OVERVIEW OF STATE-OF-THE-ART IN HYDRIDES

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- MgH_2, AlH_3
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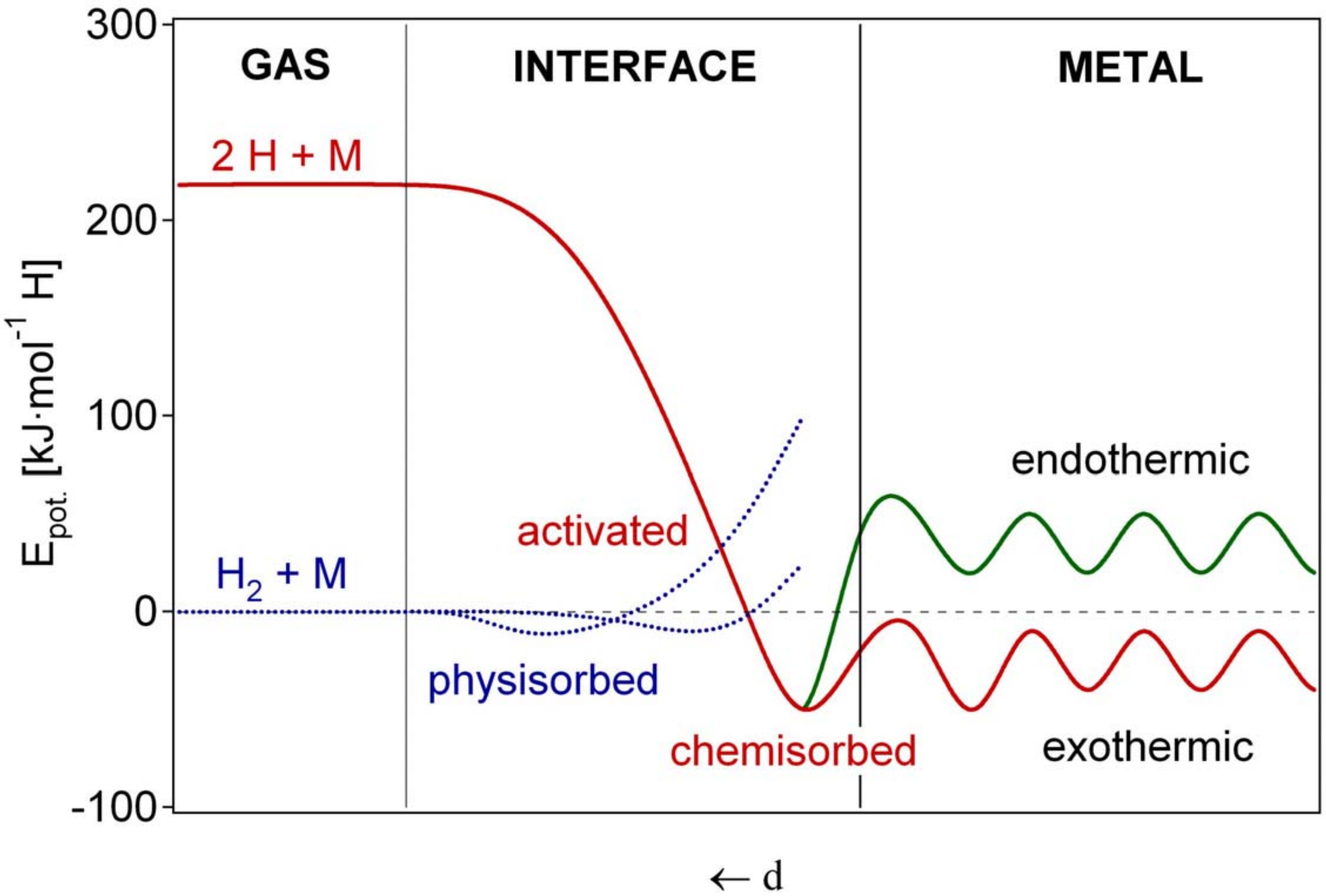
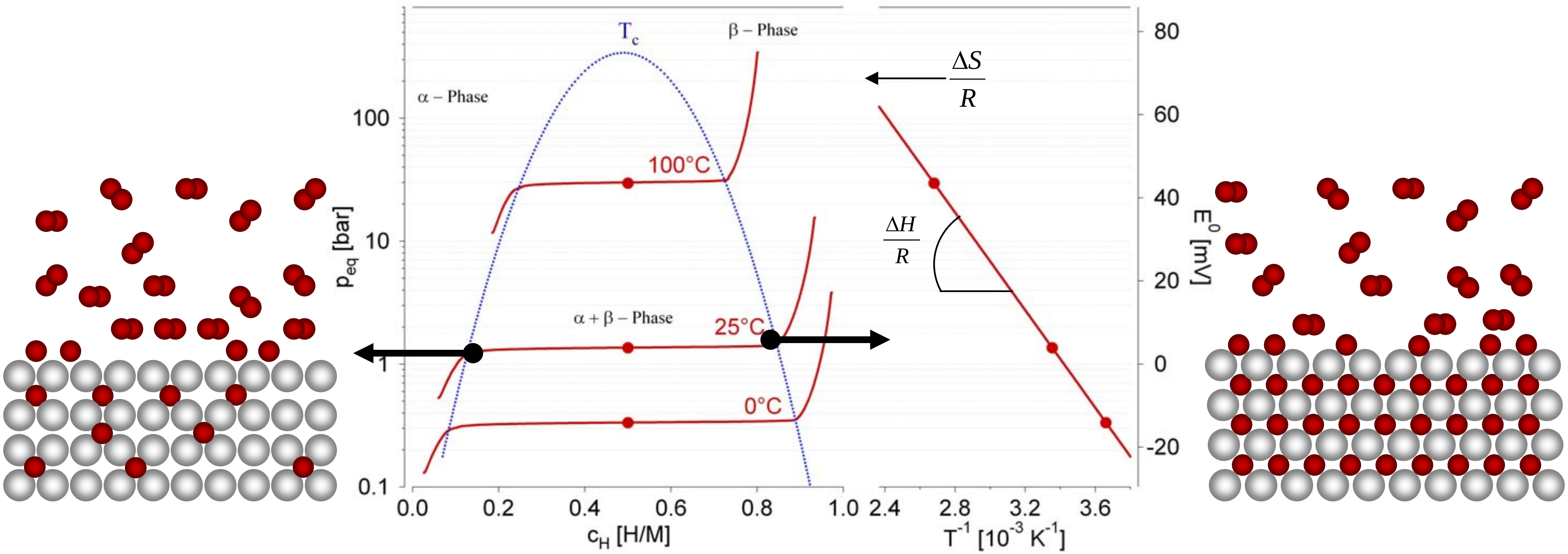
LENNARD-JONES POTENTIAL



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.

HYDROGEN ABSORPTION IN METALS



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

α-Phase: Solid Solution

MH_x $(0 < x < 0.1)$

~~H ↔ H~~, $\Delta V/V = k \cdot c_H$

β-Phase: Hydride Phase

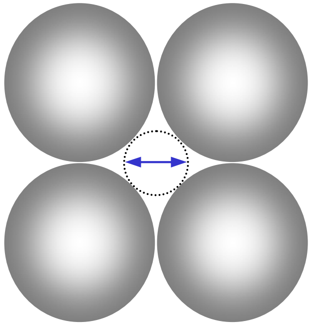
MH_x $x = \{1, 2, 3, \ldots\}$

H ↔ H

EMPIRICAL MODELS: GEOMETRY

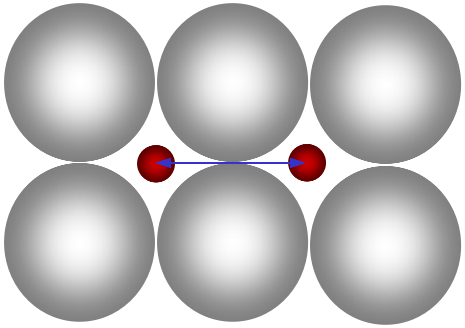
1) **Size of interstitial site:**

$r > 0.37$ 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

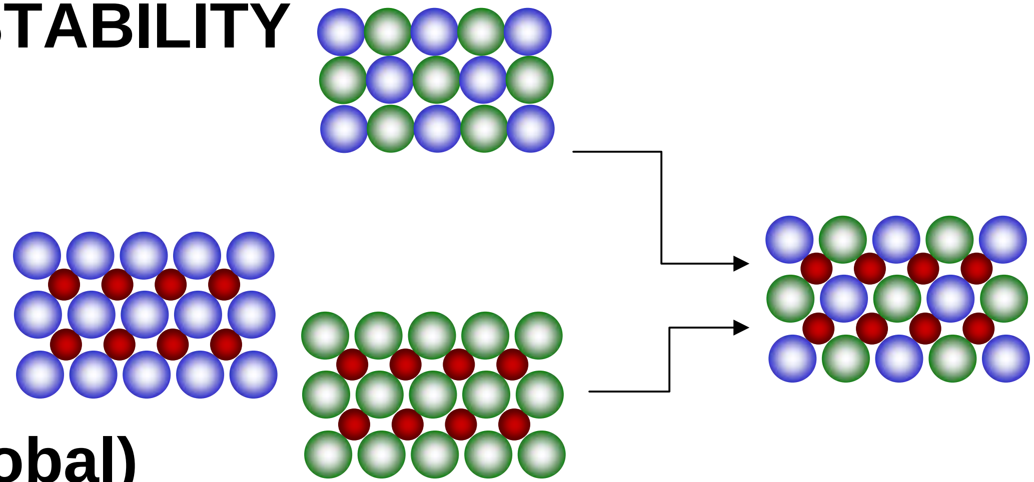
Ref.: A. C. Switendick, Z. Phys. Chem. N.F. 117 (1979), pp. 89

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

Number of hydrogen atoms:

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

EMPIRICAL MODELS: STABILITY

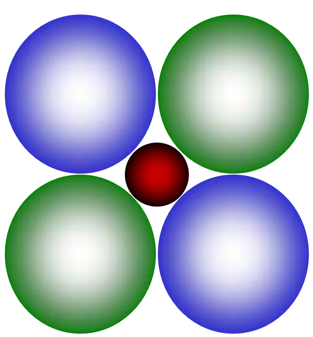


1) **Reversed stability (global)**

$$\Delta H(AB_nH_{2m}) = \Delta H(AH_m) + \Delta H(B_nH_m) - (1-F)\cdot\Delta H(AB_n)$$

Miedema Model

Ref.: H.H. Van Mal, K.H.J. Buschow and A.R. Miedema, J. Less-Common Met. 35 (1974), pp. 65



2) **Imaginary binary hydrides (local)**

$$A_mB_n + xH \rightarrow (A_mB_nH_x)$$

interstitial site

$$\Delta H([A_aB_b]H) = \Delta H(A_mH_{x\cdot a/(a+b)}) + \Delta H(B_nH_{x\cdot b/(a+b)})$$

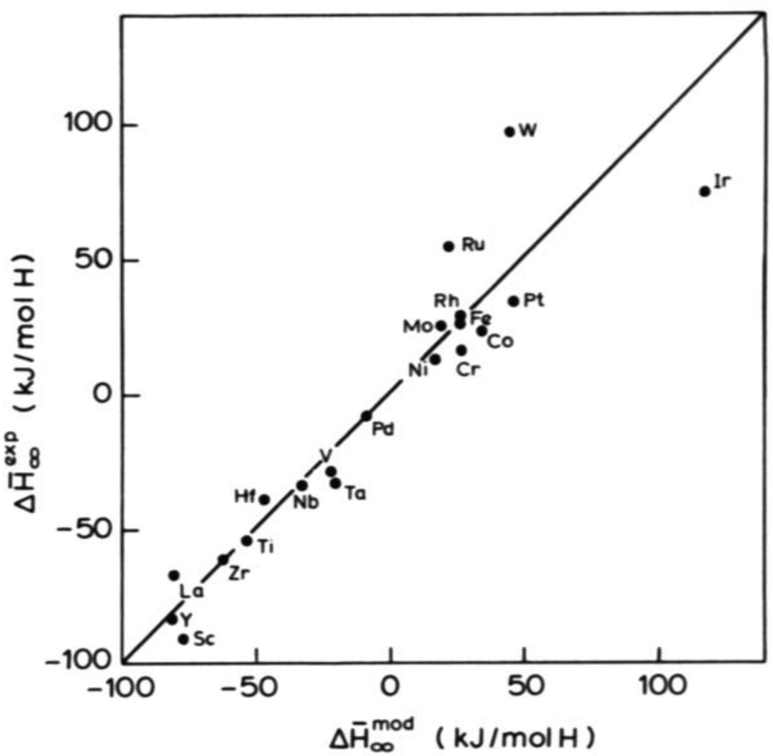
binary hydrides

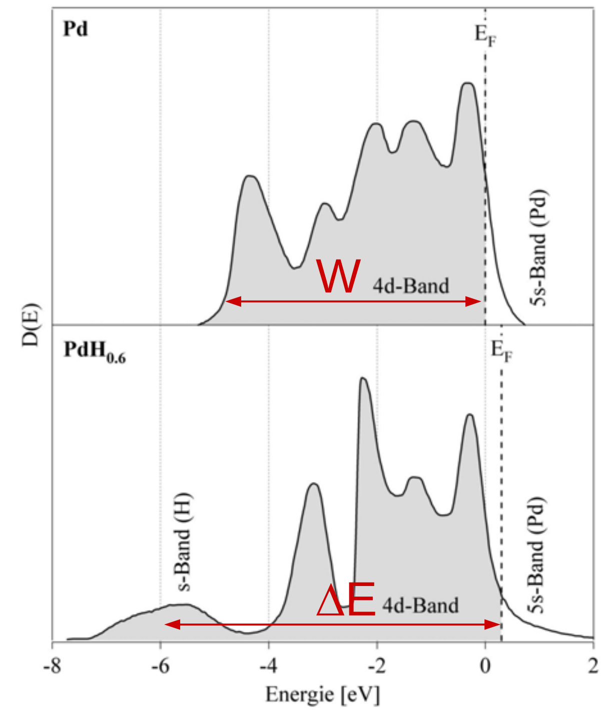
SEMI-EMPIRICAL MODEL FOR THE STABILITY

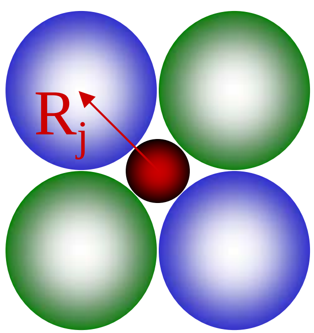
The Local Band-Structure Model

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

a = 18.6 kJ·mol^{-1}HÅ^{4}eV$^{-3/2}$
b = -90 kJ·mol^{-1}H

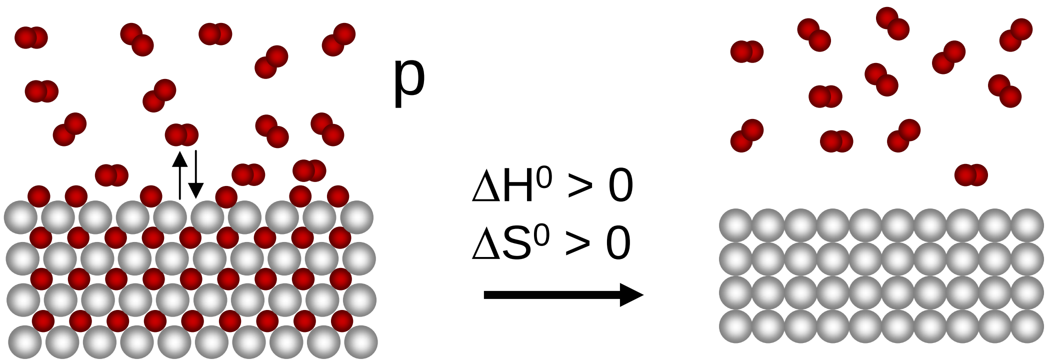






Ref.: R. Griessen, Phys. Rev. B **38** (1988), pp.3690-3698

THERMODYNAMICS OF HYDRIDES



$x\,MH_{2/x} \longrightarrow x\,M + H_2$

Equilibrium $\Delta G = 0$

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

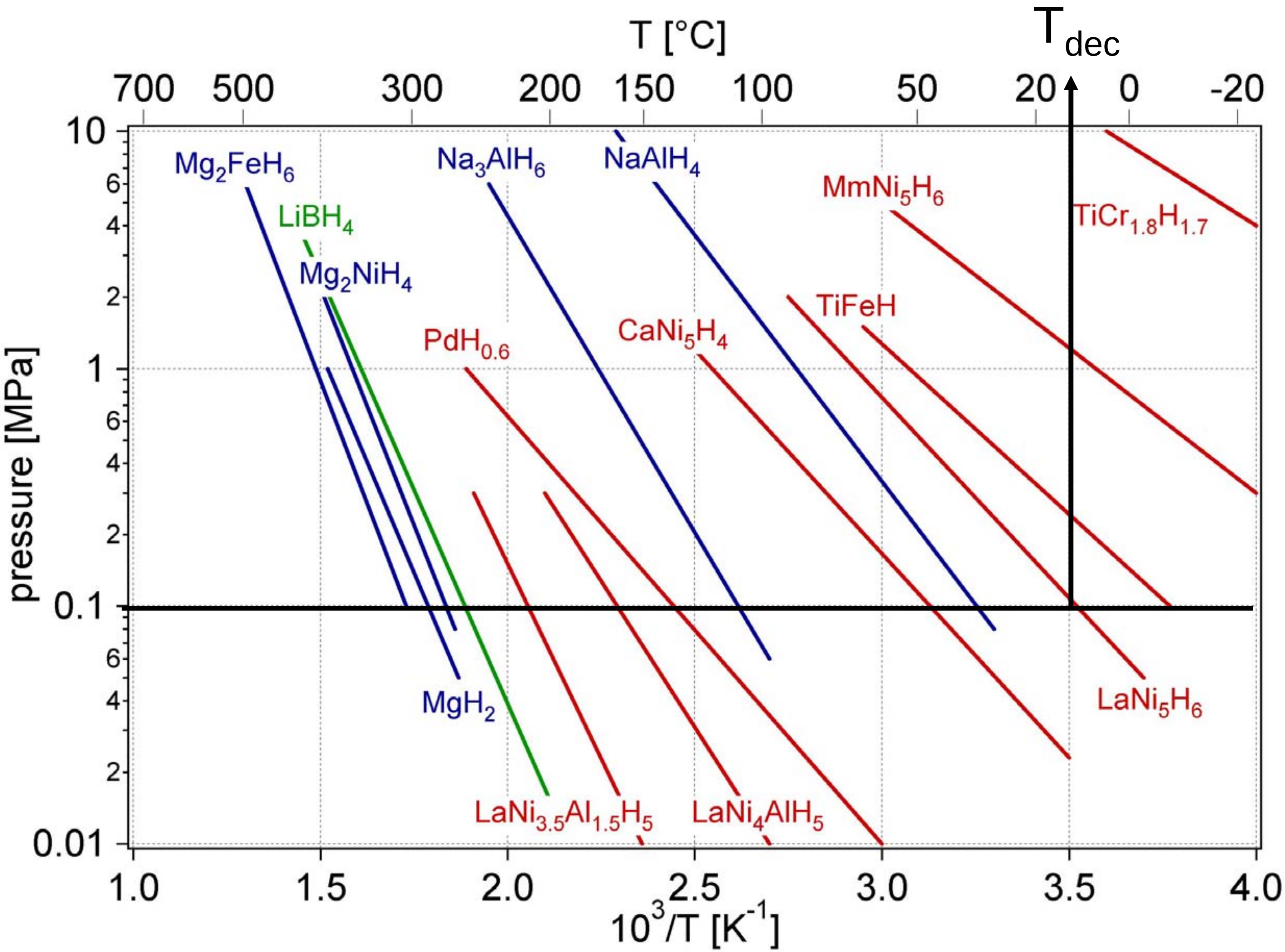
$$\Delta G^0 = -R \cdot T \cdot \ln\left(\frac{p}{p_0}\right) = \Delta H^0 - T \cdot \Delta S^0$$

Van't Hoff equation

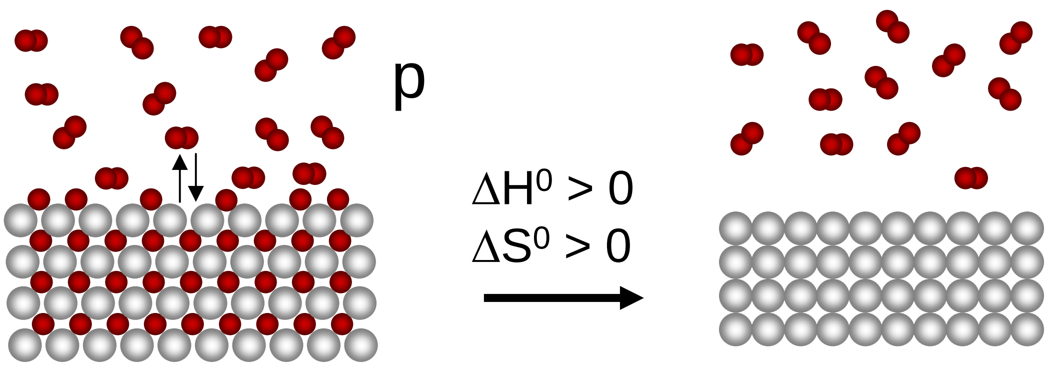
$$\ln\left(\frac{p}{p_0}\right) = -\frac{\Delta H^0}{R} \cdot \frac{1}{T} + \frac{\Delta S^0}{R}$$

for $p = p_0$ $$T_{dec} = \frac{\Delta H^0}{\Delta S^0}$$ decomposition temperature

STABILITY OF HYDRIDES: VAN'T HOFF PLOT



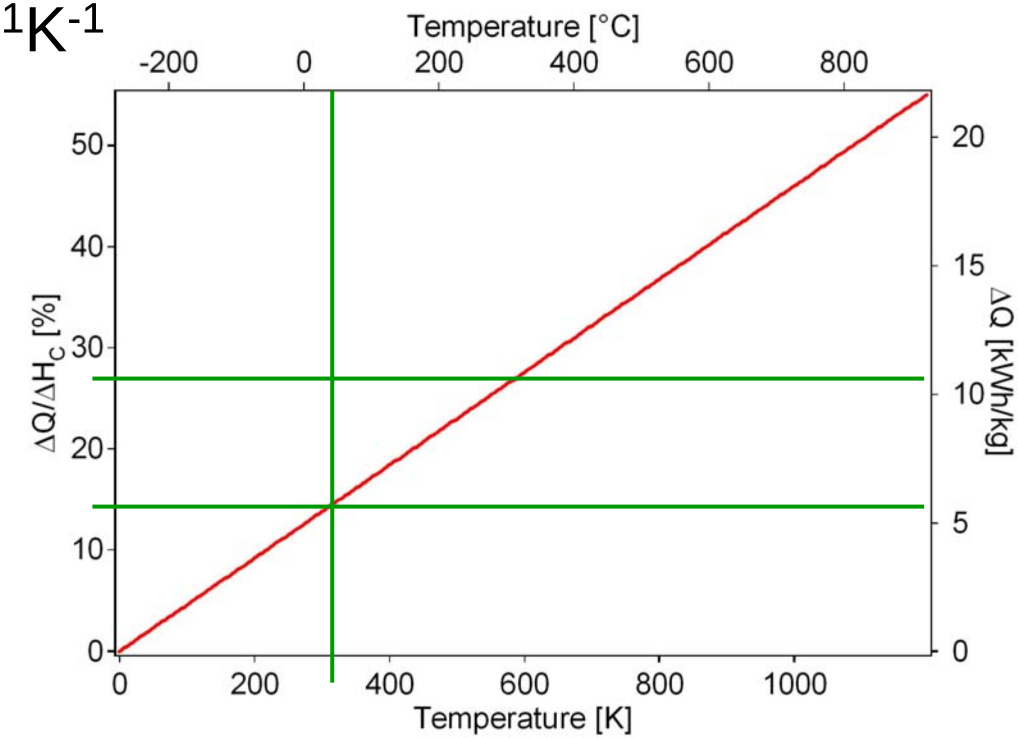
THERMODYNAMICS OF HYDRIDES



$$\Delta S^0 \approx S^0(H_2) = 130.2 \text{ J mol}^{-1}\text{K}^{-1}$$

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

$$\frac{\Delta Q}{\Delta H_V} = \frac{\Delta S^0}{\Delta H_V} \cdot T = 4.6 \cdot 10^{-4} \cdot T$$



Andreas Züttel, IfRES (2005)

HYDRIDES

Metal hydrides

MgH_2, AlH_3

$XAlH_4$, XBH_4

$-NH_2$, $=NH$

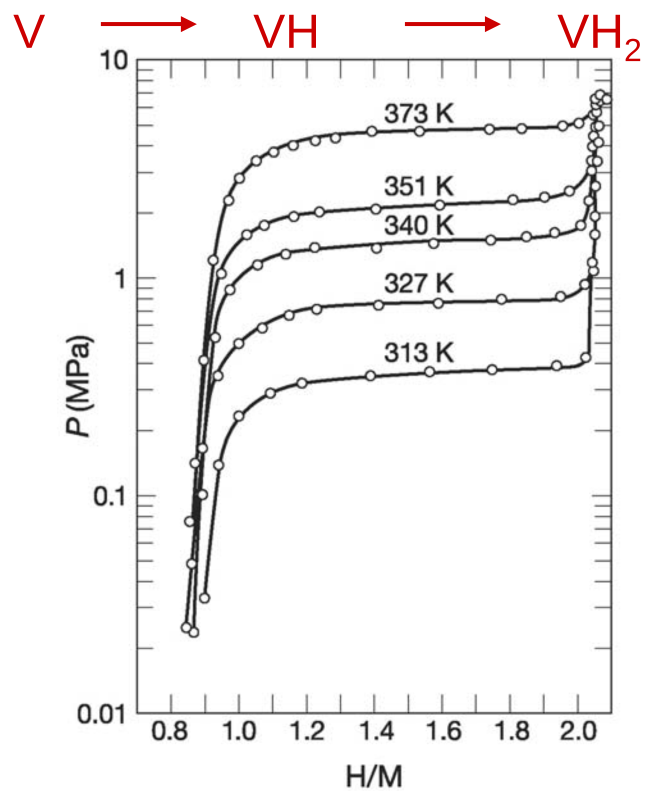
$H^{\delta+}$ and $H^{\delta-}$

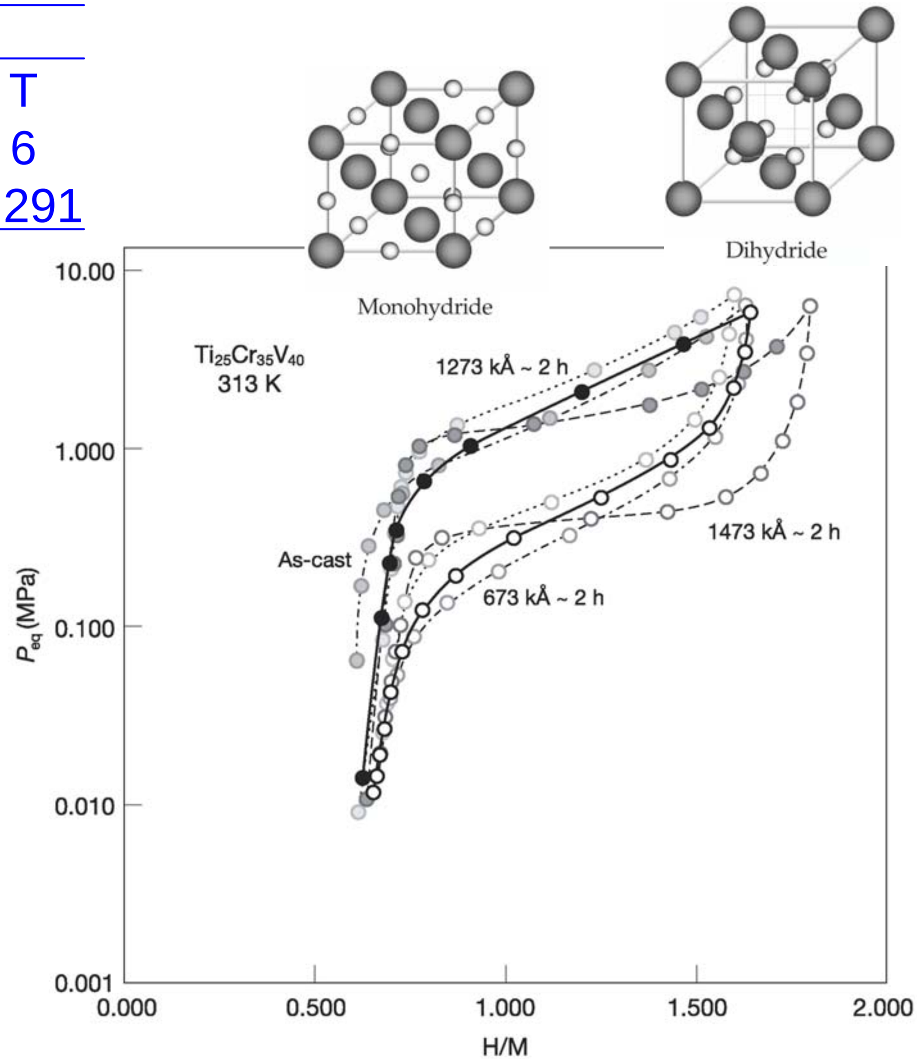
Material	H_2 [mass%]	T_{dec} [°C] 1 bar
$LaNi_5H_6$	1.49	15
$TiMn_{1.5}H_{2.5}$	1.76	
$FeTiH_2$	1.86	-10
ZrH_2	2.16	
$TiCr_{1.8}H_{3.5}$	2.43	
Mg_2NiH_4	3.62	300
VH_2	3.81	-10,
TiH_2	3.98	780
NaH	4.20	430
CaH_2	4.79	1000
Li_2NH + LiH	5.50	600
$LiNH_2$ + LiH	6.50	300
$NaAlH_4$	7.46	30, 120
MgH_2	7.66	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

BODY CENTERED CUBIC 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

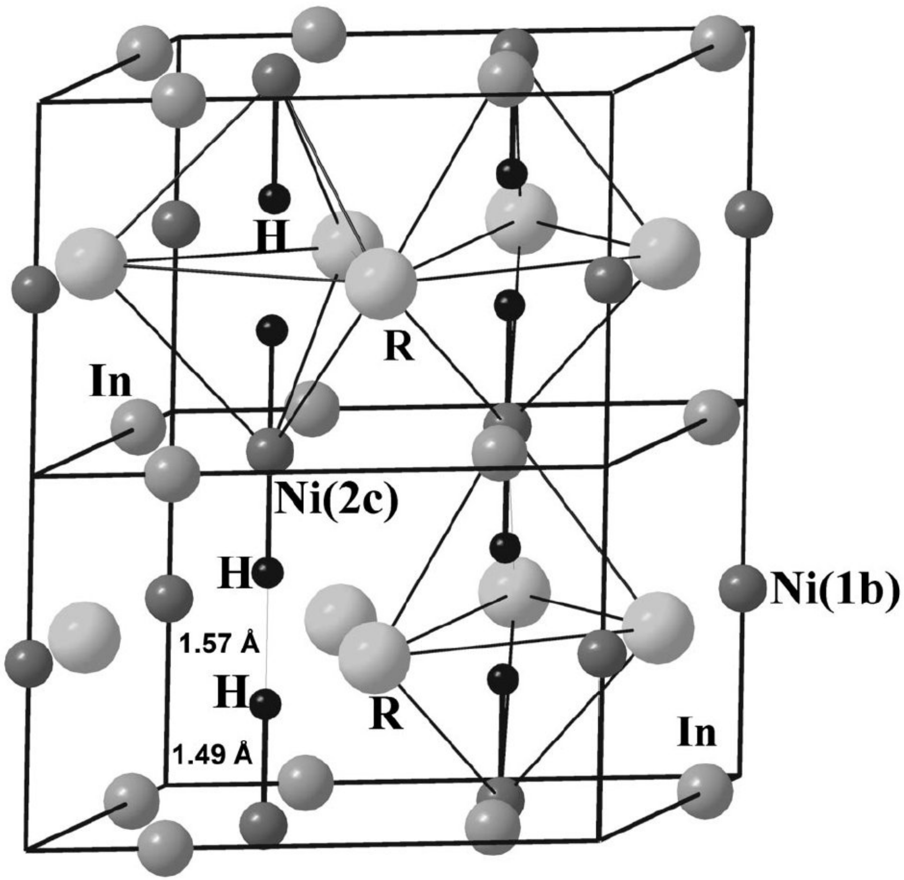


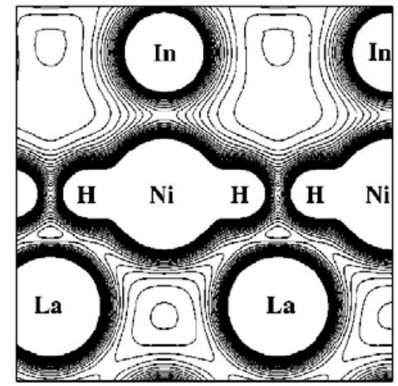


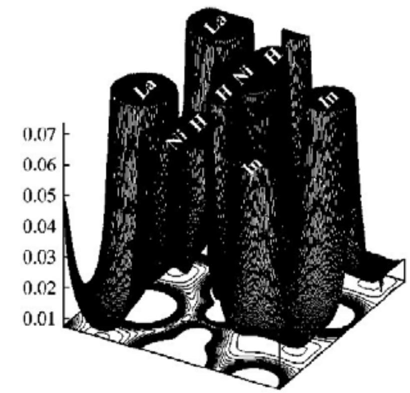
Ref.: E. Akiba and M. Okada, “Metallic Hydrides III: Body-Centered-Cubic Solid-Solution Alloys”, MRS BULLETIN/SEPTEMBER 2002 699-703

METAL HYDRIDES WITH SHORT H-H SEPARATIONS

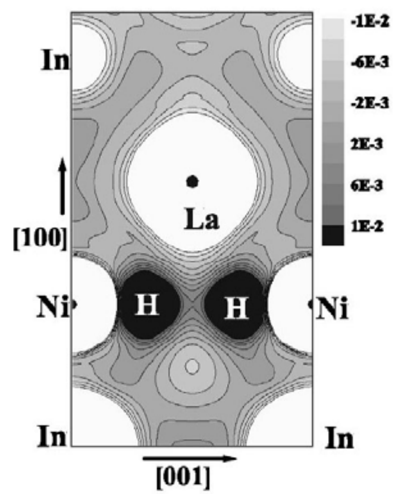
$RTInH_{1.333}$ (R = La, Ce, Pr, or Nd; T = Ni, Pd, or Pt)



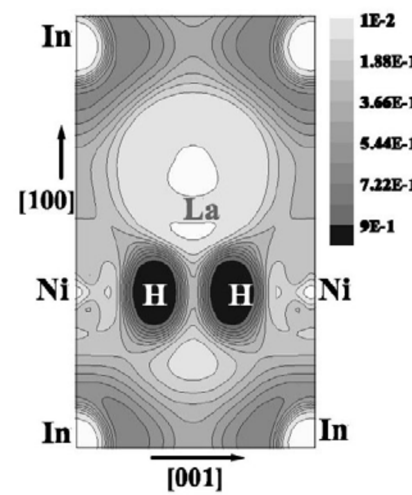




charge transfer



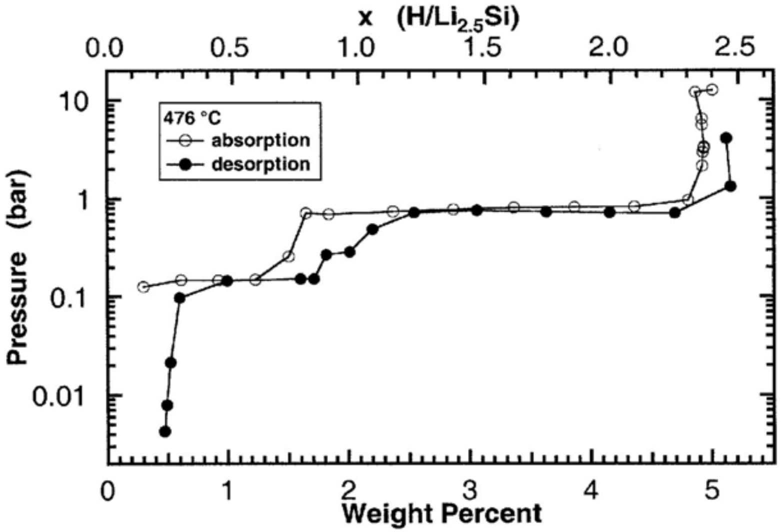
electron density

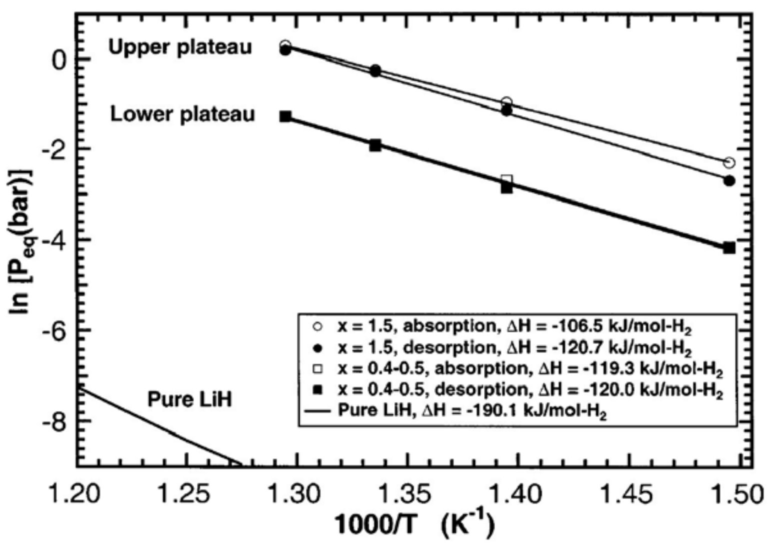


Ref.: P. Vajeeston et al. Phys. Rev. B 67 (2003), 014101

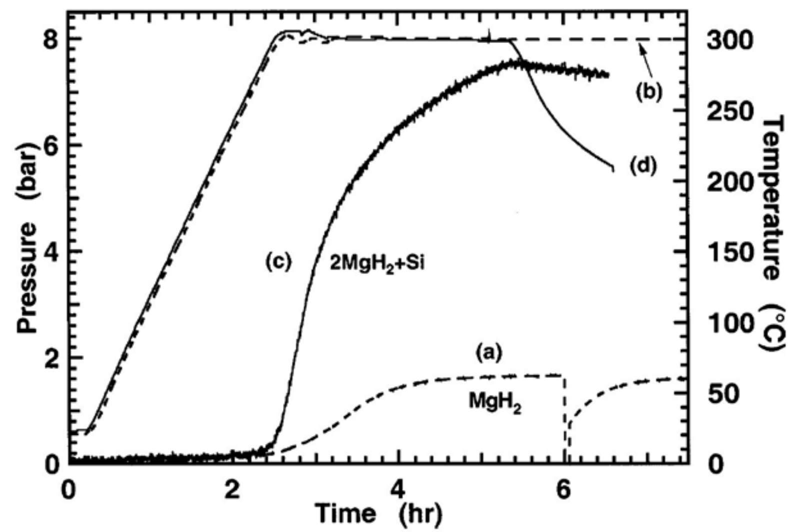
DESTABILISATION OF MgH_2

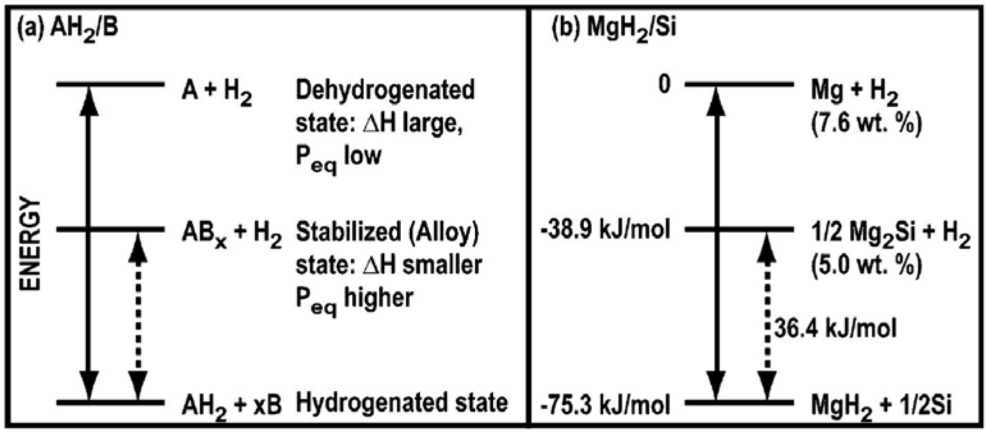
$2.5\ LiH + Si \longrightarrow Li_{2.5}Si + 1.25H_2$





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





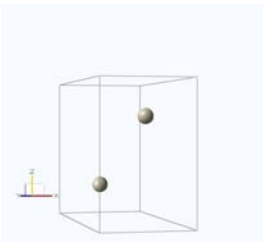
Ref.: J. J. Vajo, F. Mertens, C. C. Ahn, R. C. Bowman Jr, B. Fultz, J. Phys. Chem. B 108 (2004), 13977-13983

METASTABLE MgH_2

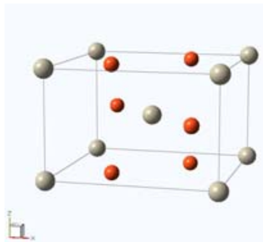
Ti and TiO_2

Ref.: Z. Xiao Guo, Department of Materials, Queen Mary, University of London, UK

Ti



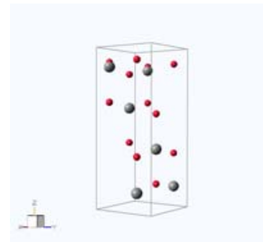
Rutile



a=0.45845 nm, ***c***=0.29533 nm
$P4_2$/mnm, 136

		x	*y*	*z*
Ti	2*a*	0	0	0
O	4*f*	0.3049	0.3049	0

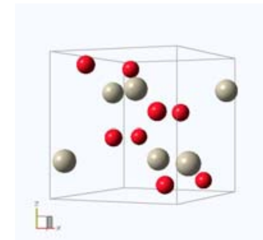
Anatase



a=0.3733 nm, ***c***=0.9370 nm
$I4_1$/amd, 141

		x	*y*	*z*
Ti	4*a*	0.5	0.75	0.375
O	8e	0.5	0.75	0.1598

TiO_2(II)

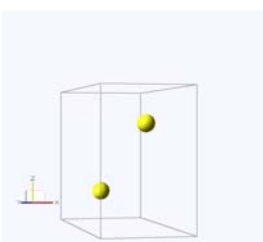


a=0.4563 nm, b= 0.5469 nm, ***c***=0.4911 nm
Pbcn, 60

	x	*y*	*z*
Ti	0	0.171	0.25
O	0.286	0.376	0.412

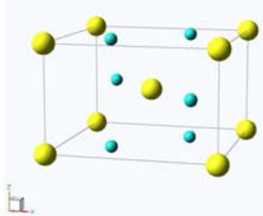
Mg and MgH_2

Mg



α-MgH_2

ΔHf = -71.149 kJ/molH_2



a=0.4501 nm, ***c***=0.3010 nm
$P4_2$/mnm, 136

		x	*y*	*z*
Mg	2*a*	0	0	0
H	4*f*	0.3040	0.3040	0

T-MgH_2 ?

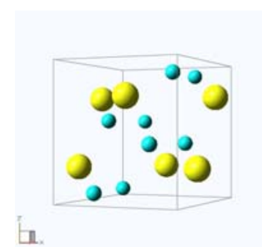
ΔHf = -58.033 kJ/molH_2

?

a=0.3840 nm, ***c***=0.9415 nm
***$I4_1$/amd*, 141**

	x	*y*	*z*
Ti	0.5	0.75	0.375
H	0.5	0.75	0.1647

γ-MgH_2

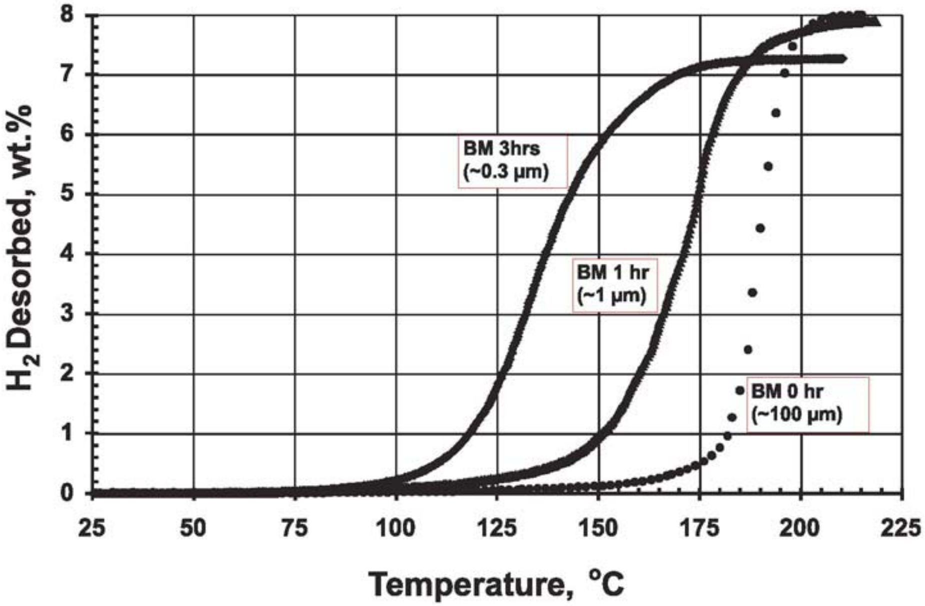


a=0.4505 nm, b= 0.54197 nm ***c***=0.49168 nm
Pbcn, 60

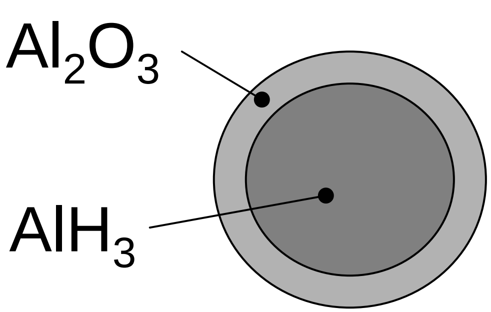
		x	*y*	*z*
Mg	4c	0	0.3313	0.25
H	8d	0.2727	0.1089	0.0794

THERMAL DECOMPOSITION OF AlH_3

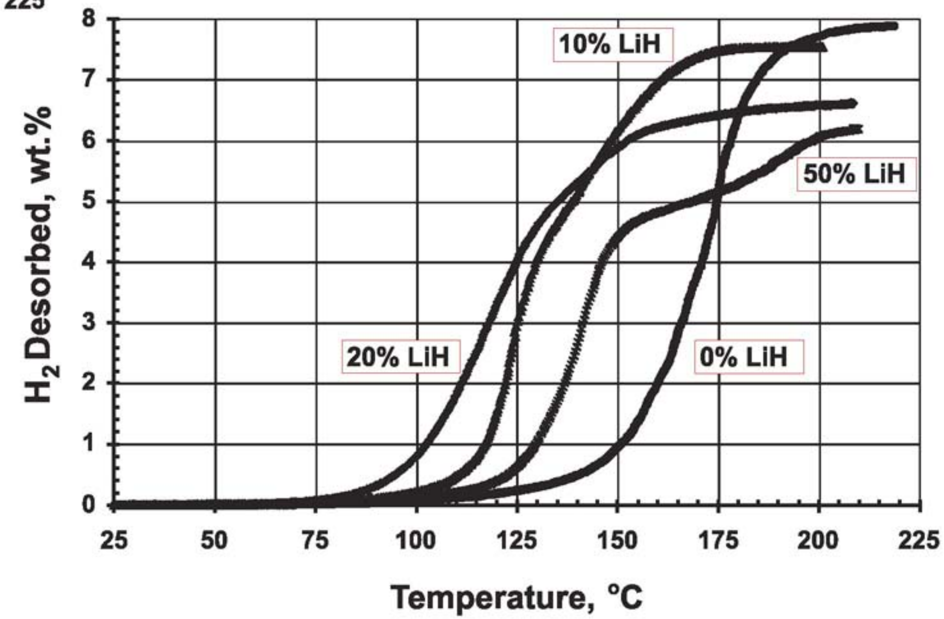
Particle size



ρ_m = 10.1 mass%
ρ_V = 149 kg m^{-3}
ΔH = 7.6 kJ mol^{-1} H_2

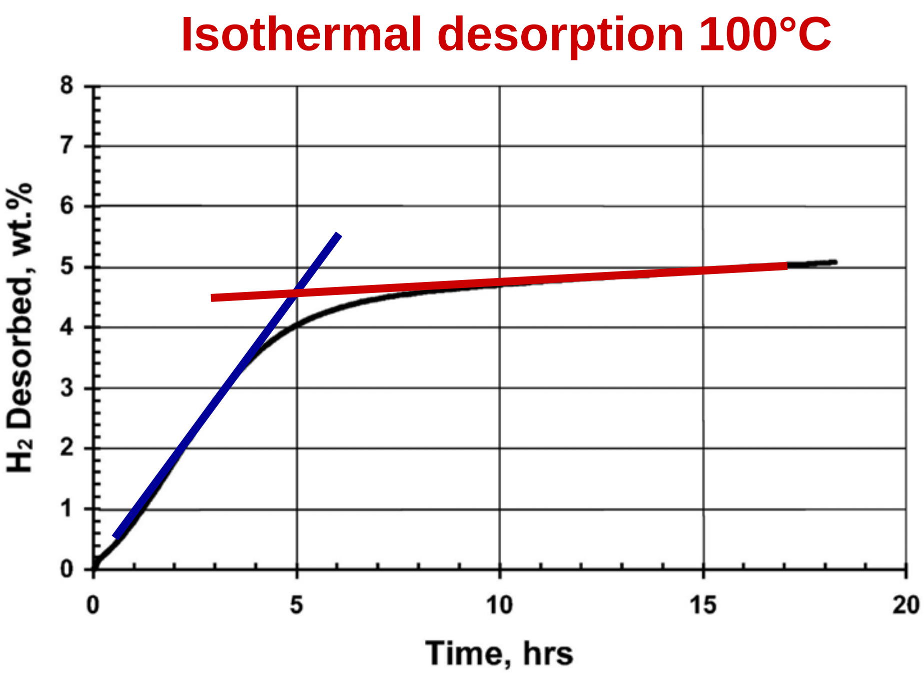


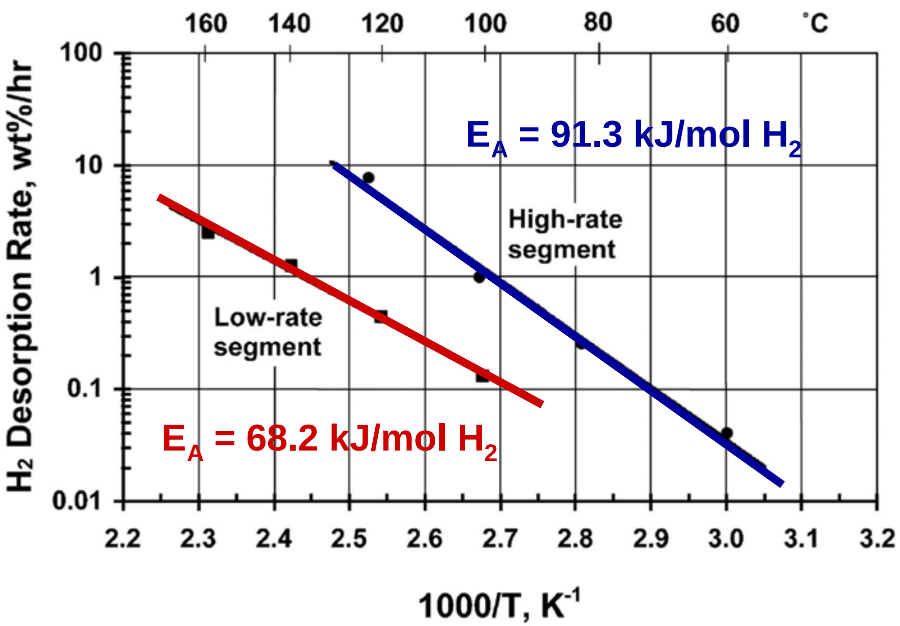
AlH_3-LiH



Ref.: G. Sandrock, J. Reilly, J. Graetz, W.-M. Zhou, J. Johnson, J. Wegrzyn, Appl. Phys. A 80 (2005), pp. 687–690

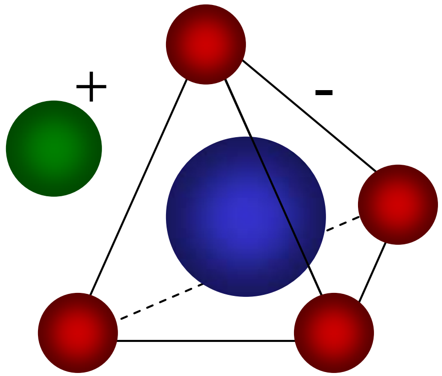
THERMAL DECOMPOSITION OF 80mol%AlH_3-20mol%LiH

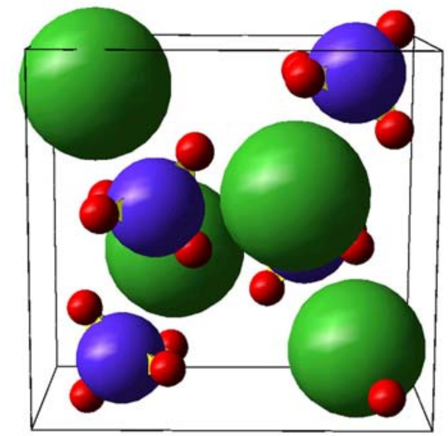




Ref.: G. Sandrock, J. Reilly, J. Graetz, W.-M. Zhou, J. Johnson, J. Wegrzyn, Appl. Phys. A 80 (2005), pp. 687–690

COMPLEX HYDRIDES





1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 2.20																	He
Li 0.97	Be 1.47											B 2.01	C 2.50	N 3.07	0 3.50	F 4.10	Ne
Na 1.01	Mg 1.23											Al 1.47	Si 1.74	P 2.06	S 2.44	Cl 2.83	Ar
K 0.91	Ca 1.04	Sc 1.20	Ti 1.32	V 1.45	Cr 1.56	Mn 1.60	Fe 1.64	Co 1.70	Ni 1.75	Cu 1.75	Zn 1.66	Ga 1.82	Ge 2.02	As 2.20	Se 2.48	Br 2.74	Kr
Rb 0.89	Sr 0.99	Y 1.11	Zr 1.22	Nb 1.23	Mo 1.30	Tc 1.36	Ru 1.42	Rh 1.45	Pd 1.35	Ag 1.42	Cd 1.46	In 1.49	Sn 1.72	Sb 1.82	Tc 2.01	I 2.21	Xe
Cs 0.86	Ba 0.97	La 1.08	Hf 1.23	Ta 1.33	W 1.40	Re 1.46	Os 1.52	Ir 1.55	Pt 1.44	Au 1.42	Hg 1.44	Tl 1.44	Pb 1.55	Bi 1.67	Po 1.76	At 1.90	Rn
Fr	Ra	Ac 1.00															

Ce 1.06	Pr 1.07	Nd 1.07	Pm	Sm 1.07	Eu 1.01	Gd 1.11	Tb 1.10	Dy 1.10	Ho 1.10	Er 1.11	Tm 1.11	Yb 1.06	Lu 1.14
Th 1.11	Pa 1.14	U 1.22	Np 1.22	Pu 1.22	Am 1.2	Cm	Bk	Cf	Es	Fm	Md	No	Lr

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

Examples:

$NaAlH_4$

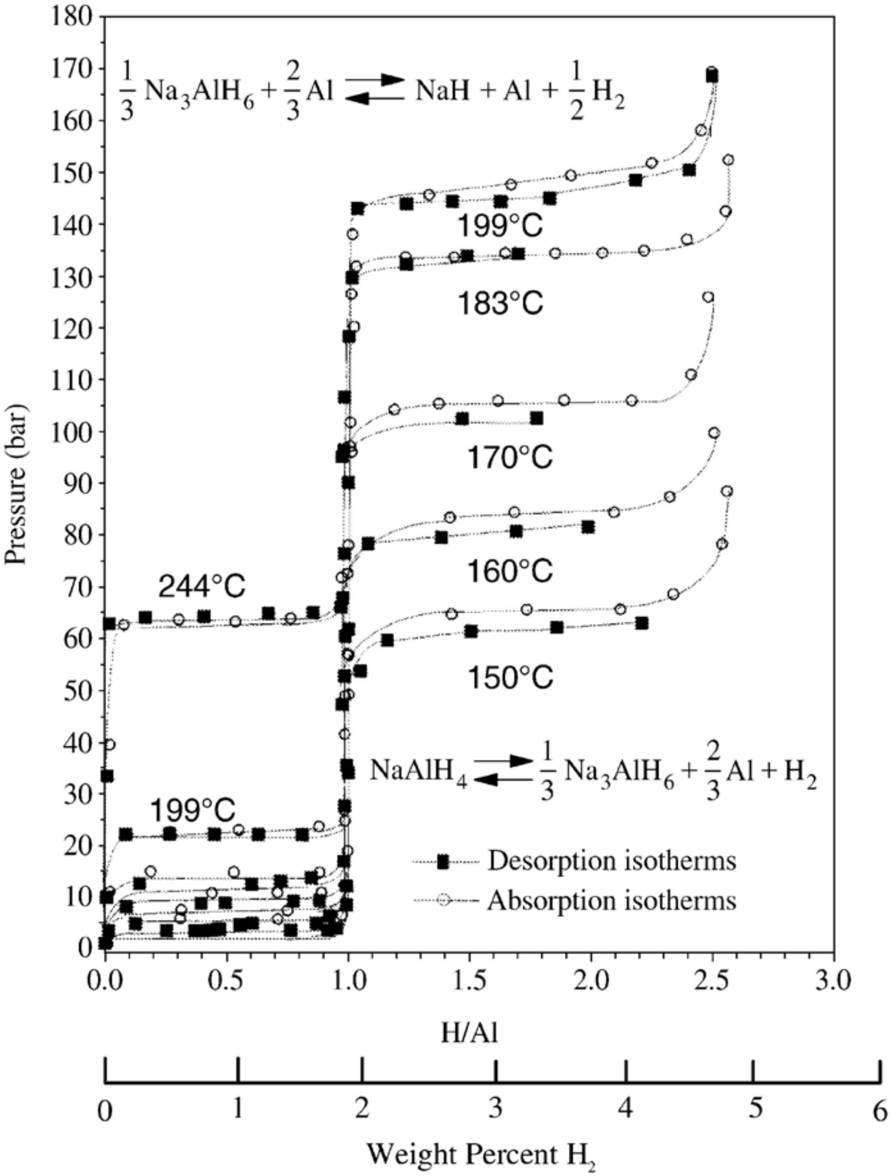
$Mg(AlH_4)_2$

$LiBH_4$

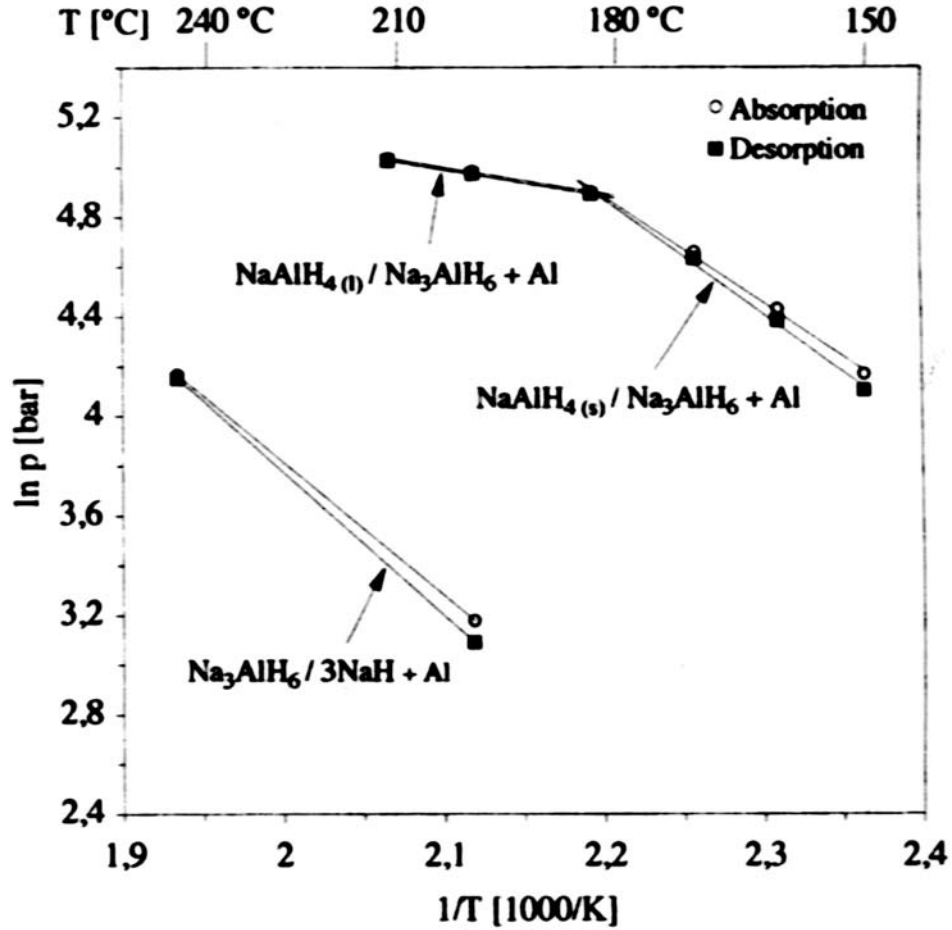
$Mg(BH_4)_2$

$Al(BH_4)_3$

STABILITY OF $NaAlH_4$

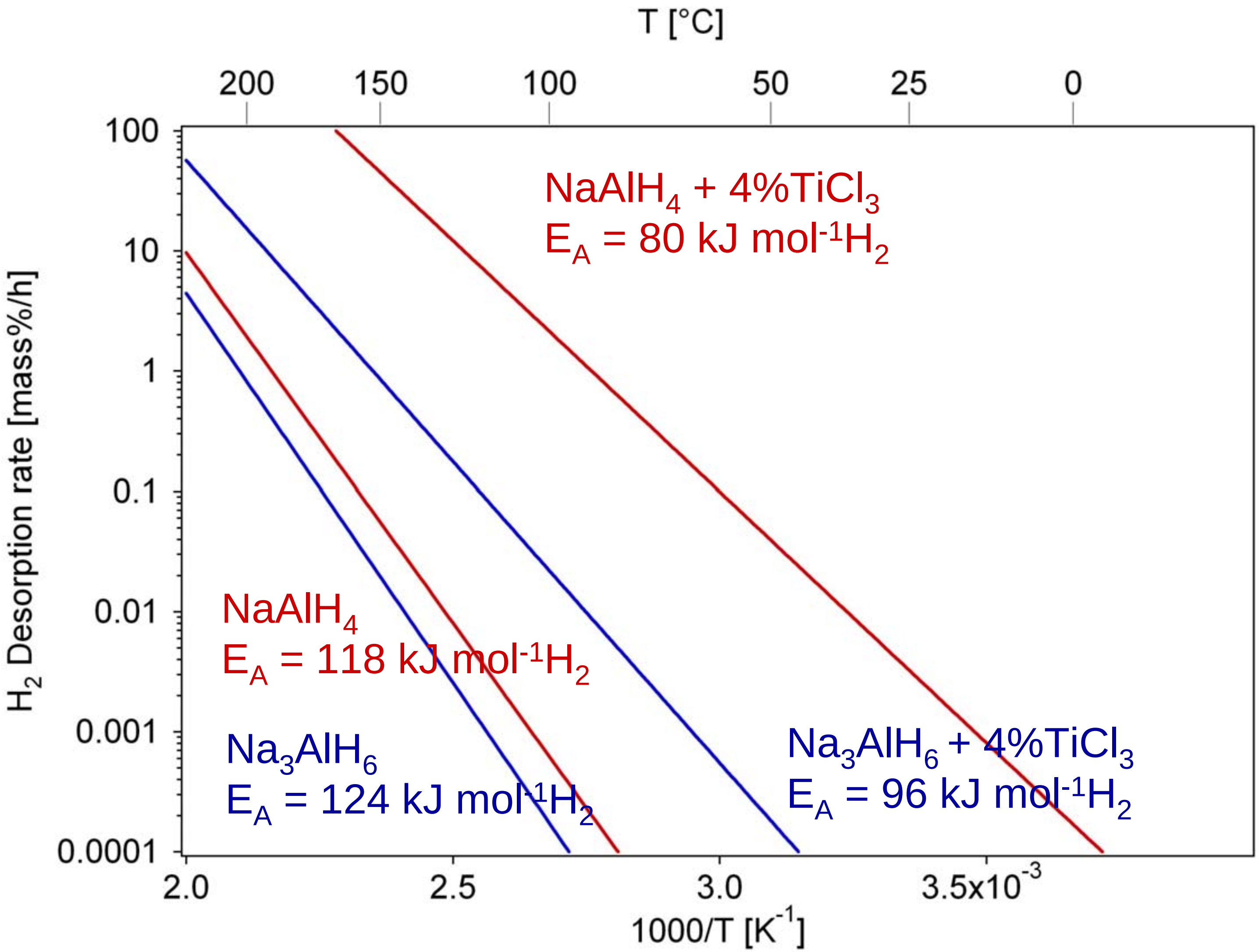


$$-\ln\left(\frac{p}{p_0}\right) = \frac{\Delta H^0}{R \cdot T} - \frac{\Delta S^0}{R}$$



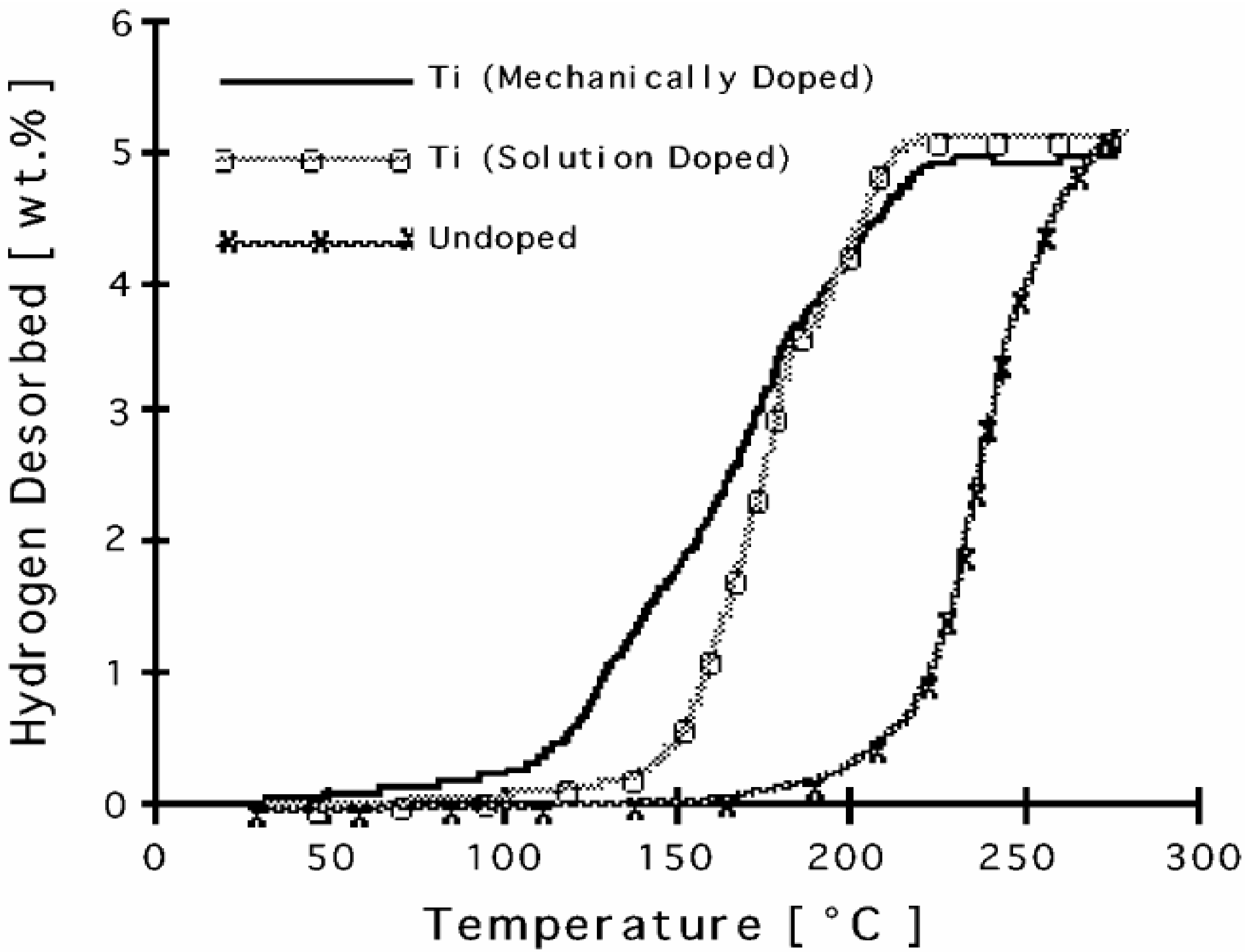
Ref.: B. Bogdanovic et al., J. Alloys and Comp. 302 (2000), pp. 36-58

ARRHENIUS PLOT OF $NaAlH_4$



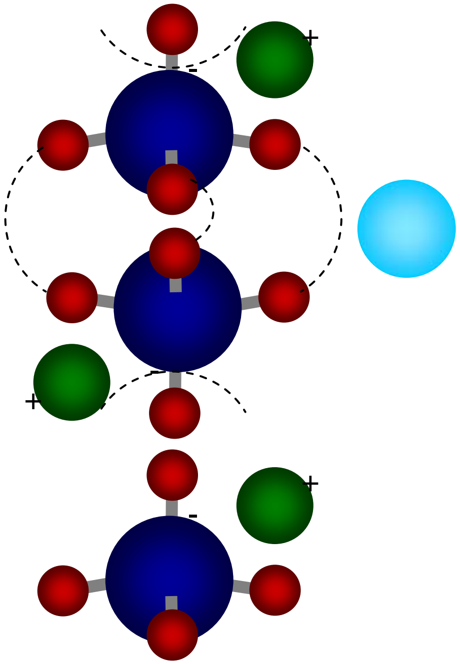
Ref.: Borislav Bogdanovic and Gary Sandrock, "Catalyzed Complex Metal Hydrides", MRS BULLETIN / SEPT. 2002 712-716 and G. Sandrock, K. Gross, and G. Thomas, *J. Alloys Compd.* **339** (2002) p. 299.

Mechanically Doped $NaAlH_4$

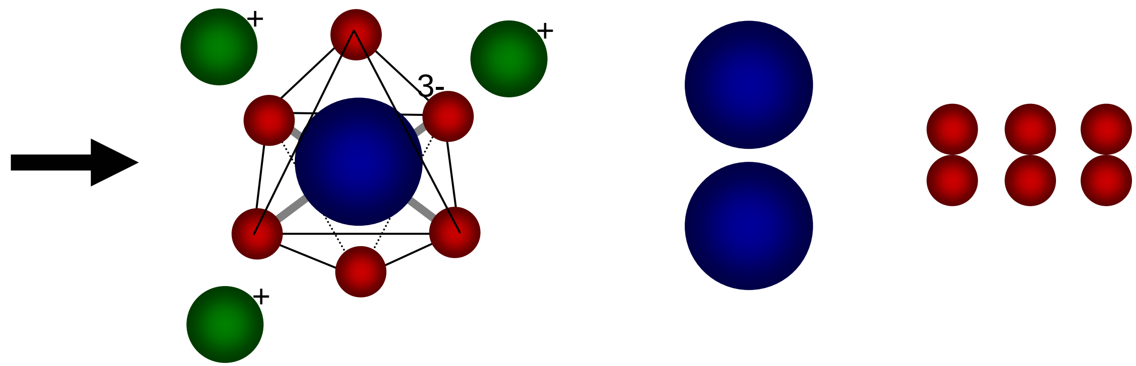


Ref.: R.A. Zidan, S. Takara, A.G. Hee, and C.M. Jensen, J. Alloys and Compounds 285 (1999), pp. 119.
C.M. Jensen and R.A. Zidan, U.S. Patent 6,471,935 (2002).

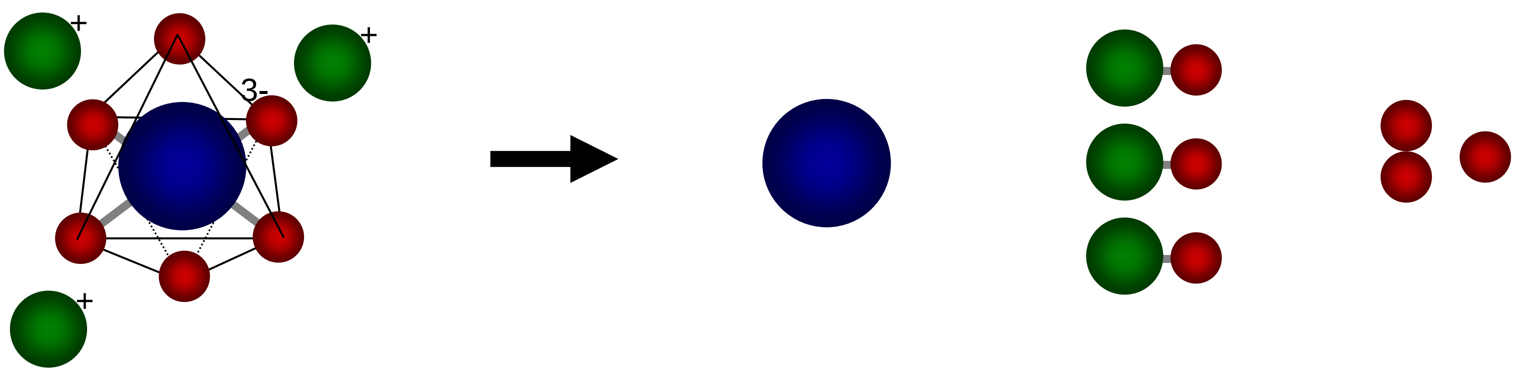
MECHANISM OF THE THERMAL DECOMPOSITION ($NaAlH_4$)



$$3\ NaAlH_4 \rightarrow Na_3\ AlH_6 + 2\ Al + 3\ H_2$$

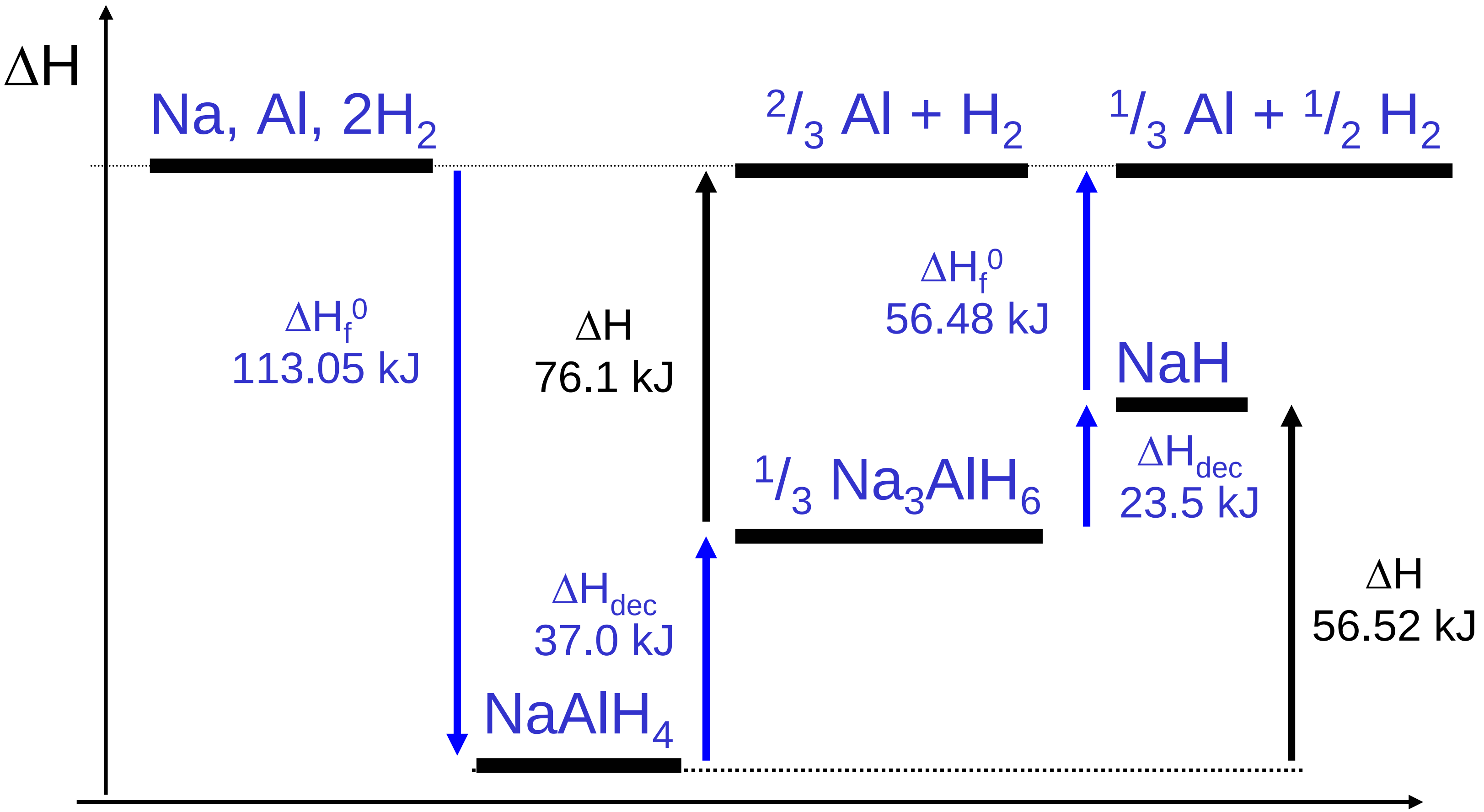


$$Na_3\ AlH_6 \rightarrow Al + 3\ NaH + {}^{3}/_{2}\ H_2$$



ENERGY LEVELS OF $NaAlH_4$

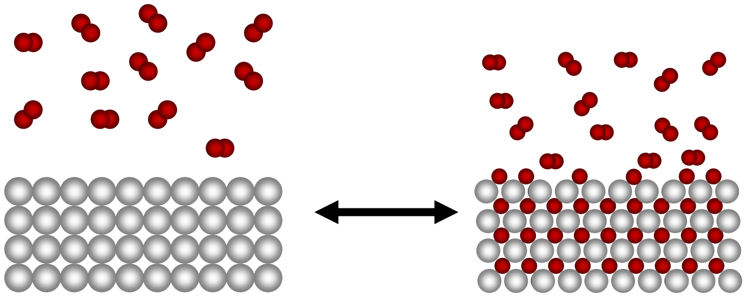
$$NaAlH_4 \rightarrow {}^{1}/_{3}\, Na_3AlH_6 + {}^{2}/_{3}\, Al + H_2 \rightarrow Al + NaH + {}^{3}/_{2}\, H_2$$

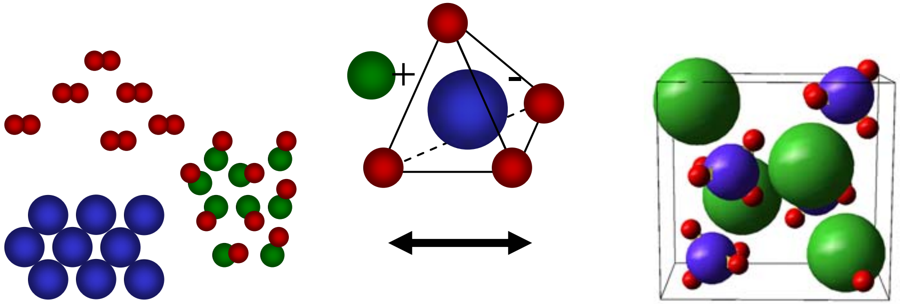


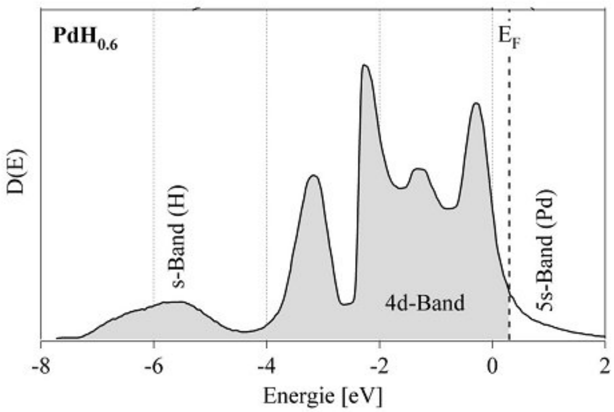
Ref.: Smith and Bass, J. Chem. Eng. Data 8 (1963), pp. 342;
Arroyo y de Dompablo M E, Ceder G, J. of Alloys and Compounds 364 (2004), pp. 6–12

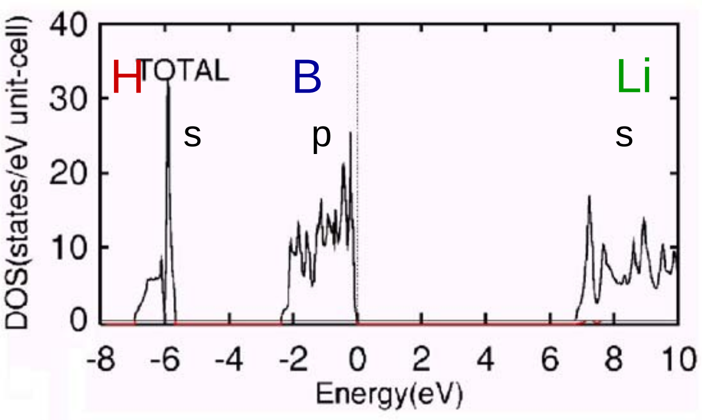
METAL HYDRIDES

COMPLEX HYDRIDES









$$MH_{2x} \longrightarrow M + x\,H_2$$

$$ABH_4 \longrightarrow AH + B + {}^3/_2\,H_2$$

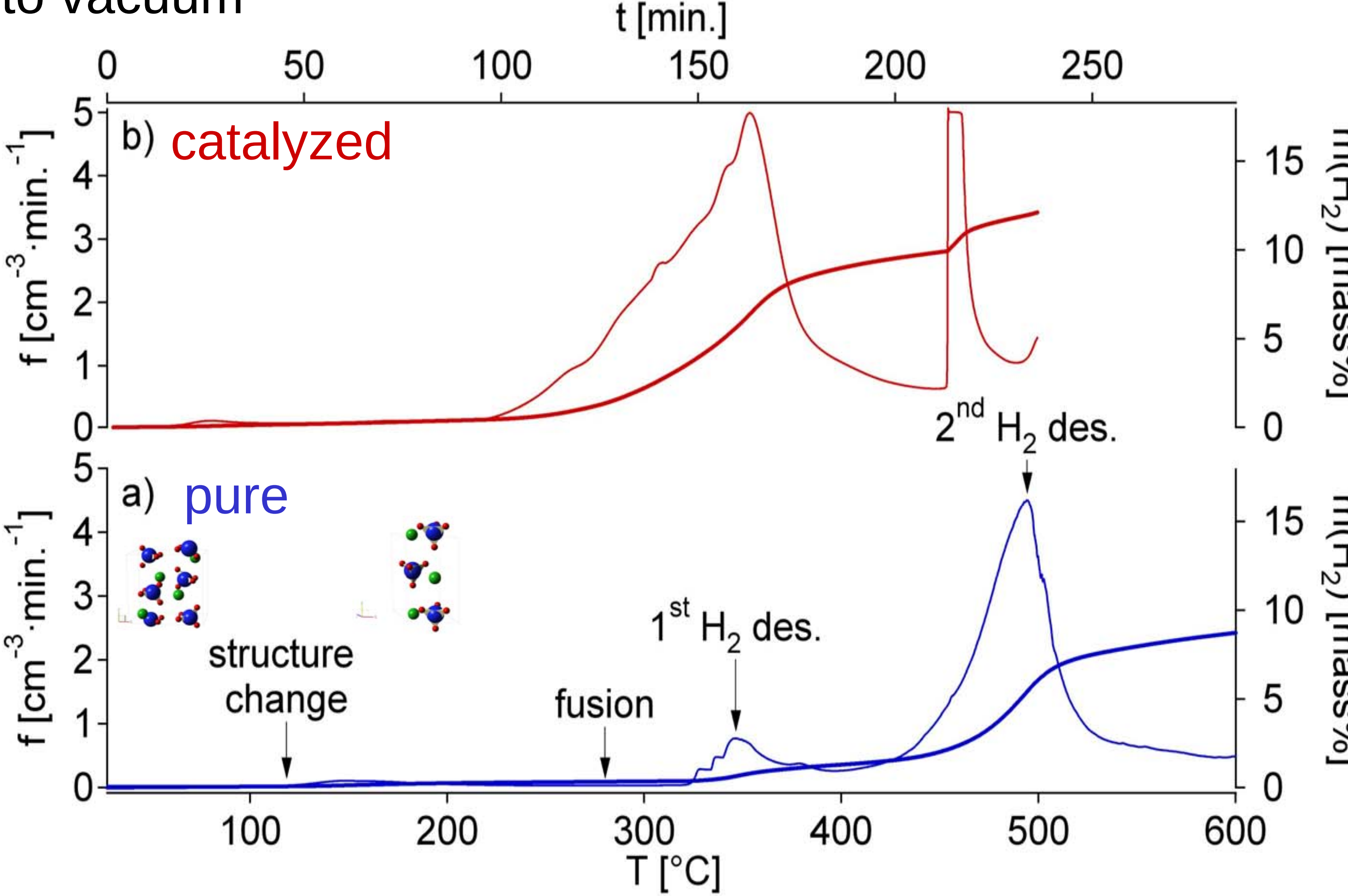
$$\Delta G = 0 = \Delta G^0 + R \cdot T \cdot \ln\left(\frac{p}{p_0}\right)$$

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

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

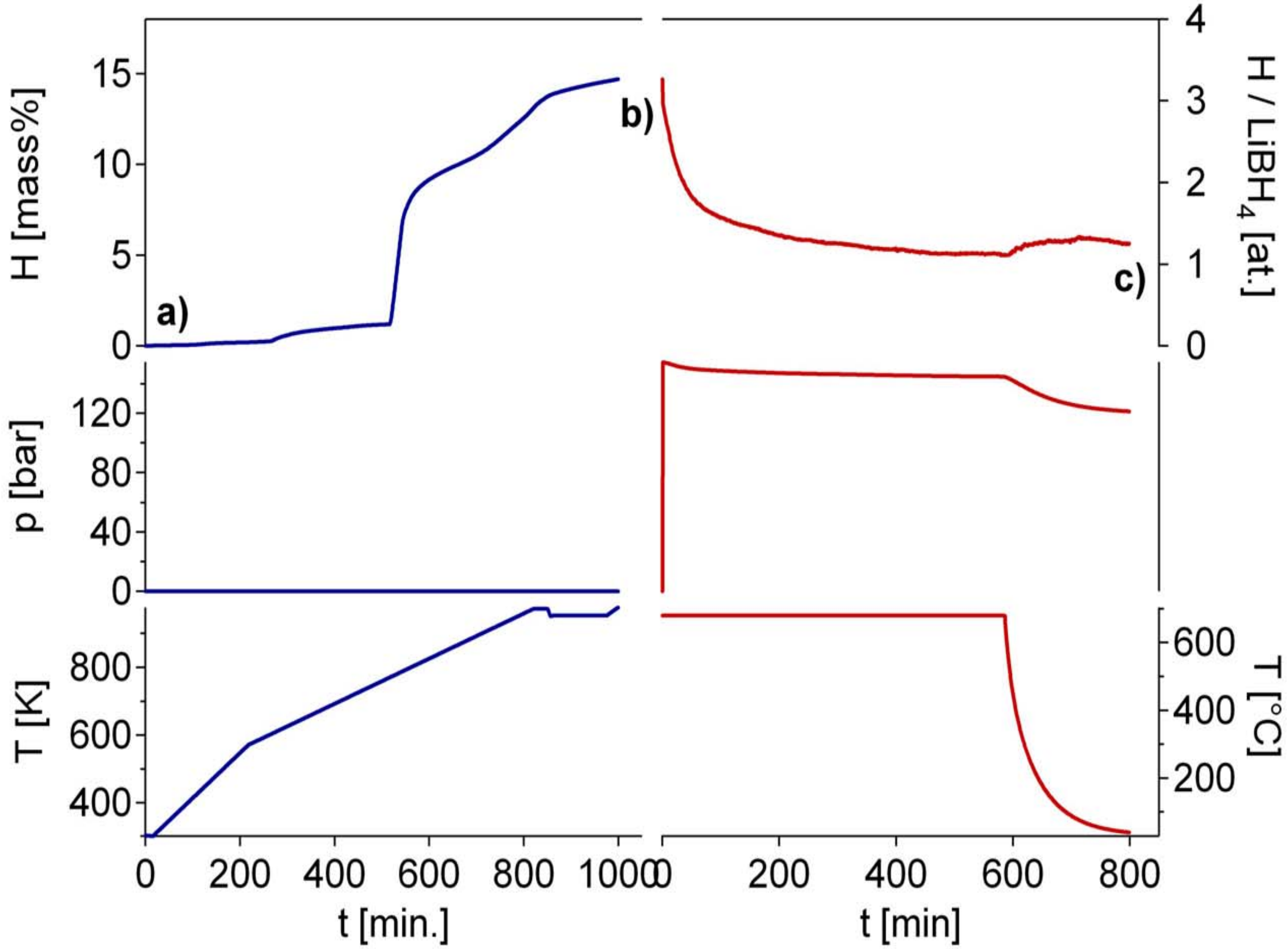
THERMAL H_2 DESORPTION FROM $LiBH_4$

into vacuum

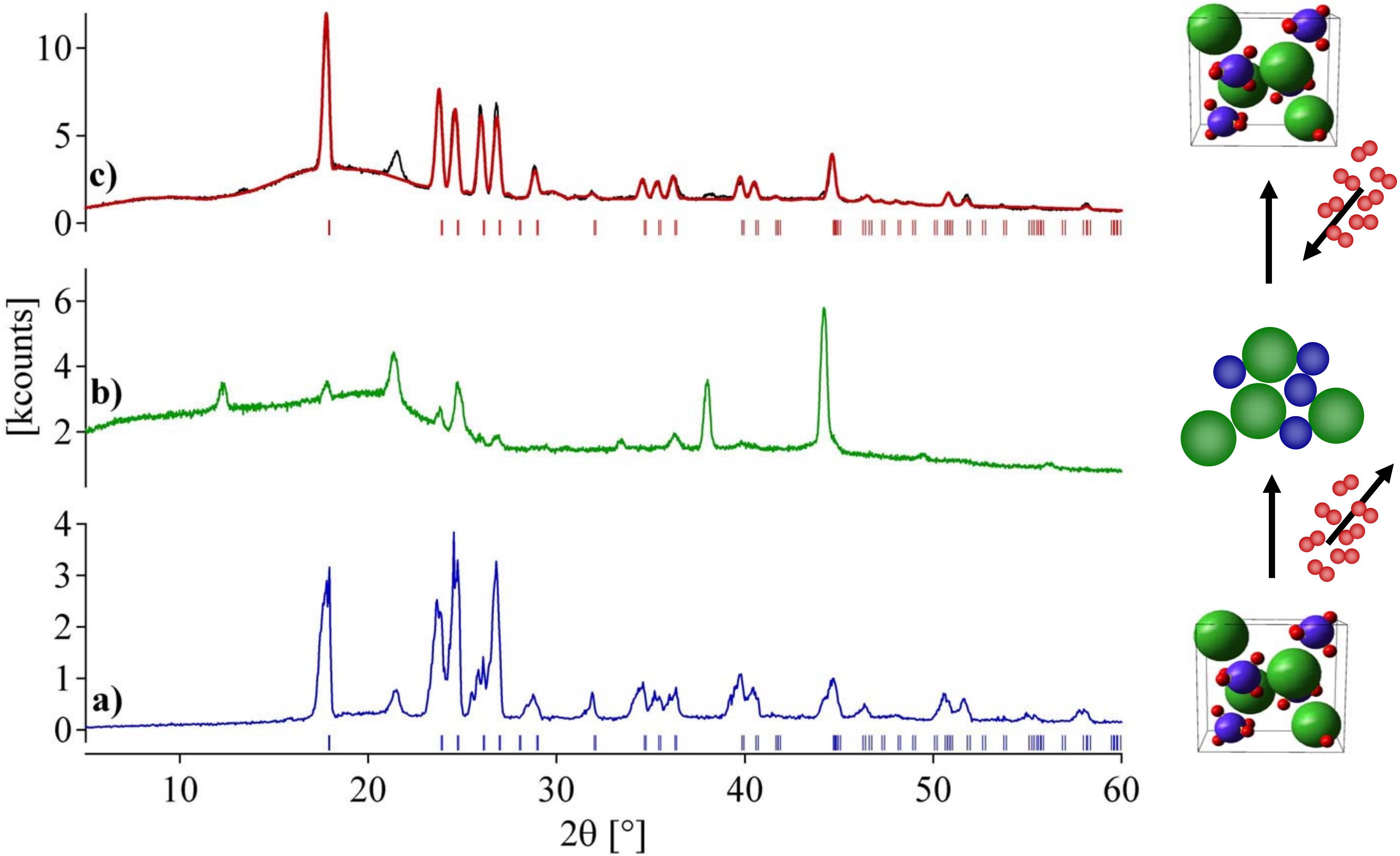


Ref.: W. G. Brown, L. Kaplan, K. E. Wilzbach, J. Amer. Chem. Soc. 74 (1952), pp. 1343-1344

REVERSIBILITY OF H_2 SORPTION FROM $LiBH_4$

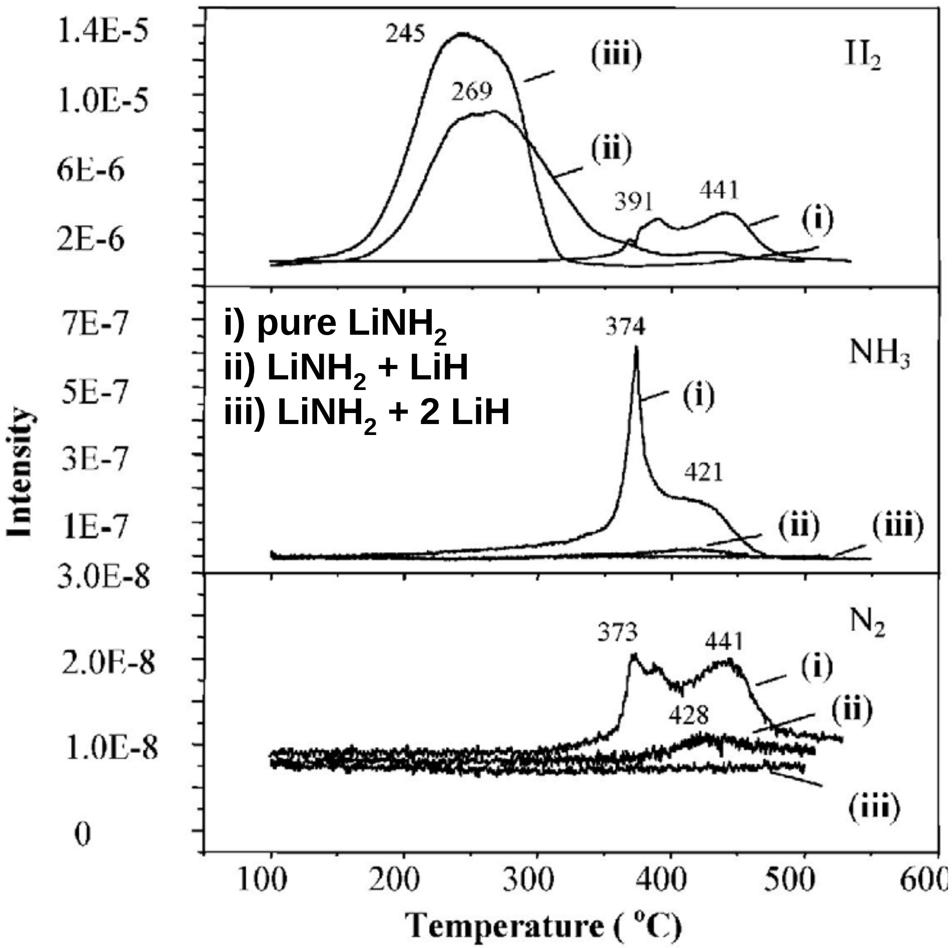


REVERSIBILITY OF $LiBH_4$



AMIDES ($LiNH_2$)

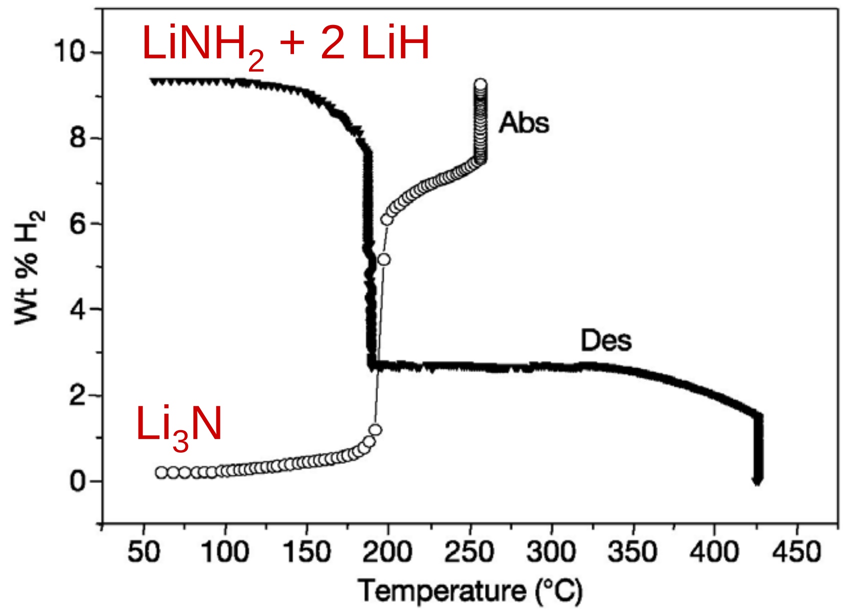
$LiNH_2 + 2LiH \rightarrow Li_3N + 2H_2$ (10.3 mass%, $\Delta H = 40\ kJ\ mol^{-1}\ H$)



$3\ LiNH_2 \rightarrow NH_3 + 3\ LiH + N_2$

$LiNH_2 + 2\ LiH \rightarrow Li_2NH + LiH + H_2$

$\rightarrow Li_3N + 2\ H_2$

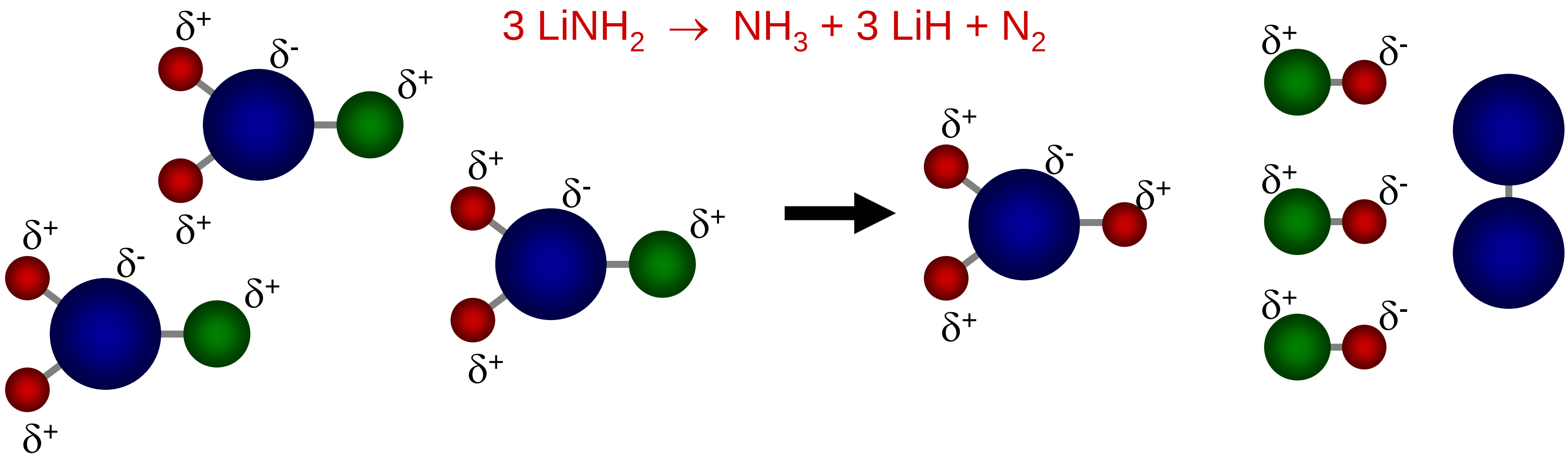


Ref.: Chen P; Xiong Z R; Luo J; Lin J; Tan K L, "Interaction of Hydrogen with Metal Nitrides and Imides", Nature 420 (21 November 2002), pp. 302-304

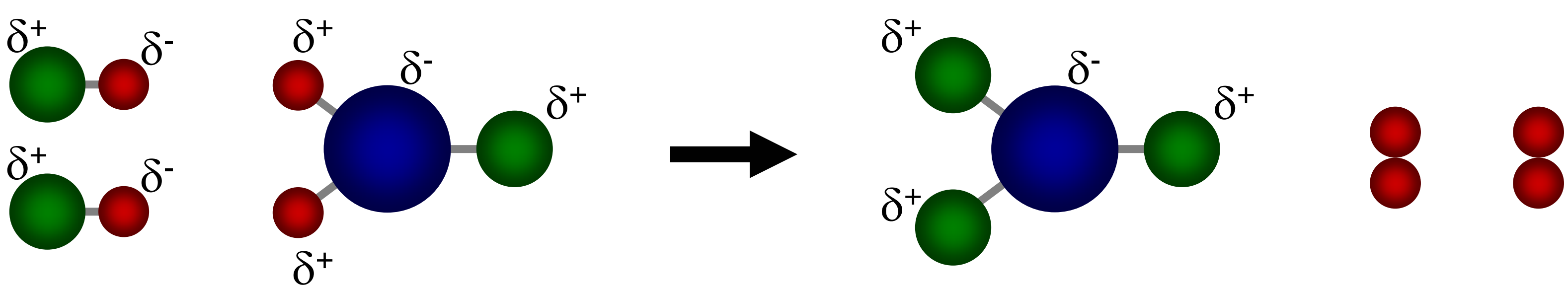
AMIDES ($LiNH_2$)

MECHANISM OF THE THERMAL DECOMPOSITION

$$3\ LiNH_2 \rightarrow NH_3 + 3\ LiH + N_2$$



$$LiNH_2 + 2\ LiH \rightarrow Li_2NH + LiH + H_2 \rightarrow Li_3N + 2\ H_2$$

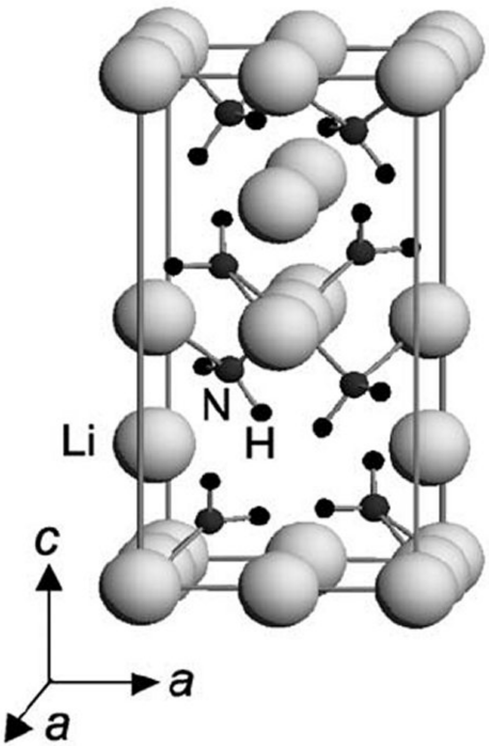


Ref.: Chen P; Xiong Z R; Luo J; Lin J; Tan K L, "Interaction between Lithium Amide and Lithium Hydride", J. Phys. Chem. B (2003), pp. 10967-10970

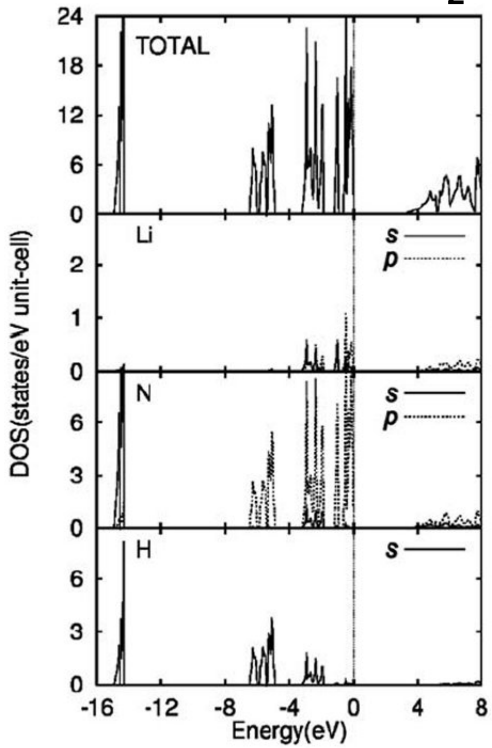
AMIDES ($Li_{1-x}Mg_xNH_2$)

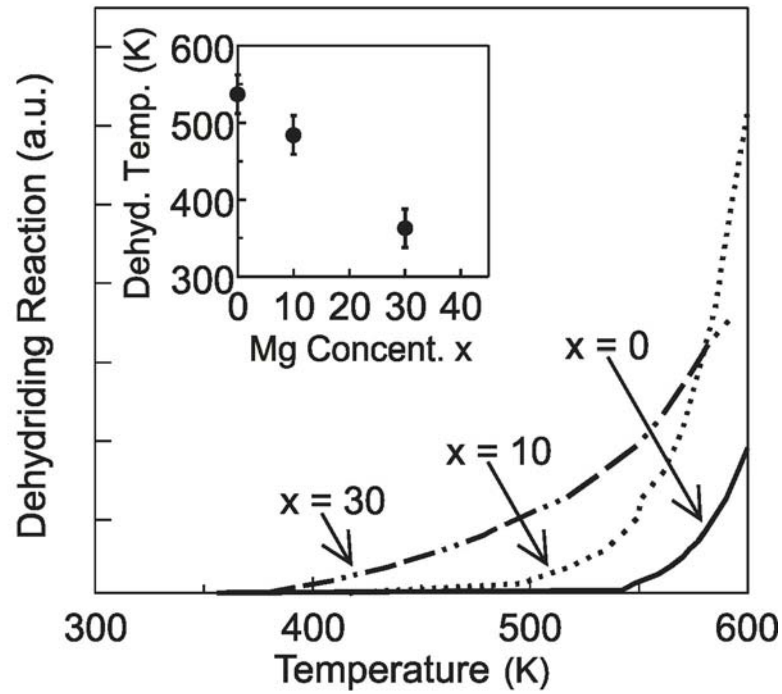
$LiNH_2 + 2LiH \rightarrow Li_3N + 2H_2$

$Li^+[NH2]^-$ destabilization by partial substitution of Li with Mg



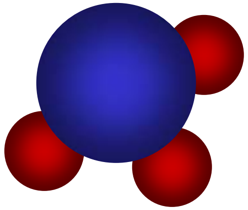
DOS of $LiNH_2$





Ref.: S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, T. Noritake, S. Towata, Appl. Phys. A (Rapid Commun., on-line June 10, (2004)

AMMONIA (NH_3)

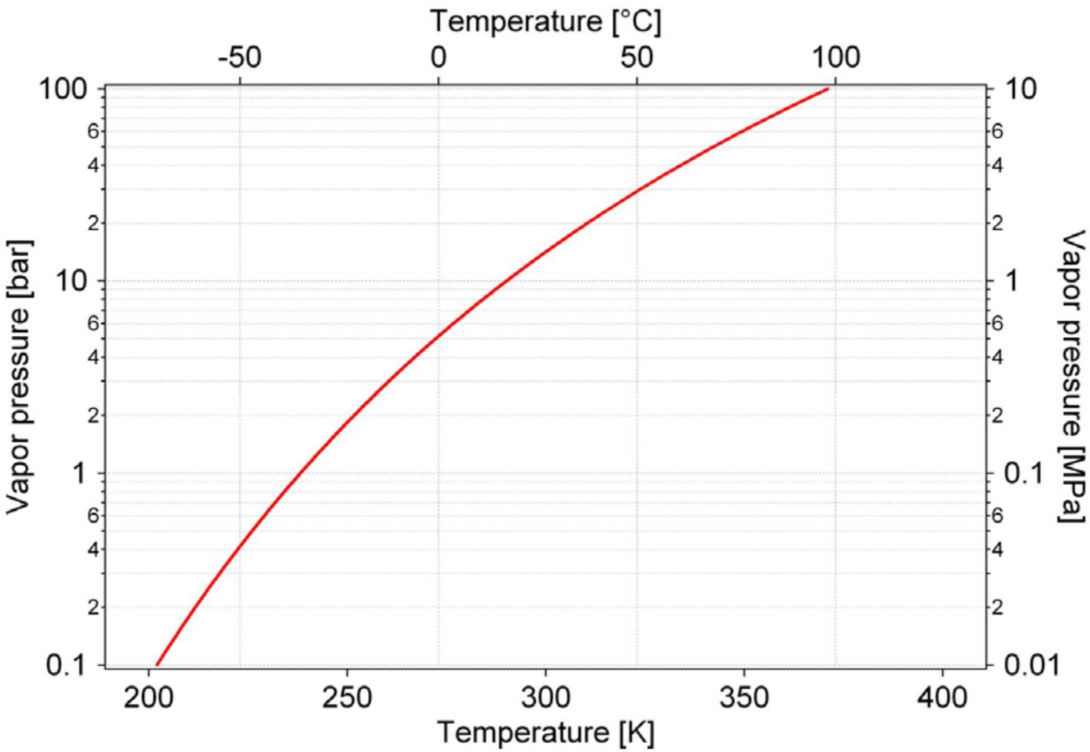


$$3H_2 + N_2 \rightarrow 2NH_3$$

17.6 mass% H_2

ΔH_f = -92.4 kJ, S^0 = 384 J K^{-1}

ΔH_f = -15.4 kJ mol^{-1}H,
S^0 = 64 J $K^{-1}mol^{-1}$H



Dissociation of NH_3 at T > 459°C

$$2NH_3 \rightarrow 3H_2 + N_2$$

TOXIC!

Ref.: G. Strickland, Int. J. Hydrogen Energy 9:9 (1984), pp. 759-766
http://www.electricauto.com/HighDensity_stor.htm

BORAZANE (BH_3NH_3)

$H_3BNH_3(s) \rightarrow H_3BNH_3(l)$ 114°C

$H_3BNH_3(l) \rightarrow H_2BNH_2(s) + H_2(g)$ 137°C

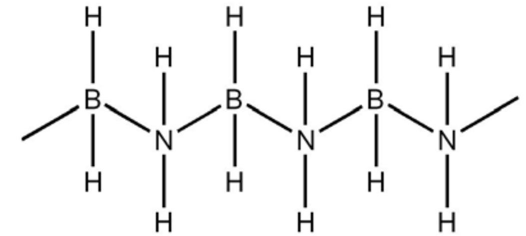
7.4 mass% H_2, $\Delta H = -21.7$ kJ mol^{-1}

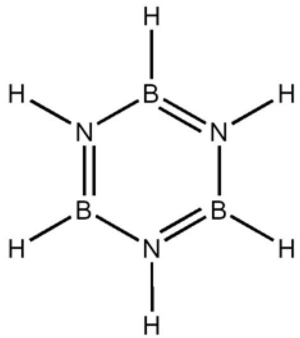
$x\ H_2BNH_2(s) \rightarrow [H_2BNH_2]_x(s)$ 125°C

$[H_2BNH_2]_x(s) \rightarrow [HBNH]_x(s) + H_2(g)$ 155°C

$[HBNH]_x(s) \rightarrow B_3N_3H_6$ + others

$[HBNH]_3(s) \rightarrow BN + 3H_2(g)$ 500°C

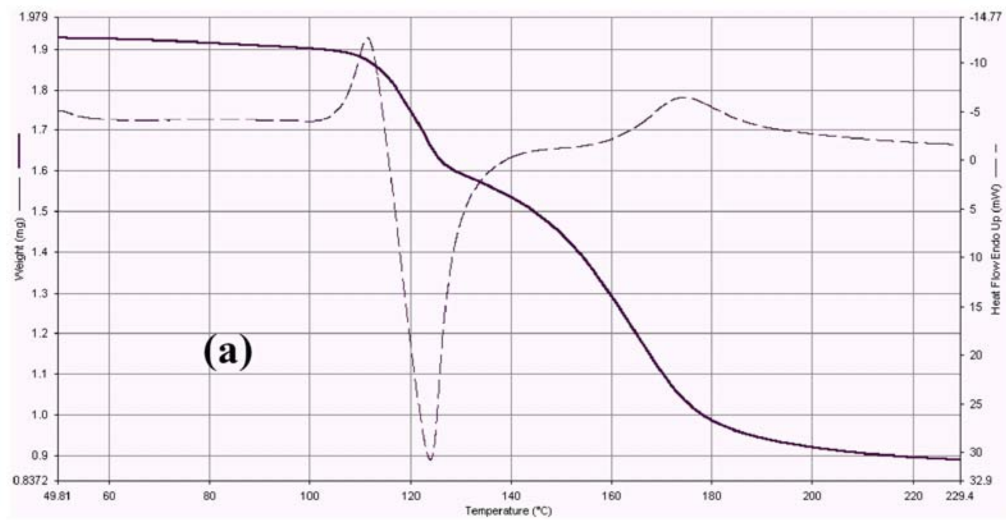




Reversibility?

$LiBH_4 + NH_4Cl \rightarrow H_3BNH_3 + LiCl + H_2$

$\Delta H_f\ (H_3BNH_3) = -178$ kJ mol^{-1}



Ref.: N. Mohajeri, T. Robertson and A. T-Raissi, FSEC FINAL REPORT FOR TASK III-B, Hydrogen Storage in Amine Borane Complexes (2003)

CONCLUSIONS

- Solid hydrides with gravimetric hydrogen density up to 18 mass% exist
- Volumetric hydrogen density > 80 kg m^{-3} for all solids
- No relation between gravimetric hydrogen density and decomposition temperature
- Desorption mechanism in complex hydrides?
- Desorption rate sample size dependent (heat transfer)
- Reversibility or synthesis of hydrides?
- Destabilization of complex hydrides?
- Stabilization and catalytic decomposition of unstable hydrides like NH_3, AlH_3.
- Reaction of multiphase compounds to complex hydrides?