New Possibilities for Hydrogen Transport

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Properties of Borazane, H_3BNH_3

Property	Borazane, H_3BNH_3	Ammonia, NH_3	Potential Problems
Hydrogen content (%)	19,5; The Hydrogen-storage density is higher than that of liquid hyrogen [1]; more hydrogen-dense than liquid hydrogen[2]	17.7	(1) NH_3 has a high Hydrogen storage capacity, but also a high decomposition temperature [3] (2) NH_3 is very toxic[3]
Boiling point (°C)	-	-33.34	
Melting point (°C)	97.61 (beginning dec. at 68°C)[1] 104°C[2], 110 – 112[4]	-77.73	
Physical state at RT	White solid[1], colorless crystals[2]	Colorless gas	
Density at RT (g cm^{-3})	780 mg mL^{-1}[2]	0.6819 g/cm^3 at -33.3°C (l); 0.73 g/cm^3 at 1.013 bar at 15°C[2]	
Toxicity/Hazard symbols	Flam.Sol 1 (100%), Acute Tox. (50%), Skin Irrit. 2 (50%), Eye Irrit. 2 (50%), Acute Tox. 4 (50%) ECHA	LD_{50} = 0.015 mL/kg (lethal dose); LC_{50} = 5000 ppm (5 mins., lethal conc.); NIOSH PEL = 50 ppm, REL = 25 ppm, IDLH = 300 ppm	
Release of hyrogen (H_2) at (°C)	80 – 150[1]	600[3]	

[1] Wikipedia: https://de.wikipedia.org/wiki/Ammiboran, accessed on 12.01.2023. [2] Wikipedia: https://en.wikipedia.org/wiki /Ammonia_borane, accessed on 12.01.2023. [3] *Physikalisch-chemische Untersuchungen zur Wasserstoffabgabe von BNH-Verbindungen*, J. Baumann, Doktorarbeit, TUB Freiberg, 2003, s. 3. [4] *Physikalisch-chemische Untersuchungen zur Wasserstoffabgabe von BNH-Verbindungen*, J. Baumann, Doktorarbeit, TUB Freiberg, 2003, s. 6.

Hydrogen (H$_2$) Transport by Ship: Energy density by weight vs. Energy density by volume

SPECIAL REPORT | Why shipping pure hydrogen around the world might already be dead in the water

Physics and cost mean that ammonia is a far more economic option for long-distance seaborne transportation, writes Leigh Collins

"Hydrogen transport by ship is technically possible for larger distances where pipelines are not an option. Because of its low energy density by volume, gaseous hydrogen is best converted into a more energy-dense liquid before being loaded onto a ship," says Irena's recent report, *Geopolitics of the Energy Transformation: The Hydrogen Factor*. "There are several vectors for hydrogen transport via ship, but ammonia is the most promising."

At normal atmospheric pressure, hydrogen contains just 3kWh of energy per cubic metre, so it either has to be compressed or liquefied to increase its energy density — to 1,411kWh/m^3 (at a pressure of 700 bar), or 2,350kWh/m^3 when super-cooled to a liquid at a balmy minus 253°C.

The volumetric energy density of ammonia is 59% higher — at 3,730kWh/m^3 when stored in its standard liquid form at minus 33.3°C.

So, assuming same-sized vessels, it would theoretically take more than three shipments of liquid hydrogen (LH$_2$) to transport the same amount of energy as two shipments of liquid ammonia (LNH$_3$).

The Suiso Frontier vessel, which is taking the world's first shipment of liquid hydrogen from southern Australia to Japan. Photo: Kawasaki Heavy Industries

In transport in tanks (e.g. ships), what matters is energy density by volume _and not_ energy density by weight

But NH₃ also has considerable problems:

And the traditional Haber-Bosch process, which is usually powered by fossil fuels, requires 9-11kWh/kg, according to multiple sources. However, powering Haber-Bosch via renewable electricity could cut this to 6.41kWh/kg, say **researchers at the UK's Cranfield University**.

While that might sound like a win for ammonia, LH_2 actually contains a lot more energy per kilogram than ammonia — 33.6kWh/kg versus 5.2kWh/kg. So while conversion to LH_2 requires the equivalent of 36% of the energy that the hydrogen contains, producing ammonia requires more energy than that held by the produced NH_3.

According to Bunro Shiowaza, a senior associate at the Sumitomo Chemical Company in Japan, **writing in the Japanese-language International Environment and Economy Institute Journal**, producing zero-carbon ammonia from green hydrogen (priced at $3/kg) would cost $480 per tonne, or $0.48/kg (*note: ammonia is only 17.65% hydrogen by mass*).

LH_2 based on green hydrogen at the same price would cost $7.15/kg — almost 15 times higher than green NH_3.

Taking all these elements into account, it is clear that ammonia would be far less expensive to transport by sea than liquid hydrogen.

Agora calculates it would be cheaper to produce green hydrogen in the EU than to import renewable H_2 by ship from places such as Chile and Australia, where high solar irradiation and strong winds means hydrogen can be produced extremely cheaply.

However, as the think-tank explains in its recent report, *12 Insights on Hydrogen,* the opposite would be true for hydrogen derivatives such as ammonia, methanol or synthetic fuel.

As the Royal Society policy briefing note points out, ammonia production currently results in about 500 million tonnes of CO_2 being released into the atmosphere each year, about 1.8% of annual global carbon emissions.

But don't we still need to trade pure hydrogen?

Yes, the world will still need a lot of pure hydrogen, probably to decarbonise heavy industry and heavy transport, rather than for use cases such as heating and cars, where electric options will be far cheaper.

And countries such as Germany, Japan and South Korea — as well as the EU — believe that they will not be able to produce enough clean hydrogen locally to meet demand. So international trade in H_2 is very much still needed.

HOW RECHARGE CALCULATED THE COST OF SHIPFULS OF AMMONIA AND LIQUID HYDROGEN

A full 160,000-cubic-metre cryogenic liquid tank (a standard size on LNG vessels where liquefied natural gas needs to be kept at minus 162°C) would contain 109,248 tonnes of liquid ammonia, which, using Shiowaza's costings of $0.48/kg, would cost $52.44m to produce.

The same tank would only be able to hold 11,376 tonnes of liquid hydrogen, which would cost $81.34m to produce at a price of $7.15/kg.

The ammonia shipment would therefore contain 596.8GWh of energy, at a cost of $87.87/MWh, whereas the hydrogen tankful would contain 404.8GWh at a cost of $200.94/MWh.

Synthesis of Borazane, H_3BNH_3

Various possibilities have been described in the literature e.g.:

$$LiBH_4 \quad + \quad NH_4Cl \quad \longrightarrow \quad H_3BNH_3 \quad + \quad LiCl \quad + \quad H_2$$

45% yield

$NaBH_4$ can be used instead of $LiBH_4$
NH_4Cl can be replaced by $(NH_4)_2CO_3$ or $(NH_4)_2SO_4$

$$LiBH_4 + NH_4Cl \rightarrow [NH_4]^+[BH_4]^- + LiCl$$ **Metathesis reaktion**

$$[NH_4]^+[BH_4]^- \rightarrow H_3N-BH_3 + H_2$$ **Proton-Hydride combination**

or e.g.:

$$2\,NaBH_4 \quad + \quad (NH_4)_2CO_3 \quad \xrightarrow{\text{THF}} \quad 2\,H_3BNH_3 \quad + \quad Na_2CO_3 \quad + \quad 2\,H_2$$
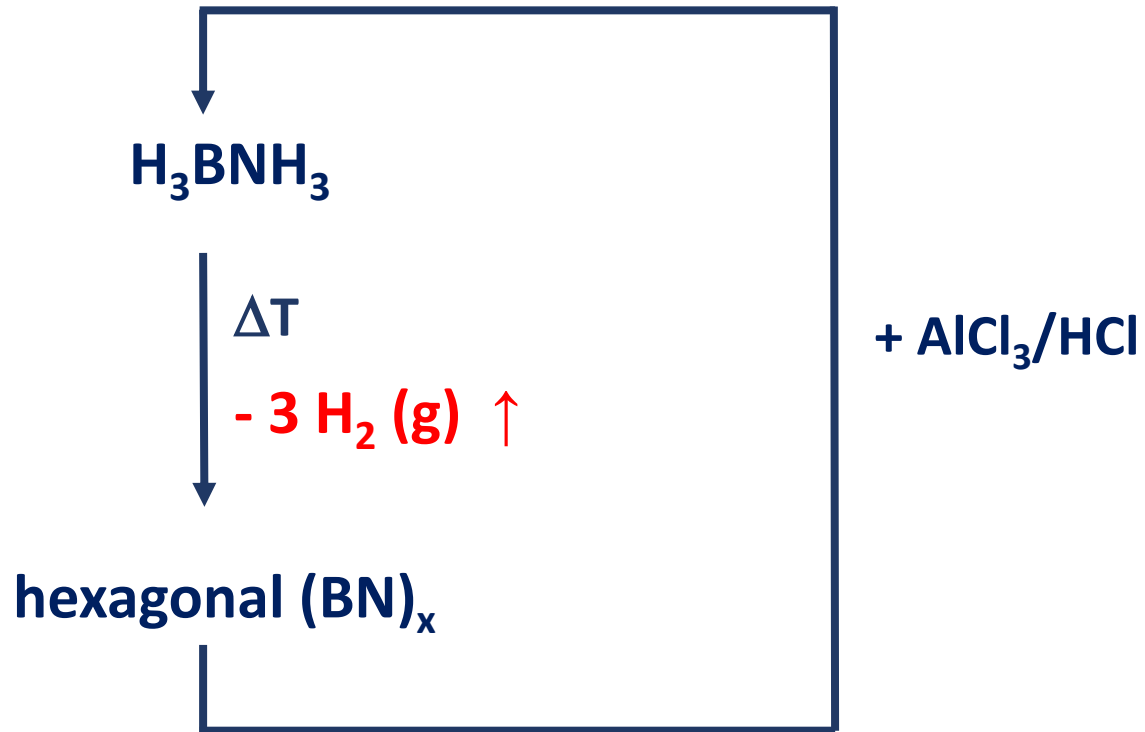
[1] *Physikalisch-chemische Untersuchungen zur Wasserstoffabgabe von BNH-Verbindungen*, J. Baumann, Doktorarbeit, TUB Freiberg, 2003, s. 5, 16.
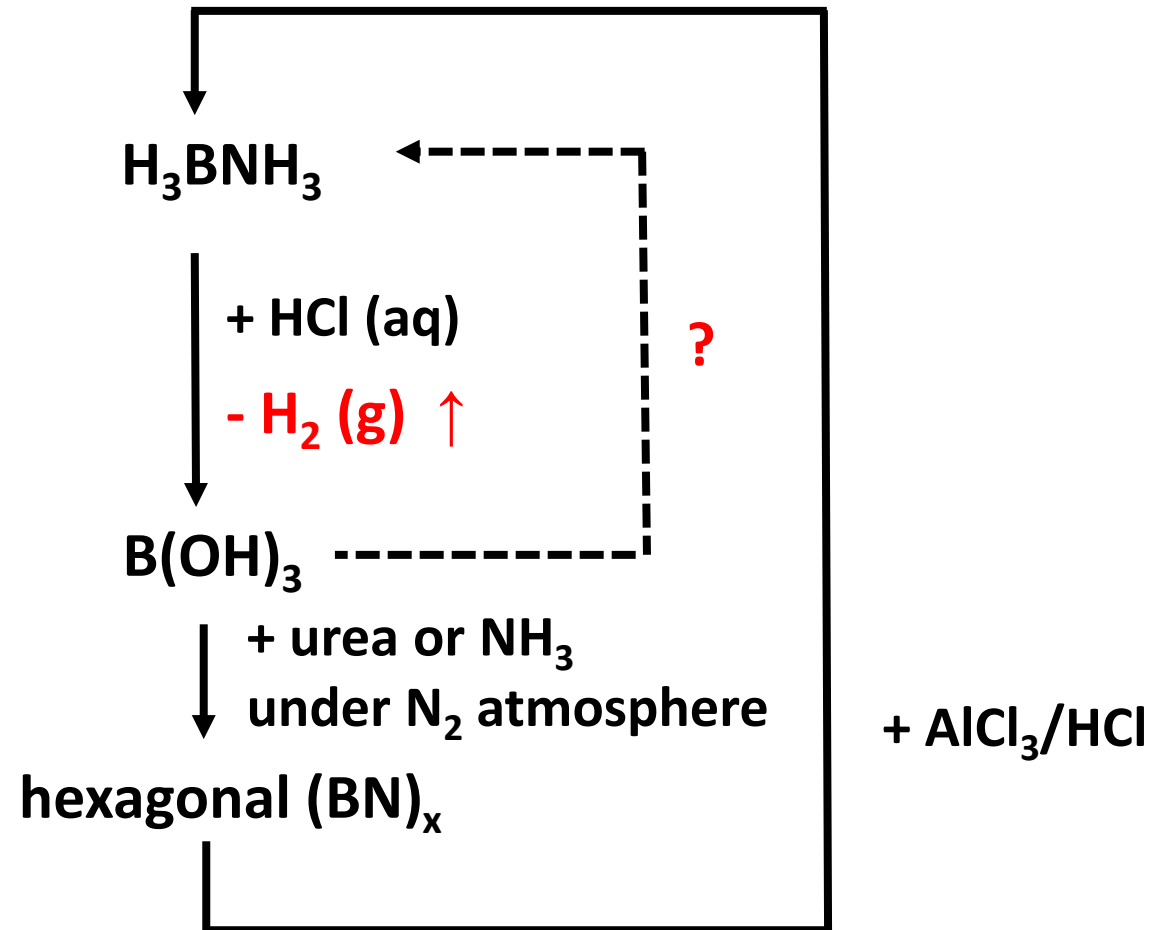[2] U. M. Dermirci, *Energies*, **2020**, *13*, 3071.

Two (abbreviated) Cycles for the Possible Synthesis and Decomposition of H_3BNH_3, with the Release of Hydrogen (H_2)
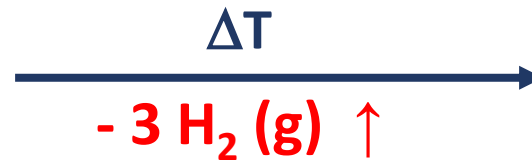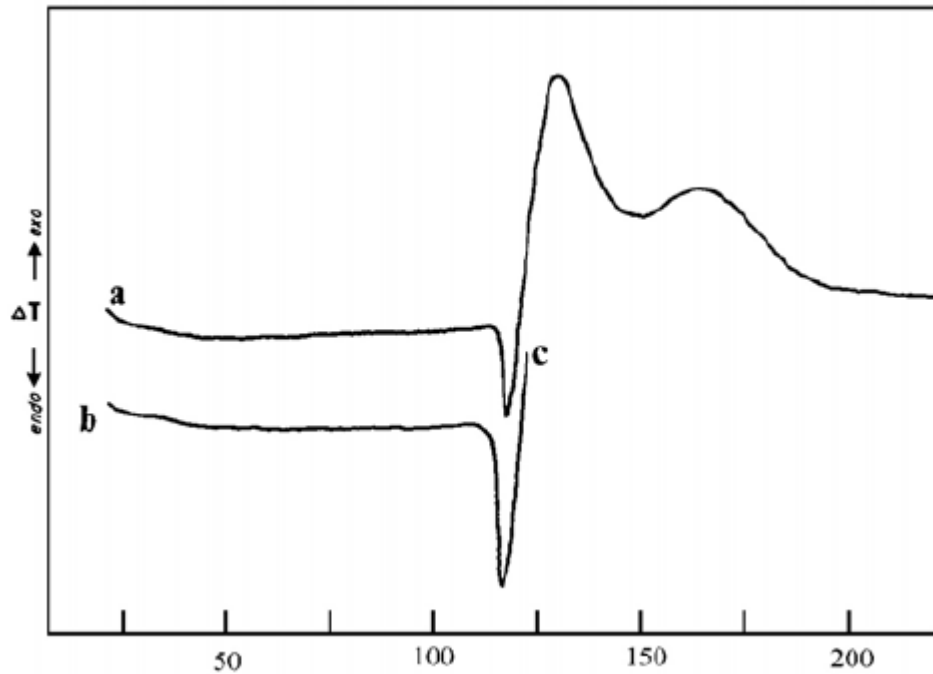
1st Possibility

2nd Possibility

H_3BNH_3

ΔT

$- 3\ H_2\ (g)\ \uparrow$

hexagonal $(BN)_x$

$+\ AlCl_3/HCl$

H_3BNH_3

$+\ HCl\ (aq)$

$-\ H_2\ (g)\ \uparrow$

?

$B(OH)_3$

$+$ urea or NH_3
under N_2 atmosphere

hexagonal $(BN)_x$

$+\ AlCl_3/HCl$

Thermal Decomposition of Borazane, H_3BNH_3

1st Possibility: H_3BNH_3 $\xrightarrow{\Delta T}$ hexagonal $(BN)_x$

$- 3 H_2 (g) \uparrow$

Thermal decomposition of Borazane (DTA) by Hu et al., up to 200°C, with $\beta = 10$ K/min

Thermal decomposition of Borazane up to 200°C under N_2, with $\beta = 5$ K/min

Decomposition processes are accompanied by the release of hydrogen.

Hu et al.: above T = 120°C, mass loss of 31.6%; up to 200°C a total of 35 mass-% lost

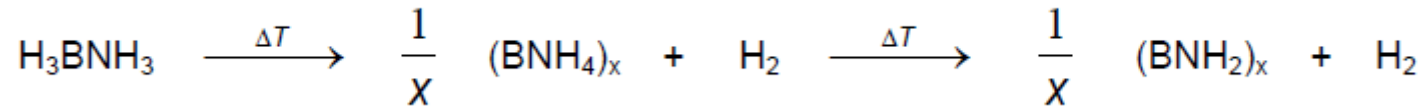*Sorokin et al.*: at T = 105°C, mass loss of ca. 6.5%; at 150°C ca. 9.8 mass-%; at 300°C ca. 12.7 mass-%

Sorokin et al.: All of the bound hydrogen in H_3NBH_3 is released with the formation of boron nitride

Physikalisch-chemische Untersuchungen zur Wasserstoffabgabe von BNH-Verbindungen, J. Baumann, Doktorarbeit, TUB Freiberg, 2003, s. 73, 21.

Hu

$$H_3BNH_3 \xrightarrow{\Delta T} \frac{1}{X} (BNH_4)_x + H_2 \xrightarrow{\Delta T} \frac{1}{X} (BNH_2)_x + H_2$$
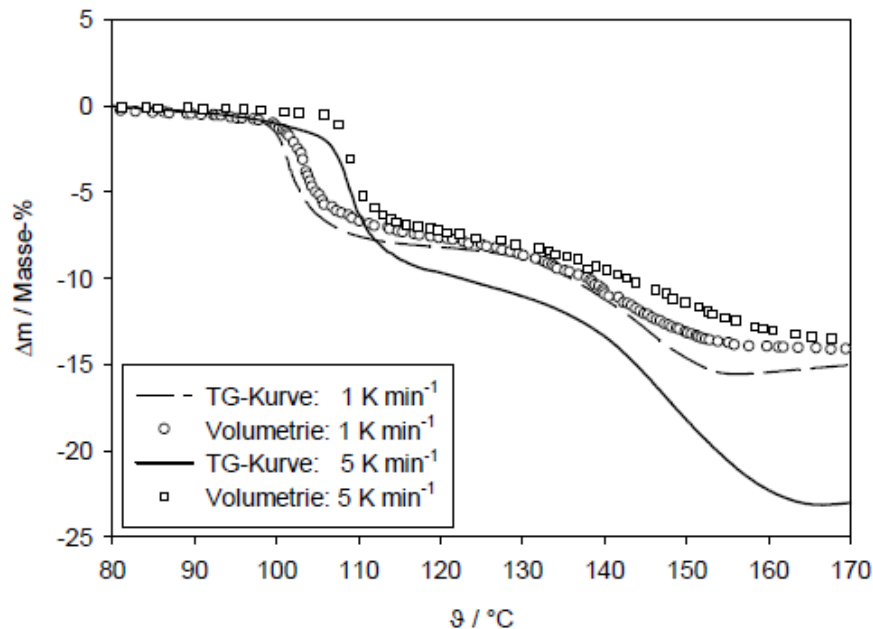
Thermal decomposition occurs through two processes
DTA, TG

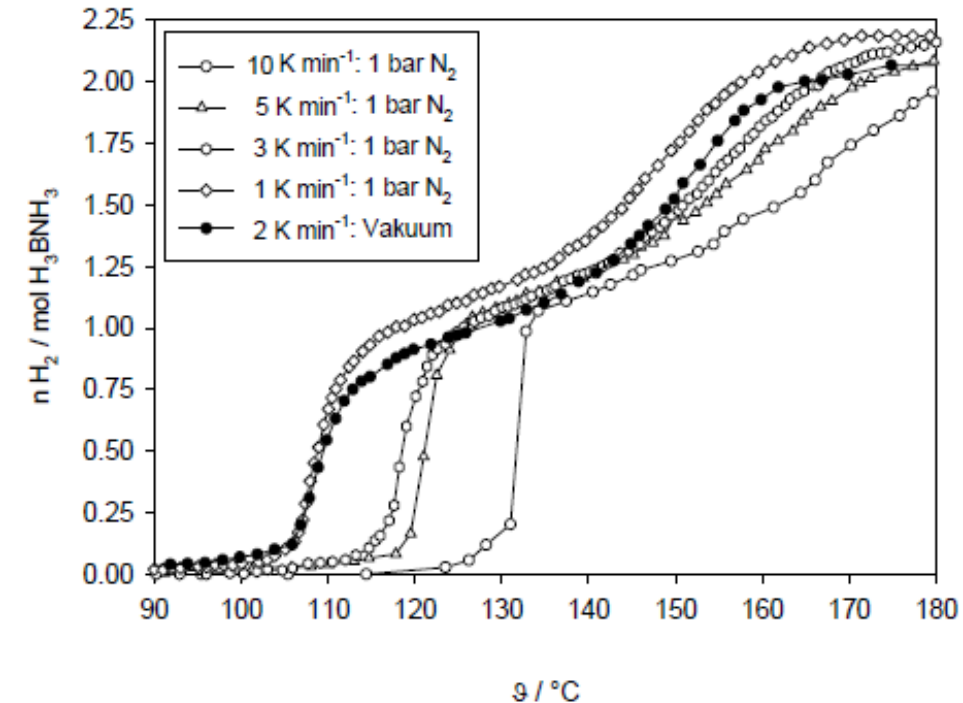**Thermal decomposition at 20 – 200°C:**
Volumetric: Value of n = (2,2 ± 0,2) mol H_2 / pro mol H_3BNH_3
(corresponds to a mass loss of Δm = 14,2 Masse-%

Comparison of the thermal decomposition
of H_3NBH_3 at various heating rates

Difference between the calculated mass loss for H_2 release and the experimentally determined value corresponds to ca. 2 mass-%.
This difference is attributed to Additional gaseous decomposition products

Volumetric investigations into the thermal decomposition of H_3NBH_3 different conditions

Physikalisch-chemische Untersuchungen zur Wasserstoffabgabe von BNH-Verbindungen, J. Baumann, Doktorarbeit, TUB Freiberg, 2003, s. 73, 21.

Thermal Decomposition of Borazane, H_3BNH_3

IR spectrum of the gaseous decomposition products showed:

At 102.5°C, 1st decomposition stage (slow): Aminoboran H_2BNH_2 as well as H_2
At 150°C, 2nd decomposition stage: Borazin, $B_3N_3H_6$ as well as H_2

Hydrogen release (H_2) in both processes
A total of 2.2 ± 0.2 mol H_2 per mol H_3NBH_3

Compounds which are involved in the decomposition:

Gas-phase: Hydrogen (H_2), monomeric Aminoborane (H_2NBH_2), Diborane (B_2H_6), Borazine ($(HBNH)_3$)
Solid state: Borazane starting material (H_3BNH_3), polymeric $(BNH_x)_z$ mixture

Steady hydrogen release is observed espite different decomposition conditions
(volumetric investigations), but

No solid final product with defined composition – probably a mixture of different polymers

$\Rightarrow$ Probably the degree of polymerisation of the polymer $(BNH_x)_y$ is dependent on the duration of decomposition
   since significant differences in the hydrogen content are observed, depending on the conditions used
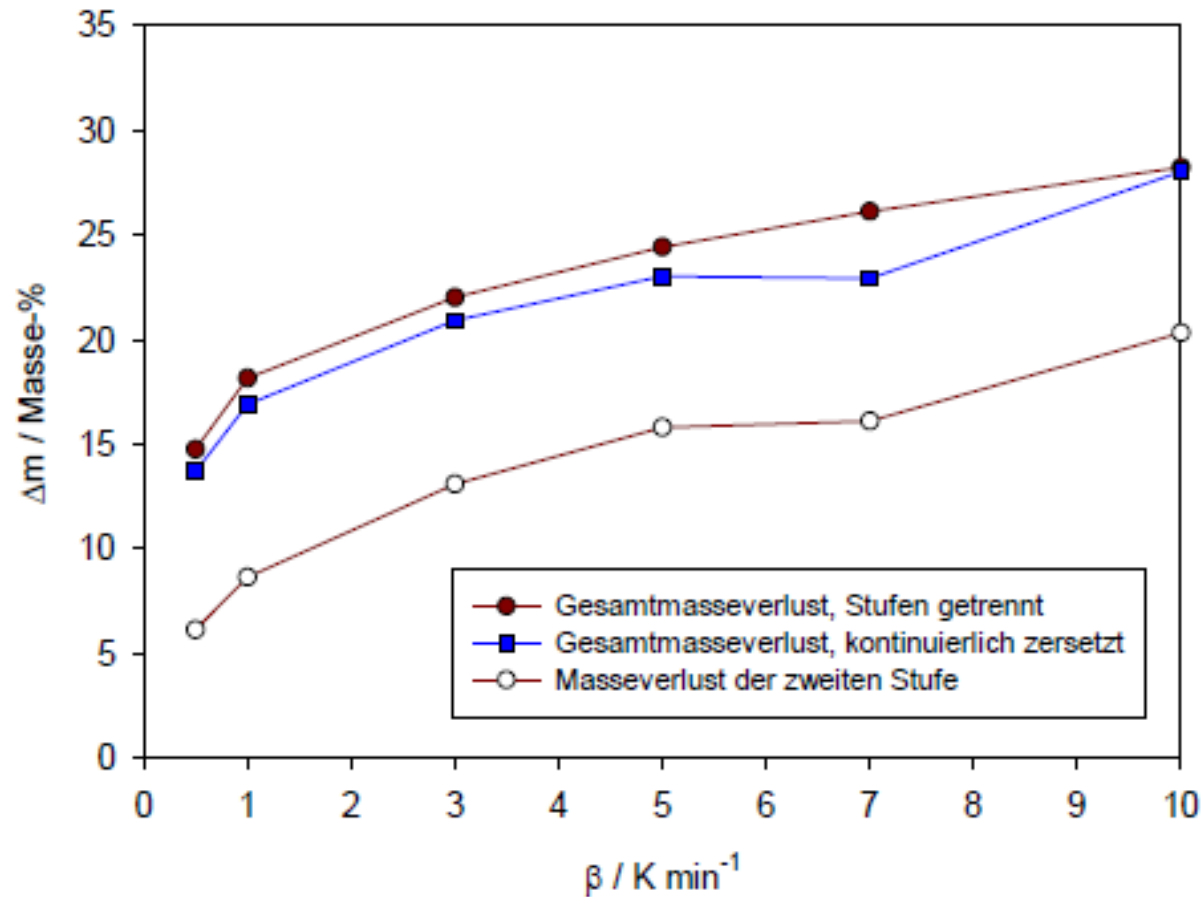
The quantity of gas released increases with increasing heating rate

**Hydrogen release (H_2) in both processes corresponds to a total of 2.2 ± 0.2 mol H_2 per mol H_3NBH_3
But the total mass loss lies between 14 masse-% to 33 mass-% depending on the conditions used for decomposition**

Physikalisch-chemische Untersuchungen zur Wasserstoffabgabe von BNH-Verbindungen, J. Baumann, Doktorarbeit, TUB Freiberg, 2003.
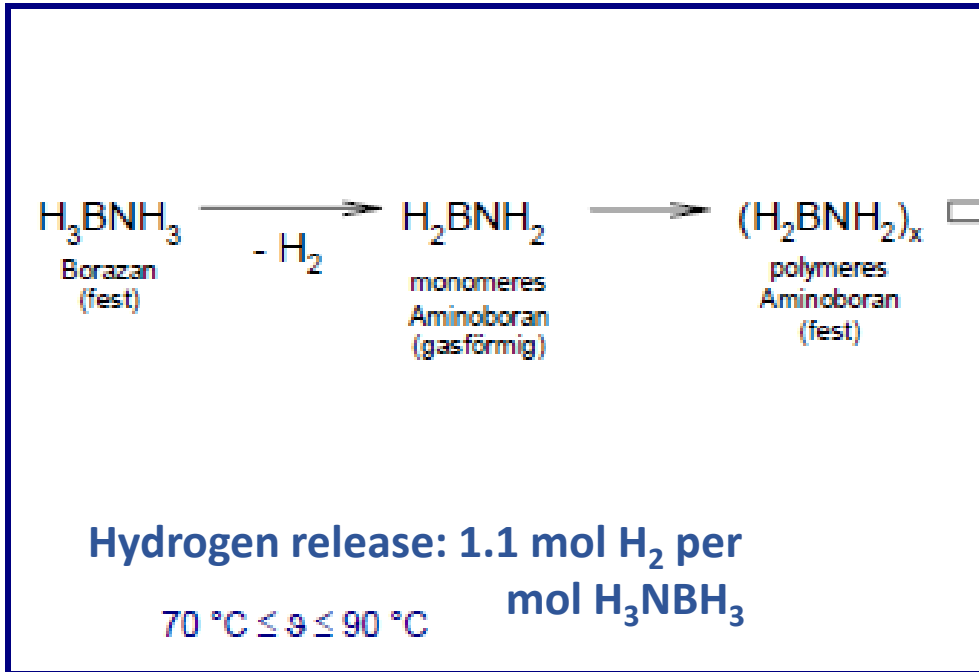
All 3 curves show an increase in the mass loss with increasing heating rate

The almost constant difference between the mass loss of the overall process and that of the 2nd decomposition stage confirm that for the 1st decomposition stage a constant mass loss results
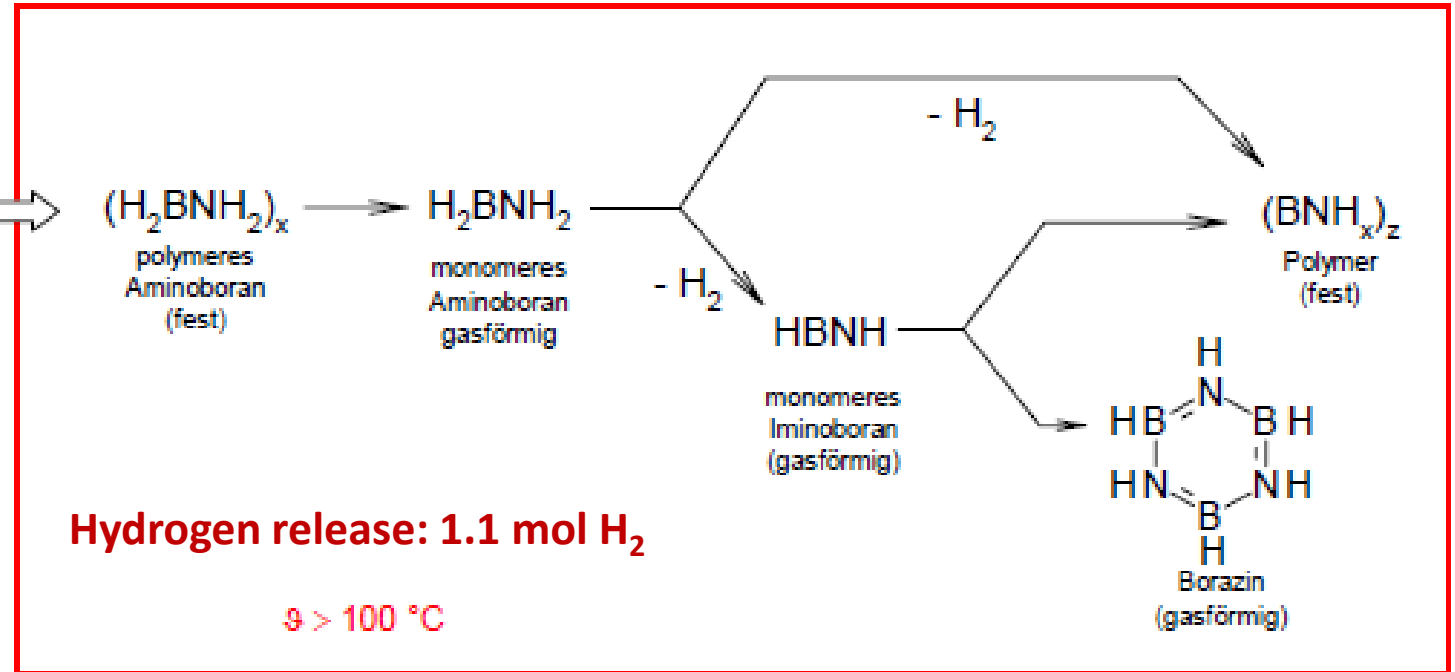

Physikalisch-chemische Untersuchungen zur Wasserstoffabgabe von BNH-Verbindungen, J. Baumann, Doktorarbeit, TUB Freiberg, 2003.

Overview of the Thermal Decomposition of Borazane, H_3BNH_3

1st stage of thermal decomposition

2nd stage of thermal decomposition

H_3BNH_3 $\xrightarrow{-H_2}$ H_2BNH_2 $\longrightarrow$ $(H_2BNH_2)_x$

Borazan (fest)

monomeres Aminoboran (gasförmig)

polymeres Aminoboran (fest)

Hydrogen release: 1.1 mol H_2 per mol H_3NBH_3

$70\ °C \leq \vartheta \leq 90\ °C$

$(H_2BNH_2)_x$ $\longrightarrow$ H_2BNH_2

polymeres Aminoboran (fest)

monomeres Aminoboran gasförmig

$\xrightarrow{-H_2}$ HBNH

monomeres Iminoboran (gasförmig)

$\xrightarrow{-H_2}$ $(BNH_x)_z$

Polymer (fest)

Borazin (gasförmig)

Hydrogen release: 1.1 mol H_2

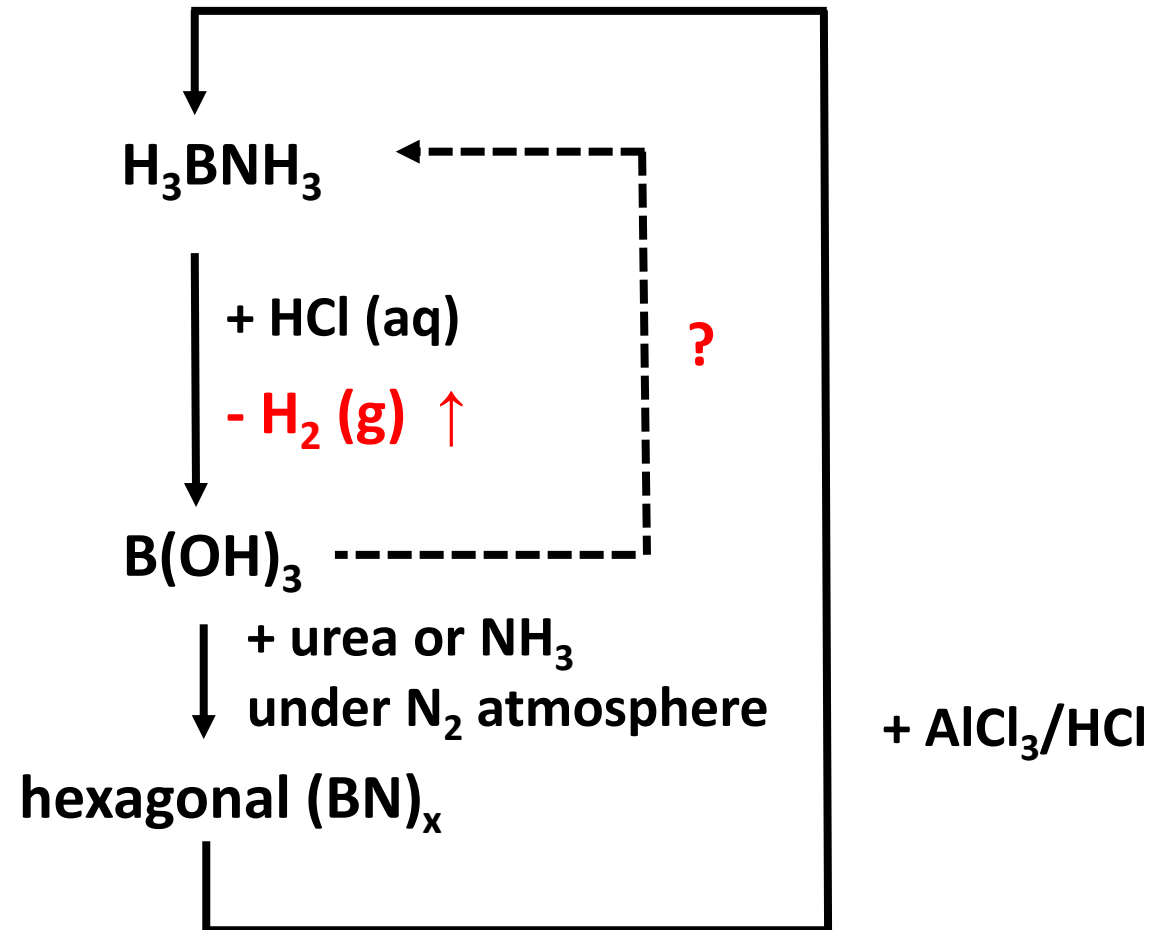$\vartheta > 100\ °C$

Hydrogen (H_2) can be released at moderate temperatures in the thermal decomposition of Borazane, H_3BNH_3

Physikalisch-chemische Untersuchungen zur Wasserstoffabgabe von BNH-Verbindungen, J. Baumann, Doktorarbeit, TUB Freiberg, 2003, s. 89.

Two (abbreviated) Cycles for the Possible Synthesis and Decomposition of H_3BNH_3, with the Release of Hydrogen (H_2)

1st Possibility

H_3BNH_3

ΔT

- 3 H_2 (g) ↑

hexagonal $(BN)_x$

+ $AlCl_3/HCl$

2nd Possibility

H_3BNH_3

+ HCl (aq)

- H_2 (g) ↑

$B(OH)_3$

?

+ urea or NH_3
under N_2 atmosphere

hexagonal $(BN)_x$

+ $AlCl_3/HCl$
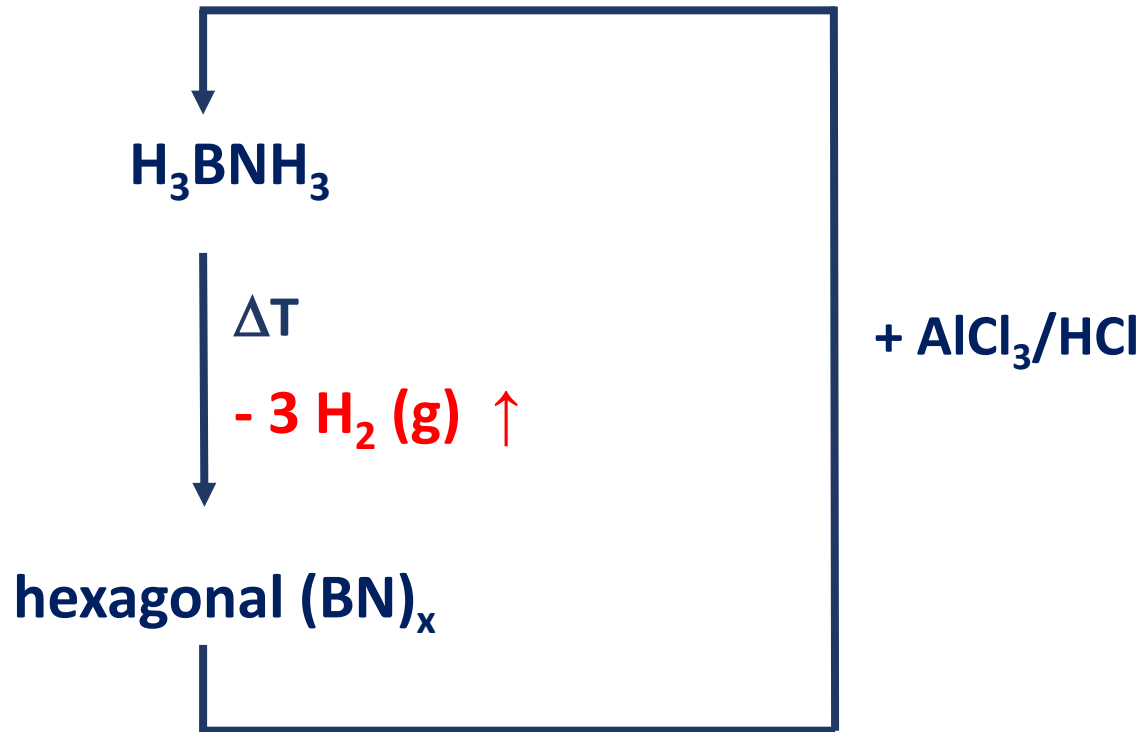
The Release of Hydrogen is Also Possible Through the Hydrolysis of Borazane, H_3BNH_3

Borazane shows considerable stability in water, with a decomposition rate of 0.4% (2,5 % solution, 24 hours at RT)

Pure Borazane doesn't decompose in the presence of moisture from the air by releasing hydrogen and ammonia

Speed of hydrogn relase on hydrolysis with a metal catalyst (Pt/Al$_2$O$_3$) or with 0.1 N hydrochloric acid
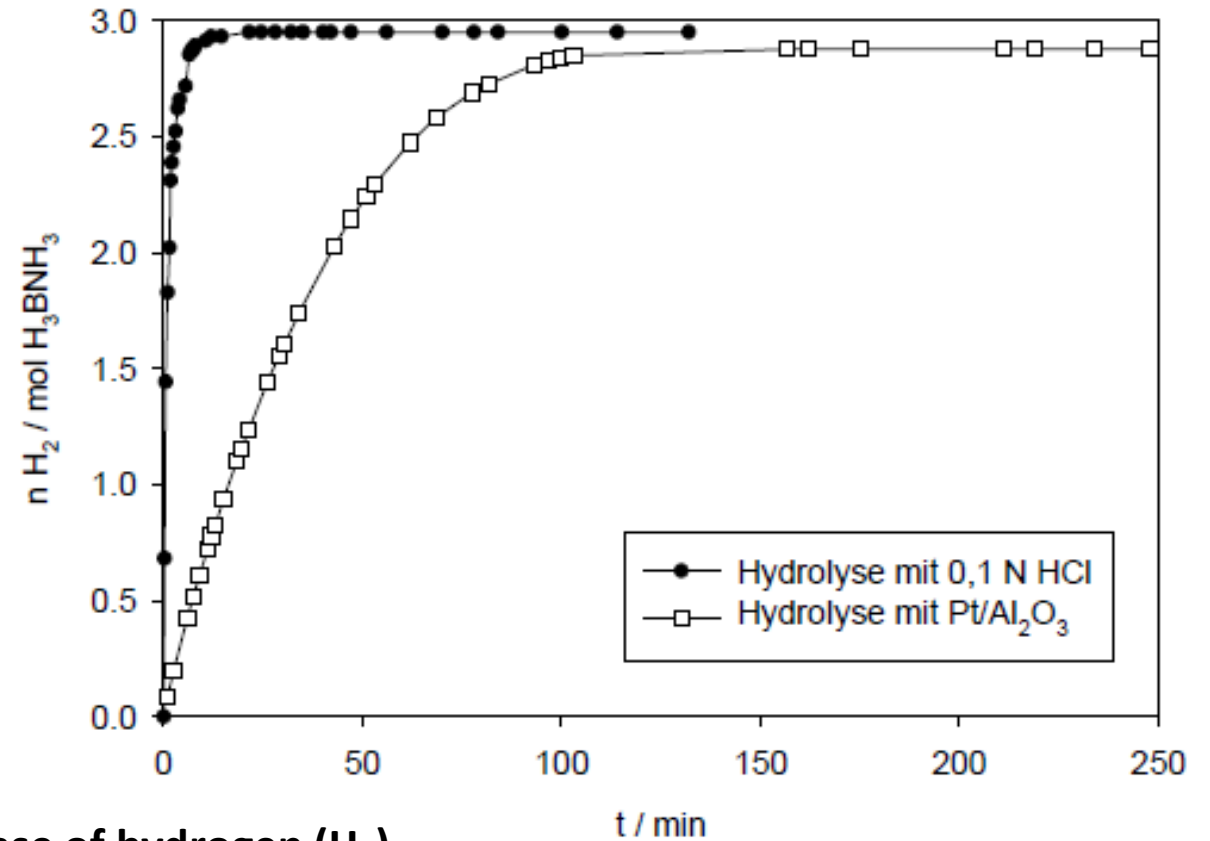
Aqueous Borazane solutions decompose:
* Immediately on contact with a metal catalyst with the release of hydrogen (H$_2$)
* Immediately on addition of an acid (without a metal catalyst)

Hydrolysis in the presence of an acid proceeds quicker than by addition of a metal catalyst

$$2\,H_3BNH_3 \;+\; 6\,H_2O \;\xrightarrow{\text{(Pt, Ni or Pd cat. (aq))}}\; [2\,B(OH)_3 \;+\; 2\,NH_3]\,(aq) \;+\; 6\,H_2$$
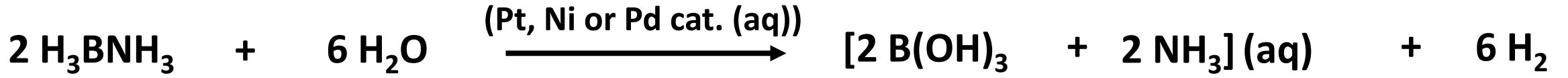
Corresponds to the hydrolysis of Borazane

Borazane can be dissolved in water, and it is relatively stable in aqueous solutions if a catalyst is not present (ca. 0.4% dec. after 24 hours; 15% dec. after 70 days)
Decomposition of Borazane (H_3BNH_3) in aqueous solution occurs only after the addition of a catalyst

Long-term stabilty study of Borazane (m = 9.43 mg) in aqueous solution
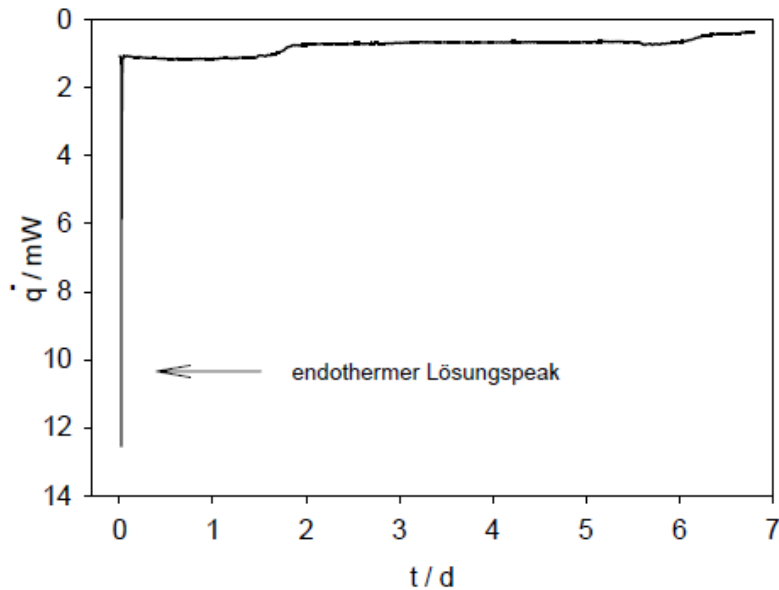
- Mit Hilfe von Leitfähigkeitsmessungen wurde nach 24 Stunden ein Hydrolysegrad von 0,4 % ermittelt. Nach insgesamt 70 Tagen beträgt der Hydrolysegrad 15 %. Es erfolgten Messungen der Leitfähigkeit von Wasser, einer Borazanlösung ohne Katalysator und einer Borazanlösung mit Katalysator (Abb. 37).

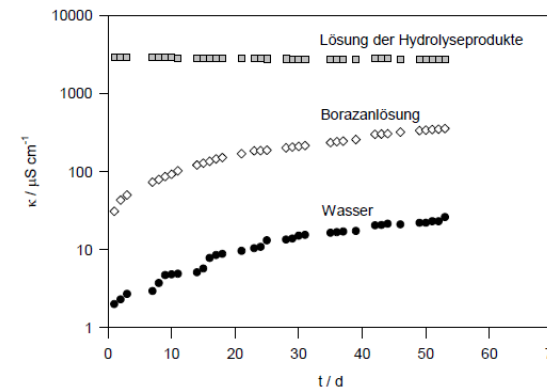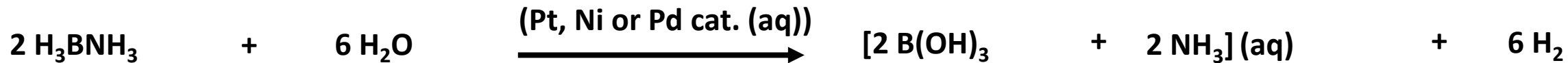Abb. 37: Leitfähigkeitsmessungen einer wässrigen Borazanlösung und einer Lösung nach erfolgter Borazanhydrolyse

Physikalisch-chemische Untersuchungen zur Wasserstoffabgabe von BNH-Verbindungen, J. Baumann, Doktorarbeit, TUB Freiberg, 2003, s. 50.

$$2\ H_3BNH_3 \quad + \quad 6\ H_2O \quad \xrightarrow{\text{(Pt, Ni or Pd cat. (aq))}} \quad [2\ B(OH)_3 \quad + \quad 2\ NH_3]\ (aq) \quad + \quad 6\ H_2$$

Based on this reaction equation, a Hydrogen release of n ~ 2.9 mol H_2/mol H_3NBH_3 was observed regardless of the Borazane concentration

Calvet-Kalorimeter

Kat. = 0.5% Pt auf Korundträger

T = 30°C

Exotherm
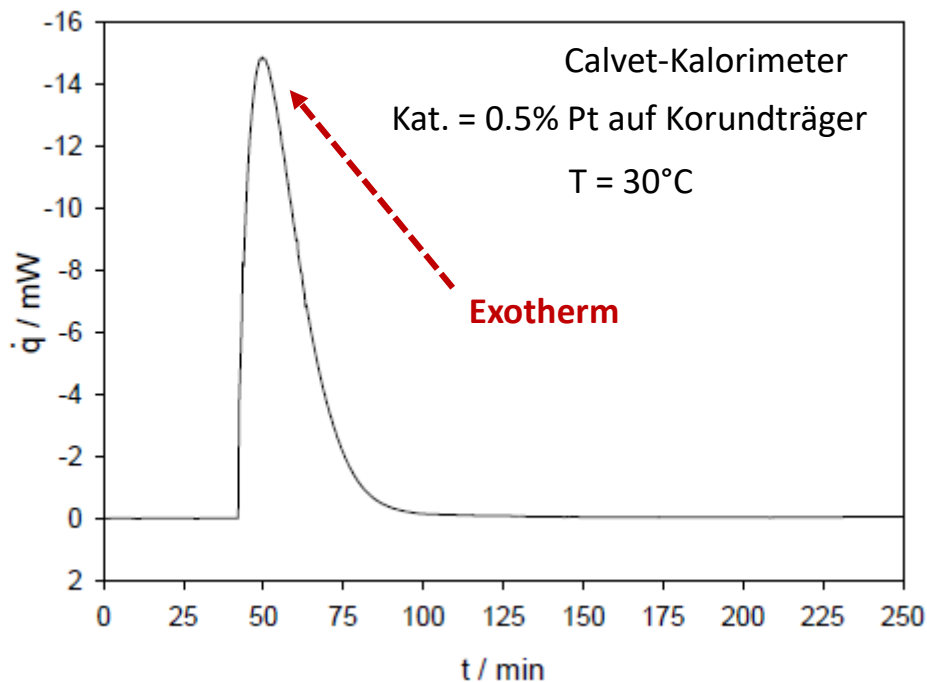
Hydrolysis of dissolved Borazane with Pt/Al_2O_3 catalyst under N_2 (30°C)

15 mg Pt/Al_2O_3
30 mg Pt/Al_2O_3
50 mg Pt/Al_2O_3

Volumetric investigation of Borazane hydrolysis with different quantities of catalyst

Hydrolysis of aq. Borazan at RT possible if Pt catalyst is present
Ni catalysata and Pd/Al_2O_3 catalysts less effective
Highest speed of hydrolysis with Pt catalyst

Hydrolysis requires at least 3 mol H_2O per mol Borazane
Duration of hydrolysis depends on quantity of catalyst present
Duration of hydrolysis independent of the concentration of the Borazane solution

Physikalisch-chemische Untersuchungen zur Wasserstoffabgabe von BNH-Verbindungen, J. Baumann, Doktorarbeit, TUB Freiberg, 2003, s. 51.

Thermodynamics of the Aqueous Hydrolysis of H_3BNH_3 in the Presence of a Catalyst

$$H_3BNH_3 \quad + \quad 3\,H_2O \quad \longrightarrow \quad B(OH)_3 \quad + \quad NH_3 \quad + \quad 3\,H_2$$

$\Delta_R H_3$: $\quad H_3BNH_3\,_{(aq)} + 3\,H_2O \quad \xrightarrow{\text{Kat.}} \quad 3\,H_2\,_{(g)} + NH_3\,_{(aq)} + H_3BO_3\,_{(aq)}$ $\qquad \Delta_R H_3 = -(179{,}2 \pm 8{,}0)\ \text{kJ mol}^{-1}$

$\Delta_L H_1$: $\quad H_3BNH_3\,_{(s)} \quad \xrightarrow{\text{H2O}} \quad H_3BNH_3\,_{(aq)}$ $\qquad \Delta_L H_1 = (16{,}4 \pm 1{,}3)\ \text{kJ mol}^{-1}$

$\Delta_L H_2$: $\quad H_3BO_3\,_{(s)} \quad \xrightarrow{\text{H2O}} \quad H_3BO_3\,_{(aq)}$ $\qquad \Delta_L H_{\text{H3BO3}} = 22{,}1\ \text{kJ mol}^{-1}$

$\Delta_L H_3$: $\quad NH_3\,_{(g)} \quad \xrightarrow{\text{H2O}} \quad NH_3\,_{(aq)}$ $\qquad \Delta_L H_{\text{NH3}} = -35{,}3\ \text{kJ mol}^{-1}$

$\Delta_R H_4$: $\quad H_3BO_3\,_{(aq)} + NH_3\,_{(aq)} \quad \longrightarrow \quad [\text{Folgeprodukte}]_{\text{H2O}}$ $\qquad \Delta_R H_4 = -(20{,}7 \pm 0{,}3)\ \text{kJ mol}^{-1}$
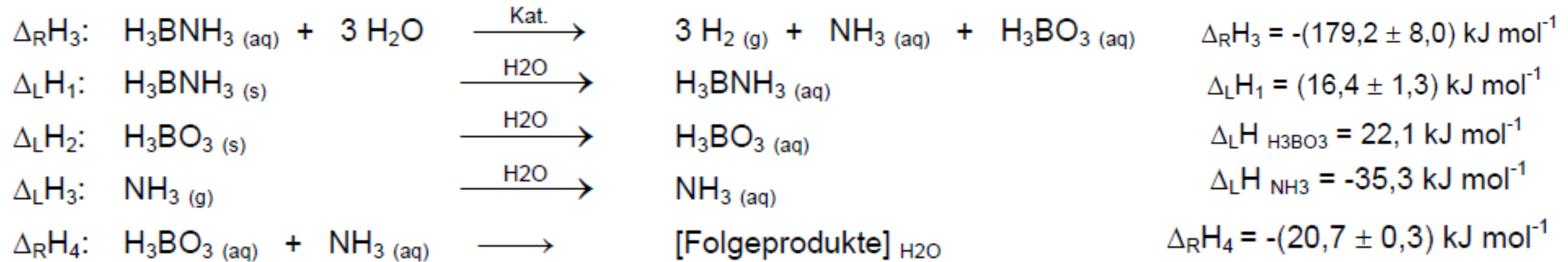
Enthalpy of Hydrolysis for H_3BNH_3/cat.:

$$\Delta_R H_{\text{H3BNH3 / Kat}} = \Delta_R H_3 + \Delta_L H_1 - \Delta_L H_2 - \Delta_L H_3 - \Delta_R H_4$$

$$\Delta_R H_{\text{H3BNH3 / Kat}} = -(129 \pm 8)\ \text{kJ mol}^{-1}$$

Standard enthalpy of formation for H_3BNH_3/cat.:

$$\Delta_B H_{\text{H3BNH3 / Kat.}} = \Delta_B H_{\text{H3BO3}} + \Delta_B H_{\text{NH3}} - 3\,\Delta_B H_{\text{H2O}} - \Delta_R H_{\text{H3BNH3 / Kat}}$$

$$\Delta_B H_{\text{H3BNH3 / Kat.}} = -(153 \pm 8)\ \text{kJ mol}^{-1}$$

Physikalisch-chemische Untersuchungen zur Wasserstoffabgabe von BNH-Verbindungen, J. Baumann, Doktorarbeit, TUB Freiberg, 2003, s. 63.

Hydrolysis of H₃BNH₃ in Acidic Media

$$H_3BNH_3 \quad + \quad HCl\ (aq) \quad \xrightarrow{\text{(in acidic medium)}} \quad (B(OH)_3 \quad + \quad 2\ NH_4Cl)\ aq,\ HCl \quad + \quad 3\ H_2$$
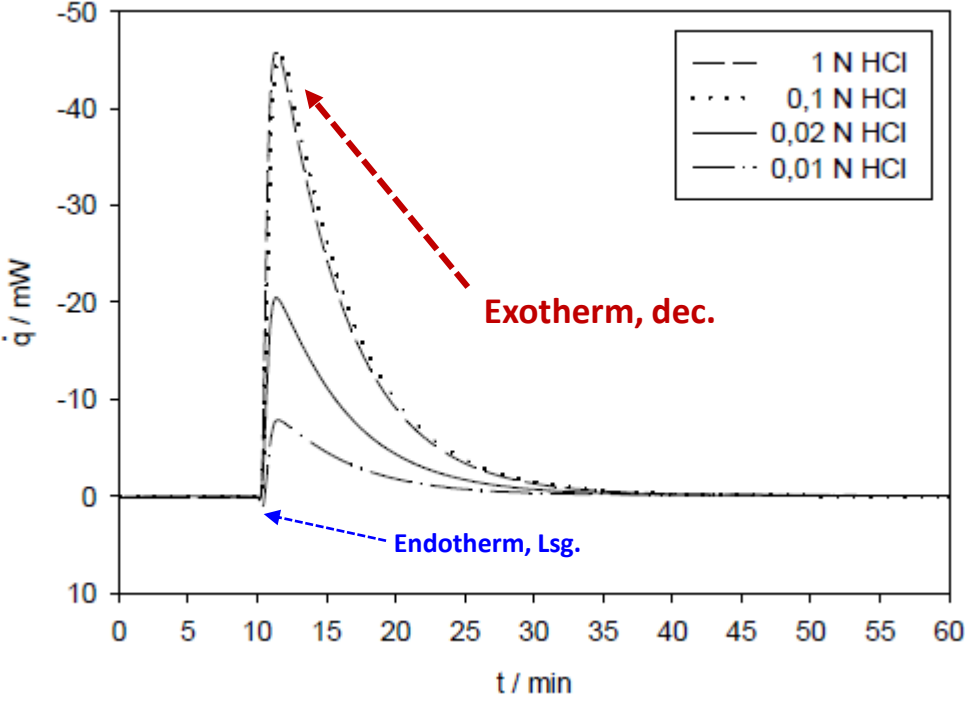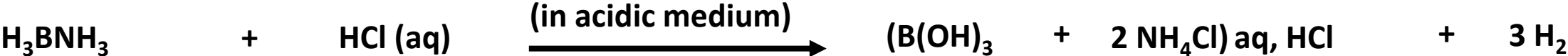
Acidic hydrolysis of solid Borazane with different concentrations of hydrochloric acid under N_2, at 30°C
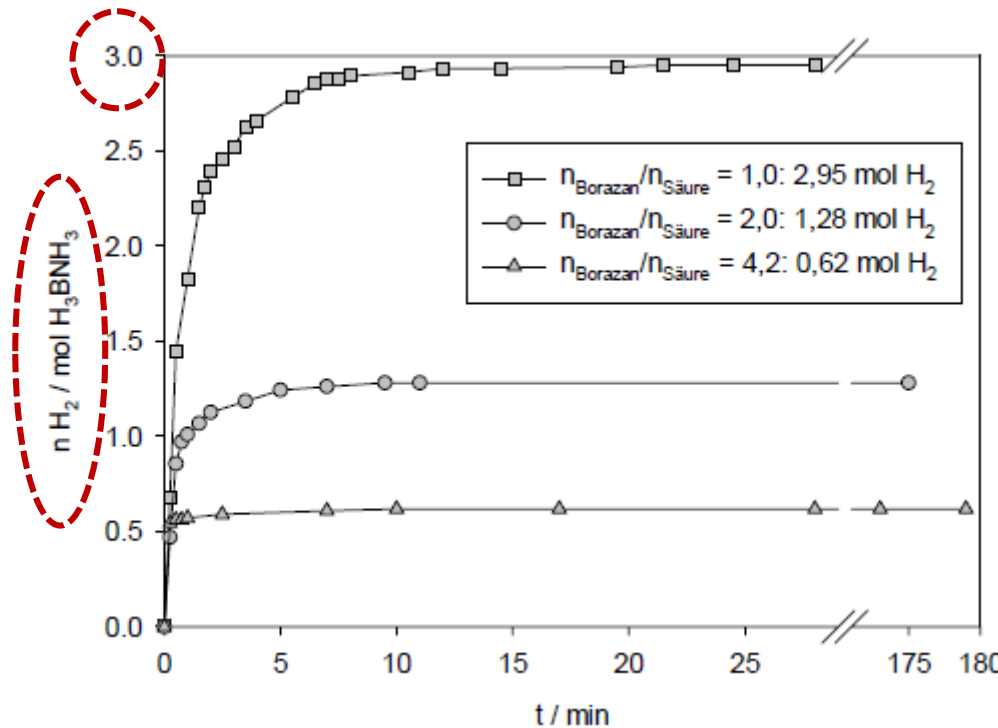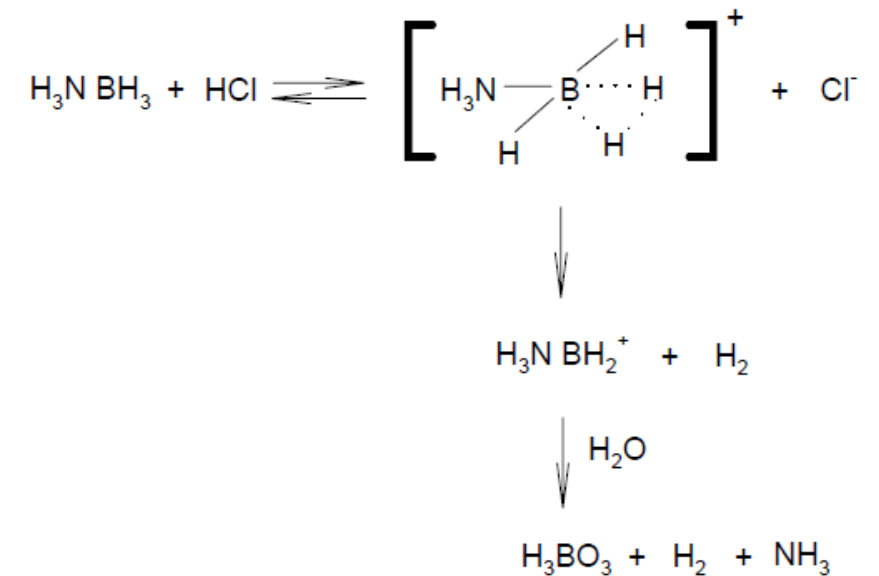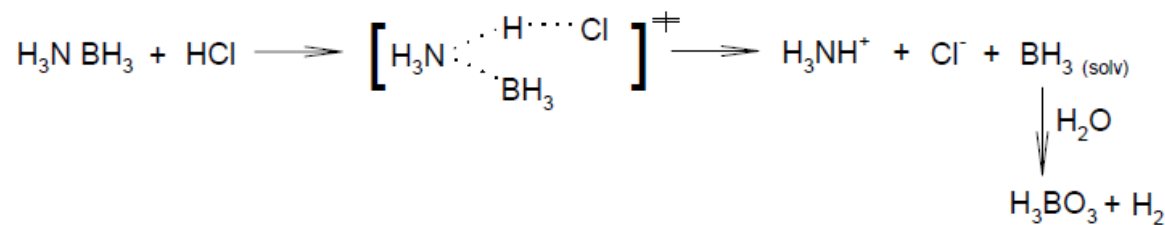
Complete hydrolysis occurs with $n_{Borazane}/n_{HCl} = 1$ i.e. 2.95 mol Hydrogen are formed

Hydrolysis of aq. Borazane at RT possible if Pt catalyst is present
Ni catalysts and Pd/Al₂O₃ catalysts less effective
Highest speed of hydrolysis with Pt catalyst

Physikalisch-chemische Untersuchungen zur Wasserstoffabgabe von BNH-Verbindungen, J. Baumann, Doktorarbeit, TUB Freiberg, 2003, s. 51.

Aqueous hydrolysis with a catalyst:

* Low speed of hydrolysis in comparison with acidic hydrolysis
* Release of hydrogen can be controlled by the addition/removal of the catalyst

$$H_3N\,BH_3 + HCl \longrightarrow \left[H_3N \cdots \begin{array}{c} H \cdots Cl \\ BH_3 \end{array} \right]^+ \longrightarrow H_3NH^+ + Cl^- + BH_{3\,(solv)}$$

$$\downarrow H_2O$$

$$H_3BO_3 + H_2$$

$$H_3N\,BH_3 + HCl \rightleftharpoons \left[\begin{array}{c} H \\ H_3N - B \cdots H \\ H \quad H \end{array} \right]^+ + Cl^-$$

$$\downarrow$$

$$H_3N\,BH_2^+ + H_2$$

$$\downarrow H_2O$$

$$H_3BO_3 + H_2 + NH_3$$

Aqueous acid Hydrolysis :

* Higher speed in comparison with the hydrolysis involving a catalyst
* Complete hydrolysis only if at least 1 Borazan:1 HCl ratio
* The release of hydrogen can be controlled by the acid concentration. It is unknown whether an incomplete hydrolysis can be re-started to release hydrogen again on addition of acid

Physikalisch-chemische Untersuchungen zur Wasserstoffabgabe von BNH-Verbindungen, J. Baumann, Doktorarbeit, TUB Freiberg, 2003.

Comparison of the Thermal Decomposition as well as of the Hydrolysis of Borazane, H_3BNH_3

Which method is more promising – thermal decomposition or hydrolysis of Borazane?

* Amount of hydrogen released:

Thermal decomposition:	maximum 2.2 mol H_2/1 mol Borazane released (up to 200°C), corresponds to a mass-based energy density of 14 mass-% hydrogen
Hydrolysis:	2.9 mol H_2/1 mol Borazane released, 5 mass-% higher than in the thermal decomposition

* Technical Aspects:

Thermal decomposition:	Speed is only acceptable at temperatures above 80°C, significantly lower temperature in comparison with MgH_2 or $MgNiH_4$ (H_2 release begins above 280°C)
Hydrolysis:	occurs at RT, no elevated temperature necessary
Thermal decomposition:	Hydrogen release could only be separated into two steps, each with the release of 1.1 mol H_2
Hydrolysis:	In principle, the release of hydrogen could be stopped by removal of the catalyst, introduces the possibility of hydrogen release in portions
Thermal decomposition:	The speed of hydrogen release is determined by the heating rate, the heating rate is also responsible for the composition of the product
Hydrolysis:	The speed of hydrogen release can be controlled by controlling the presence of the catalyst
Hydrolysis:	Possible applications of the aqueous Borazane solution for use direct in the combustion cell with the hyrogen release occurring directl at the Pt electrode

Physikalisch-chemische Untersuchungen zur Wasserstoffabgabe von BNH-Verbindungen, J. Baumann, Doktorarbeit, TUB Freiberg, 2003, s. 99.

Overview of the two Decomposition Processes of Borazane, H_3BNH_3

Thermal Decomposition of Solid Borazane

* Two exothermic processes (in region 25 – 200°C)
* 1.1 mol H_2 released per process
* Total of 2.2 mol H_2 released
* Process strongly influenced by the heating rate (at $\beta > 0.5$ K/min decomposition processes overlap)

* **1st stage of decomposition:**
$\Rightarrow$ formation of H_2NBH_2 followed by polymerisation to form $(BNH_x)_z$-Polymer.

* **2nd stage of decomposition:**
$\Rightarrow$ Polymeric $(H_2BNH_2)_x$ converted to H-poor, $(BNH_x)_z$ solid
$\Rightarrow$ Decomposition reaction is strongly influenced by the β
$\Rightarrow$ At elevated β, the formation of Borazin $(HBNH)_3$ and monomeric H_2BNH_2 increases
$\Rightarrow$ Hydrogen generation can be optimized in which the formation of additional gaseous products is minimised

Hydrolysis of Aqueous Borazane Solutions

* Borazane dissolved in water shows considerable stability
* Hydrolysis occurs only after addition of a catalyst
* Total of 2.95 mol H_2 released
* Acid hydrolysis without catalyst also possible

* Hydrolysis occurs by H_2 release forming $B(OH)_3$ und NH_3

* 19 mass-% released H_2, higher than in the thermal decomposition
* Hydrolysis occurs at RT
* Controllable with the amount of catalyst used
* Hydrolysis can be stopped by removal of the catalyst

Physikalisch-chemische Untersuchungen zur Wasserstoffabgabe von BNH-Verbindungen, J. Baumann, Doktorarbeit, TUB Freiberg, 2003, s. 100.

How can Borazane be Regenerated?

3.2 BNH_x-Abfall Recycling und die Wiedergewinnung von BH₃NH₃

In den folgenden Abschnitten dieser Arbeit werden vor dem Hintergrund der drei wichtigen Verfahrensschritte des Recyclingschemas (BNH_x-Aufschluss, Hydrodehalogenierung und Basenaustausch) (Abb. 46) die wichtigsten Ergebnisse präsentiert. Als bedeutendster Teilbereich der folgenden Ergebnisse soll die heterogen katalysierte Hydrodehalogenierung von Et₃NBX₃-Addukten unter der Anwendung des bisher aufwendig charakterisierten amorphen Nickelborids im Vordergrund stehen.
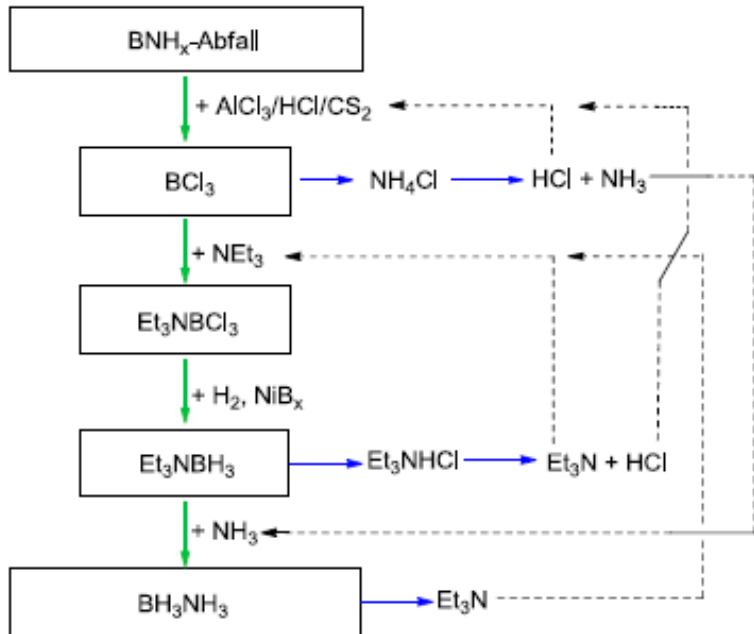
Abb. 46 BNH_x-Recyclingschema basierend auf dem Supersäureaufschluss, der Hydrodehalogenierung von Et₃NBCl₃ und dem Basenaustausch mit Ammoniak.
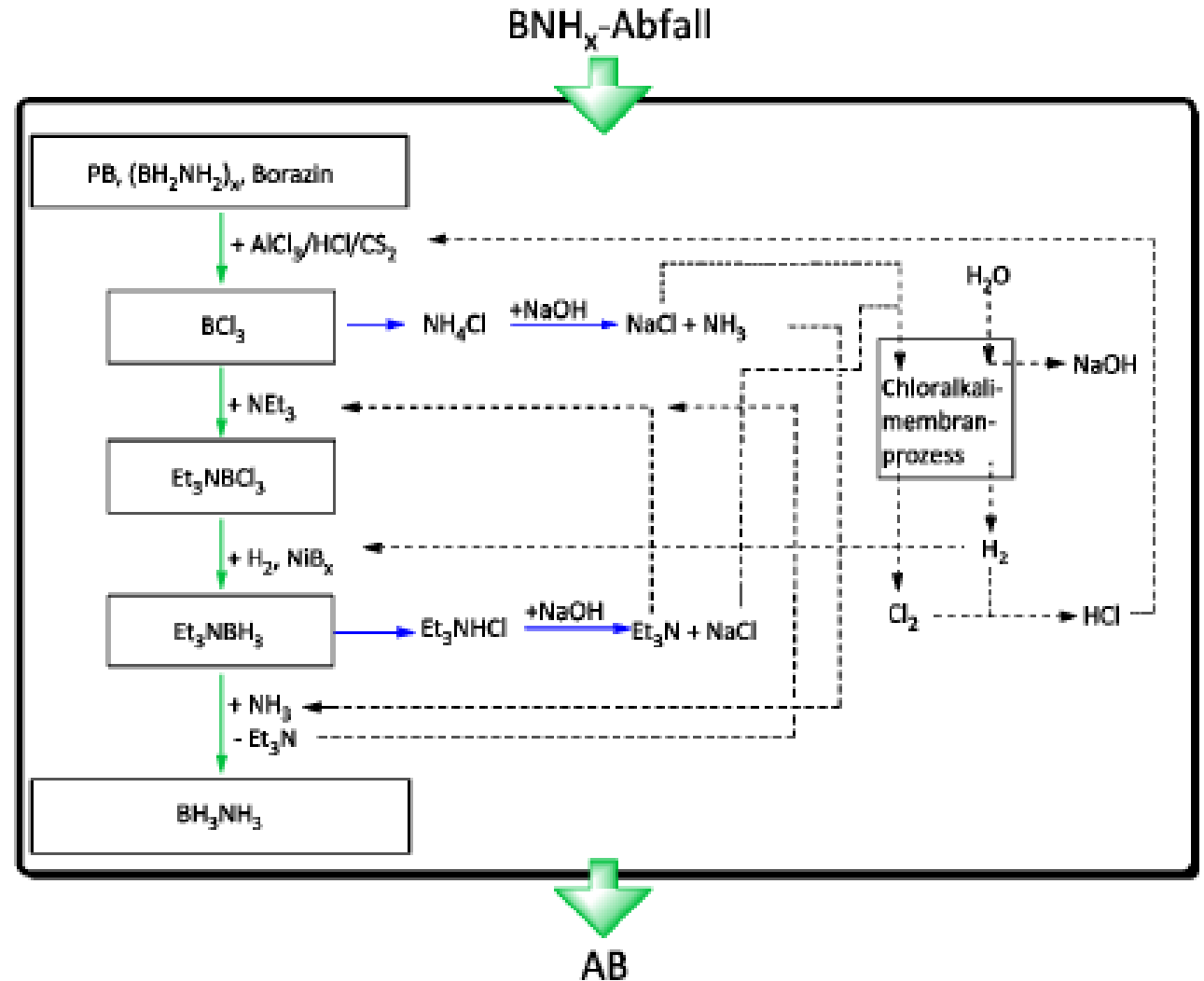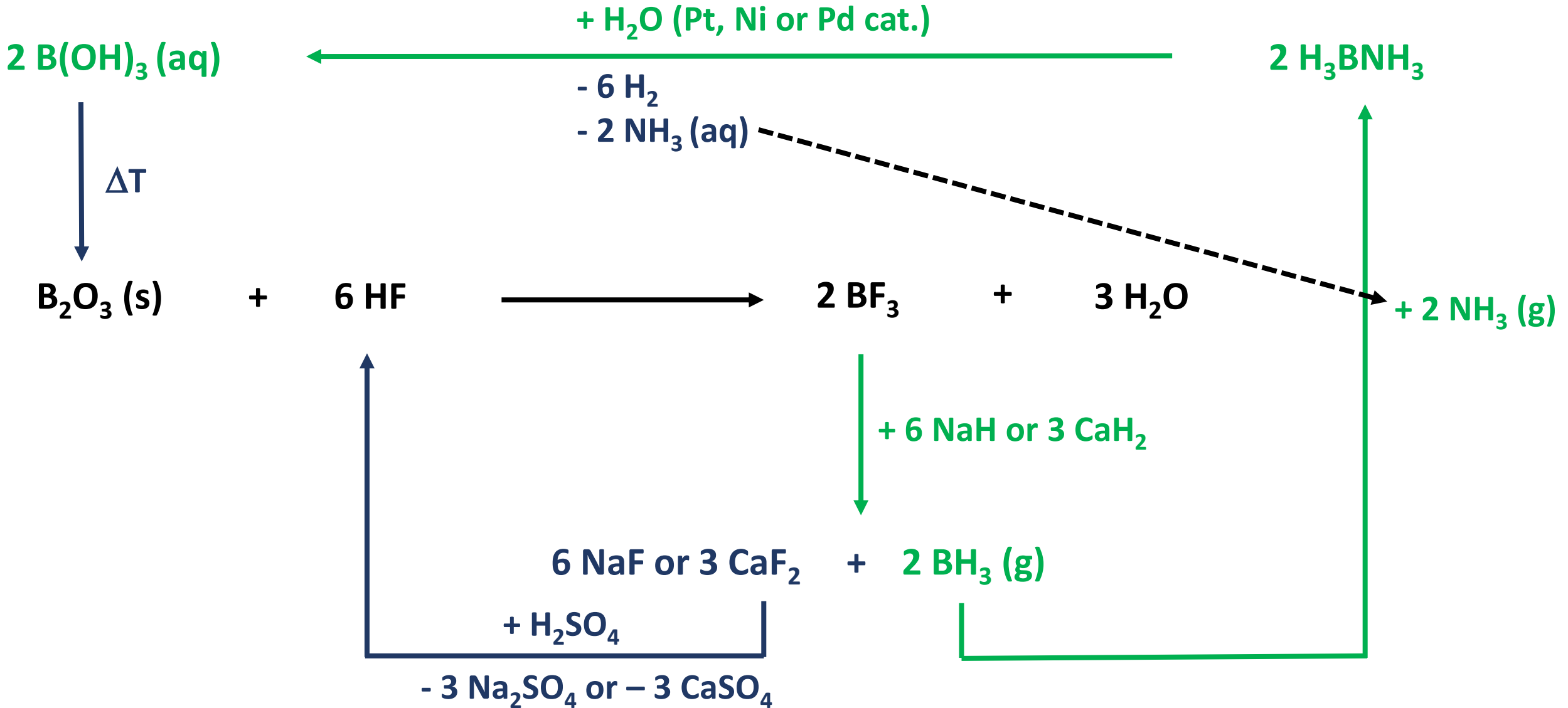
Abb. 88 Fließschema des BNH_x-Abfallrecyclings in Kombination mit der Chloralkalielektrolyse.

Heterogen katalysierte Hydrodehalogenierung von Borhalogeniden im Rahmen eines in sich geschlossenen BNH_x-Recyclingkonzepts , C. Reller, Doktorarbeit, TUB Freiberg, 2014, s. 102, 182.

Possible Complete Cycle for the Synthesis and Decomposition of H_3BNH_3, with the Release of Hydrogen (H_2)

$+ H_2O$ (Pt, Ni or Pd cat.)

$2 B(OH)_3$ (aq) $2 H_3BNH_3$

$- 6 H_2$
$- 2 NH_3$ (aq)

ΔT

B_2O_3 (s)   +   6 HF $\longrightarrow$ $2 BF_3$ + $3 H_2O$ $+ 2 NH_3$ (g)

$+ 6$ NaH or 3 CaH$_2$

6 NaF or 3 CaF$_2$ + $2 BH_3$ (g)

$+ H_2SO_4$

$- 3 Na_2SO_4$ or $- 3 CaSO_4$

A More Detailed Look at the Individual Reaction Equations

B_2O_3 (s) + 6 HF $\longrightarrow$ 2 BF_3 + 3 H_2O

BF_3 + 3 NaH $\longrightarrow$ BH_3 + 3 NaF

BF_3 + $^3/_2$ CaH_2 $\longrightarrow$ BH_3 + $^3/_2$ CaF_2

BH_3 + NH_3 $\longrightarrow$ H_3BNH_3

A More Detailed Look at the Individual Reaction Equations

$$2 \, B(OH)_3 \, (aq) \xrightarrow{\Delta T} B_2O_3 \, (s) \quad + \quad 3 \, H_2O$$

$$2 \, NaF \quad + \quad H_2SO_4 \longrightarrow 2 \, HF \quad + \quad Na_2SO_4$$

$$CaF_2 \quad + \quad H_2SO_4 \longrightarrow 2 \, HF \quad + \quad CaSO_4$$
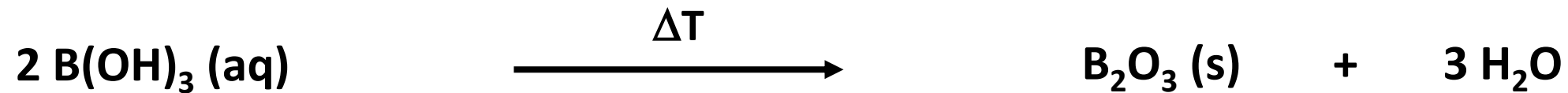
Already well-investigated and well-known industrial process for the production of HF

The Production of „Green" Hydrogen, Ammonia and Borazane in Egypt and Transport to Europe