Hydrogen Storage in Ammonia and Aminoborane Complexes

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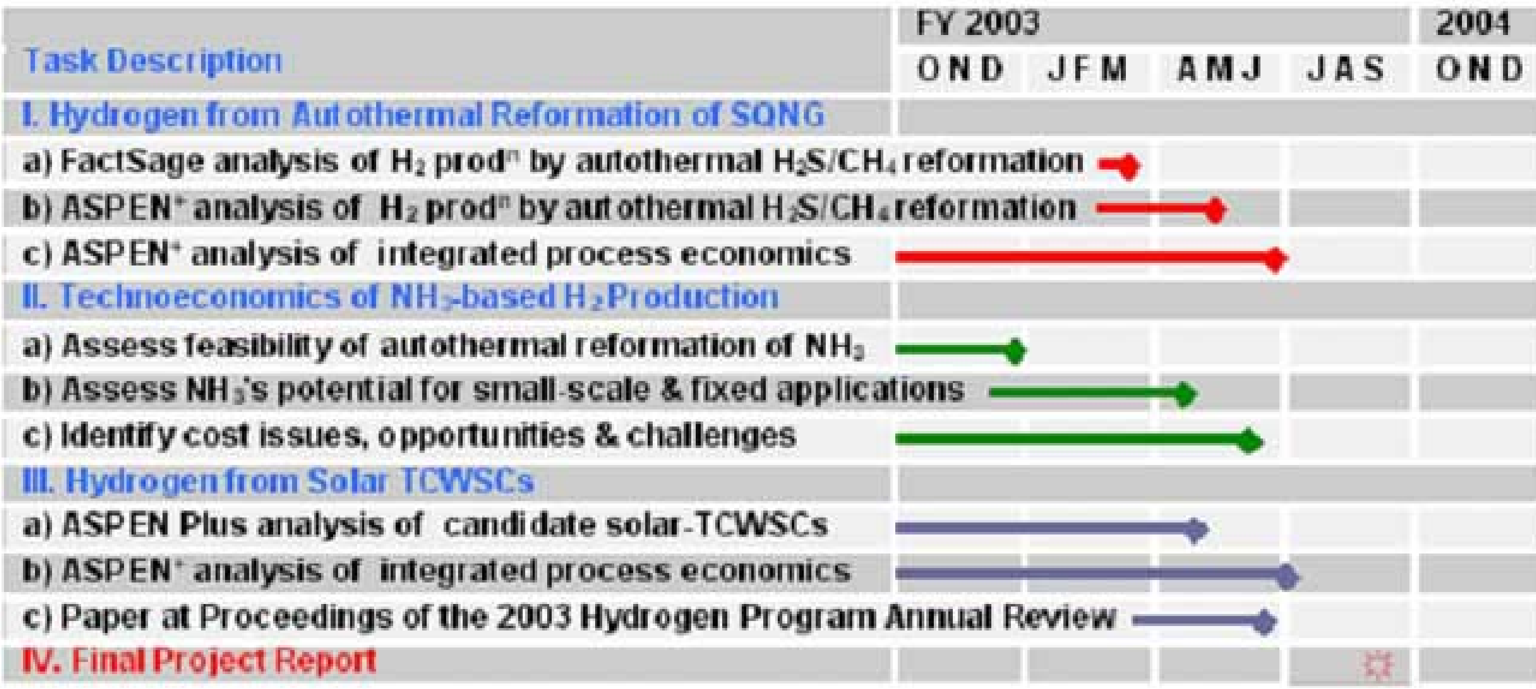
Goals and Objectives

Analyze issues of performance, cost & safety of three hydrogen technological areas:

- Thermochemical decomposition of SQNG
- Storage in NH_3 & NH_3-based complexes
- Thermochemical cycles water splitting cycles

All Milestones

(Technical Analysis of Hydrogen Production)



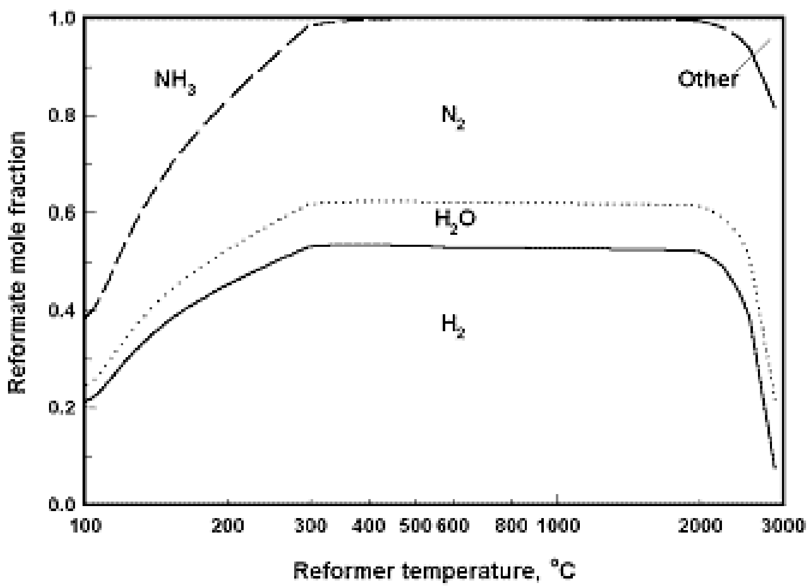
? End of the Project

Advantages of Ammonia

- Costs about $150 per short ton or less than $6.25 per million BTU of H_2 contained
- Contains17.8 wt% hydrogen
- Enjoys established infrastructure for its transportation, distribution, storage and utilization
- Stores 30% more energy by liquid volume than LH_2
- Easily reformed using 16% of the energy in the fuel
- Reformate for AFC use requires no shift converter, selective oxidizer or co-reactants
- No need for final hydrogen purification stage

Disadvantages of Ammonia

- Requires sub-ambient T and/or elevated P storage
- Safety concerns with the wide spread use as transportation fuel
- Requires some means for on-board reformation to liberate hydrogen – autothermal reformation is one approach



Chemical Hydrides (CHs) as Hydrogen & Ammonia Storers

- CHs are secondary storage methods (expendable) and their use requires:
  - Compatibility with PEMFC (no H_2S, CO or NH_3)
  - Load following capability without complex controls
- CHs fall into two classes:
  - Hydrolysis hydrides -

    H_2 is produced by reaction with H_2O, NH_3, H_2S, etc.
  - Pyrolysis hydrides -

    Decomposition by heat generates hydrogen

Hydrolysis Hydrides

Reaction	wt% H_2 Yield	Capacity Wh/kg
$LiH + H_2O \rightarrow LiOH + H_2$	7.7	1,460
$LiAlH_4 + 4\ H_2O \rightarrow LiOH + Al(OH)_3 + 4\ H_2$	7.3	1,380
$LiBH_4 + 4\ H_2O \rightarrow LiOH + H_3BO_3 + 4\ H_2$	8.6	1,630
$NaBH_4 + 4\ H_2O \rightarrow NaOH + H_3BO_3 + 4\ H_2$	7.3	1,380

Pyrolysis Hydrides

- Combination of a hydride with an ammonium halide, stabilized with polymeric binders (*e.g.* PTFE):

  $NH_4F + LiBH_4 = LiF + BN + 4\ H_2$ (~ 13.6 wt % H_2)
- NH_4X + MH formulations render compound storable, and insensitive to air & moisture
- $Mg(BH_4)_2.2NH_3/LiNO_3/PTFE$: 85/7½/7½ wt %

  - gives 12.84 wt% of 99.8% pure H_2
  - impurities include CO, NH_3 & CH_4
- $NH_3BH_3/N_2H_4.2BH_3/(NH_4)_2B_{10}H_{10}/\ NH_4NO_3$: 50/30/9.8/10.2 wt %

  - gives 16.52 wt% of >94% pure H_2
  - impurities include borazine $B_3N_3H_6$
- These reactions are highly exothermic & unstoppable

Amine-Borane Complexes

- $NH_4BH_4 = BN + 4\ H_2$ (24.5 wt % H_2)

  Unstable above -20 ^oC, unsuitable

- Ammonia borane (AB) complex:

  $NH_3BH_3 = BN + 3\ H_2$ (20 wt % H_2)

  Requires heating, decomposition at stages from ~130-450 ^oC

Pyrolysis of AB Complex

- $H_3BNH_3\ (l) \rightarrow H_2BNH_2\ (s) + H_2\ (g)$ ~137°C
  $\Delta H_r \sim 22$ kJ/mol
- $x\ (H_2BNH_2)\ (s) \rightarrow (H_2BNH_2)_x\ (s)$ ~125°C
- $(H_2BNH_2)_x\ (s) \rightarrow (HBNH)_x\ (s) + x\ H_2\ (g)$ ~155°C
- $(HBNH)_x\ (s) \rightarrow$ borazine + other products
- $(HBNH)_3 \rightarrow 3\ BN + 3\ H_2$ >> 500°C
- $(H_2BNH_2)_x\ (s) \rightarrow (BN)_x\ (s) + 2x\ H_2\ (g)$ ~450°C

Ref:
G. Wolf, et al., Thermochimica Acta 343(1-2): 19-25, 2000.
V. Sit, et al., Thermochimica Acta, 113, 379-82, 1987.
M.G. Hu, et al., Thermo-chimica Acta, 23(2), 249-55, 1978.
R.A. Geanangel & W.W. Wendlandt, Thermochimica Acta, 86, 375-78, 1985.

AB Complex

Property	Description
Formula	NH_3BH_3
Molecular weight	30.86
Odor	Ammonia-like
Density, g/mL	0.74
Melting point	112-114°C, slow decomp^n at approx. 70°C
Heat of formation	$\Delta H_f° = -42.54 \pm 1.4$ kcal/mol
Heat of combustion	$\Delta H_c° = -322.4 \pm 0.7$ kcal/mol

Drawback to AB Use

- Cost of NH_3BH_3 Production at present feedstock costs & technologies is too high

Required mass, volume and cost of chemical hydrides for specified targeted duty*

Storer	Mass, kg	Volume, l	Cost, US$
LiH [1]	1.7	3.7	109
CaH_2 [1]	4.5	4.0	104
$NaBH_4$ (35 wt% aqueous) [2]	6.21	6.21	102
H_3BNH_3	2.38	3.21	390-525

* To run a 1 kW AFC for 8 hours

1. V.C.Y. Kong, et al., Int. J. Hydrogen Energy, 24, 665-75, 1999.
2. S.C. Amendola, et al., Proceedings of the Power Sources Conference, 39th, 176-79, 2000.

Literature Search Results

- Approx. 1,450 articles related to borazine and borazine reactions of which about 50 or so related to the molecular modeling/ ab initio calculations
- About 300 articles involving borazane reactions including 50^{+} articles related to the molecular modeling/ ab initio calculations
- Only a dozen articles related to cyclotriborazane including one involving ab initio calculations (1977)
- Very few publications or studies related to the synthesis of cyclotriborazane or hydrogenation of borazine

Synthesis of AB Complex

- Indirect methods:

$$LiBH_4 + NH_4Cl \xrightarrow{DEE} LiCl + H_3BNH_3 + H_2$$

$$2\ LiBH_4 + (NH_4)_2SO_4 \xrightarrow{DEE} Li_2SO_4 + 2\ H_3BNH_3 + 2\ H_2$$

S.G. Shore & R.W. Parry, J. Am. Chem. Soc., 77, 6084-5, 1955
S.G. Shore & K.W. Böddeker, Inorg. Chem. 3(6): 914-15, 1964
M.G. Hu, et al., J. Inorg. Nucl. Chem. 39(12): 2147-50, 1977

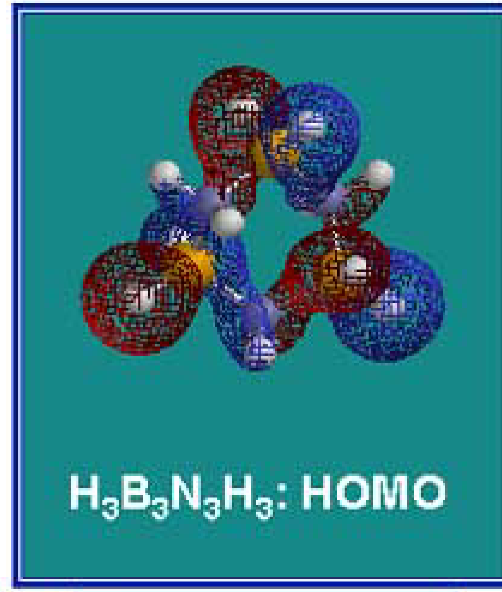
- Direct method:

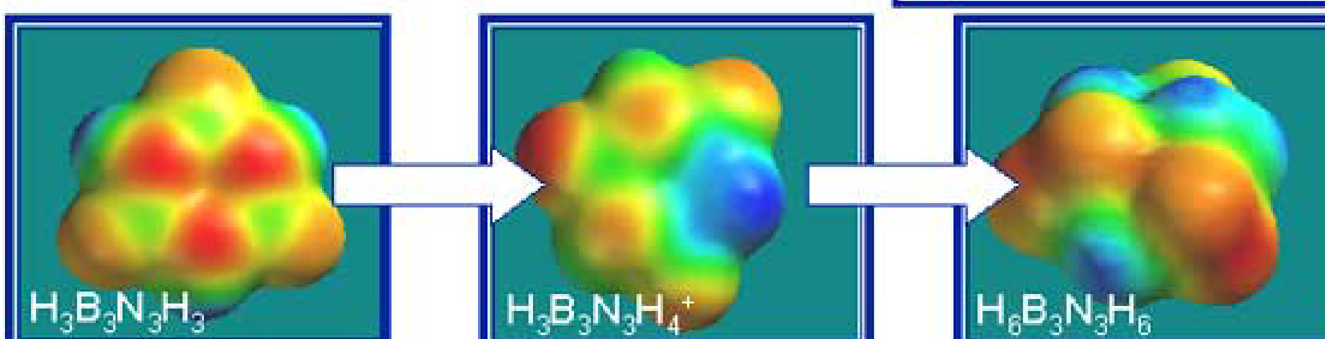
$$B_2H_6 + 2\ NH_3 \rightarrow 2\ H_3BNH_3$$

V.P. Sorokin, et al., Zh. Neorgan. Khim. 8, No. 1, 66; CA 58, 10962d, 1963
R.A. Geanangel & S.G. Shore, Prep. Inorg. React. 3: 123-238, 1966

Molecular Orbital Calculations

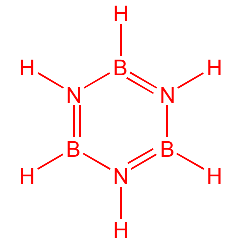
- Electrostatic potential for predicting H_2 bonding interactions
- Enthalpies of hydrogenation/dehyd.
- Potential energy surfaces
- Transition energies and structural information
- Vibrational frequencies



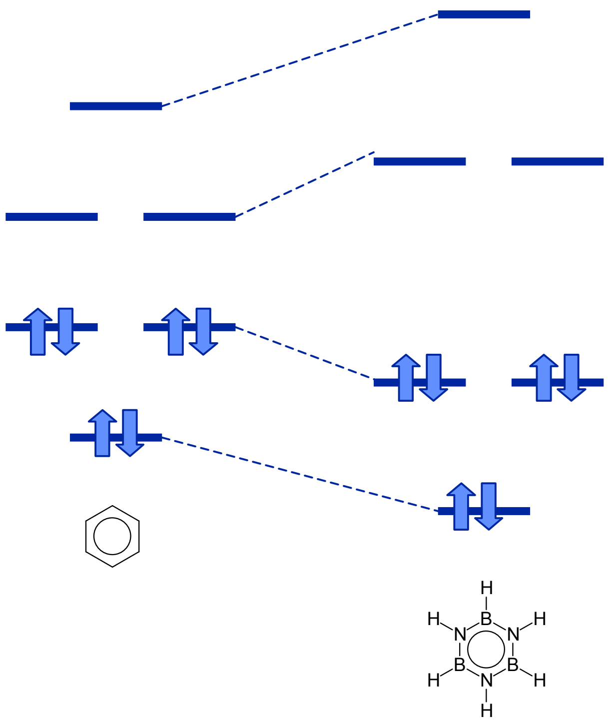


Electrostatic potential surfaces for the Isolated Molecules

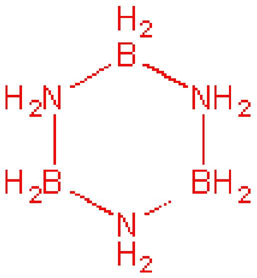
Borazine



- mp at –58°C & bp at 53°C) is stable in gas phase up to 500°C
- isoelectronic with benzene (*inorganic benzene)*
- Charge localisation on N makes borazine more susceptible to addition reactions and thus less stable than benzene



Cyclotriborazane

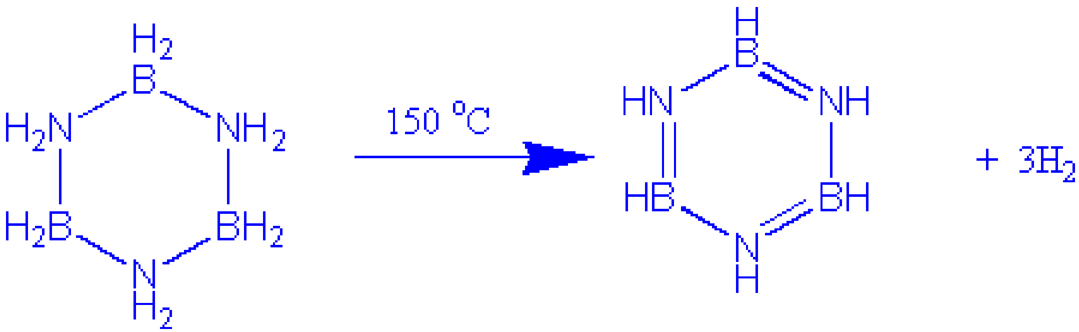


- Known synthesis routes:

  $2B_3N_3H_6.3HCl+6NaBH_4 \rightarrow 2B_3N_3H_{12}+6NaCl+3B_2H_6$ (1)

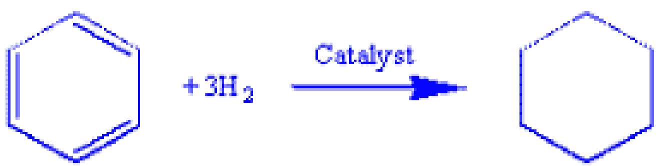
  $BH_2(NH_3)_2BH_4+NaC{\equiv}CH \rightarrow BH_2NH_2+NaBH_4+HC{\equiv}CH+NH_3$ (2)

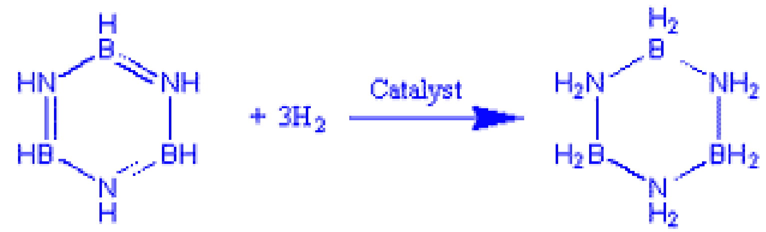
- Crystalline [3]
- Does not react with water [3]
- Cylcotriborazane contains 6.47% H_2 by weight [1]



1) Dahl, G.H. & Schaeffer, R. *J. Am. Chem. Soc.* **1961**, 83, 3032.
2) Shore, S.G. & Hickam, C.W. *Inorg. Chem.* **1963**, 2, 638.
3) Boddeker, K.W., et al. *J. Am. Chem. Soc.* **1966**, 88, 4396.

Borazine Hydrogenation





Catalyst	T (°C)	P (atm)
Ni Raney (L)	150	15
Pt (G)	200	11.25

- $\Delta H_{hydrogenation}$ = -30.1 kcal/mol [1]
- Cat. Activity: Rh>Ru>>Pt>>Pd>Ni>Co [3]

- $\Delta H_{hydrogenation}$ = 28.1 kcal/mol [1]
- Past attempts [2]
  - Ni at 70°C, 150°C & 200°C
  - Pd at 40-50°C
  - Unknown amorphous solid residue

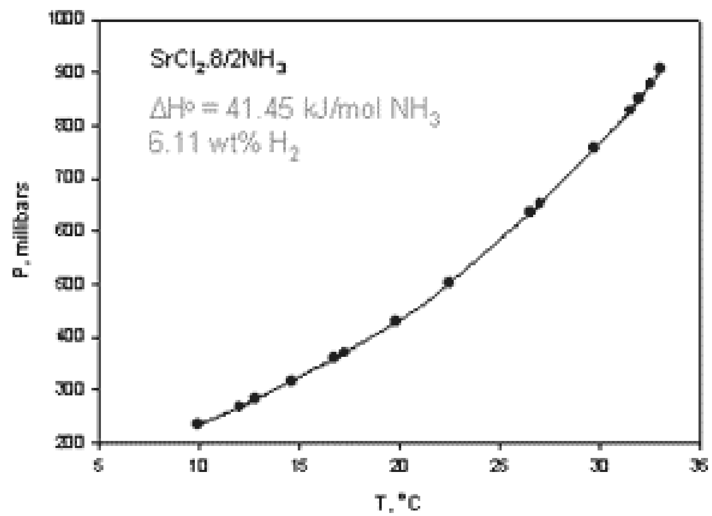
1) Gaussian 03: x86-Win32-G03RevB.01 3-Mar-2003; DFT B3LYP 6-31G.
2) Wiberg, E.; Bolz, A. *Berichte der Deutschen Chemischen* **1940**, 73B, 209.
3) Greenfiled, H. *Ann. N. Y. Acad. Sci.* **1973**, 214, 233.

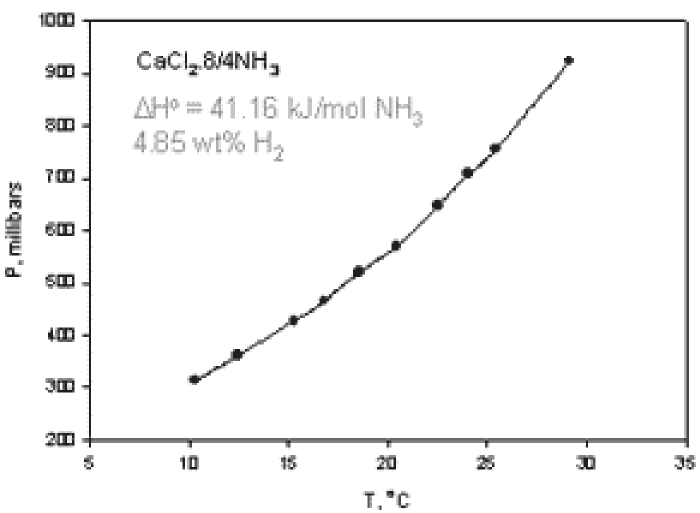
Advantageous Properties of Ammonia Complexes

- Can store large amounts of ammonia as high as the weight of the absorbing salt
- Many compounds and combinations are available
- Vapor pressure is independent of ammonia concentration, over very broad concentration ranges
- Ammonia complexes are solid state and thus not gravity sensitive

Metallic Salt Ammonia Complexes

- Solid-gas reaction pairs for chemical heat pumps [1]
- $MgCl_2$, $CaCl_2$, $CaBr_2$ & $SrBr_2$ can be used for NH_3 storage via heating to 200°C byTSA & $CaCl_2$-$CaBr_2$ mixed halides via evacuation to 10 kPa by PSA [2]

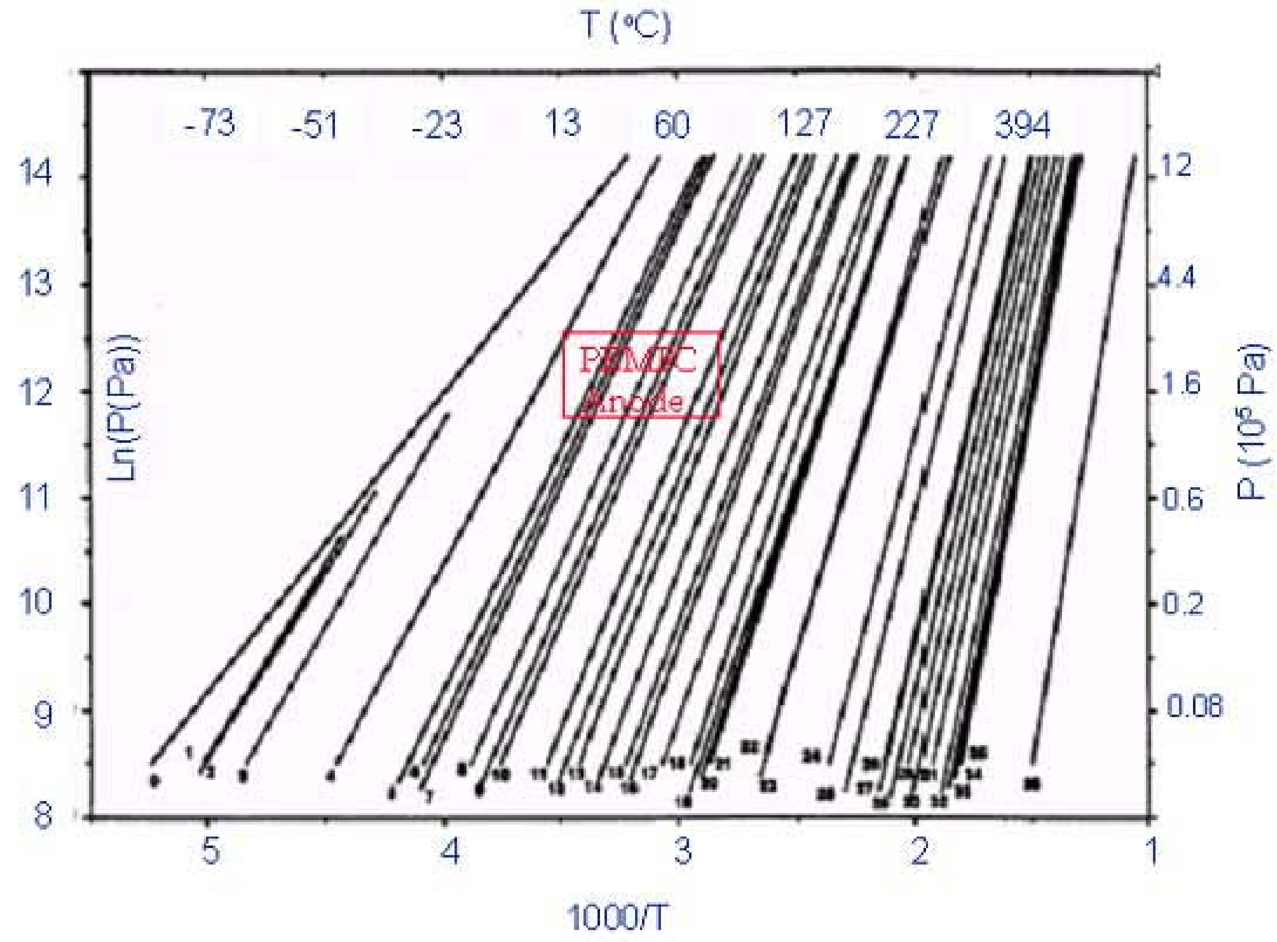




1. *Wentworth, W.E. TES Seminar, Stockholm, **1980**, 371.*
2. *Liu, C.Y. & Aika, K.-I. Chem. Lett. **2002**, 798.*

Equilibrium Lines for Various Chlorides/NH_3 Reactions

No		ΔH (J mol^{-1})
0	NH_3	23,366
1	Zn10-6	29,588
2	Ca10-6	31,387
3	Sn9-4	31,806
4	Pb8-3,25	34,317
5	Ba8-0	37,665
6	Sn4-2,5	38,920
7	Pb3,25-2	39,339
8	Ca8-4	41,013
9	Sr8-1	41,431
10	Ca4-2	42,268
11	Zn6-4	44,779
12	Pb2-1,5	46,035
13	Pb1,5-1	47,290
14	Mn6-2	47,416
15	Zn4-2	49,467
16	Cu5-3,3	50,241
17	Fe6-2	51,266
18	Cu3,3-2	56,497
19	Co6-2	53,986
20	Pb1-0	55,660
21	Mg6-2	55,660
22	Ni6-2	59,217
23	Ca2-1	63,193
24	Ca1-0	69,052
25	Mn2-1	71,019
26	Mg2-1	74,911
27	Fe2-1	76,167
28	Co2-1	78,134
29	Ni2-1	79,515
30	Zn2-1	80,352
31	Mn1-0	84,202
32	Fe1-0	86,880
33	Mg1-0	87,048
34	Co1-0	88,303
35	Ni1-0	89,810
36	Zn1-0	104,625



Neveu, P., Castaing, J. Heat Recovery & CHP, Vol. 13, No. 3, 1993.

Conclusions

- Successful implementation of chemical hydrides for vehicular FC applications requires:
  - Substantial reduction in their production costs
  - Development of new and/or innovative synthesis routes for their preparation
- Alkali earth metal halides and/or mixed halides may provide a promising route via ammonia to reversibly store hydrogen for PEMFC applications