Hydrogen storage.
(I) Metal hydrides and ammonia borane.

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Summer School on “Materials for the hydrogen economy”
University of Iceland, Reykjavik, Iceland, August 19, 2010

Outline

- Hydrogen economy
- Why is hydrogen storage so troublesome?
- Hydrogen storage targets
- Metal hydrides and chemical storage
- Organic liquid carrier
- Ammonia borane

(II) Hydrogen hydrates and hydrogen clathrates of ammonia borane

Hydrogen economy

- Fossil fuels economy

Gasoline:
13 kWh/kg
10 000 kWh/m^3

$$2C_nH_{2n+2} + (3n+1)O_2 \rightarrow 2nCO_2 + (2n+2)H_2O$$

Dependence on hydrocarbons and limited resources

Environmental problems

- Hydrogen economy

Hydrogen:
39 kWh/kg
3.5 kWh/m^3

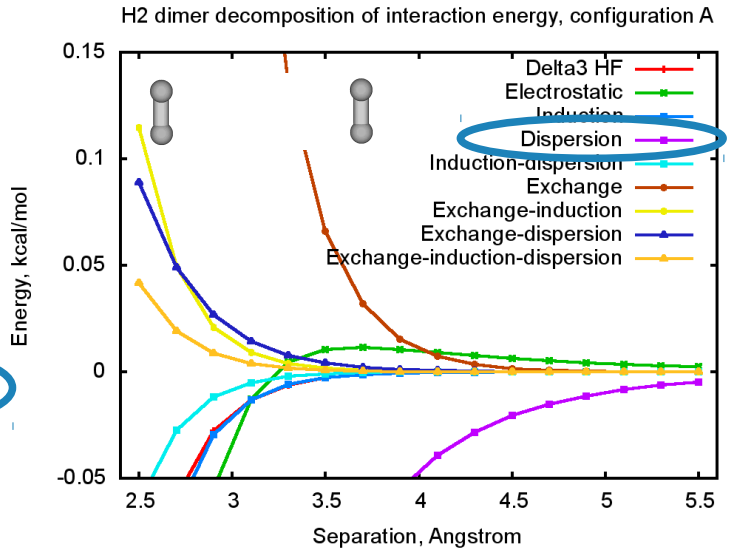
$$H_2O + Energy \rightarrow H_2 + \tfrac{1}{2}O_2$$
$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O + Energy$$

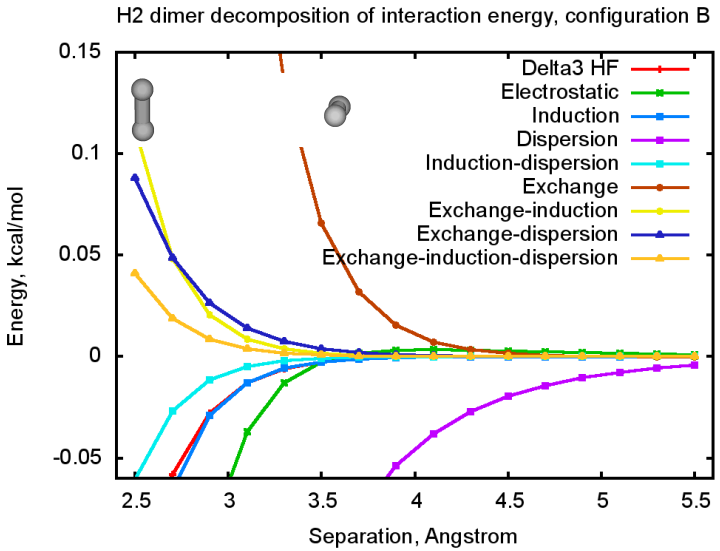
*The picture is adapted from www.wikipedia.org

Why is hydrogen storage so troublesome?

Decomposition of intermolecular interaction energy for H_2 dimer

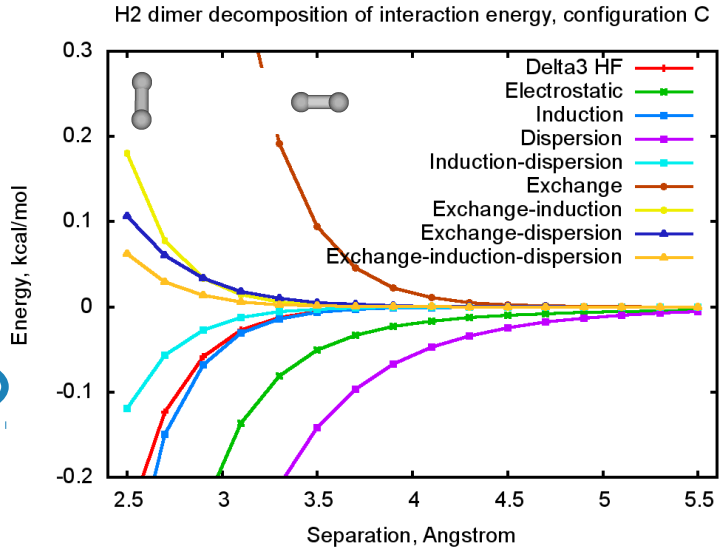
R_{min}	3.5
E_{min}	-0.036
elst	0.010
exch	0.072
ind	-0.003
disp	-0.115
inddisp	-0.001





R_{min}	3.5
E_{min}	-0.047
elst	-0.003
exch	0.072
ind	-0.003
disp	-0.113
inddisp	-0.001

R_{min}	3.3
E_{min}	-0.101
elst	-0.081
exch	0.210
ind	-0.014
disp	-0.210
inddisp	-0.006



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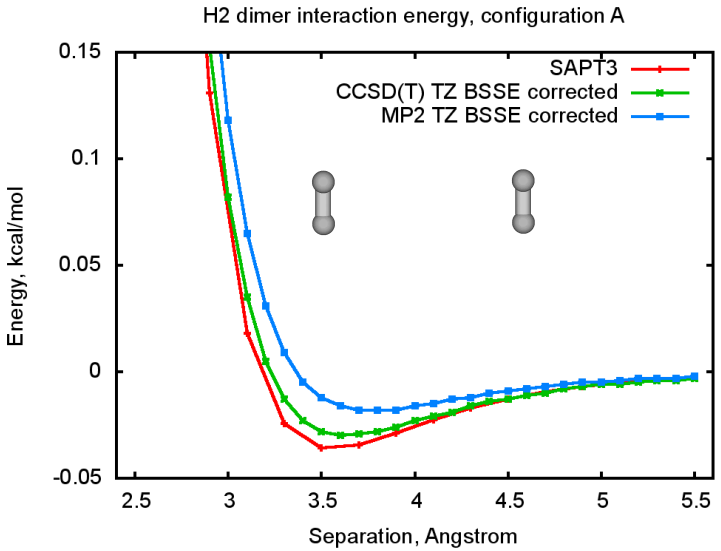

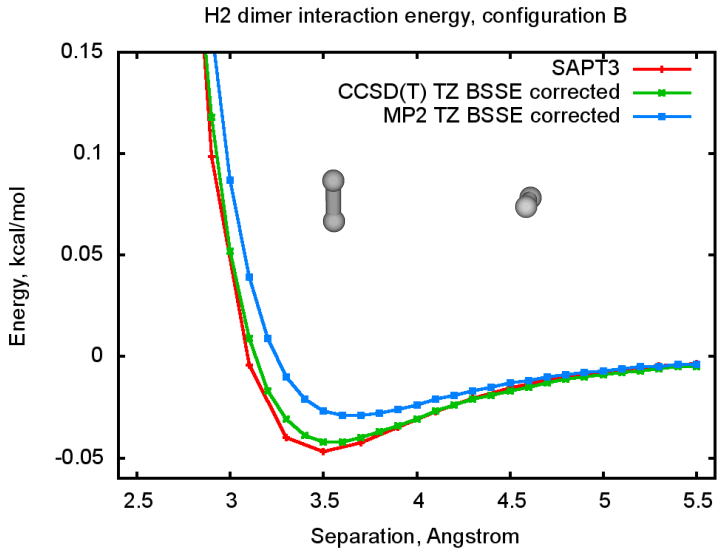

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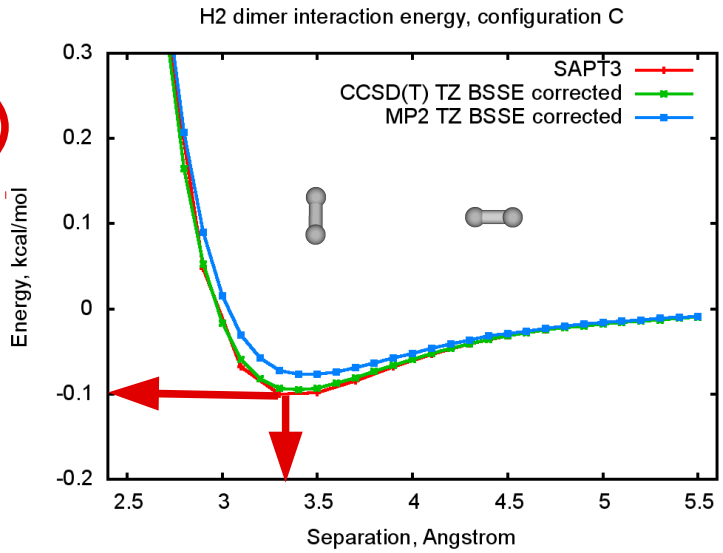
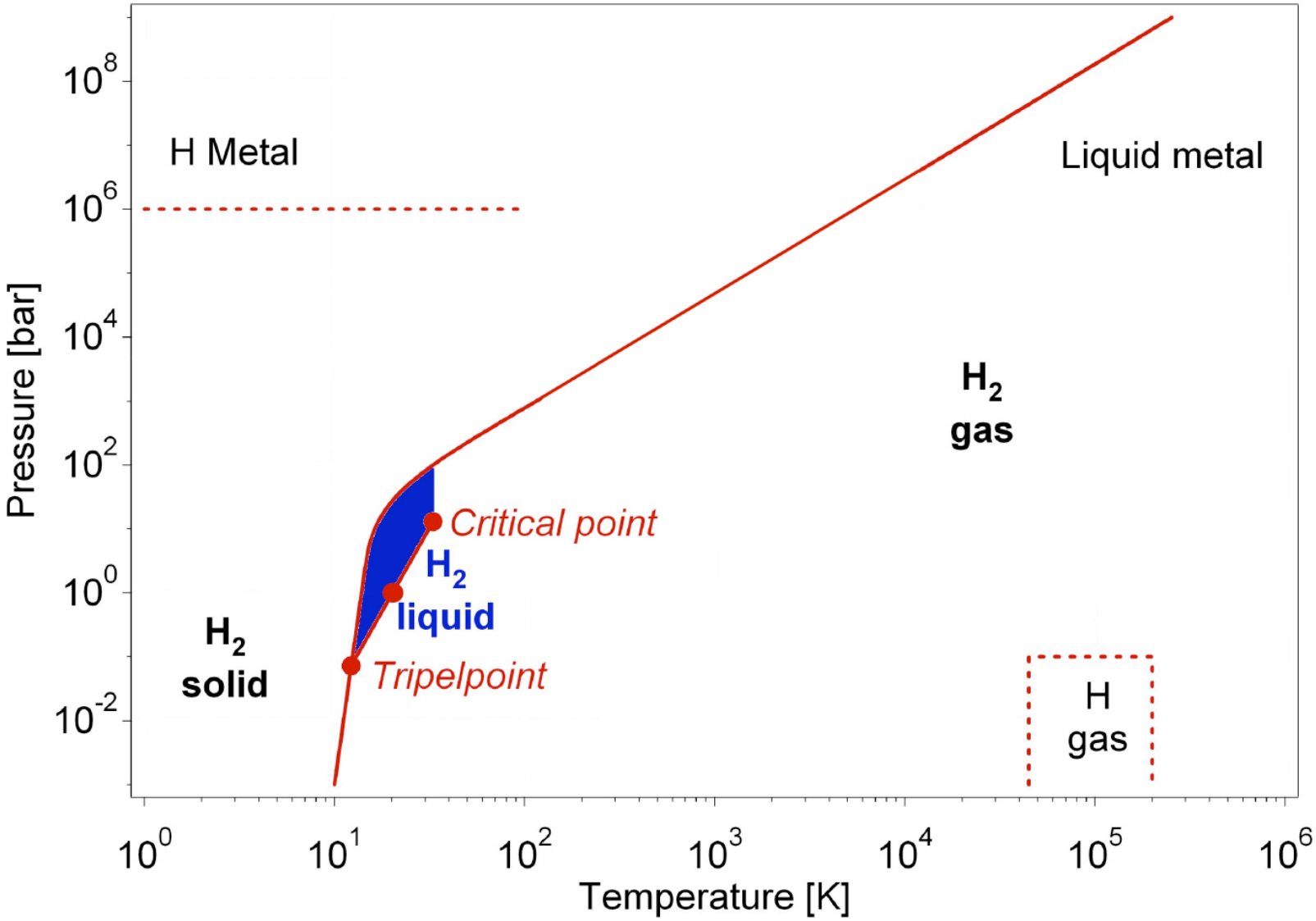


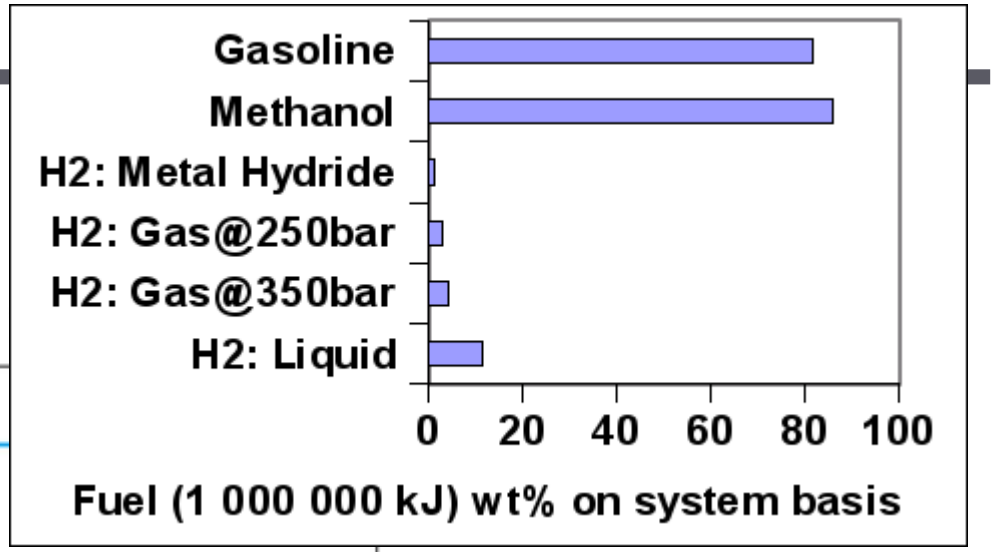
Confer:
kT~0.05 kcal/mol at 25K

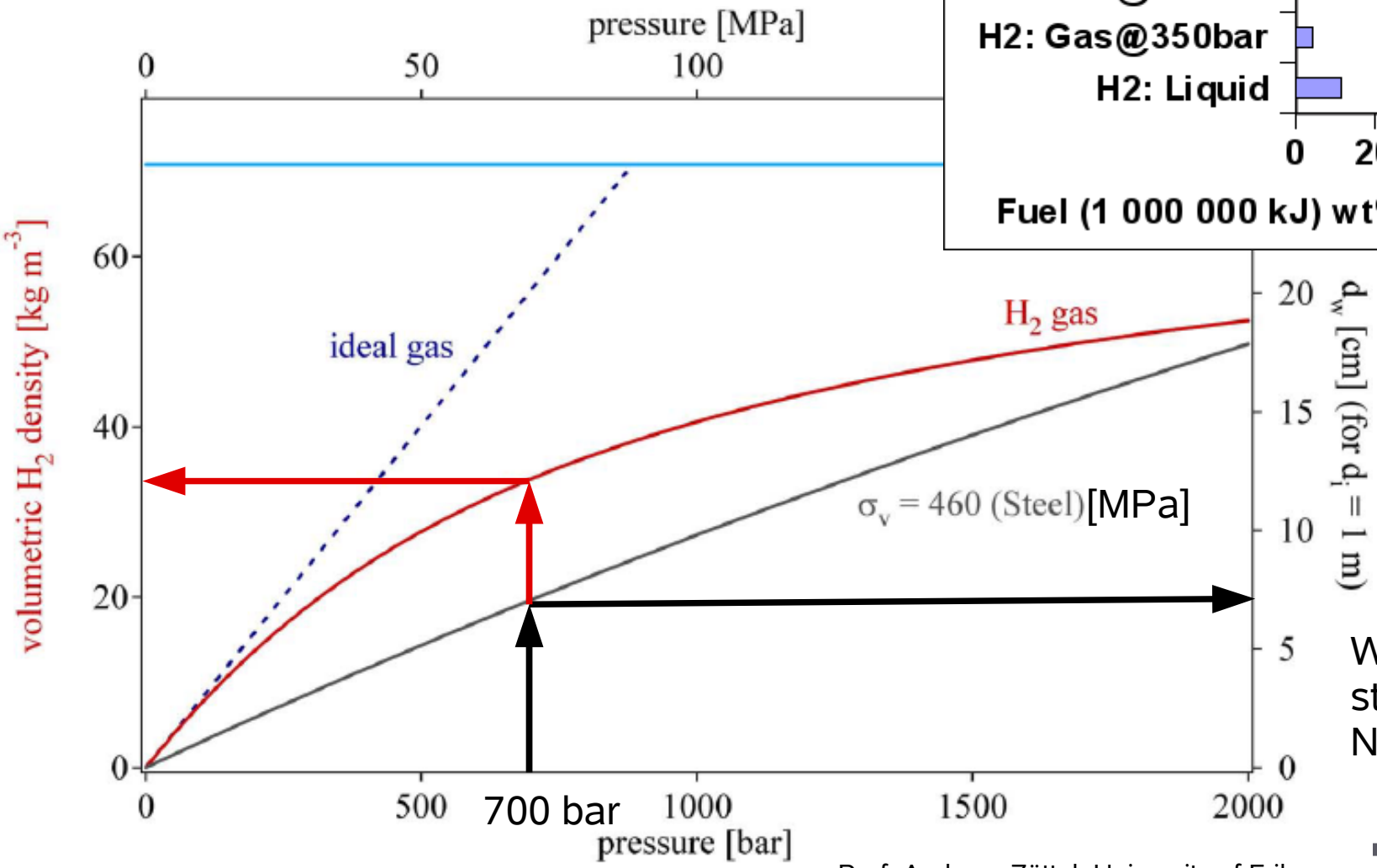
Why is hydrogen storage so troublesome?



W. B. Leung, N. H. March, and H. Motz, Primitive phase diagram for hydrogen, Physics Letters 1976, 56A(6), 425-426, as represented by Prof. Andreas Zuttel

Why is hydrogen storage so troublesome?





Hydrogen Fuel Cell Engines and Related Technologies, College of the Desert, Palm Desert, CA, USA

Wall thickness of the steel cylinder ~ 7 cm
NB: ρ ~ 7800kg/m3

Prof. Andreas Züttel, University of Fribourg

Why is hydrogen storage so troublesome?

Interaction of H2 with other materials

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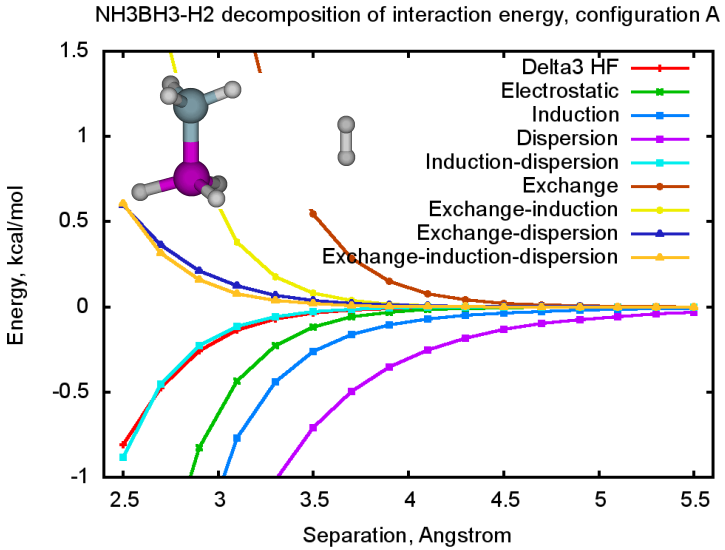
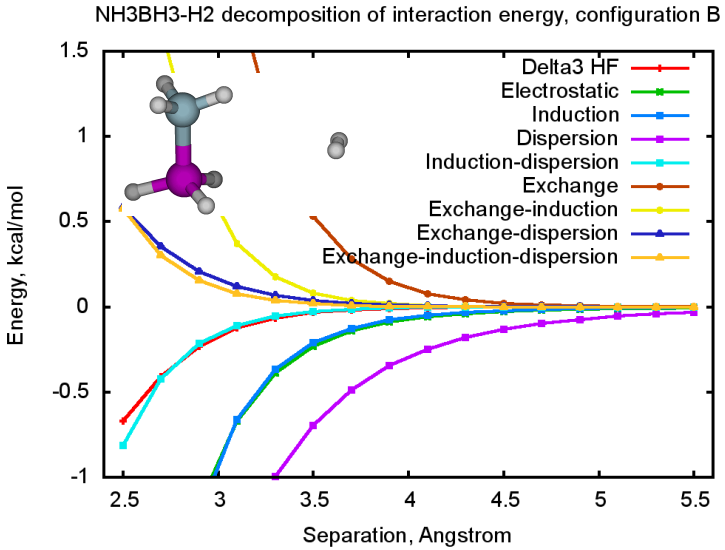
E_{min}	-0.503
elst+δHF	-0.297
exch	1.307
ind	-0.439
disp	-1.018
inddisp	-0.056





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elst+δHF	-0.455
exch	1.277
ind	-0.367
disp	-0.996
inddisp	-0.054

R_{min}	3.5
E_{min}	-0.418
elst+δHF	-0.158
exch	0.896
ind	-0.284
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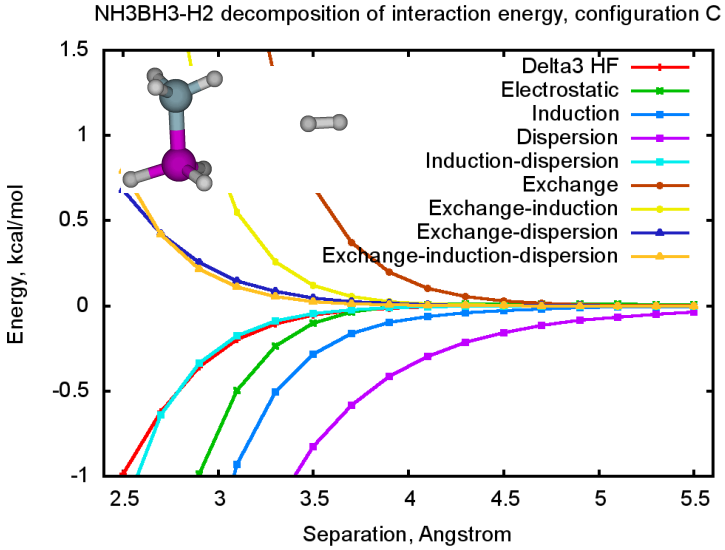
inddisp	-0.046



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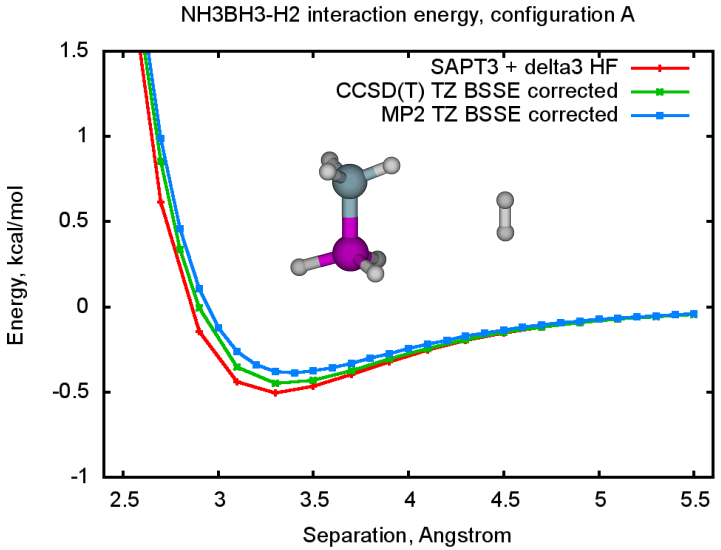

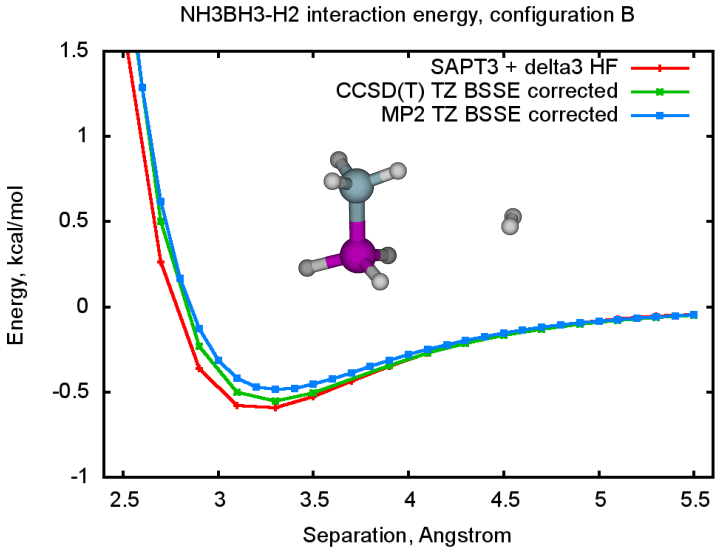

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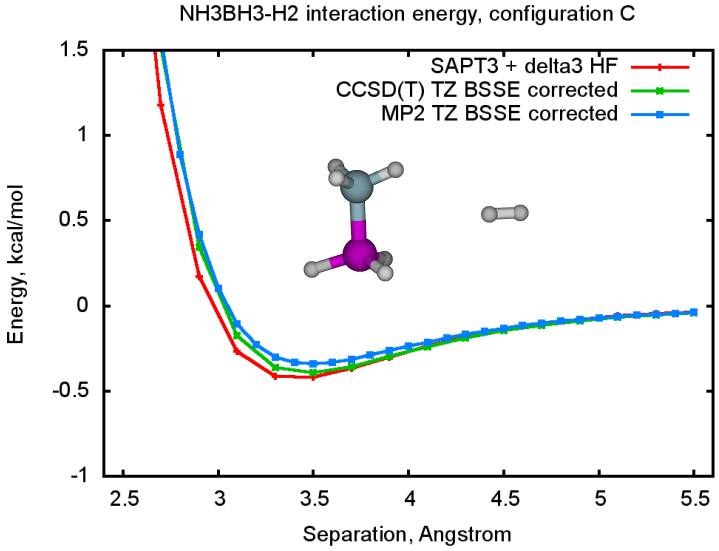


Homework 1

Assume that the phase change from H2 gas to H2 liquid happens when the kinetic energy of the gaseous species is counterbalanced by the potential energy of their interaction with the nearest neighbor. Neglect the zero point energy.

1) Calculate the interaction energy in three ways (i) as a simple average, (ii) as the weighted average over three configurations of H2 dimer and (iii) assuming that the Boltzmann distribution is valid.

2) Estimate the transition temperature (gas-liquid and liquid-solid) treating gaseous H2 as small spherical particles (three degrees of freedom) and as the diatomic gas (five degrees of freedom).

3) Compare your results with the phase diagram and discuss explicit and implicit assumptions made.

4) Assume that each hydrogen molecule is surrounded by a sphere of its own space radius of which could be found as the equilibrium distance between two interacting molecules (~3.5/2 Å). Calculate the density and compare it with the experimental value. Consider a cube instead of the sphere. To which phase the calculated density could correspond?

Optional: Evaluate effect of the zero point energy 1/2ħω, ω = √(V''/m). To find the second derivative of the potential V'' fit given curves for H2 dimer to some analytical form of the potentials, e.g. Lennard-Jones, Kihara.

Equilibrium energies of the three configurations of H2 dimer, kcal/mol:

A: -0.036
B: -0.047
C: -0.101

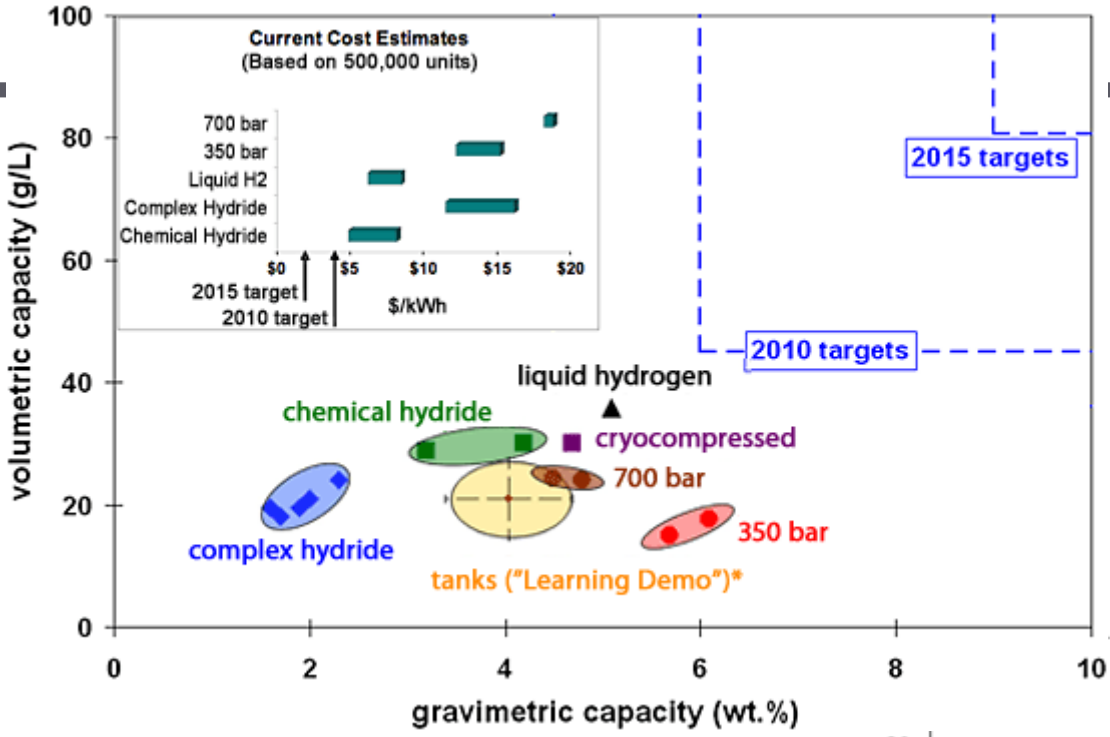
Translational kinetic energy of a particle and total internal energy for the diatomic gas:

$$\bar{E}_k = \frac{m v_{rms}^2}{2} = \frac{3}{2} kT \qquad U = \frac{5}{2} kT$$

Boltzmann factor:

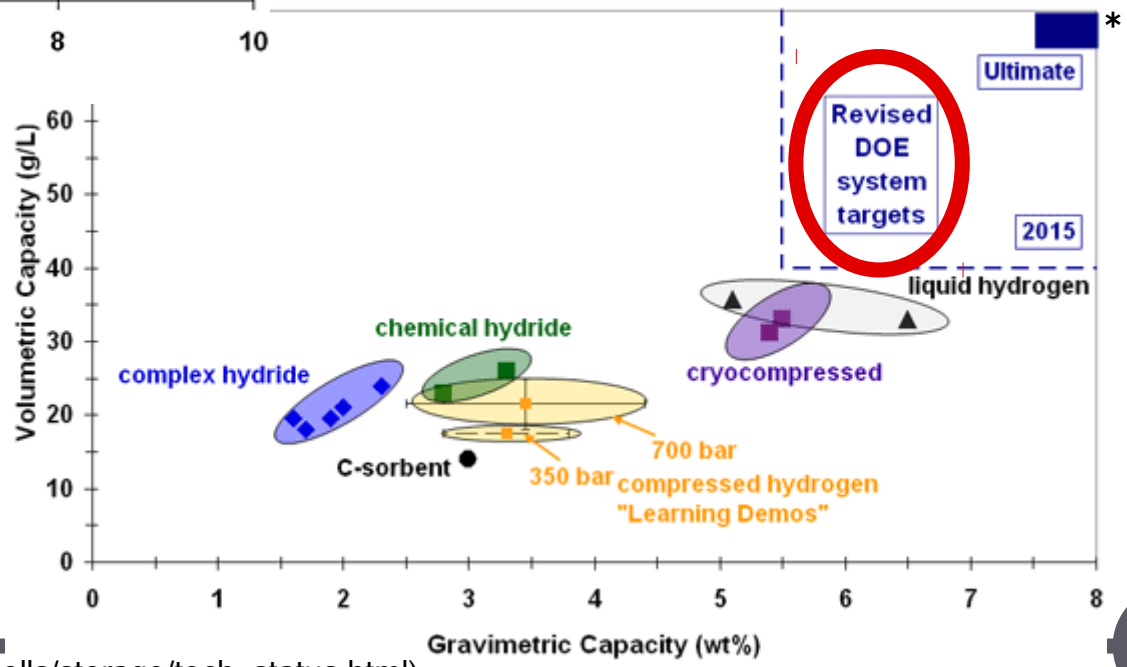
$$\frac{\exp\left(-\frac{E_i - E_{min}}{kT}\right)}{\sum_i \exp\left(-\frac{E_i - E_{min}}{kT}\right)}$$

Hydrogen storage targets



← Old

New →



*US DOE (http://www1.eere.energy.gov/hydrogenandfuelcells/storage/tech_status.html)

Metal hydrides

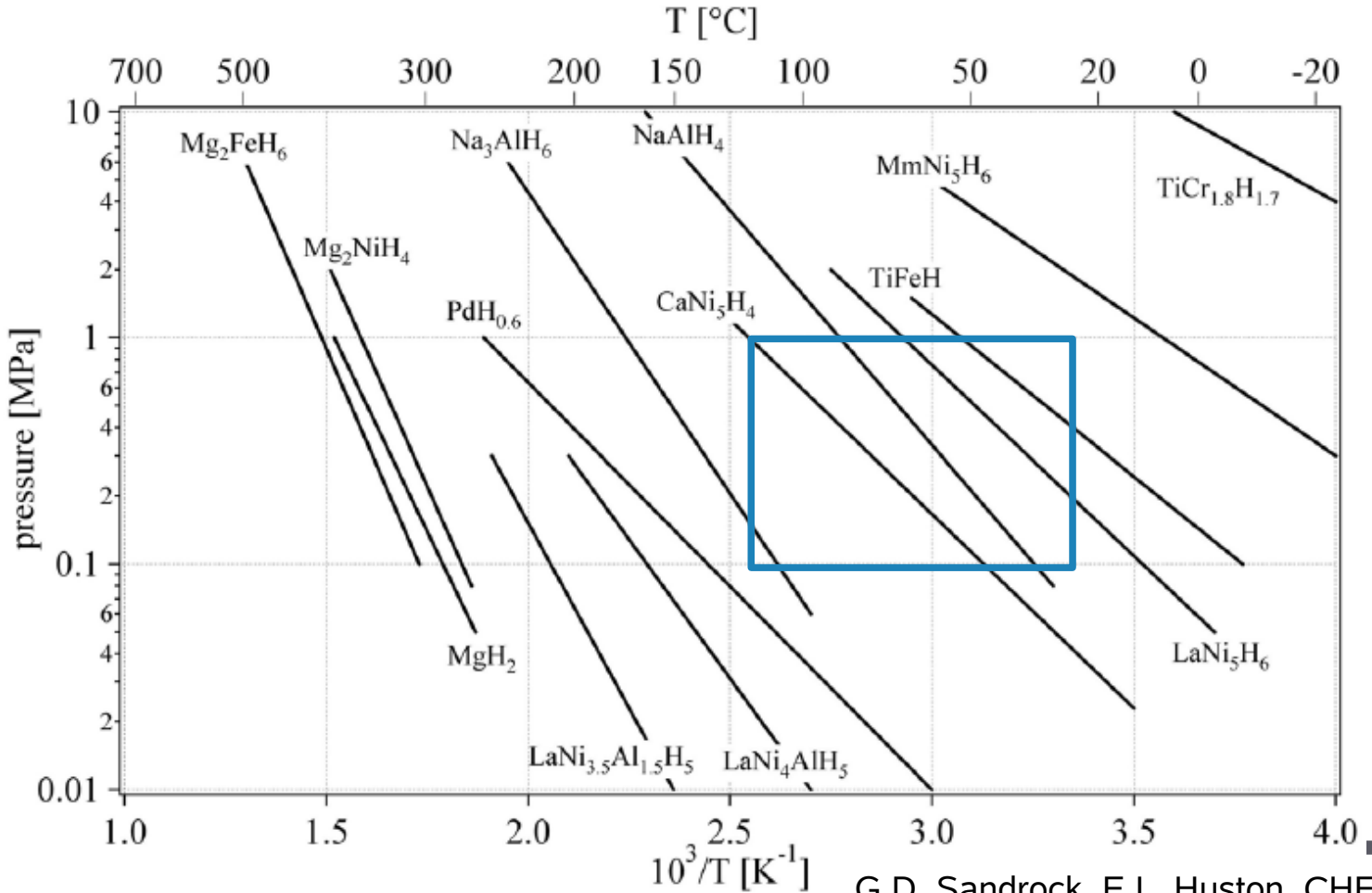
$M + H_2 \rightarrow MH_2$

ΔH = –(20...25) kJ/mol H2 : easy regenerable

ΔH = –(25...60) kJ/mol H2 : high performance heat exchangers

ΔH = –(60...100) kJ/mol H2 : off-board regeneration

In addition to thermal management issues a certain range of pressure (1...10 atm) and temperature (25...[70]...120°C) dictated by operating conditions of PEM fuel cells is required (best demonstrated by the Van't Hoff diagram).



Other classification:

1) Metal hydrides: reversible hydrogen storage and release via heating, possibility of on-board regeneration;

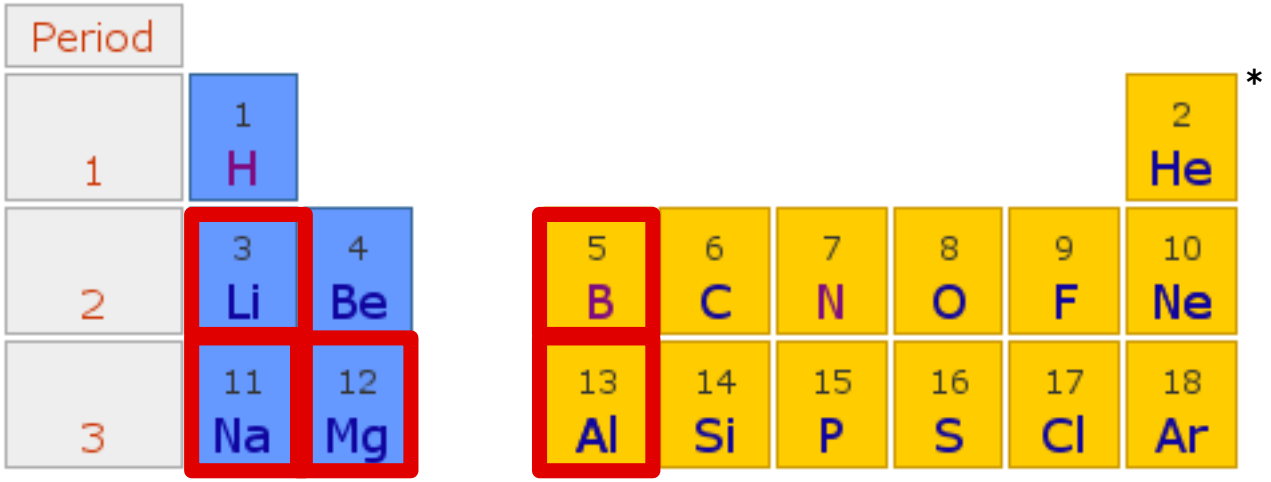
2) Chemical hydrides (or chemical hydrogen storage): hydrogen is released in chemical reaction with water (usually), off-board regeneration.

Gravimetric density of H_2!

G.D. Sandrock, E.L. Huston, CHEMTECH 11, p. 754 (1981)

Metal hydrides

Taking into account gravimetric density requirements (5.5 wt% according to revised DOE targets) one can easily exclude from consideration simple interstitial metal hydrides (FeTiH, $LaNi_5H_6$) and limit attention to the elements of the first three periods of the periodic table (Li, B, Na, Mg, Al).



*http://www.webelements.com/

Metal hydrides

- Promising metal hydride systems:
  - Complex aluminohydrides ($LiAlH_4$, $NaAlH_4$)
  - Lithium amide based hydride system ($LiNH_2$+MgH_2)
  - Destabilized metal hydrides ($LiBH_4$+MgH_2)
- Chemical storage systems:
  - Sodium borohydride ($NaBH_4$+H_2O)
  - Sodium hydride (NaH+H_2O)

Metal hydrides

The alanates (complex aluminohydrides)

Typical 3-step dehydrogenation mechanism

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2,$$

$$Li_3AlH_6 \rightarrow 3LiH + Al + \frac{3}{2}H_2,$$

$$3LiH \rightarrow 3Li + \frac{3}{2}H_2$$

Temperature required to complete the second step is 200ºC[1](7.9 wt% H2).

The first step is effectively irreversible due to extremely high equilibrium pressure of H2 (~10^4 bar).

$$3NaAlH_4 \leftrightarrow Na_3AlH_6 + 2Al + 3H_2,$$

$$Na_3AlH_6 \leftrightarrow 3NaH + Al + \frac{3}{2}H_2,$$

$$3NaH \rightarrow 3Na + \frac{3}{2}H_2$$

When catalyzed with Ti dopants[2]:

(**i**) the first reaction occurs at 1 atm and >33ºC releasing 3.7 wt% H2;

(**ii**) the second reaction occurs at >110ºC releasing 1.8 wt% H2;

(**iii**) The rehydrogenation conditions are 150 atm and 170ºC.

Issues: slow kinetics; low packing density of the powder (~50%); low practical density of H2 (4 wt%).

[1]Zaluski, L., Zaluska, A., and Strom-Olsen, J. O. Journal of Alloys and Compounds 290(1-2), 71-78 (1999)
[2]Bogdanovic, B. and Schwickardi, M. Journal of Alloys and Compounds 253-254, 1-9 (1997); Bogdanovic, B. and Schwickardi, M. Applied Physics A: Materials Science & Processing 72(2), 221-223 (2001)

Metal hydrides

Lithium amide based hydride system

$$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2$$

6.5 wt% can be stored reversibly at 1 atm and 285ºC[1].

$$2LiNH_2 + MgH_2 \leftrightarrow Li_2Mg(NH)_2 + 2H_2$$

Partial substitution of Li by Mg destabilizes amide/hydride system and lowers the reaction temperature to 200ºC[2]. 4.5 wt% of H2 can be stored reversibly.

Issues: high temperature of hydrogen release; ammonia contamination of hydrogen fuel (ISO standard <0.1 ppm).

[1]Chen, P., Xiong, Z., Luo, J., Lin, J., and Tan, K. L. Nature 420, 302 (2002); [2]Luo, W. Journal of Alloys and Compounds 381(1-2), 284 (2004)

Metal hydrides

Destabilized metal hydrides

$$LiBH_4 \rightarrow LiH + B + \frac{3}{2}H_2$$

For the reaction to proceed temperature of 400ºC is required at 1 atm.

$$LiBH_4 + \frac{1}{2}MgH_2 \leftrightarrow LiH + \frac{1}{2}MgB_2 + 2H_2$$

Addition of MgH2 in the presence of TiCl3 stabilizes the right side of the reaction or destabilizes its left side. The required temperature is reduced to 225ºC at 1 atm[1].

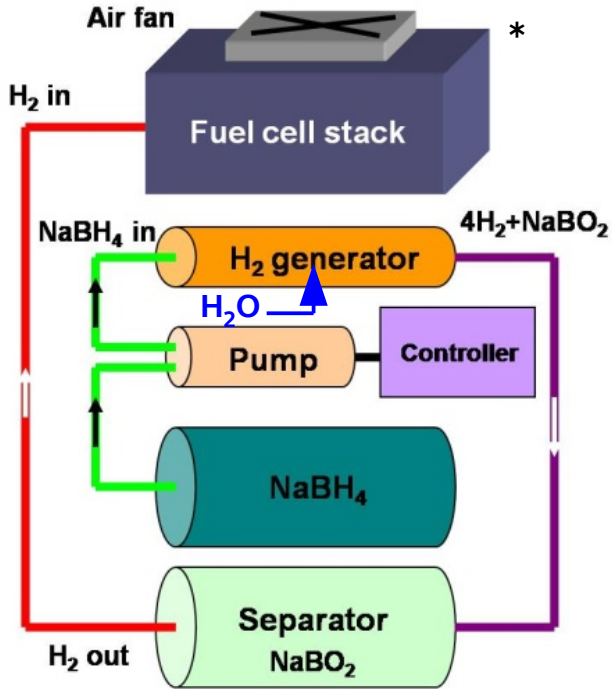
The reversible storage up to 10 wt% has been demonstrated.

Issues: high temperature of hydrogen release; slow kinetics.

[1]Vajo, J. J., Skeith, S. L., and Mertens, F. The Journal of Physical Chemistry B 109(9), 3719–3722 (2005)

Metal hydrides

Chemical hydrogen storage



*

$$NaBH_4 \rightarrow NaH + B + \frac{3}{2}H_2$$

The direct thermal decomposition of sodium tetrahydridoborate requires temperatures of >400ºC and results in 10.6 wt% of H2

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$$

A hydrolysis reaction of the hydride with water which is controlled by pH and use of catalysts proceeds even at temperatures close to 0ºC[1]. A non-catalytic process is possible with application of steam[2,3].

One half of the released hydrogen is due to water and low concentrations of $NaBH_4$ are used to prevent precipitation of $NaBO_2$.

Issues: practical storage capacity is only 4 wt% H2; sodium metaborate $NaBO_2$ can only be regenerated off-board with required energy of 900 kJ/mol[4].

[1]Ai-Jen Hung, Shing-Fen Tsai, Ya-Yi Hsu, Jie-Ren Ku, Yih-Hang Chen and Cheng-Ching Yu, International Journal of Hydrogen Energy, 33(21), 6205-6215 (2008)

[2]Ingersoll, J., Mani, N., Thenmozhiyal, J., and Muthaiah, A. Journal of Power Sources 173(1), 450-457 (2007)

[3]Marrero-Alfonso, E. Y., Gray, J. R., Davis, T. A., and Matthews, M. A. International Journal of Hydrogen Energy 32(18), 4717-4722 (2007)

[4]Felderhoff, M., Weidenthaler, C., von Helmolt, R., and Eberle, U. Physical Chemistry Chemical Physics 9, 2643-2653 (2007)

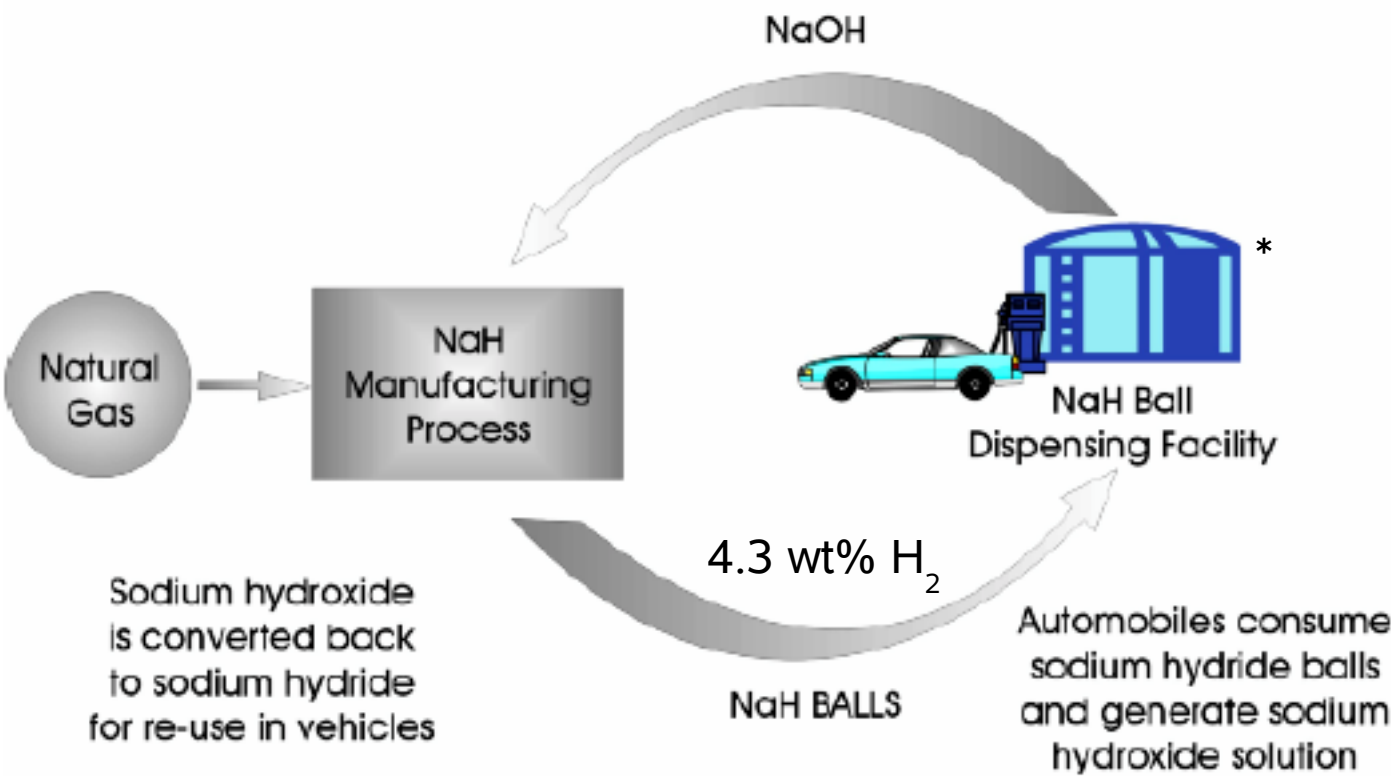
*http://rocket.kaist.ac.kr/diafice/FCUAV.files/slide0001.htm

Metal hydrides

Sodium hydride based H_2 storage and delivery system

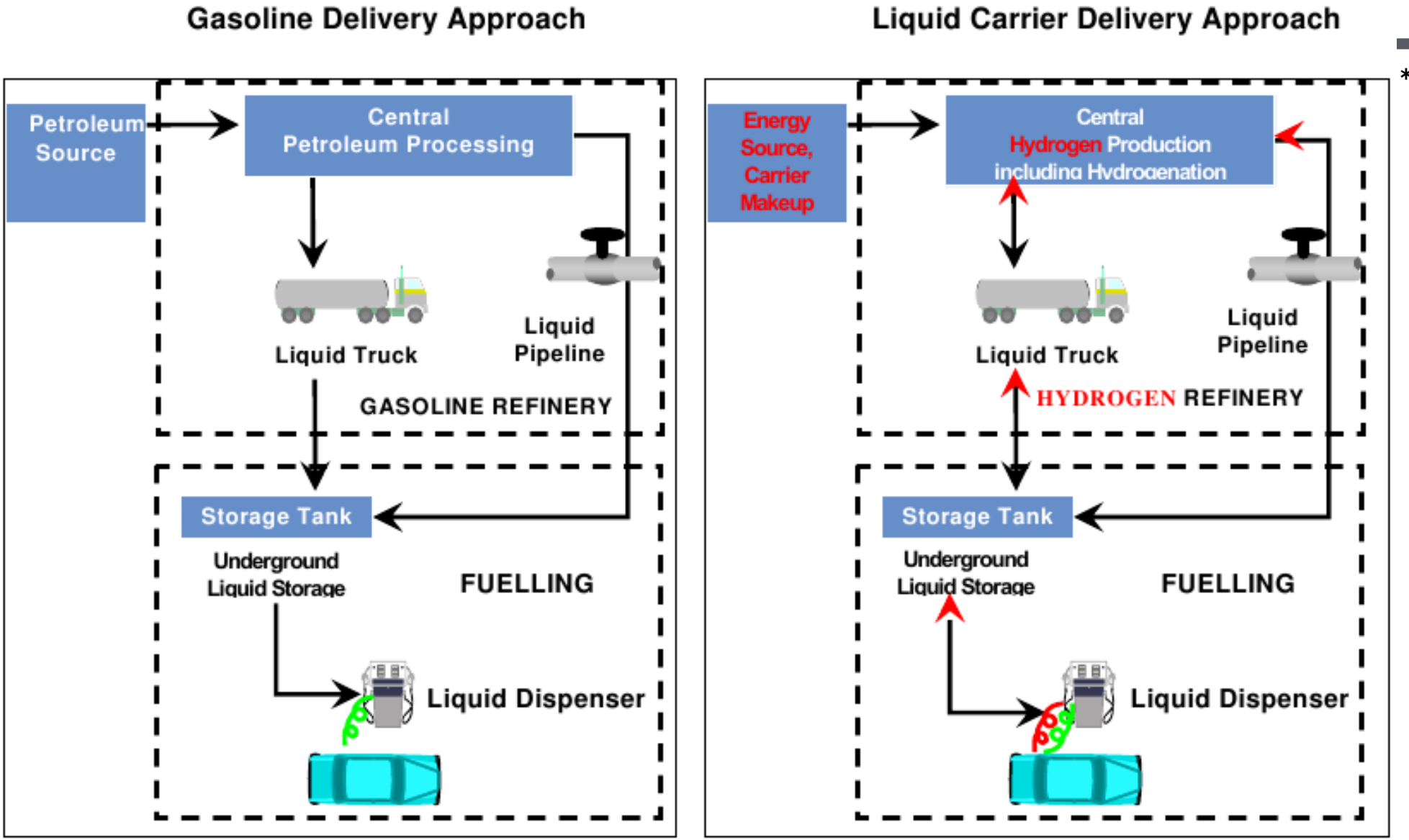
$$2\ NaOH + Heat \rightarrow 2\ NaH + O_2$$

$$NaH\ (solid) + H_2O\ (liquid) \rightarrow NaOH\ (liquid) + H_2\ (gas)$$



*Proceedings of the 2000 US DOE Hydrogen Program Review

Organic liquid carrier



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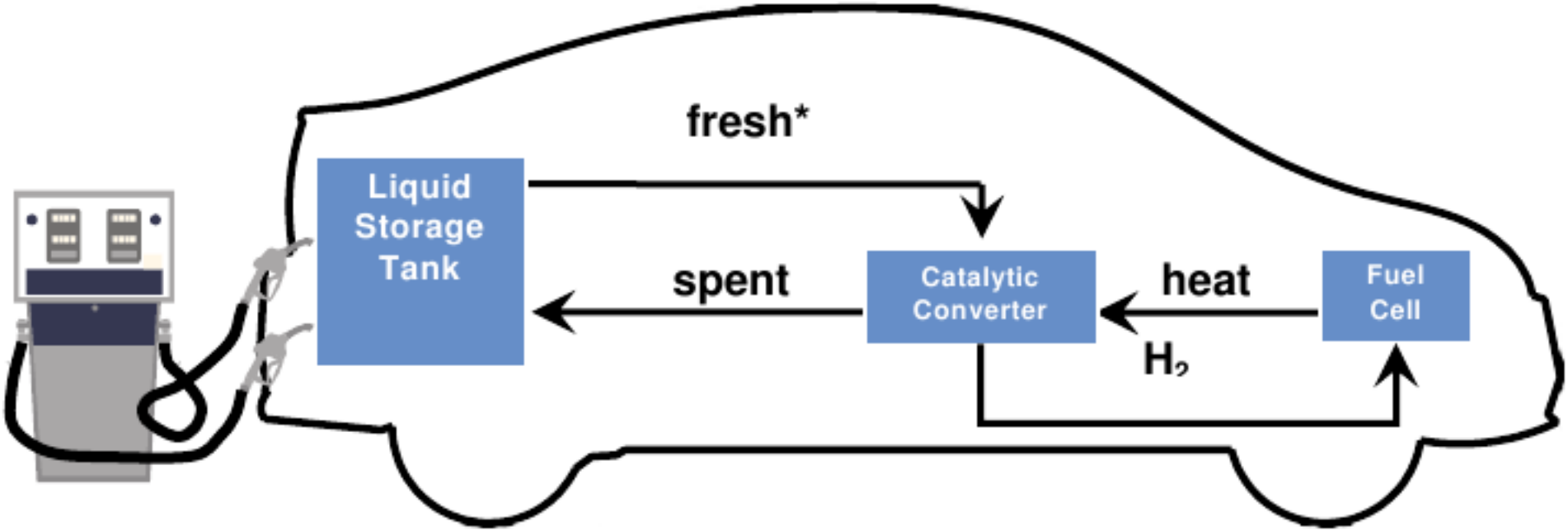
*A.C. Cooper, K.M. Campbell, G.P. Pez, Air Products and Chemicals Inc., World Hydrogen Energy Conference (WHEC) 16, 13-16 June 2006, Lyon, France

Organic liquid carrier



*A.C. Cooper, K.M. Campbell, G.P. Pez, Air Products and Chemicals Inc., World Hydrogen Energy Conference (WHEC) 16, 13-16 June 2006, Lyon, France

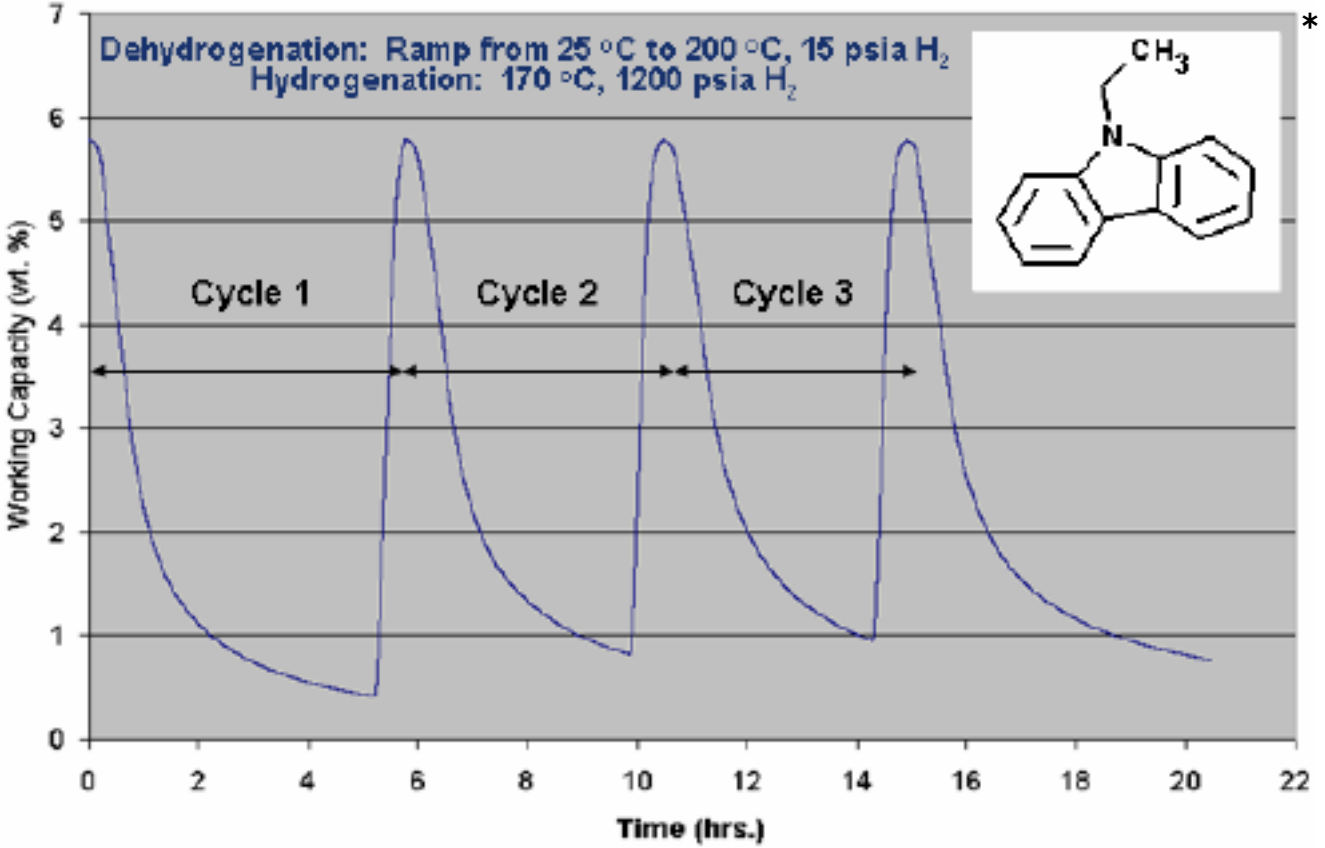
Organic liquid carrier

N-ethylcarbazole in a stirred tank reactor system

e.g. perhydro-N-ethylcarbazole

e.g. N-ethylcarbazole

$$LQ^*H_2 + \text{heat } (\Delta H) \underset{P > 50 \text{ atm.}}{\overset{\text{Catalyst}\ P < 10 \text{ atm.}}{\rightleftharpoons}} LQ + H_2$$



Somewhat <u>systematic tuning of the enthalpy of the hydrogenation</u> is possible via:

(**1**) Change of number of rings of polyaromatic hydrocarbons;

(**2**) Nitrogen substitution.

*A.C. Cooper, K.M. Campbell, G.P. Pez, Air Products and Chemicals Inc., World Hydrogen Energy Conference (WHEC) 16, 13-16 June 2006, Lyon, France

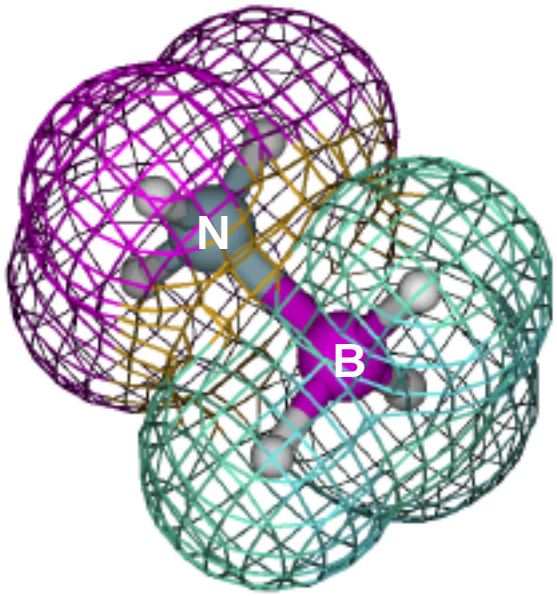
Homework 2

- Calculated weight and volume of FeTiH (5880 kg/m^3) required to store 4 kg of H2.
- Given that the price of Lanthanum is $5/g* estimate the price of La in $LaNi_5H_6$ required to store 4 kg of H2.
- Estimate amount of heat to be dispersed by a heat-exchanger in 5 min of the refueling process given by M + H2 → MH2. Take 4 kg as the amount of fuel and assume ΔH = -40 kJ/mol H2. Compare your results with performance of an average air conditioner (cooling power ~3.5 kW).

*http://periodic.lanl.gov/elements/57.html

Ammonia Borane (AB, NH_3BH_3)

General information



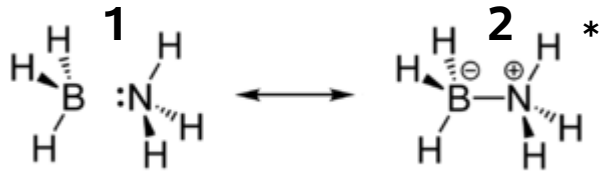
B-N, Å:	1.67
N-H, Å:	1.02
B-H, Å:	1.21
BNH, deg:	111
NBH, deg:	105

- Excellent gravimetric density of hydrogen (19.6 wt%)
- Release of hydrogen below 85ºC, although slowly
- Dipole moment 5.2 D (cf. water 1.85 D)
- Isoelectronic with ethane but forms molecular solid at ambient conditions
- Melts at 114ºC (ultra-pure material melts at 125ºC[1])

[1]Stephens, F. H., Pons, V., and Baker, R. T. Dalton Transactions (25), 2613-2626 (2007)

Ammonia borane
Molecular structure

- Donor-acceptor complex bound by a dative bond
- Bond strength is ~ the average of covalent and van der Waals bonds
- The complex can be described by two resonance structures



1. No bond exists between the BH3 and NH3 moieties. The nitrogen lone pair completely retains in the amine moiety. Interactions between NH3 and BH3 are of van der Waals type.

2. The nitrogen lone pair in NH3 is equally shared by the acceptor BH3 and forms a typical covalent (dative) bond.

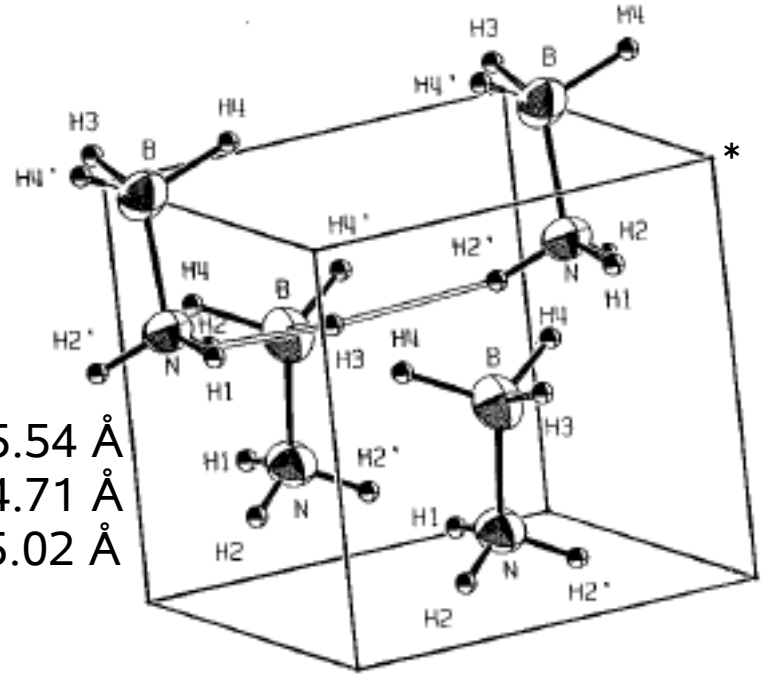
The complex is a linear combination of the no-bond and dative structures, with less importance of the latter ionic structure.

The BN bond strength is 31 kcal/mol, about 1/3 of the bond in ethane.

*Mo et al., J. Am. Chem. Soc. 2004, 126, 3974-3982

Ammonia borane

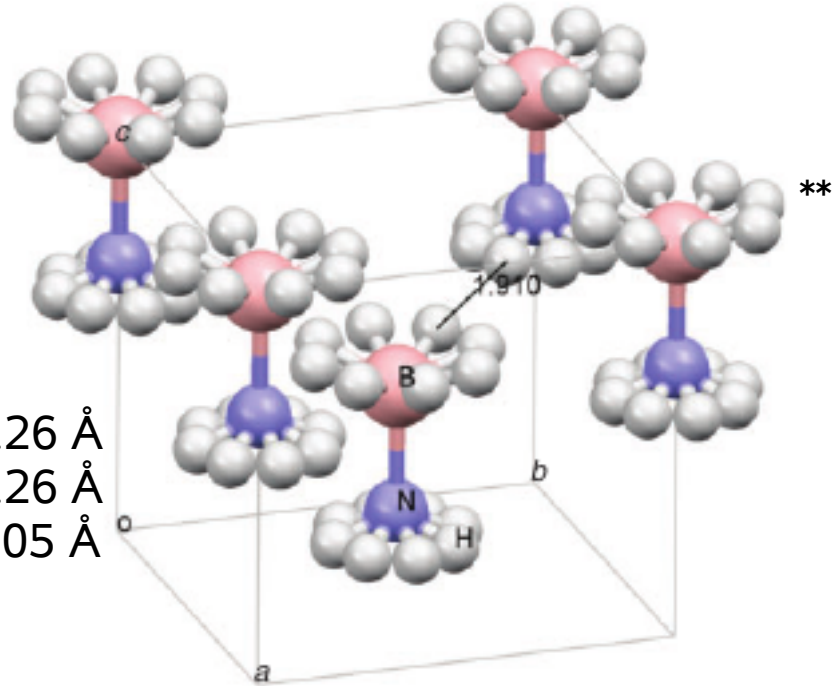
Crystal structure (ambient pressure)



*

a: 5.54 Å
b: 4.71 Å
c: 5.02 Å

Transition temperature ~220K



**

a: 5.26 Å
b: 5.26 Å
c: 5.05 Å

1) The orthorhombic phase ($Pmn2_1$)

The shortest H...H contacts (H2-H3, 2.02 Å) are smaller than the sum of the van der Waals radii 2.4Å.

2) The tetragonal phase (I4mm)

At high temperature hydrogen atoms orbit around B and N atoms.

– The BN bond length in the crystal (1.58 Å) is significantly shorter than that in the gas phase (1.67 Å) due to cooperative dipole-dipole interactions.

– The crystal is stabilized by unconventional dihydrogen bonds where the NH proton interacts with the BH bond as a whole.

*Klooster et al., J. Am. Chem. Soc., 121(27), 6337, 1999; **Bowden et al., Aust. J. Chem., 60, 149, 2007

Ammonia borane
Dehydrogenation (solid state)

$H_3N{-}BH_3 \longrightarrow 1/x\,(H_2N{-}BH_2)_x + H_2$ **~125ºC**

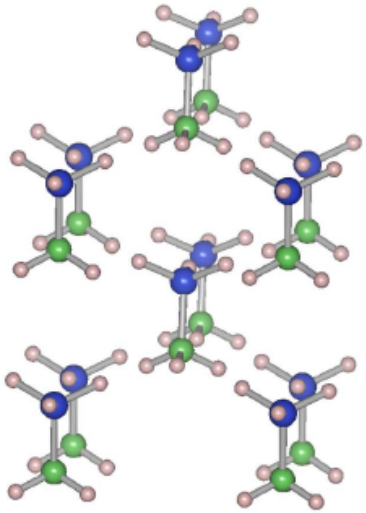
$(H_2N{-}BH_2)_x \longrightarrow (HN{-}BH)_x + x\,H_2$ **150-200ºC**

$(HN{-}BH)_x \longrightarrow x\,BN + x\,H_2$ **>1200ºC**

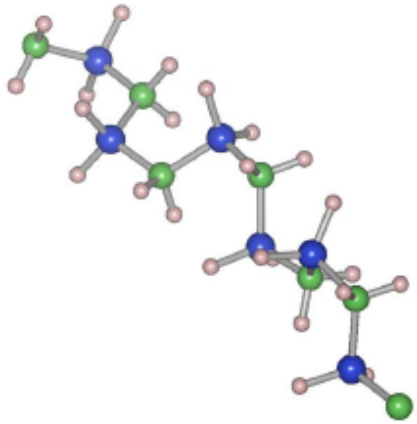
Could be divided into **polymeric** and **cyclic** routes

$(HN{-}BH)_x$ = polyiminoborane, borazine, polyborazine, cross-linked materials, mostly poorly defined and characterized

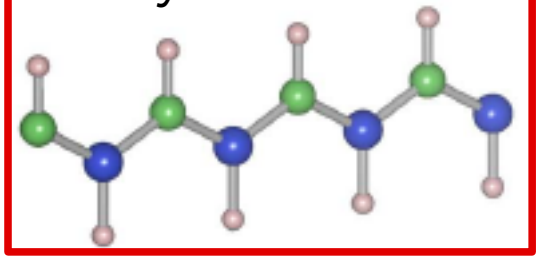
Ammonia borane



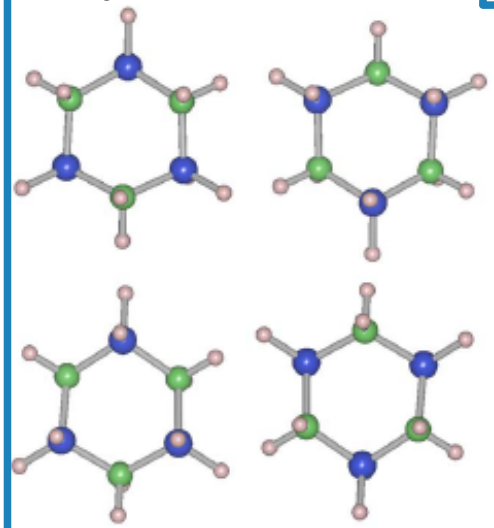
Polyaminoborane



Polyiminoborane

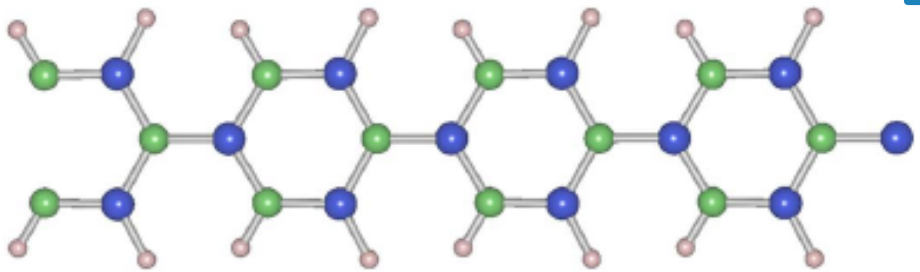


Cyclotriborazane

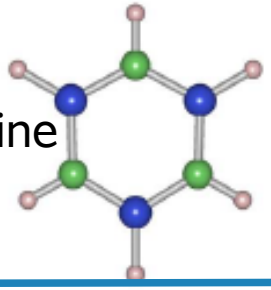


The term Polyborazine refers to all polymers containing borazinic rings B_3N_3

Polyborazylene



Borazine

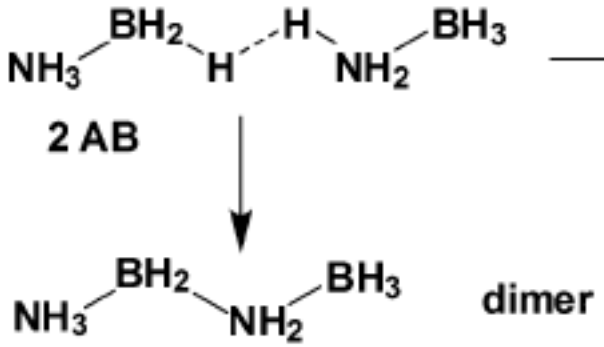


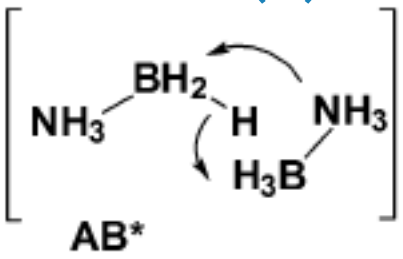
Staubitz et al., Chemical Reviews, 2010, 110(7); C.R. Miranda and G. Ceder, J. Chem. Phys. 126, 2007, 184703

Ammonia borane

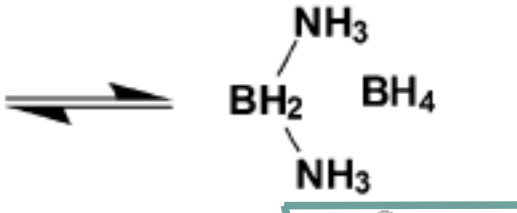
Dehydrogenation (solid state)

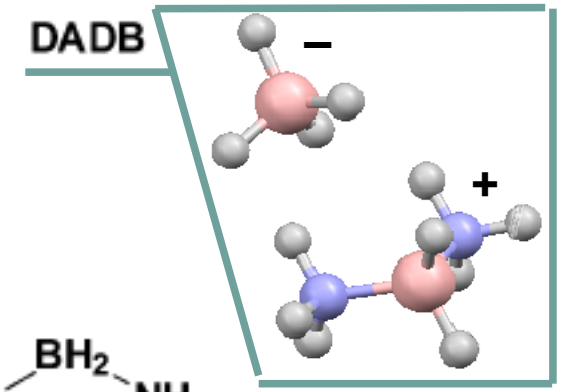
(1) Induction: Disruption of dihydrogen bonding



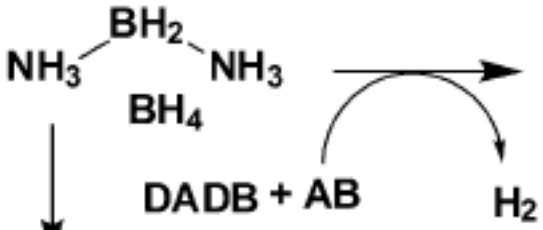


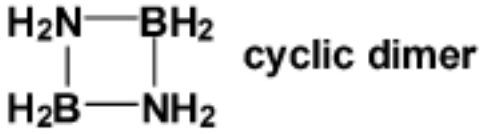
(2) Nucleation: Formation of DADB

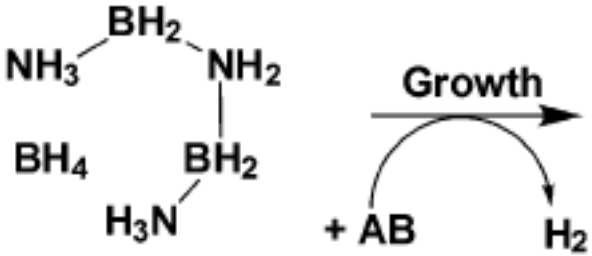


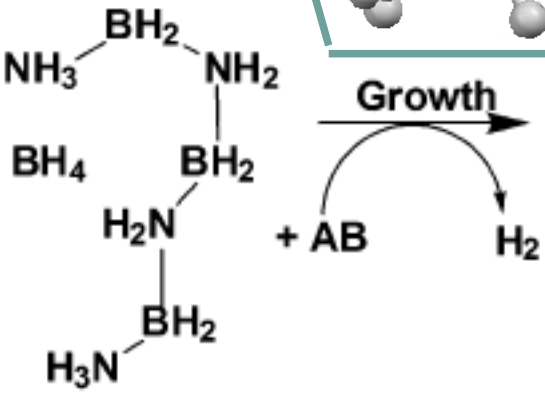


(3) Growth: Reaction of DADB with AB





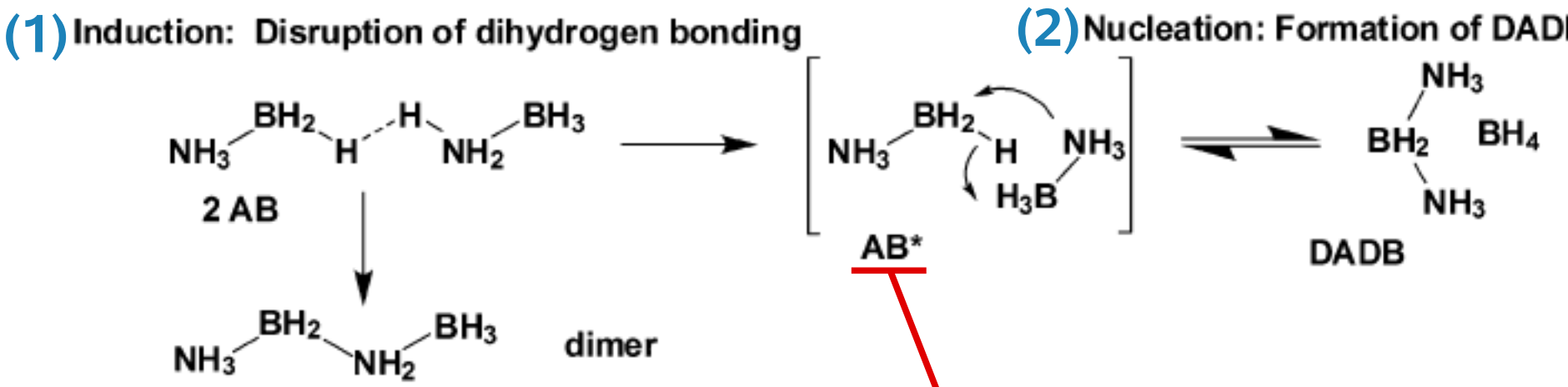




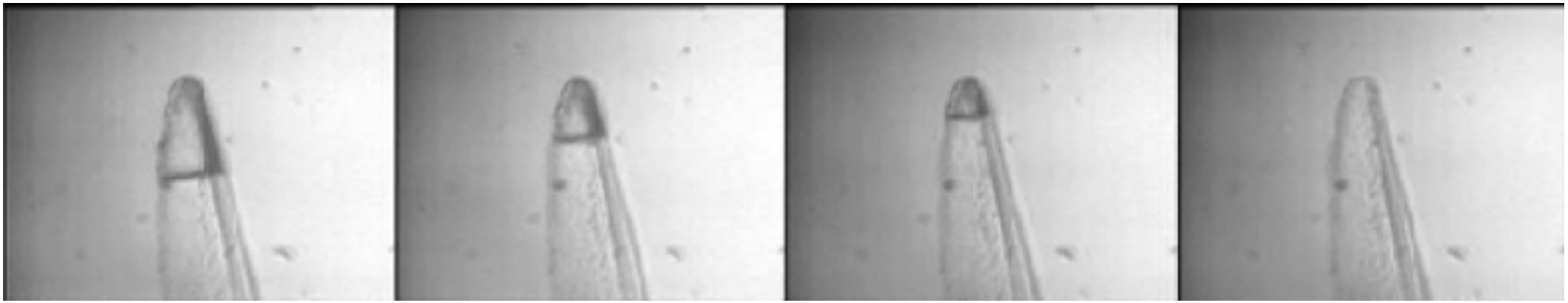
Stowe et al., Phys. Chem. Chem. Phys., 2007, 9, 1831

Ammonia borane

Dehydrogenation (solid state)



Visualization of the formation of a new mobile phase AB* (the induction)

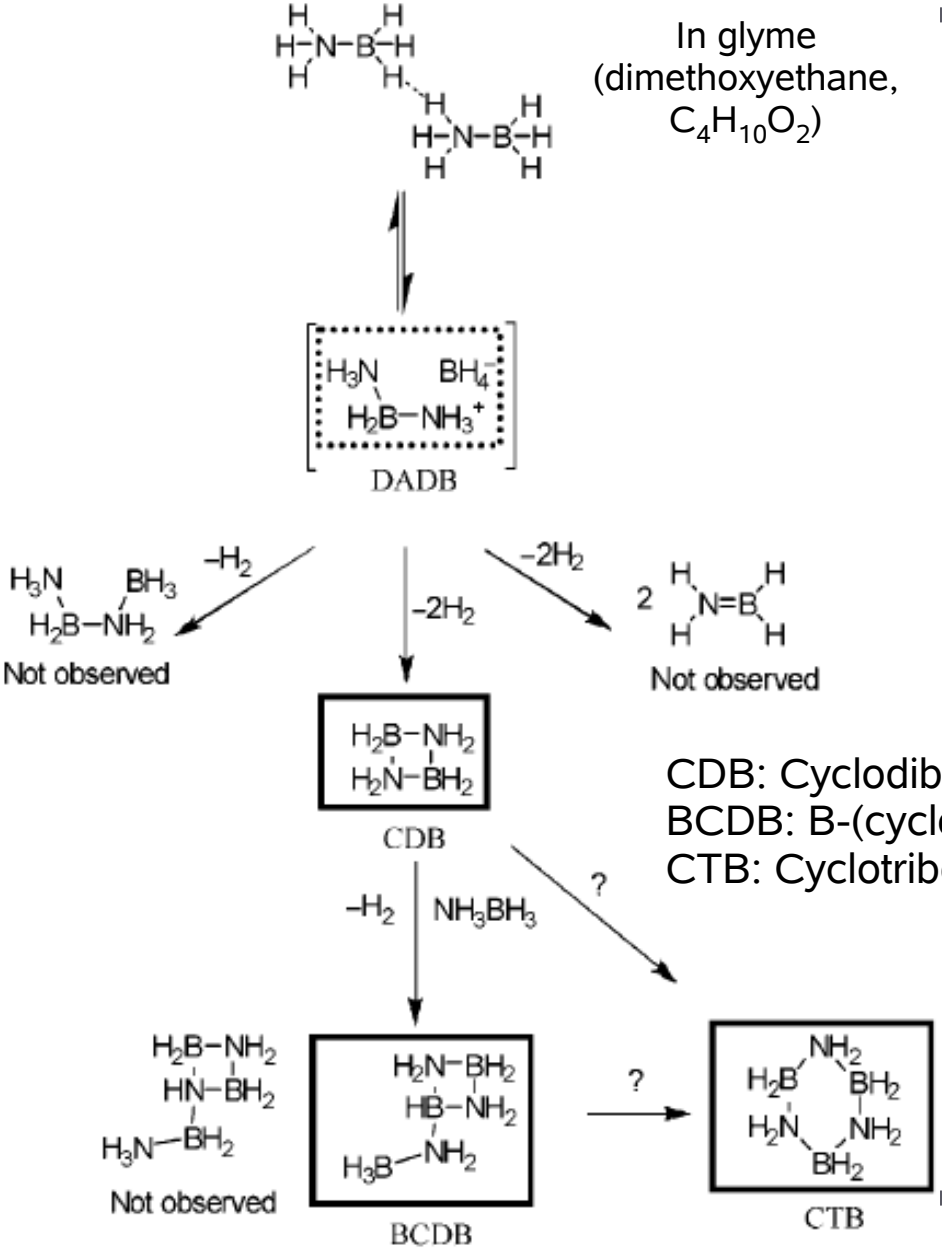


Optical micrograph images of a single crystal of AB heated to 90°C showing a traveling phase front.

Heldebrant et al., Chem. Mater., 2008, 20, 5332.

Ammonia borane

Dehydrogenation (in solution and hydrolysis)



AB undergoes rapid **hydrolysis** when added to an acidic solution:

$$H_3NBH_3 + H^+ + 3H_2O \rightarrow 3H_2 + B(OH)_3 + NH_4^+$$

H^+ interacts with the nitrogen atom, resulting in formation of $NH4^+$ and release of BH_3 which is rapidly hydrolyzed.

CDB: Cyclodiborazane;
BCDB: B-(cyclodiborazanyl)aminoborohydride;
CTB: Cyclotriborazane.

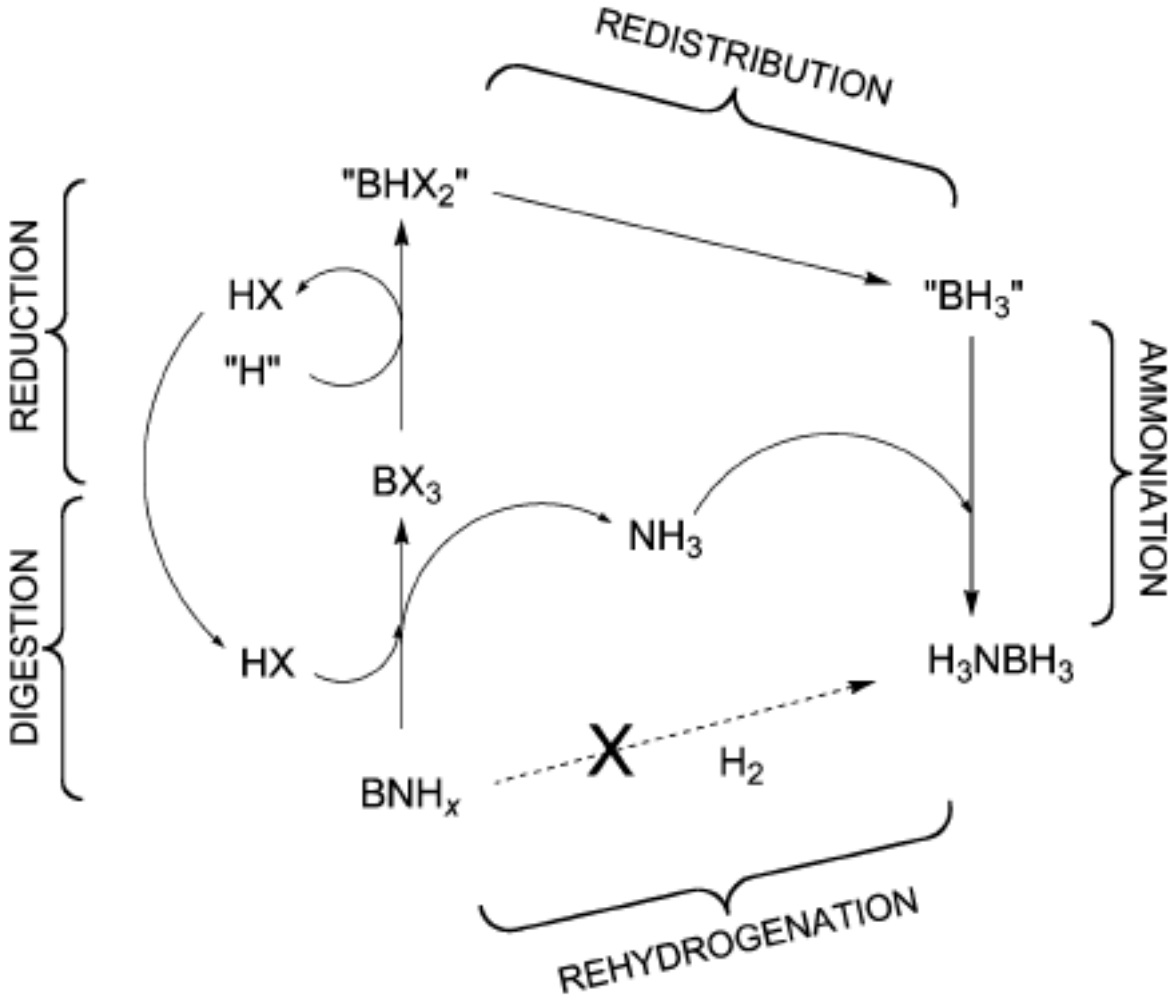
Shaw et al., Angew. Chem. Int. Ed., 47, 7493, 2008;
F.H. Stephens, V. Pons, R.T. Baker, Dalton Trans., 2613-2626, 2007

Ammonia borane
Regeneration

For the regeneration it is important to note that:

The **hydrolysis reaction** to form $B(OH)_3$ (**$\Delta H = -227$ kJ/mol**) is much more exothermic than the **dehydrogenation reaction** to form $[B_3N_3H_4]_n$ (**$\Delta H \leq -60.8$ kJ/mol**)

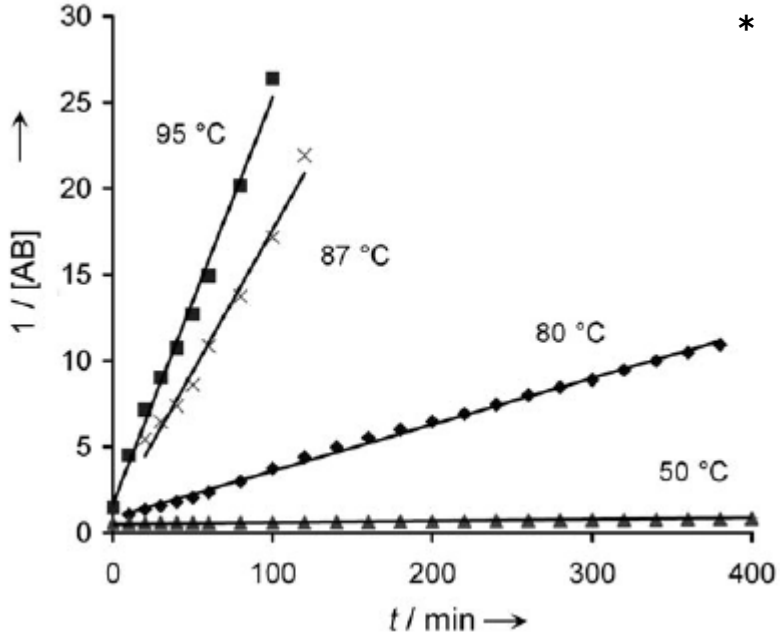
Trifluoroacetic acid (CF_3COOH) treatment to form $B(OOCCF_3)_3$



F.H. Stephens, V. Pons, R.T. Baker, Dalton Trans., 2613-2626, 2007

Homework 3

- Experimental dependence of the concentration of AB ([AB], mol/L) in glyme upon time is given in the figure
- Integrate the rate laws (below) of the 0th, 1st, and 2nd orders
- From the integrated rate laws, using the diagram, determine the order of the thermal decomposition reaction of AB in the solution
- Suggest how to determine the initial concentration $[AB]_0$ and the rate constant *k*
- Discuss practical implications of the order of this reaction (dehydrogenation temperature, kinetics)



*

$$-\frac{d[AB]}{dt} = k \qquad -\frac{d[AB]}{dt} = k[AB] \qquad -\frac{d[AB]}{dt} = k[AB]^2$$

*Shaw et al., Angew. Chem. Int. Ed., 47, 7493, 2008

Storage of hydrogen in materials

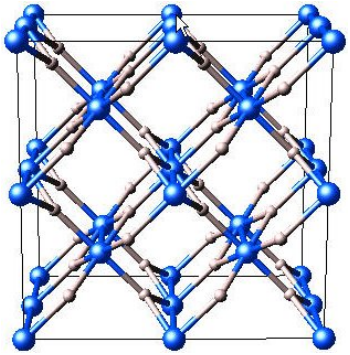
Instead of a summary

- Strong binding (e.g. metal hydrides) means high operating temperature of hydrogen release and frequently slow kinetics at lower temperatures

- Weak binding (MOF's, carbon nanotubes, hydrogen hydrates) provides poor gravimetric and volumetric density but hydrogen is easily accessible

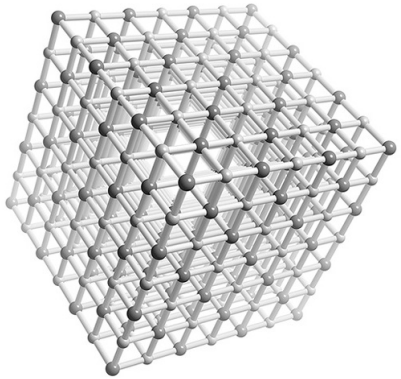
Strong binding: often high hydrogen content and poor kinetics

Magnesium hydride (MgH_2)



http://www.materialsdesign.com/mgh2_heat_of_formation.htm

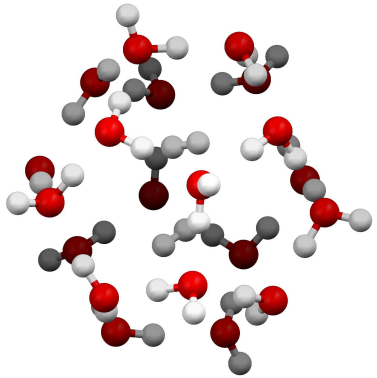
Lithium hydride (LiH)



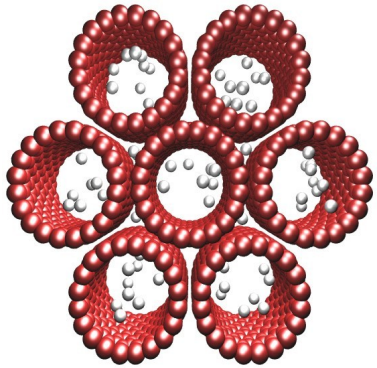
http://www.3dchem.com/inorganicmolecule.asp?id=373

Weak binding: small amount of easily accessible hydrogen

Hydrogen hydrates



Single-walled carbon nanotubes



http://www.nanotechnologies.qc.ca/projets/hydrogene/

Acknowledgments

- Anja Kobel, Heriot-Watt University, UK
  - Molecular structure of AB