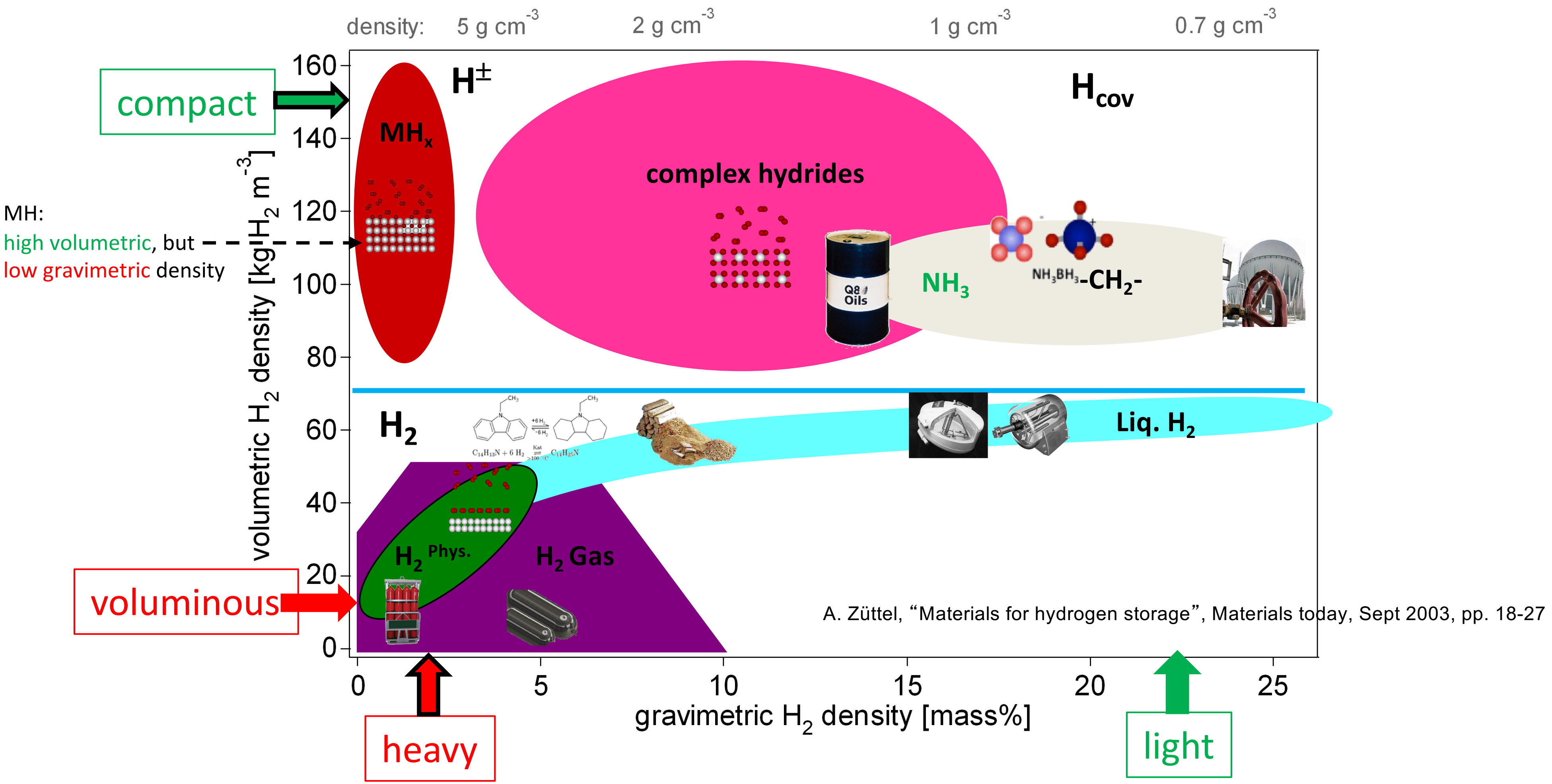
Well-established regulations and **norms**

- Energy density

  by volume : diesel : GNL : NH_3 : H_2-liq : H_2-compressed

  1 2 3 5 10 m^3

Hydrogen Storage Density comparison



compact

MH:
high volumetric, but
low gravimetric density

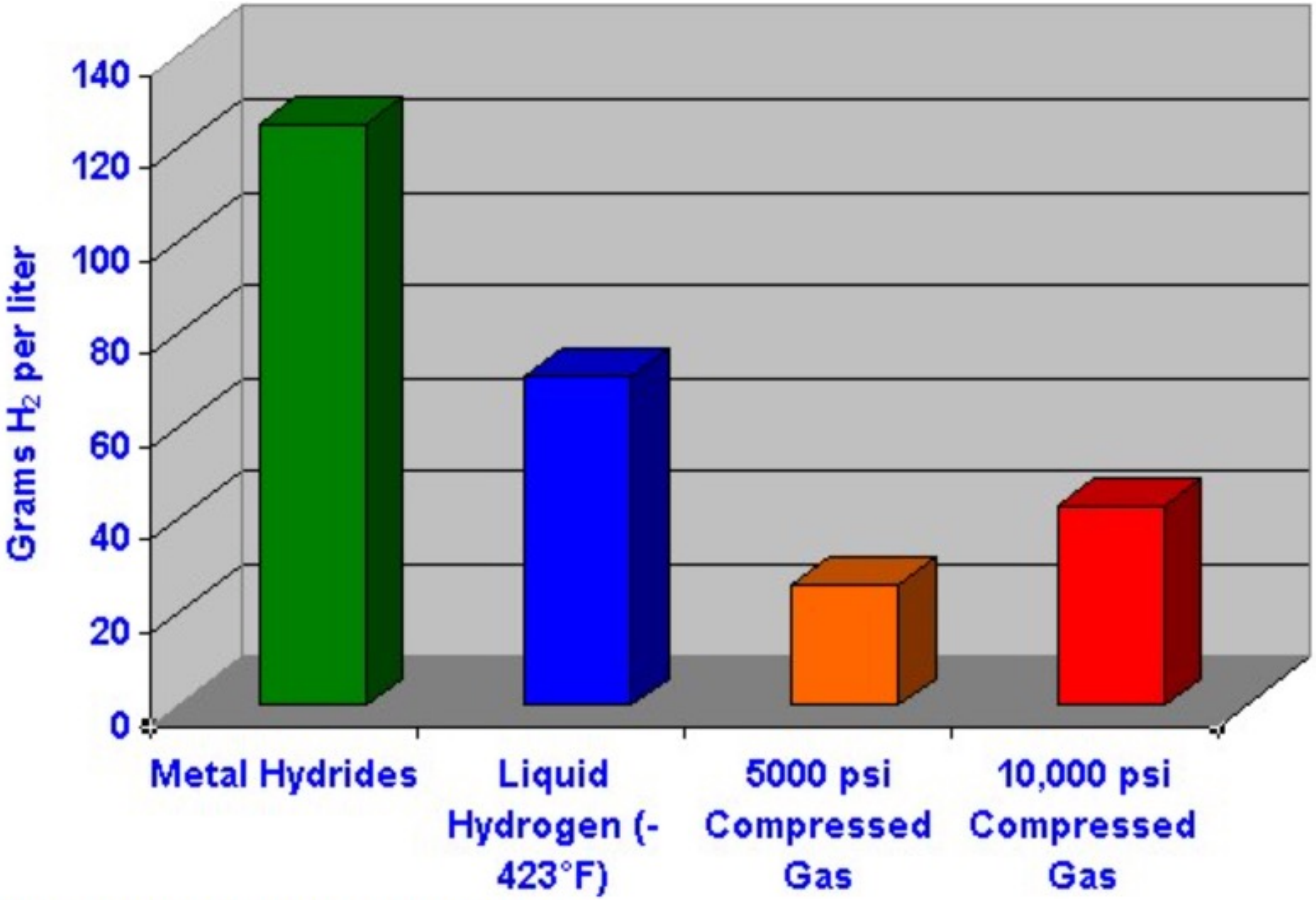
voluminous

heavy

light

A. Züttel, "Materials for hydrogen storage", Materials today, Sept 2003, pp. 18-27

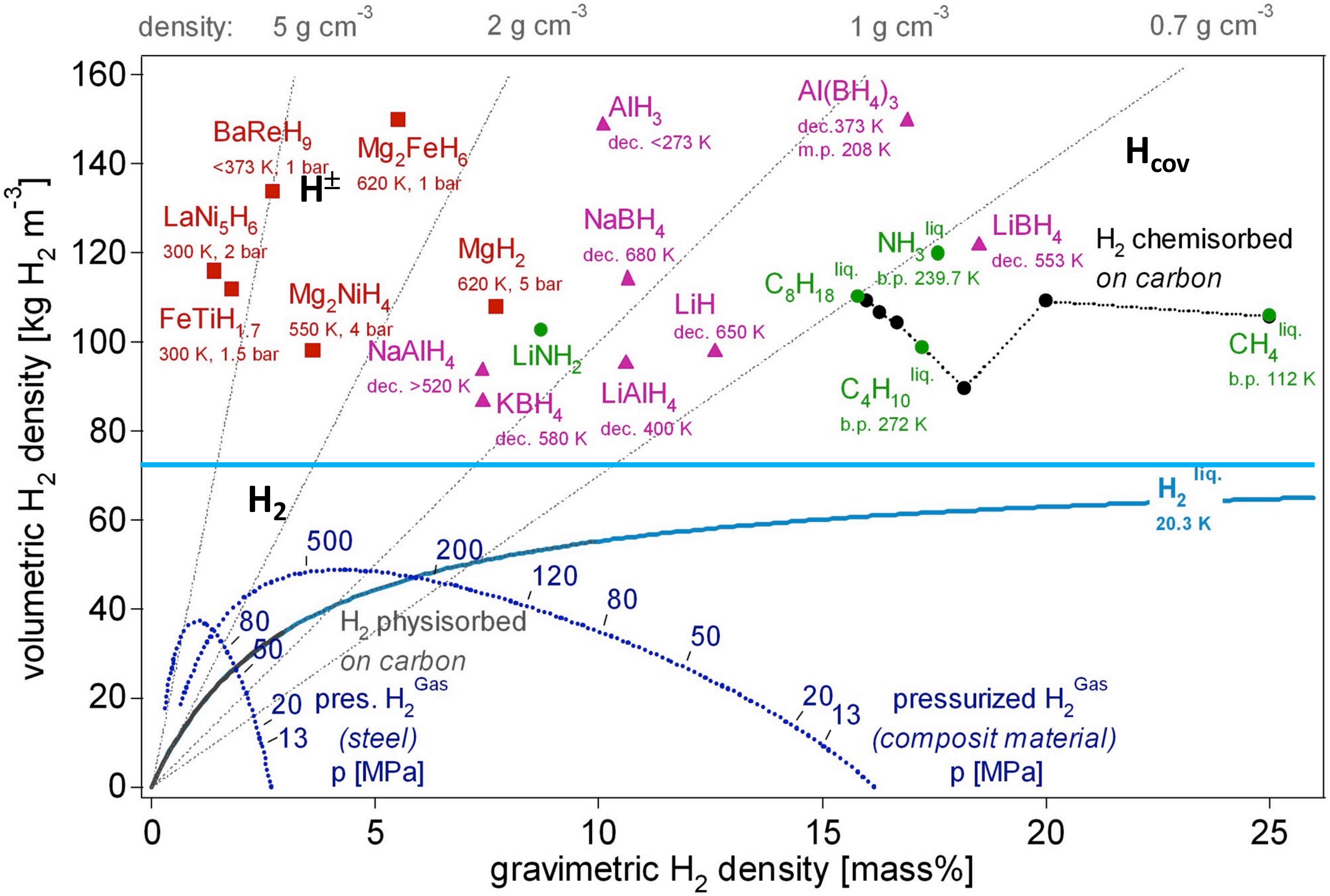
slide from Prof A Züttel, EPFL



Metal Hydride Hydrogen Storage

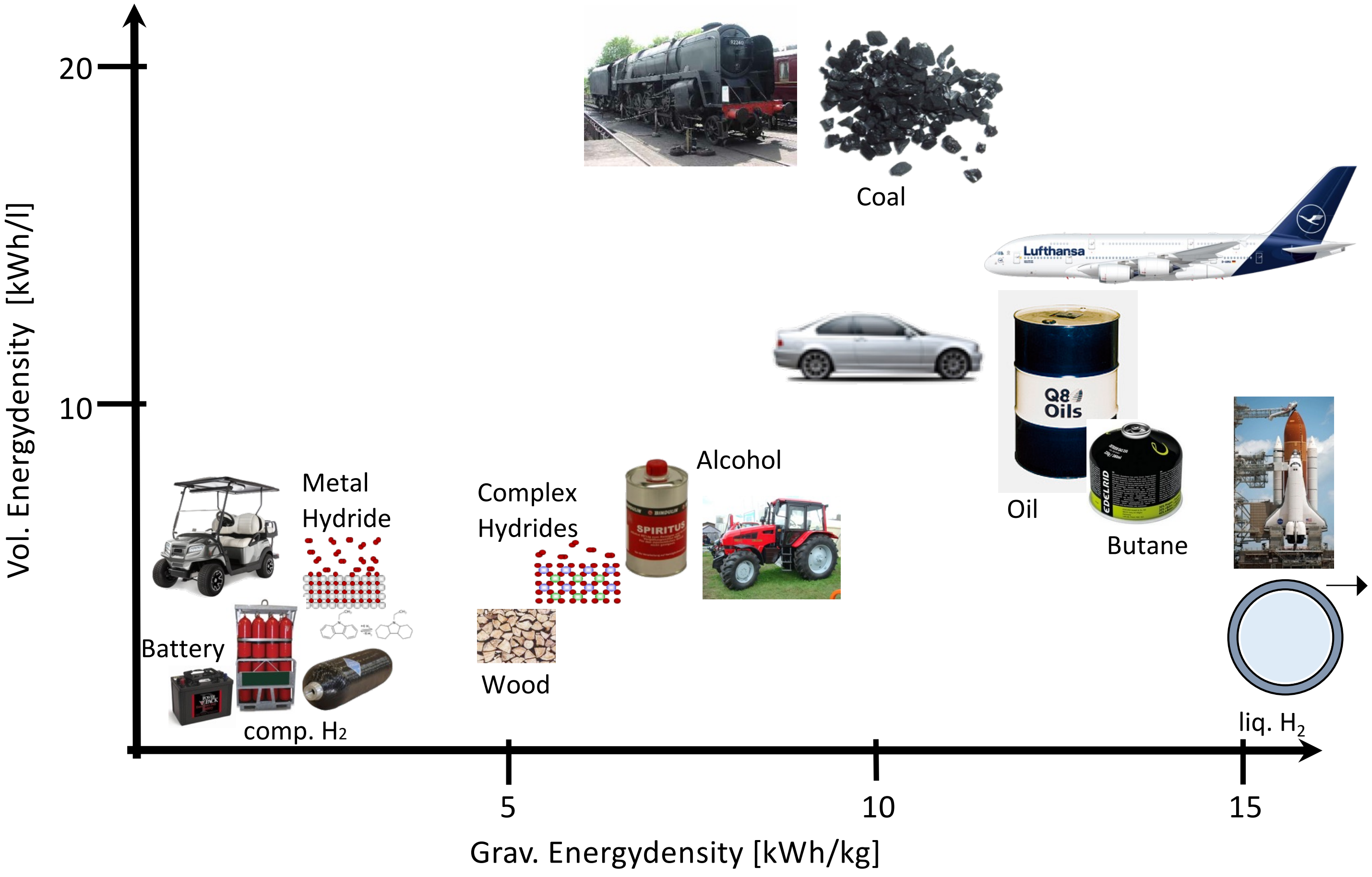
Metal hydrides have a very high volumetric density – but low gravimetric density

Hydrogen Storage Materials comparison



A. Züttel, "Materials for hydrogen storage", Materials today, Sept 2003, pp. 18-27

Energy density of fuels overall



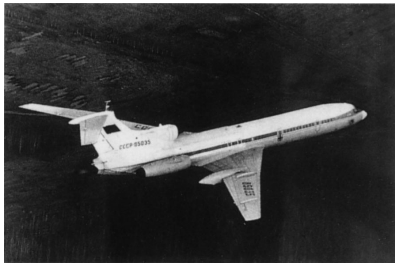
slide from Prof A Züttel, EPFL

Hydrogen Storage in Mobility

Francois Isaac de Rivaz (1813)

Hindenburg (1937)

Karl Kordesch: Austin A40 (1966)



Tupolev 155 (1988)

Saturn (1963)

Space Shuttle (1981)

Necar 1 (1994)

NuBus, 250kW (2002)

Hy.move (2009)

Necar 4 (2002)

Hyundai Nexo hydrogen car FCEV (2018)

slide from Prof A Züttel, EPFL

BMW (1978)

Ratrac (2004)

Toyota Mirai (2014)

Coradia iLint (2018)

Comparison H_2 storage (Linde AG)

	c-H2(g)	LH2	LOHC	MOFS	M-hydride	Complex hydrides	Salt hydrides
ρ (kg /m^3)	50bar: 4 700bar:36	71	57	material-dependent	material-dependent	material-dependent	material-dependent
wt% stored	100	100	6.2	5-9 (cryo) 0.5-1 (amb.)	1.4-2 ($LaNi_5$,AB_2)	5.6 ($NaAlH_4$)	7.7 (MgH_2)
T	20°C	-253°C	150-200C ads 300C desorp.	-176°C ads. Des.:vacuum	0-30°C	70-170C ads. (20-150 bar) 100-200C des. (1bar)	250-300C ads. (10-15 bar) 300-350C des. (1bar)
Storage time	unlimited	limited (boil-off)					
Compression as % LHV	6%	22-34%	49% (if no heat avail.)	18% (if no heat avail.)		55% (if no heat avail.)	
Status	commercial	commercial	emerging	R&D		R&D	
Challenge	transport limited (low ρ)	boil-off	purity, stability weight	T_adsorpt P_desorb weight		T ads/des. P_desorb weight	
TRL	9	9	4	3	7	3-4	3-4

Linde AG presentation EFCF July 2019: Industrial perspective on H_2 purification, compression, storage and distribution

Hydrogen Distribution

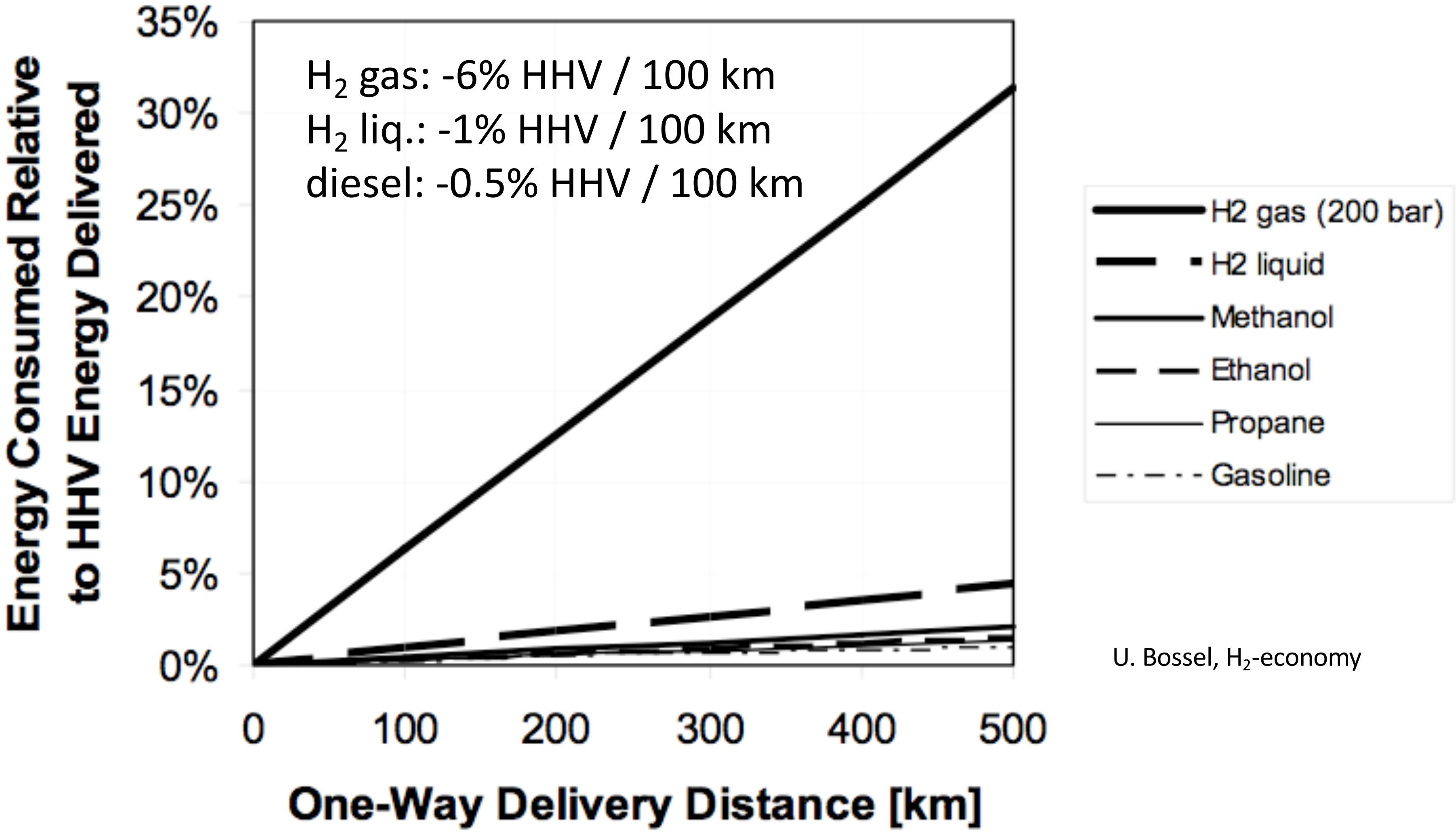
1. by road (delivery trucks)
2. by pipeline
3. by on-site generation (electrolysis) at filling station

HRS H_2 dispension needs (Linde)

Vehicle	H_2 kg/day	Number of vehicles supplied			
		$cH_2(g)$ truck	LH_2 truck	LH_2 plant 5 tpd	LH_2 plant 50 tpd
car	0.4	2500	8750	12500	125000
bus	30	33	117	167	1667
truck	100	10	35	50	500
train	250	4	14	20	200
ship	2000	0.5	1.75	2.5	25
large ship	10000	0.1	0.35	0.5	5

Linde AG presentation EFCF July 2019: Industrial perspective on H_2 purification, compression, storage and distribution

1. By road transport



H_2 gas: -6% HHV / 100 km
H_2 liq.: -1% HHV / 100 km
diesel: -0.5% HHV / 100 km

U. Bossel, H_2-economy

2. Onsite electrolysis => exercise

- Q: How big an electrolyser is needed to produce the daily amount of H_2 for a filling station (HRS), under the following assumptions?:
  - 1000 cars/day, equivalent of 50 L gasoline/car (LHV_gasoline: 33MJ/L
  - car average consumption : 7L/100km
  - a FCEV consumes 1 kg H_2/100km (HHV_H_2 : 142 MJ/kg)
  - electrolyser efficiency 78% HHV
  - compression energy needed to 400 bar
  - the electrolyser operates 50% of the time

3. By pipeline

- NG pipelines are **not** fully **compatible** for H_2 use (diffusion loss, brittleness, compressor,…)
- energy carried: $Q(W) = V(m^3/s).\rho(kg/m^3).HHV(MJ/kg) =$ section $A (m^2)$*flow $f(m/s).\ \rho(kg/m^3).HHV(MJ/kg)$
- with $\rho_{CH4}=0.71$ vs $\rho_{H2}=0.09$, and $HHV_{H2}=142$ vs $HHV_{CH4}=53$, the H_2-velocity has to be 3.1 times higher
- pumping power $P(W)=A.f.\Delta p=A.f.½(L/D)\rho f^2\zeta$
- ratio $P_{H2}/P_{CH4}=(\rho_{H2}/\rho_{CH4}).(f_{H2}/f_{CH4})^3=(0.09/0.71).(3.1)^3 = 3.85$
- $f_{CH4}=10m/s$, one compressor every 150 km consumes ca. 0.3% of the passing energy stream

  → for H_2,ca. 0.3%*3.85 = 1.16%

European Gas network

Vested infrastructure
42% of buildings heated by NG
112 million households

<u>Consumption</u>: 5375 TWh
(23% of energy)
<u>Storage</u>: 1200 TWh

= large reserve for injection of
H_2 (and green methane)

Eurogas Statistical Report 2018

Limits of H_2 injection into the NG grid

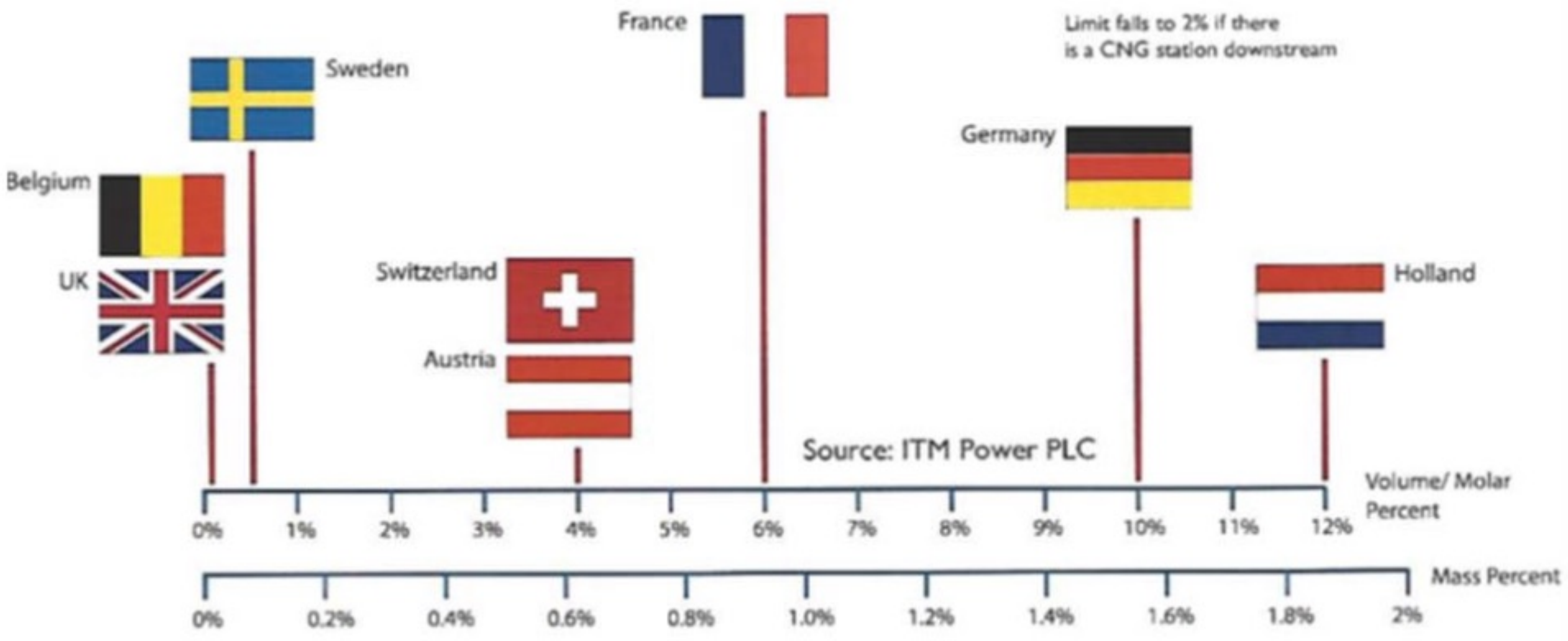


Figure 34: Hydrogen injection limit in national gas networks [71]

fch.europa.eu
June2017
STUDY ON EARLY BUSINESS CASES FOR H2
IN ENERGY STORAGE AND POWER TO H2 APPLICATIONS
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Green Hydrogen for a European Green Deal : 2x40 GW Initiative (January 2020, FCHJU)

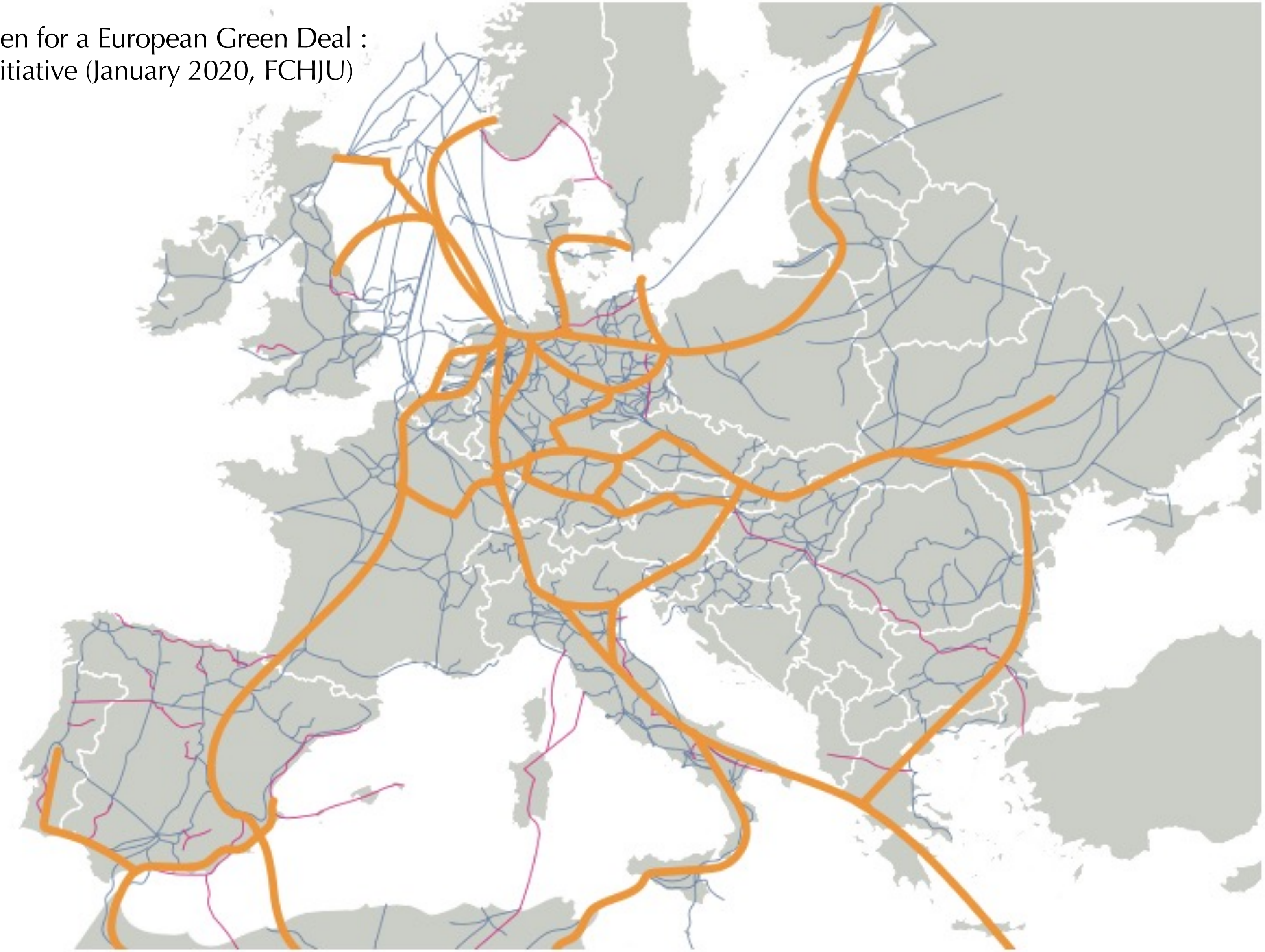

Figure 7 *European Transnational Hydrogen Backbone - The natural gas infrastructure in Europe (blue and red lines) and an outline for a hydrogen backbone infrastructure (orange lines). The main part of the hydrogen backbone infrastructure consists of re-used natural gas transport pipelines with new compressors. A "new" hydrogen transport pipeline must be realised from Italy to Greece and from Greece to the Black See, also along the South Coast of the Iberian Peninsula a dedicated hydrogen pipeline has to be realised.*

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- H_2 transport by pipeline (15-30 GW) is 10-20x cheaper than electricity transport by cable (1-2 GW); a pipeline adds only 0.2€/kgH_2 to the cost
- Capacity of the gas grid is >10x larger than of the electricity grid
  - e.g. NG pipeline Libya-Algeria-Italy-Spain = 60 GW
  - e.g. electricity line Morocco-Spain = 0.7 GW
- Natural gas is stored in large quantities in empty gas fields, porous rock formations and salt caverns (200bar). About 15-20% of the total gas consumption is stored to balance gas production and consumption
- 40 GWe H_2 in EU 2030 = 4.4 MtH_2 = 173 TWh
- Additional 100-150GWe in PV/wind are expected

Recap on H_2

- Regarded as important intermediate energy vector, because:
  1. it can store large quantities of renewable electricity (wind, PV, …) via electrolysis technologies
  2. it can be used in all sectors (industry, heating, power, mobility)
- Most hope is invested in (heavy duty) mobility and (heavy) industry, as these are difficult to decarbonise
- Different electrolyser technologies are likely to co-exist. The main challenges are:
  1. large scale deployment (TWe capacity will be needed) : manufacturing, materials, footprint
  2. storage, and transport, of H_2 (volume, weight)