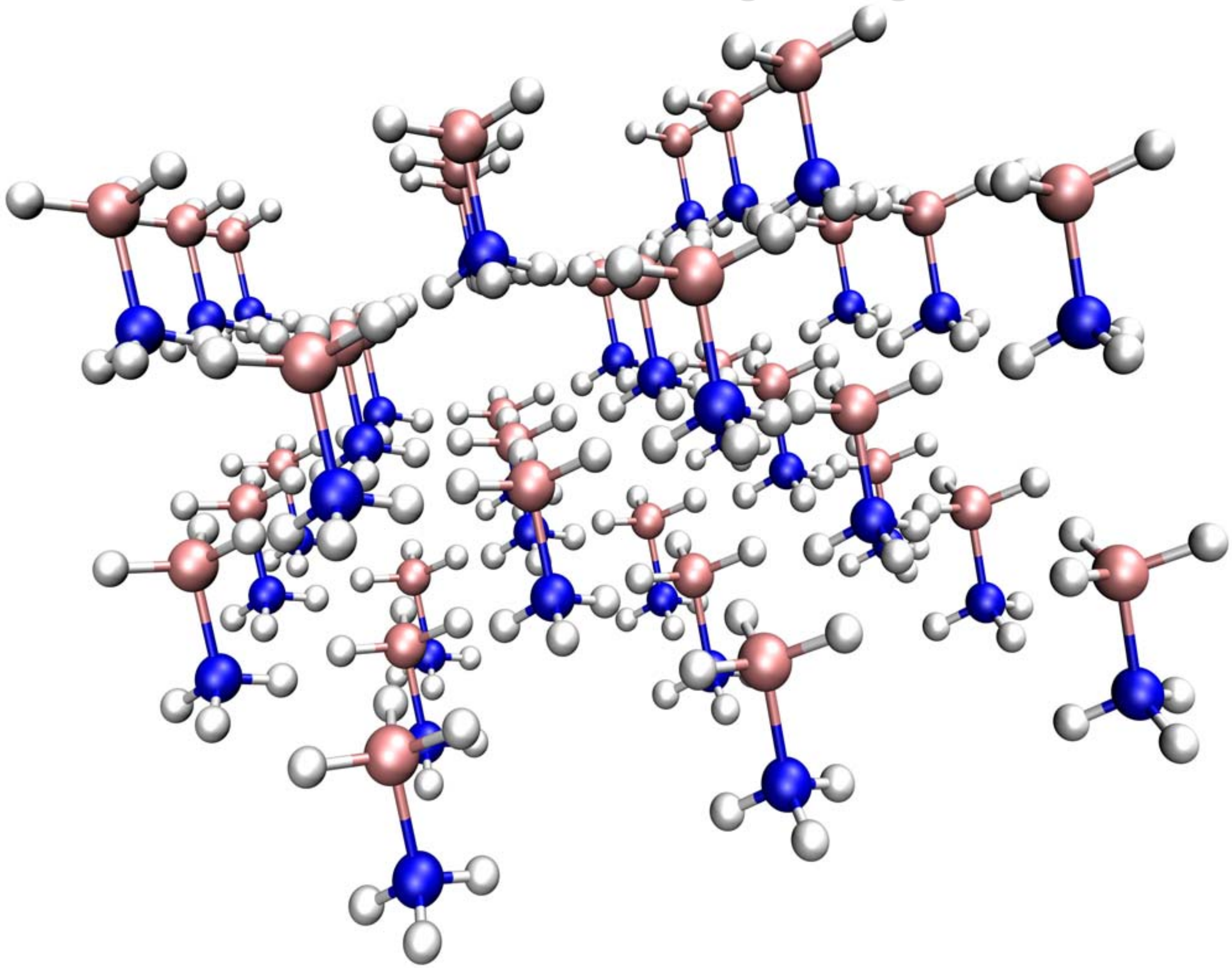
Mechanistic Studies of Hydrogen Formation from Amine-borane (NH_3BH_3) Complexes.



R. Scott Smith, Bruce D. Kay, Liyu Li, Nancy Hess, Maciej Gutowski, Benjamin Schmid & Tom Autrey

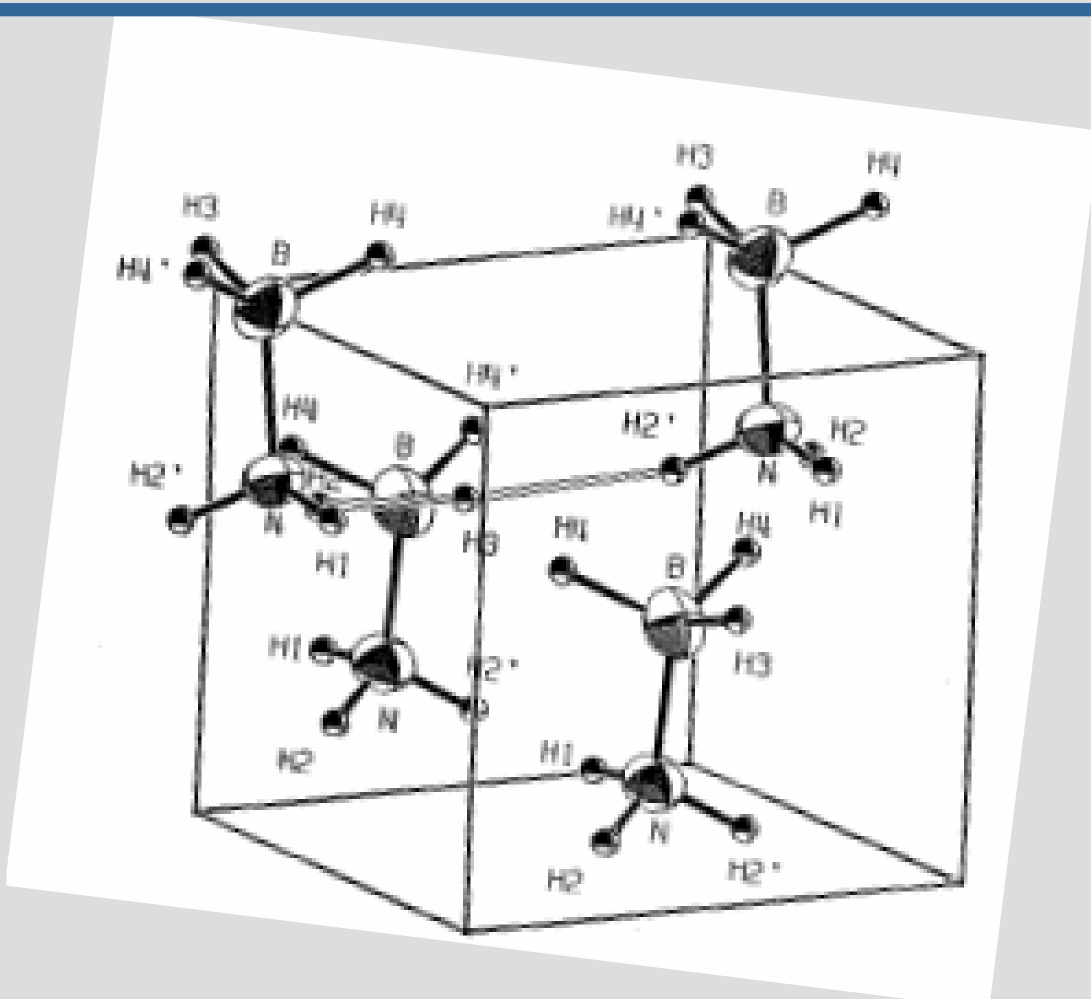
Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Ammonia Borane vs Ethane
Any similarities?

Isoelectronic Isomers

	$H_3N \rightarrow BH_3$	$H_3C—CH_3$
MW	30.81	30.07
Mp[˚C]	114	-172
bonding	dative	covalent
*D*Ho[kcal/m]	31	90
M[D]	5.2	0
R[A]	1.66	1.53
Wt% H2	19%	19%

Nonclassical Dihydrogen Bond



$\overset{-}{\mathrm{B}\color{red}{\mathrm{H}}}\ \text{---}\ \overset{+}{\color{blue}{\mathrm{H}}\mathrm{N}}$

Hydride atoms act as Proton acceptor

WT Klooster, TF Keotzle, PEM Siegbahn, TB Richardson,
RH Crabtree JACS 1999 121, 6337

Mechanism of H_2 formation?

	T (°C)
$NH_3BH_3 \rightarrow (NH_2BH_2)_n + H_2 + ?$	<120
$(NH_2BH_2)_n \rightarrow (NHBH)_n + H_2 + ?$	>120

How is the H_2 released?

mechanism (*solid state*)

What is the activation barrier?

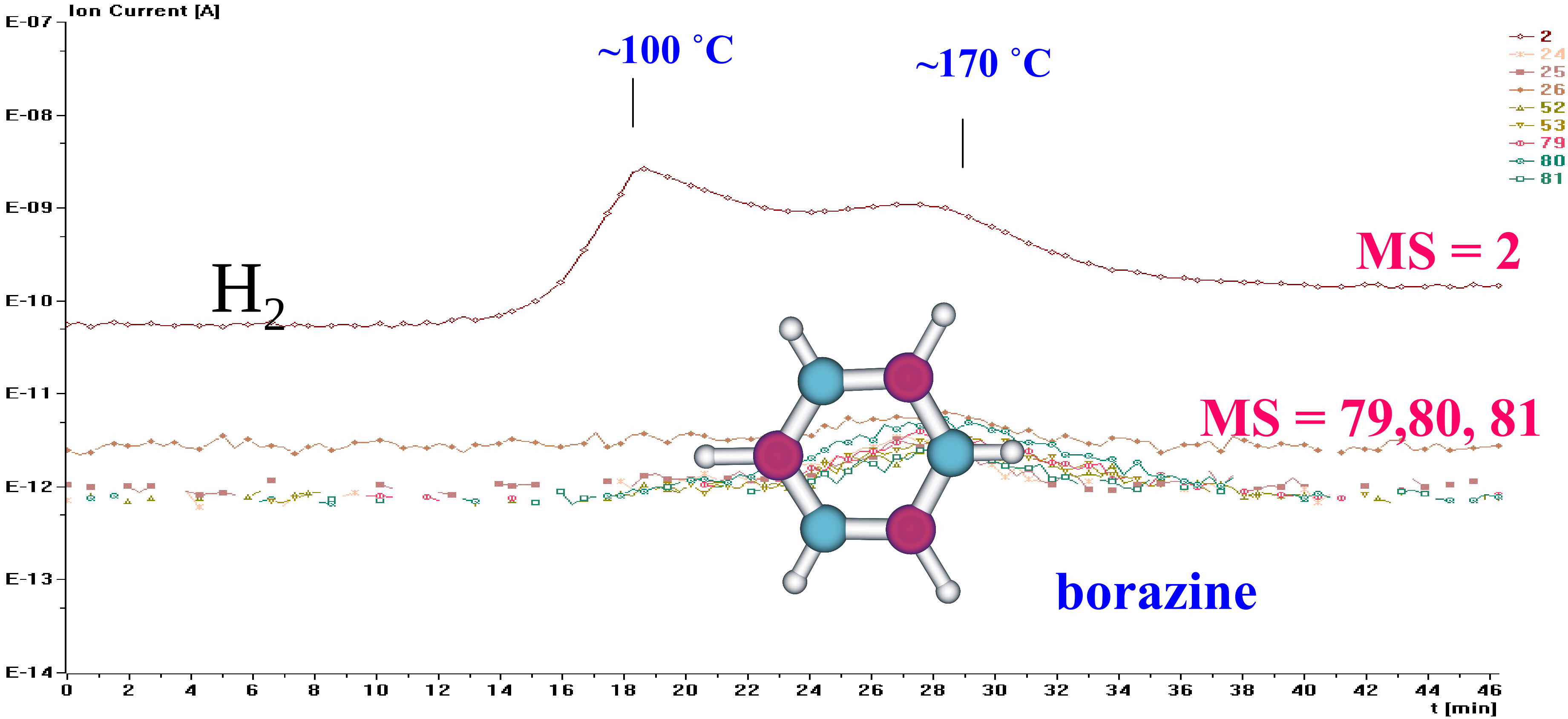
can we change it with catalysis, (*other*)

Are there other 'products'?

is the hydrogen clean? (*borazine*)

Volatile Products from NH_3BH_3

$NH_3BH_3 \rightarrow$ Products + $H_2 \rightarrow$ Products + H_2



DSC: 20 – 200 ˚C (5 ˚C/min, Ar 40 ml/min)

Reaction Pathways to H_2

$$NH_3BH_3 \rightarrow NH_2{=}BH_2 + H_2$$

$$nNH_2{=}BH_2 \rightarrow (NH_2BH_2\text{-}NH_2BH_2)_n$$

intramolecular

Or

intermolecular

$$2\ NH_3BH_3 \rightarrow NH_3BH_2\text{-}NH_2BH_3 + H_2$$

Label with deuterium, isotope studies

Product Ratio $H_2:D_2:HD$?

Bimolecular

$NH_3BH_3 + ND_3BD_3 \rightarrow NH_3BH_2\text{-}ND_2BD_3 + HD$

$NH_3BH_3 + NH_3BH_3 \rightarrow NH_3BH_2\text{-}NH_2BD_3 + H_2$

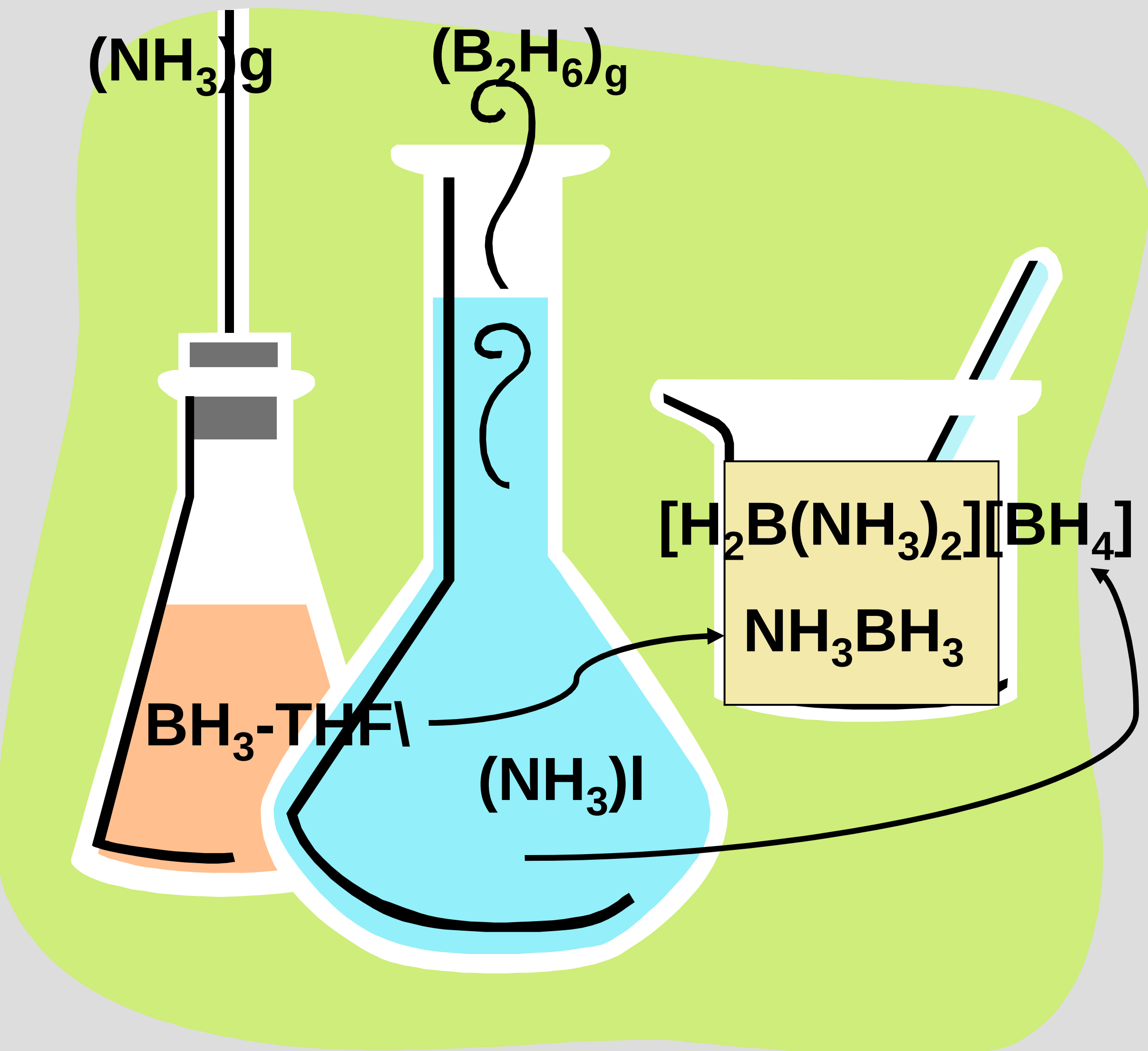
$ND_3BD_3 + ND_3BD_3 \rightarrow ND_3BD_2\text{-}ND_2BD_3 + D_2$

Unimolecular

$NH_3BH_3 + ND_3BD_3 \rightarrow NH_2BH_2 + ND_2BD_2 + H_2 + D_2$

Litmus test: observation of HD in mass spectrometer

Synthesis of Ammonia borane,



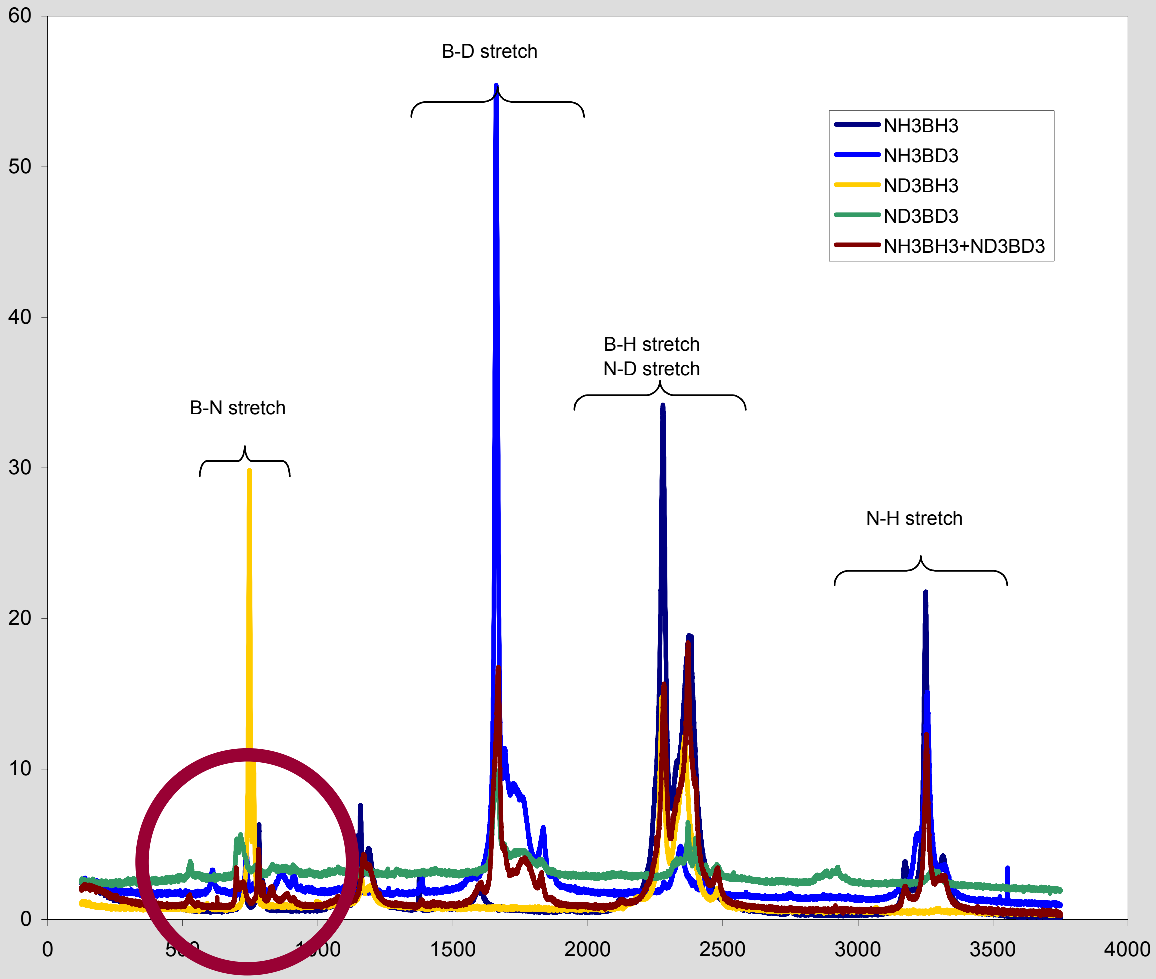
NH_3BH_3 :bubble NH_3 thru BH_3-THF

NH_3BD_3 : bubble NH_3 thru BD_3-THF

ND_3BH_3 exchange NH with D_2O

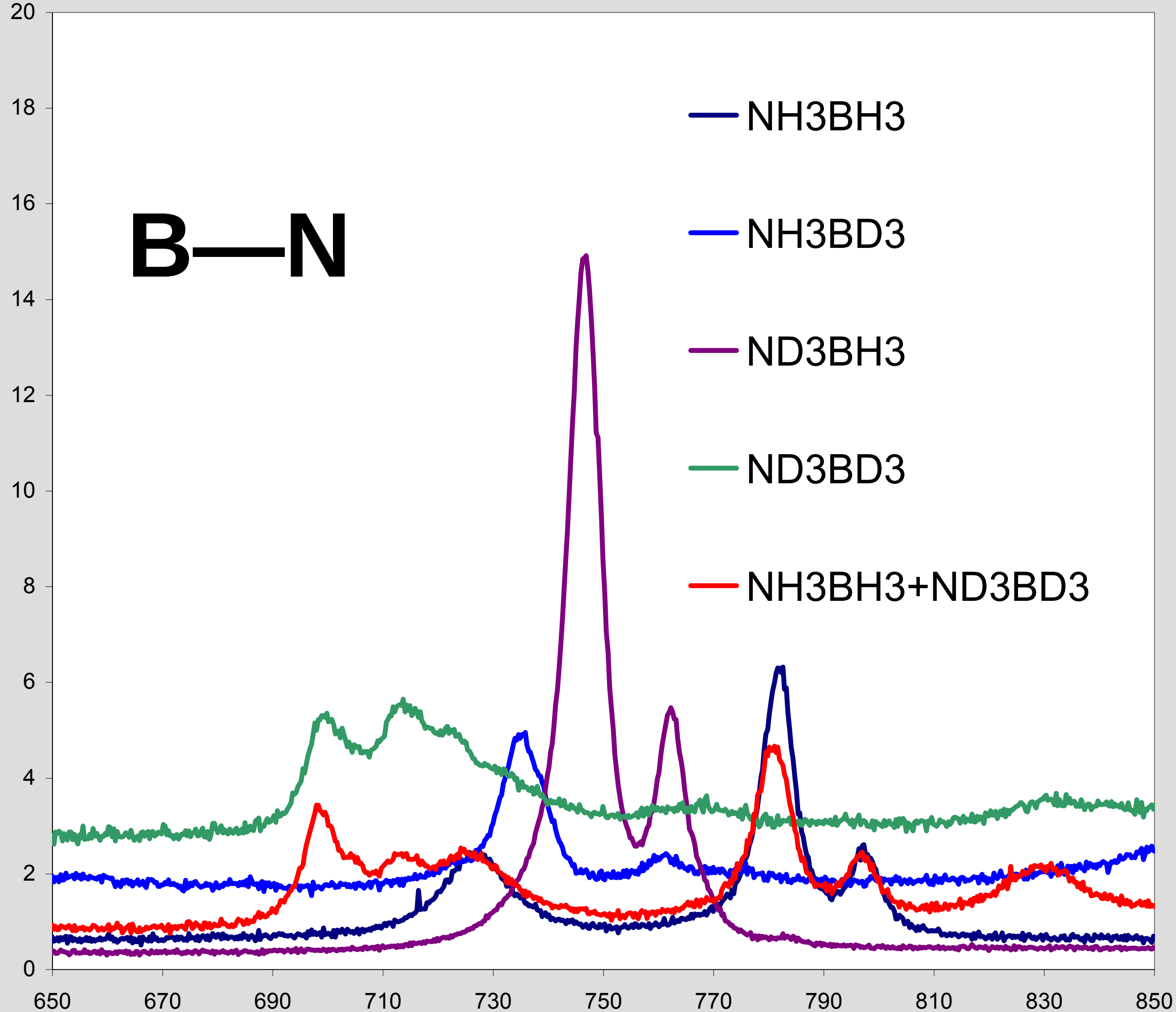
ND_3BD_3 bubble NH_3 thru BD_3-THF; exchange NH with D_2O

Raman Spectroscopy

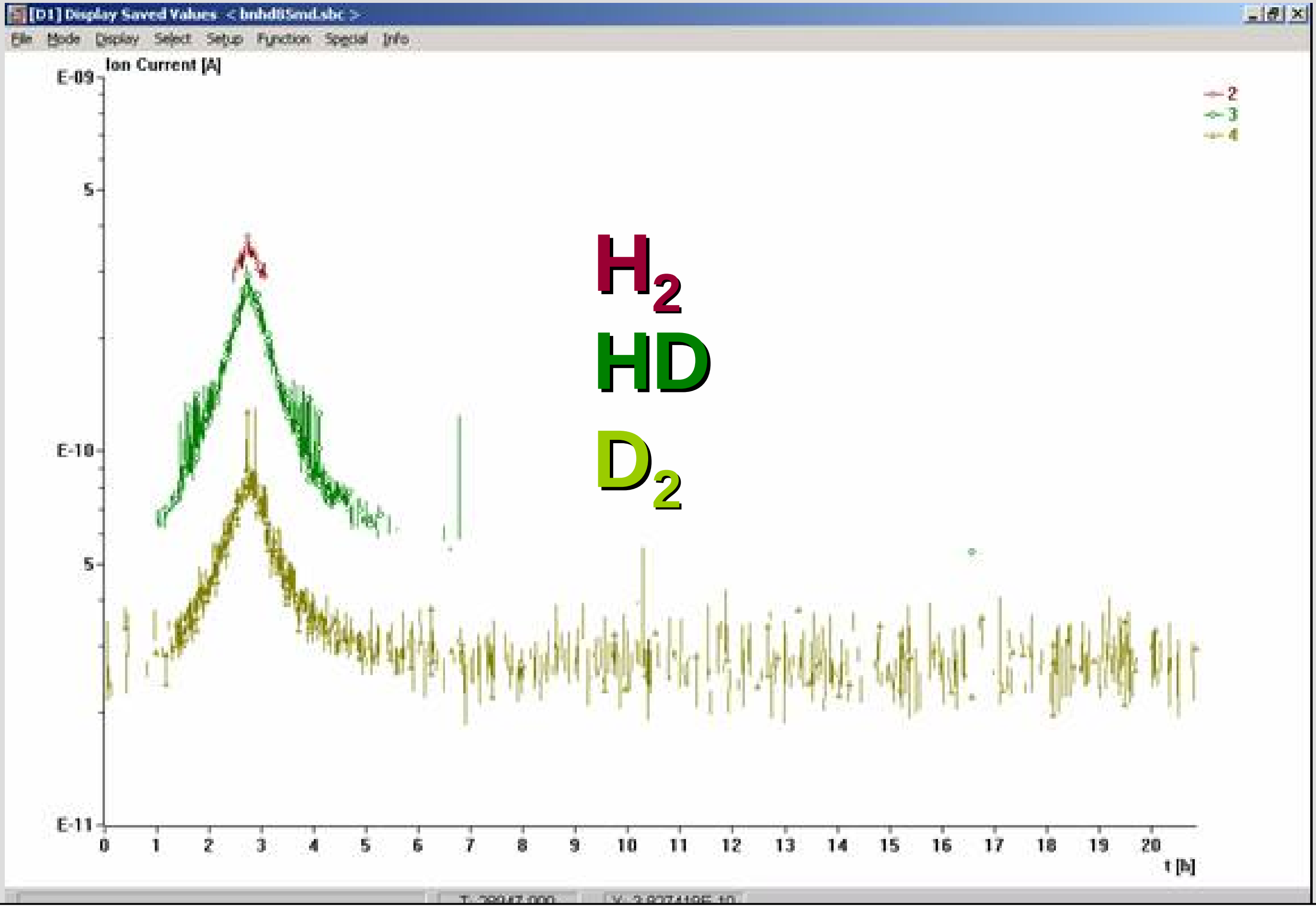


- dissolve NH_3BH_3 in THF
- dissolve ND_3BD_3 in THF
- mix together
- remove solvent
- hope that there is no exchange
- Use Raman to confirm your faith

No exchange! Only NH_3BH_3 + ND_3BD_3



MS of TPD (1:1 NH_3BH_3 : ND_3BD_3)



Bimolecular H_2 Formation from NH_3BH_3

Reaction Pathway

$NH_3BH_3 + NH_3BH_2\text{-}NH_2BH_3$

$\rightarrow NH_3BH_2\text{-}NH_2BH_2\text{-}NH_2BH_3 + H_2$

$NH_3BH_3 + NH_3BH_2NH_2BH_2\text{-}NH_2BH_3$

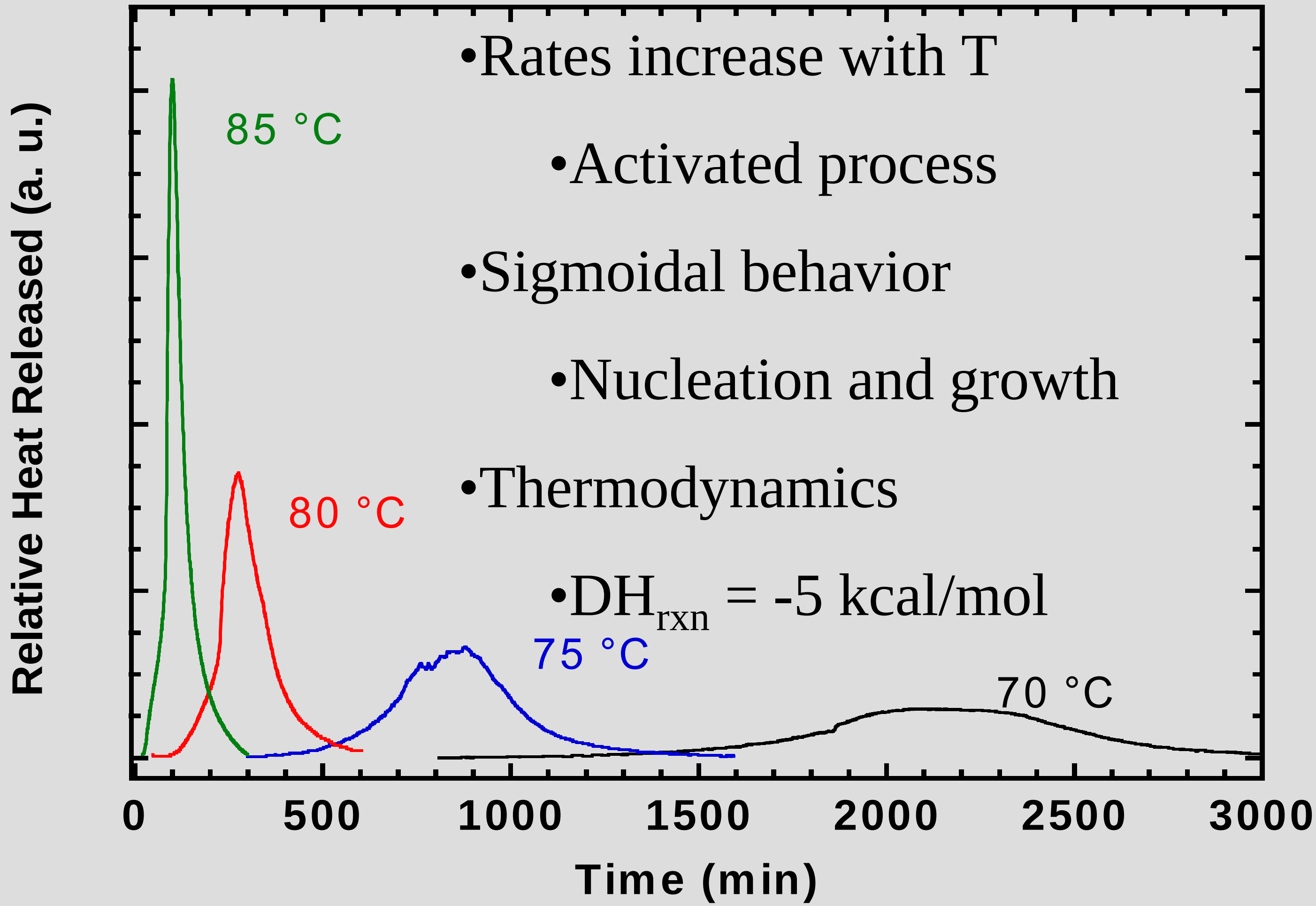
$\rightarrow NH_3BH_2\text{-}NH_2BH_2\text{-}NH_2BH_2\text{-}NH_2BH_3 + H_2$

Mechanism for polymerization?

Activation barrier?

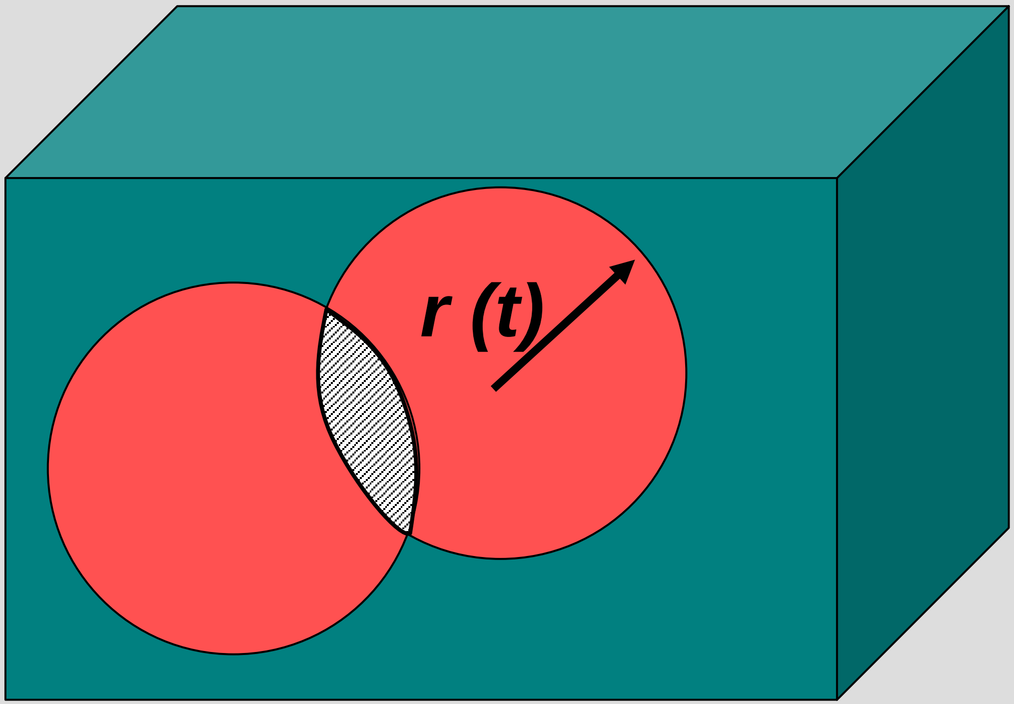
$NH_3BH_3(s) \rightarrow (NH_2BH_2)(s) + H_2$

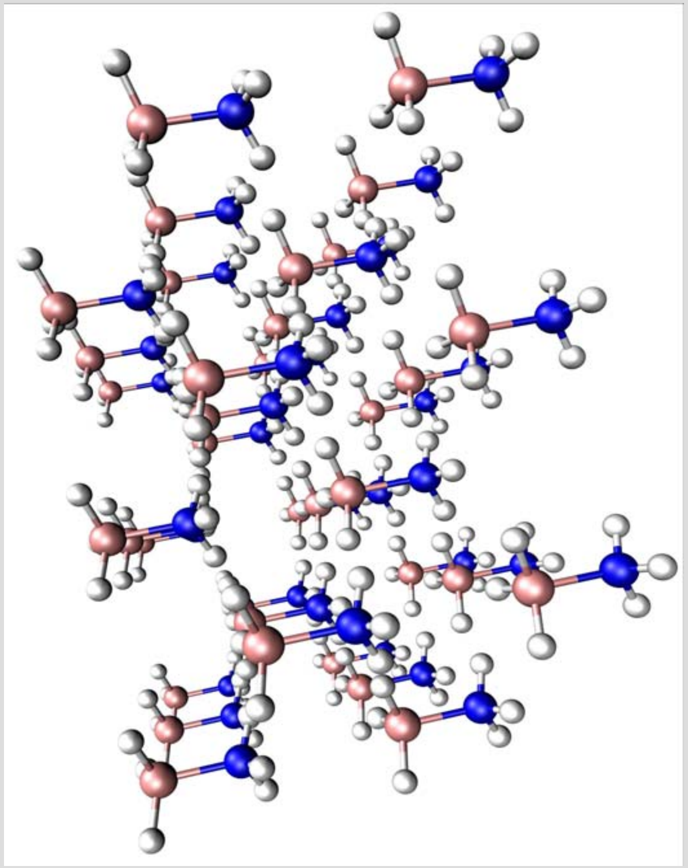
Isothermal DSC



- Rates increase with T
  - Activated process
- Sigmoidal behavior
  - Nucleation and growth
- Thermodynamics
  - DH_{rxn} = -5 kcal/mol

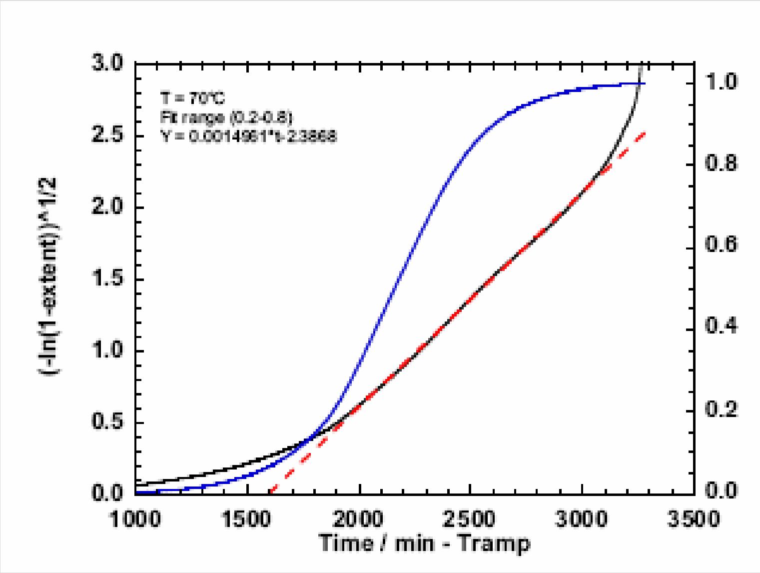
Phase Transformation Kinetics - Avrami Equation

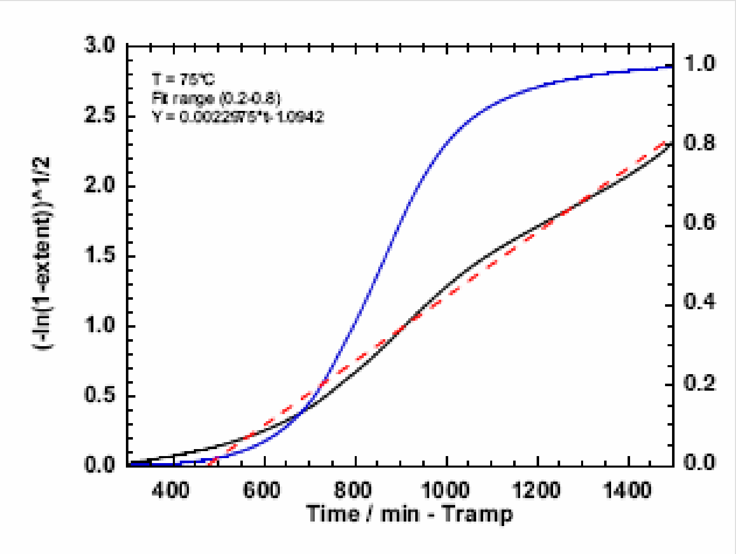


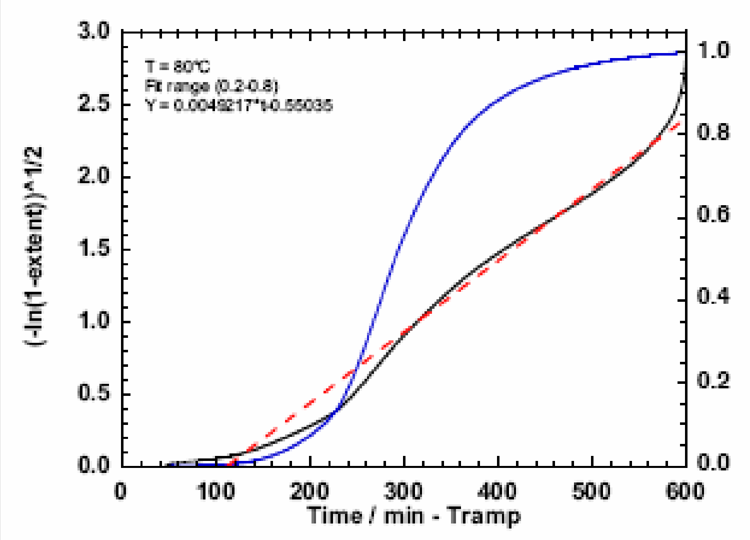


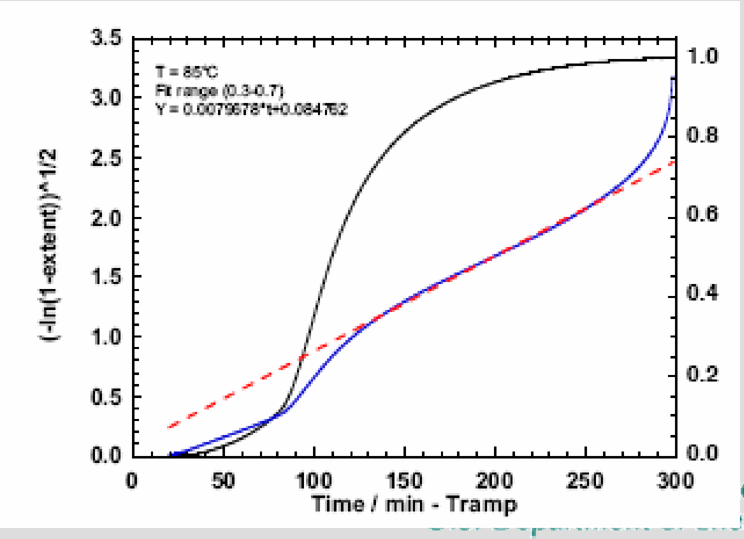
Avrami Equation $X_{Crystal} = 1 - \exp(-(kt)^n)$

Rate from 2D Growth vs. Temperature

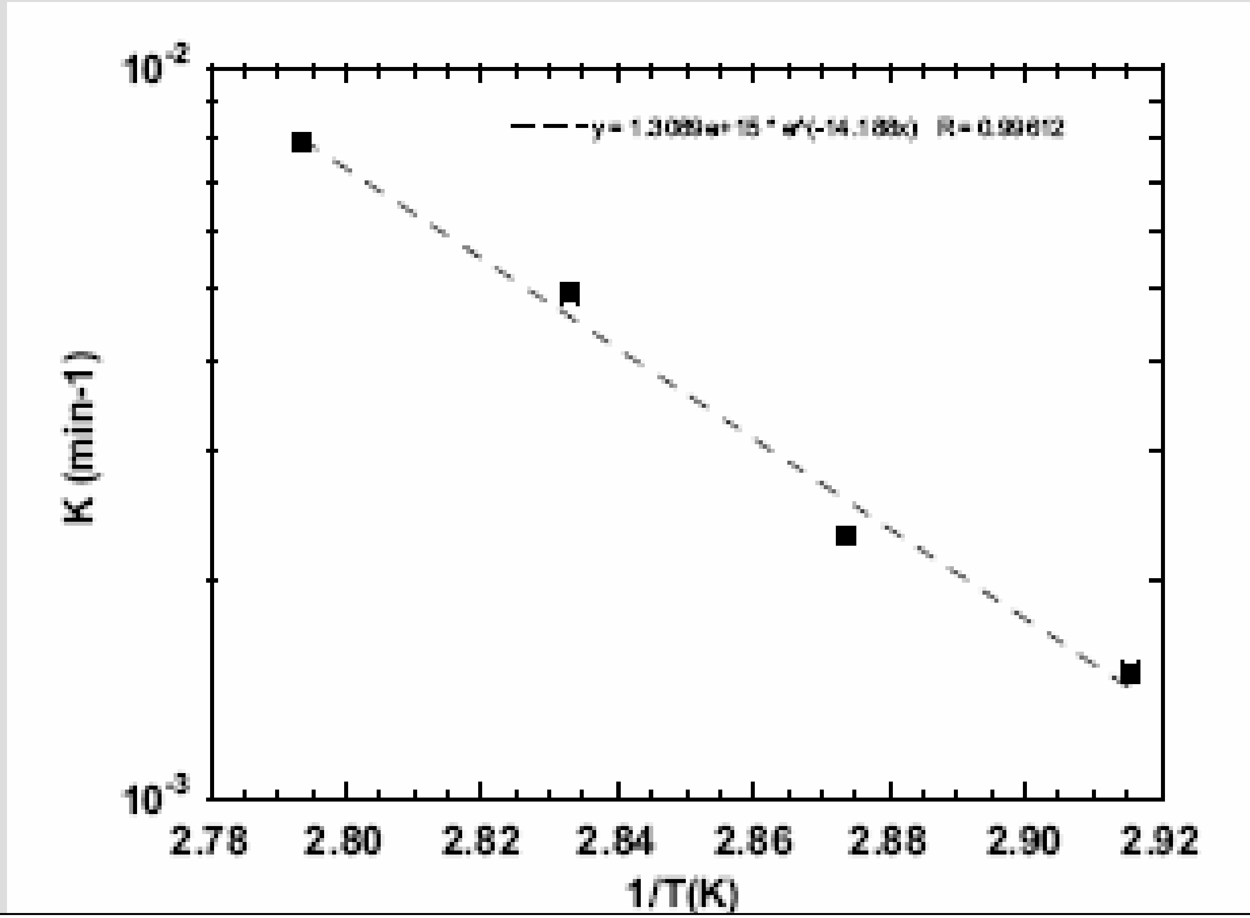






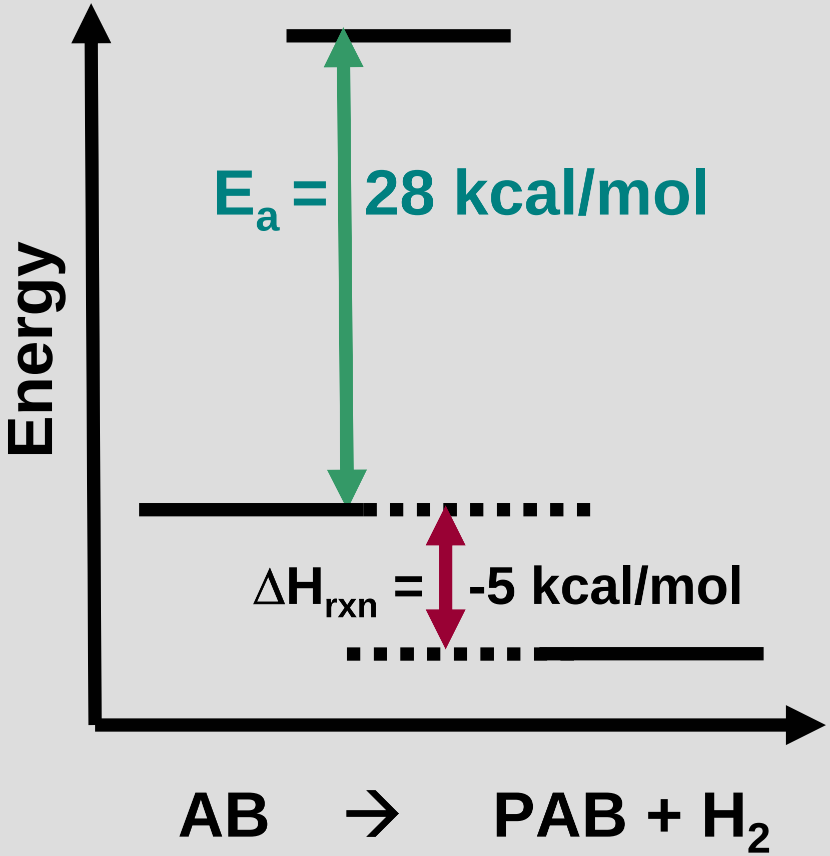


Arrhenius treatment of H_2 formation

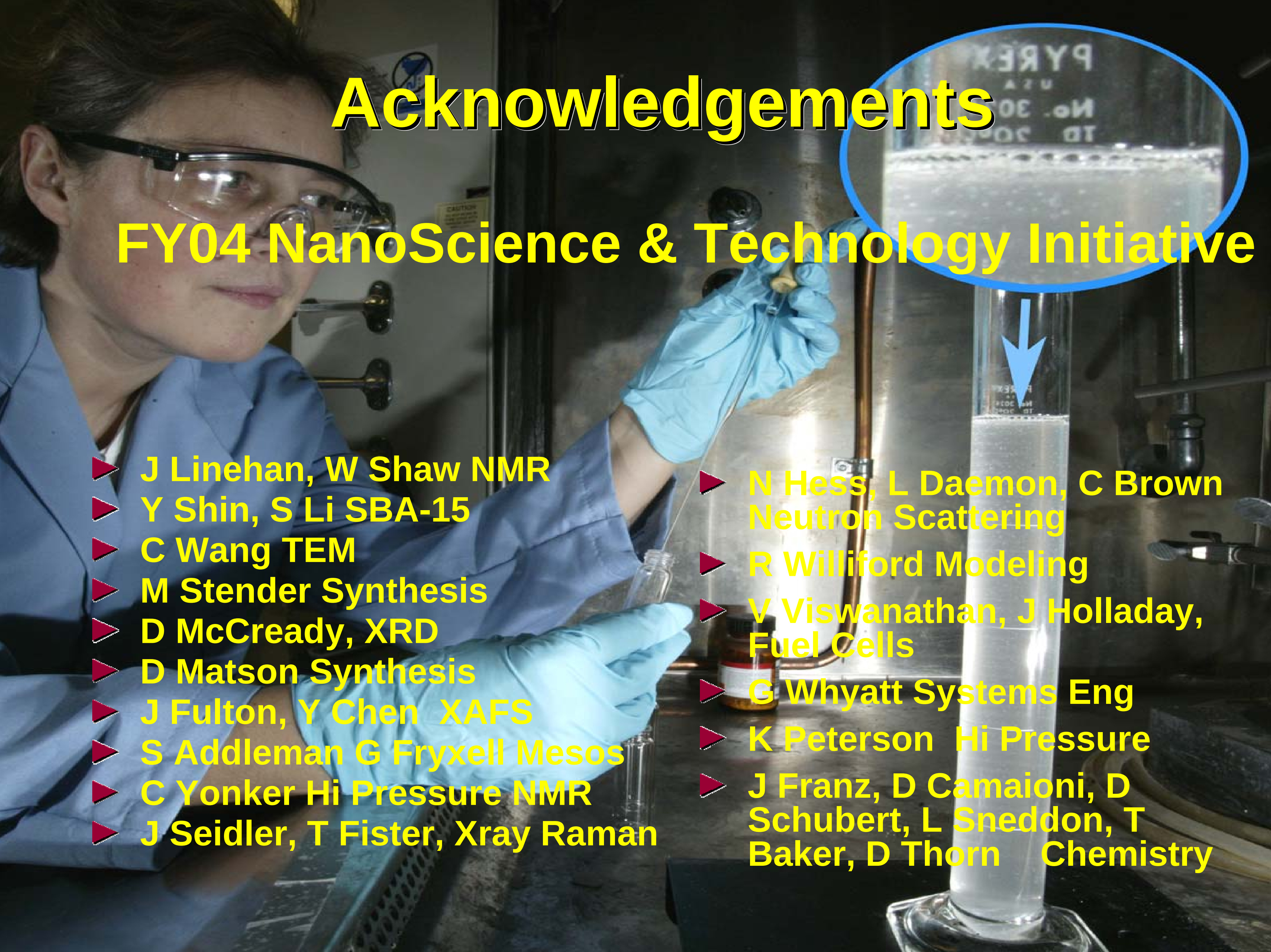


Activation barrier for H_2 formation from solid state ammonia borane is ca. 28 kcal/mol.

Conclusions



- Bimolecular dehydrocoupling leads to H_2
- Kinetic Model (nucleation & growth)
  - Rate limiting nucleation and 2-3D growth
  - What is the nucleation event?
  - Can we 'seed' the reaction to enhance the rate?



Acknowledgements

FY04 NanoScience & Technology Initiative

- J Linehan, W Shaw NMR
- Y Shin, S Li SBA-15
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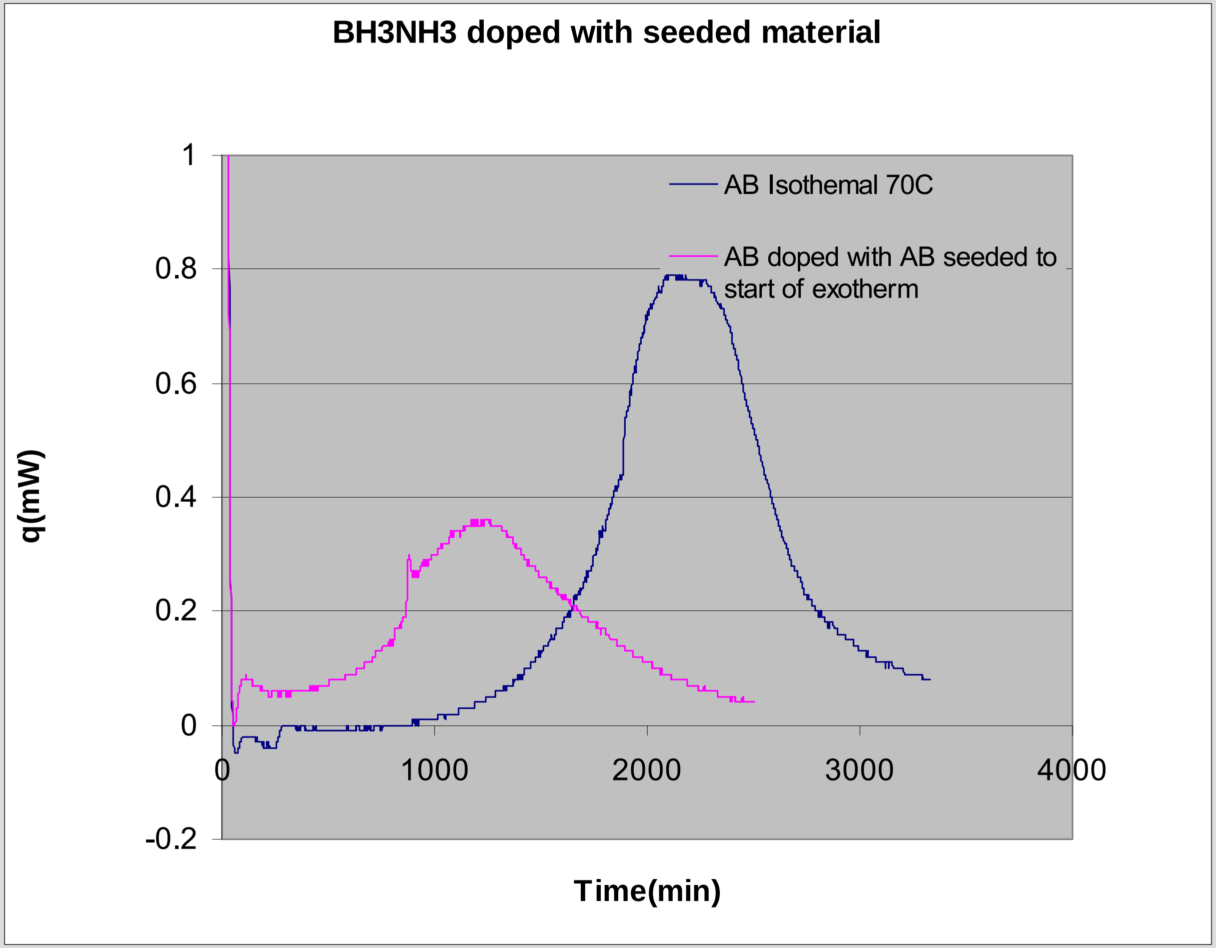
- M Stender Synthesis
- D McCready, XRD
- D Matson Synthesis
- J Fulton, Y Chen XAFS
- S Addleman G Fryxell Mesos
- C Yonker Hi Pressure NMR
- J Seidler, T Fister, Xray Raman

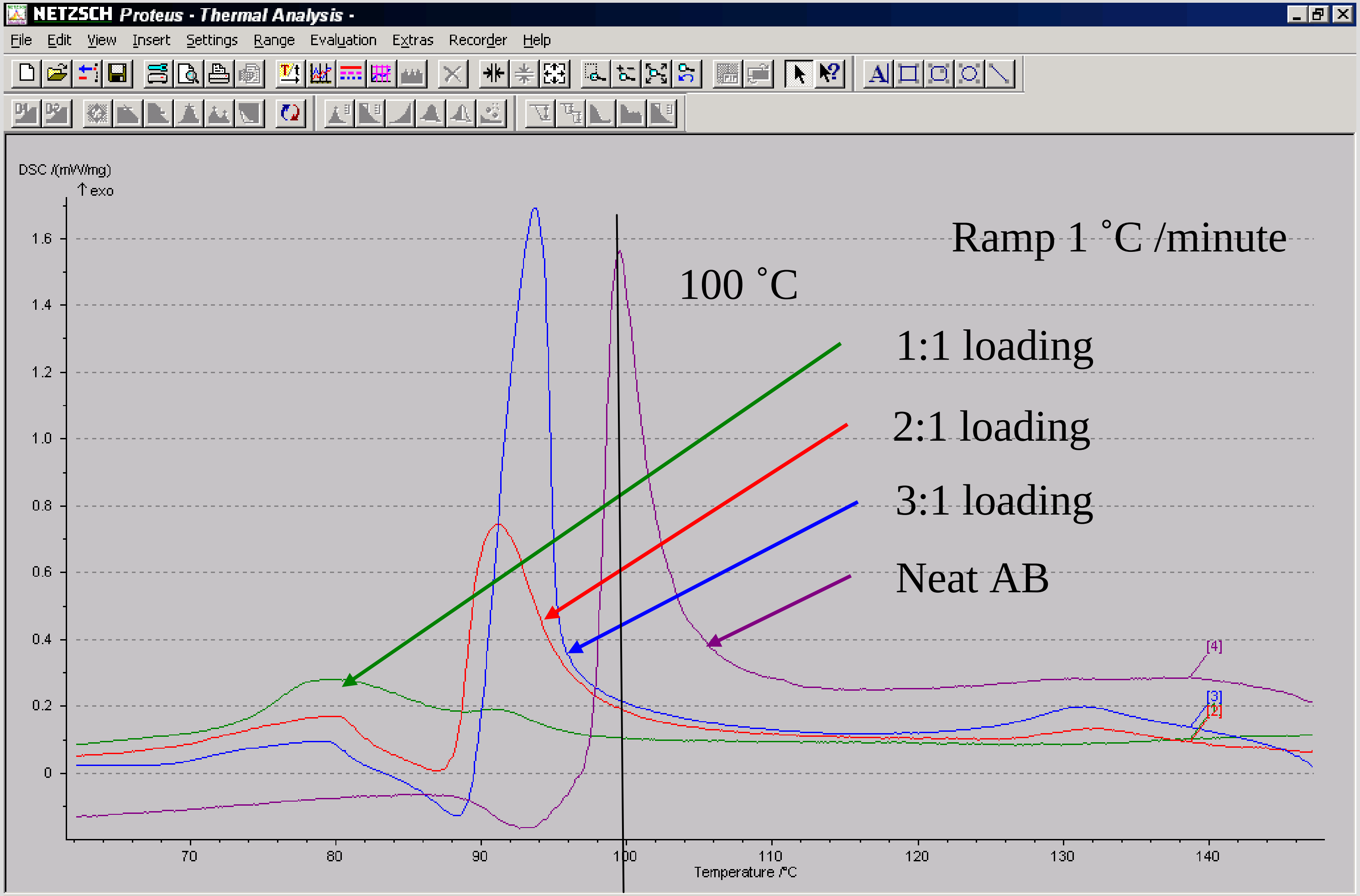
- N Hess, L Daemon, C Brown Neutron Scattering
- R Williford Modeling
- V Viswanathan, J Holladay, Fuel Cells
- G Whyatt Systems Eng
- K Peterson Hi Pressure
- J Franz, D Camaioni, D Schubert, L Sneddon, T Baker, D Thorn Chemistry

Future Work: Nucleation Seeding



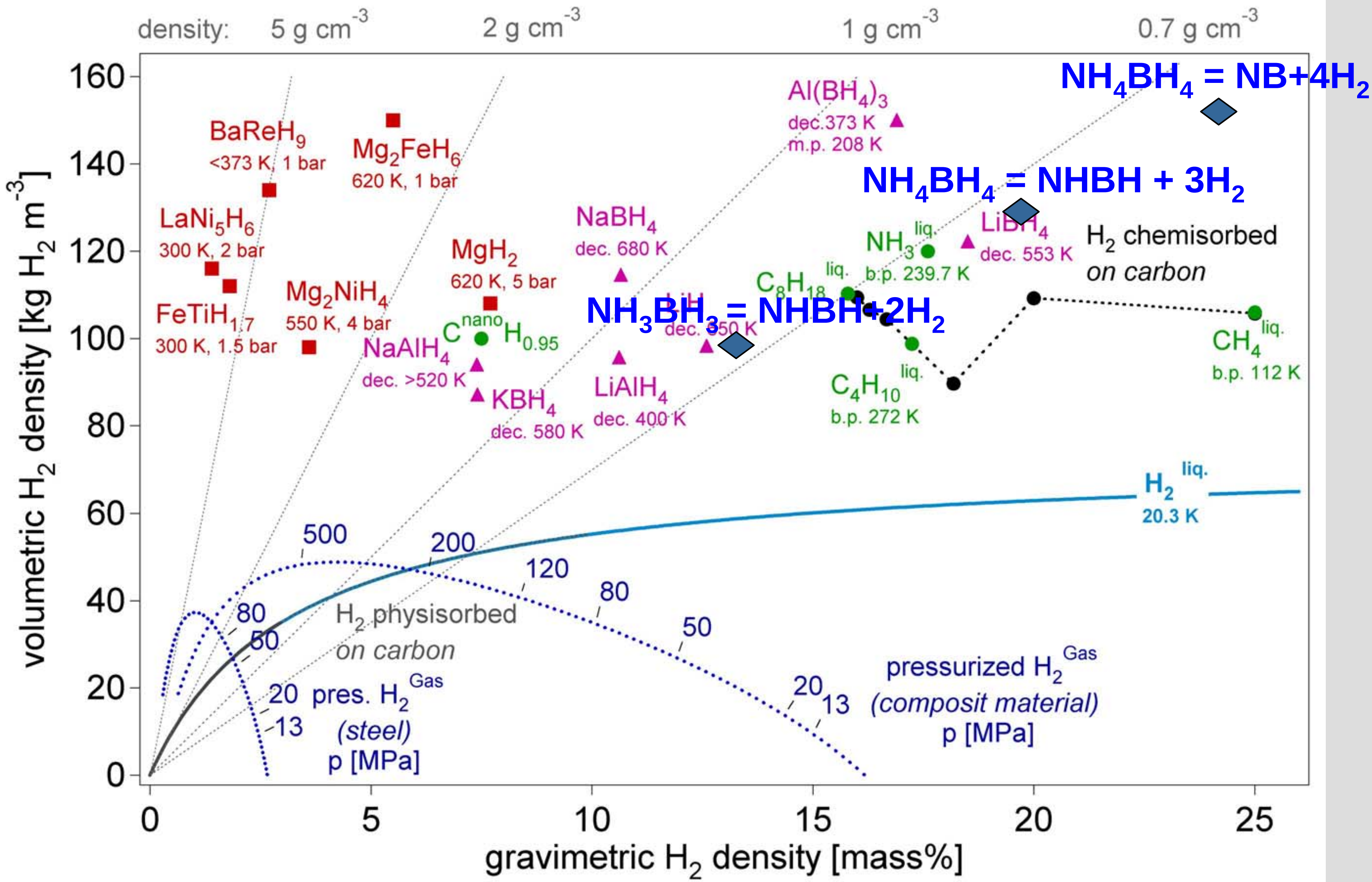
What is nucleation 'event'?
increases rate of H_2 release

Future work: Increasing AB loading density



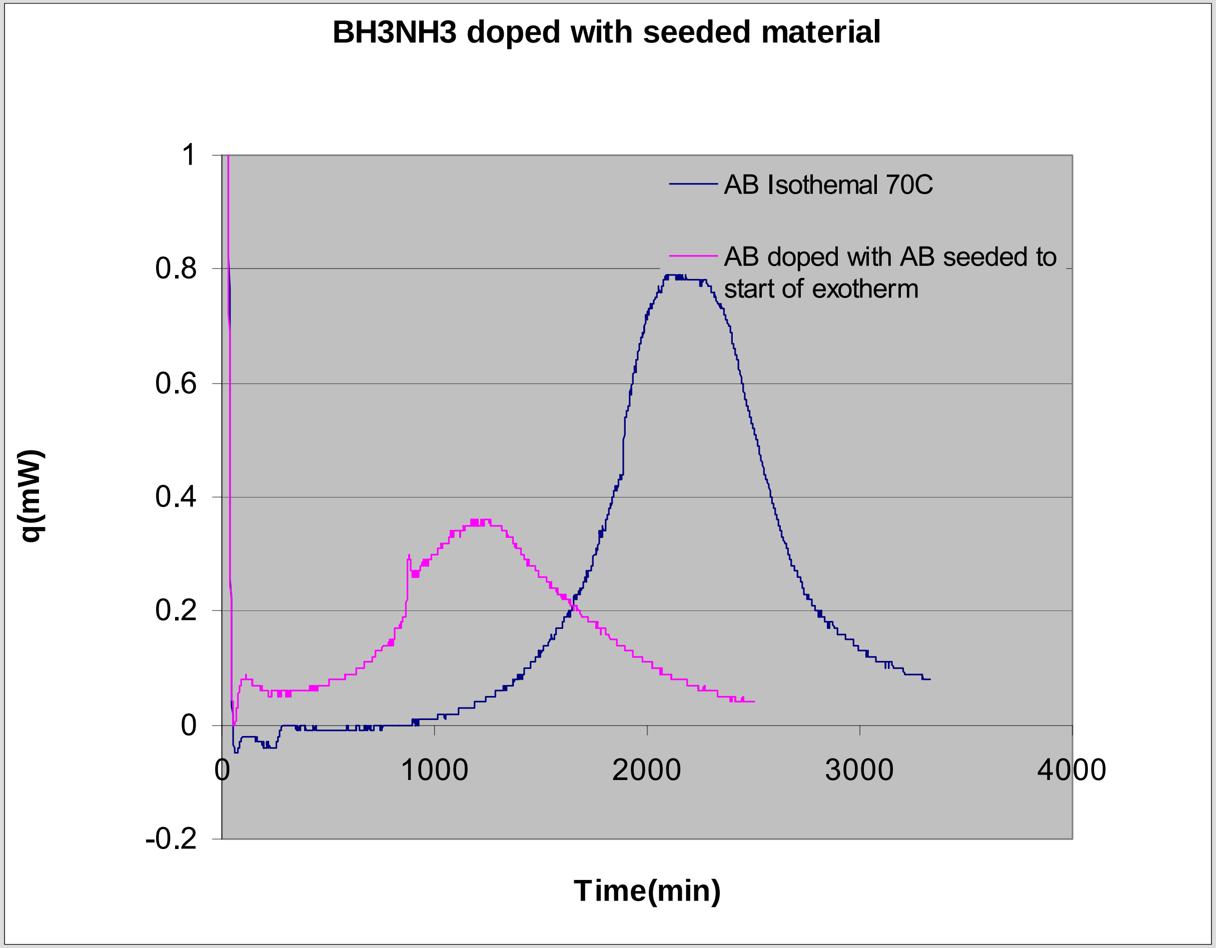
What is optimum loading density to balance reactivity and selectivity?

Materials for H_2 Storage

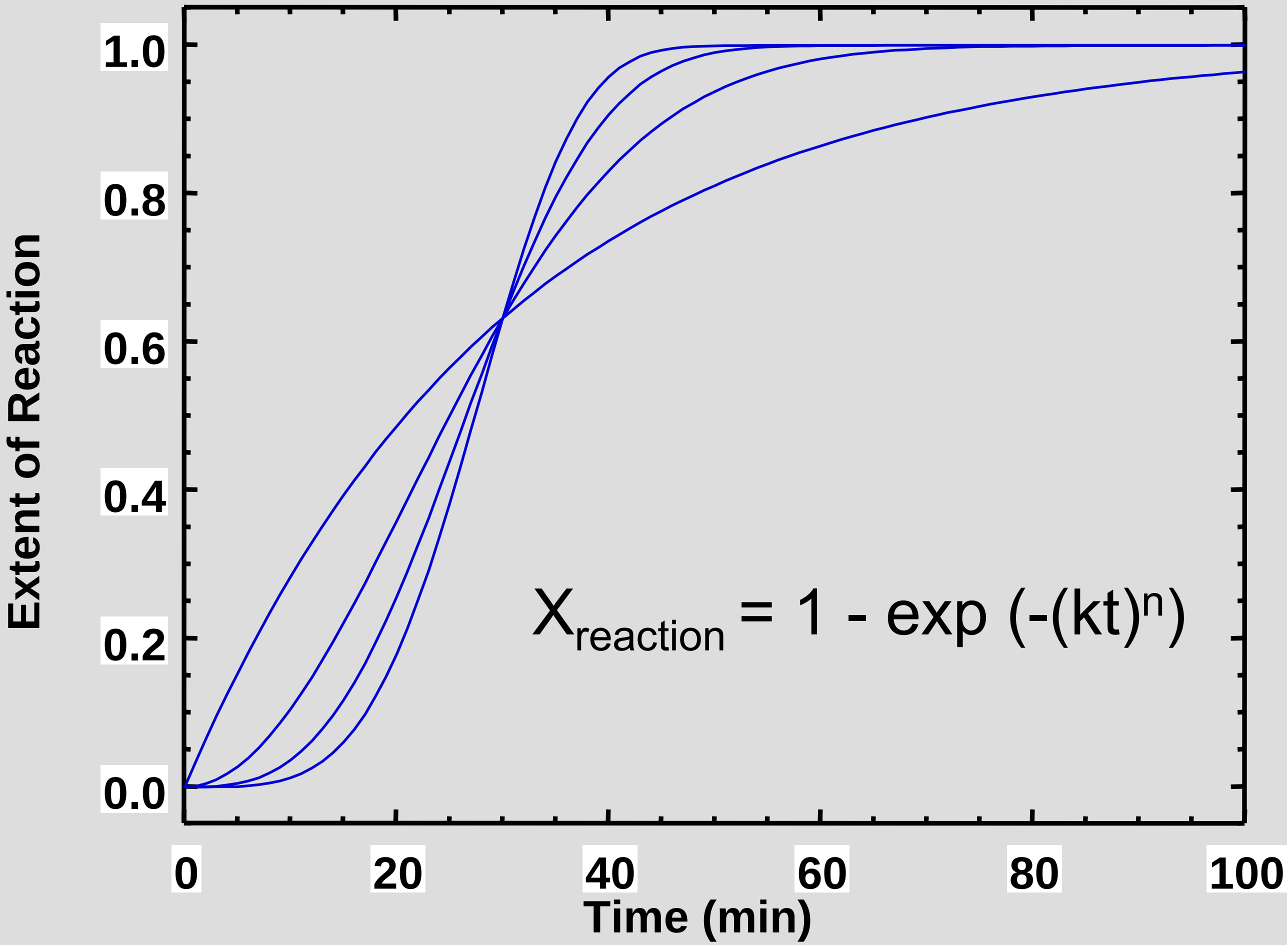


Ref: A. Züttel, “Materials for hydrogen storage”, materials today, Septemper (2003), pp. 18-27

Nucleation Seeding



Avrami Equation with Various Values of n



***n* = 4**
Constant Nucleation + 3D Growth, sphere

***n* = 3**
Nucleation at start + 3D Growth, sphere

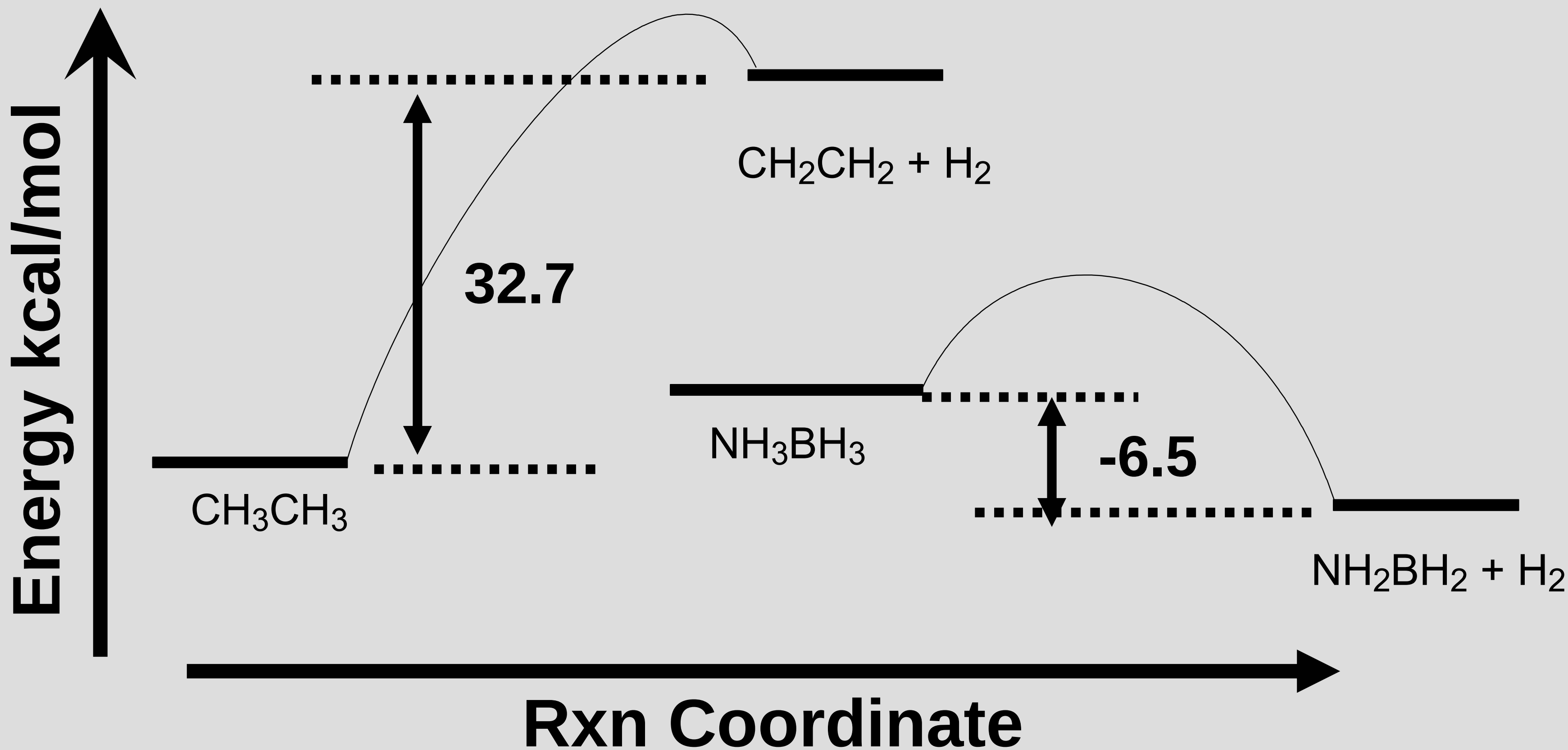
***n* = 2**
Nucleation at start + 2D Growth, cylinder

***n* = 1**
Nucleation at start + 1D Growth, Plate

Changes in Bonding

	isolated BH_3, NH_3	$H_3N—BH_3(g)$	$H_3N—BH_3(s)$
B—H	1.160	1.216	1.15
N—H	1.014	1.014	0.96
∠HBH	120	113.8	102
∠ NHN	107.6	108.7	113
∠ N—H --- H			156
∠B—H --- H			106
NH---HB			2.02

Enthalpy Calculations (Theory)



- **Kinetic verses thermodynamic control**

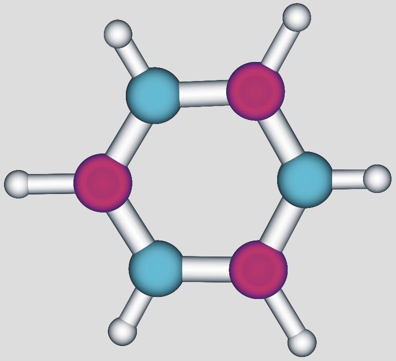
Reaction Pathways

$NH_3BH_3 + NH_3BH_2\text{-}NH_2BH_3$
$\rightarrow NH_3BH_2\text{-}NH_2BH_2\text{-}NH_2BH_3 + H_2$

$NH_3BH_3 + NH_3BH_2NH_2BH_2\text{-}NH_2BH_3$
$\rightarrow NH_3BH_2\text{-}NH_2BH_2\text{-}NH_2BH_2\text{-}NH_2BH_3 + H_2$ $\leq 120\ ^\circ C$

$\geq 120\ ^\circ C$

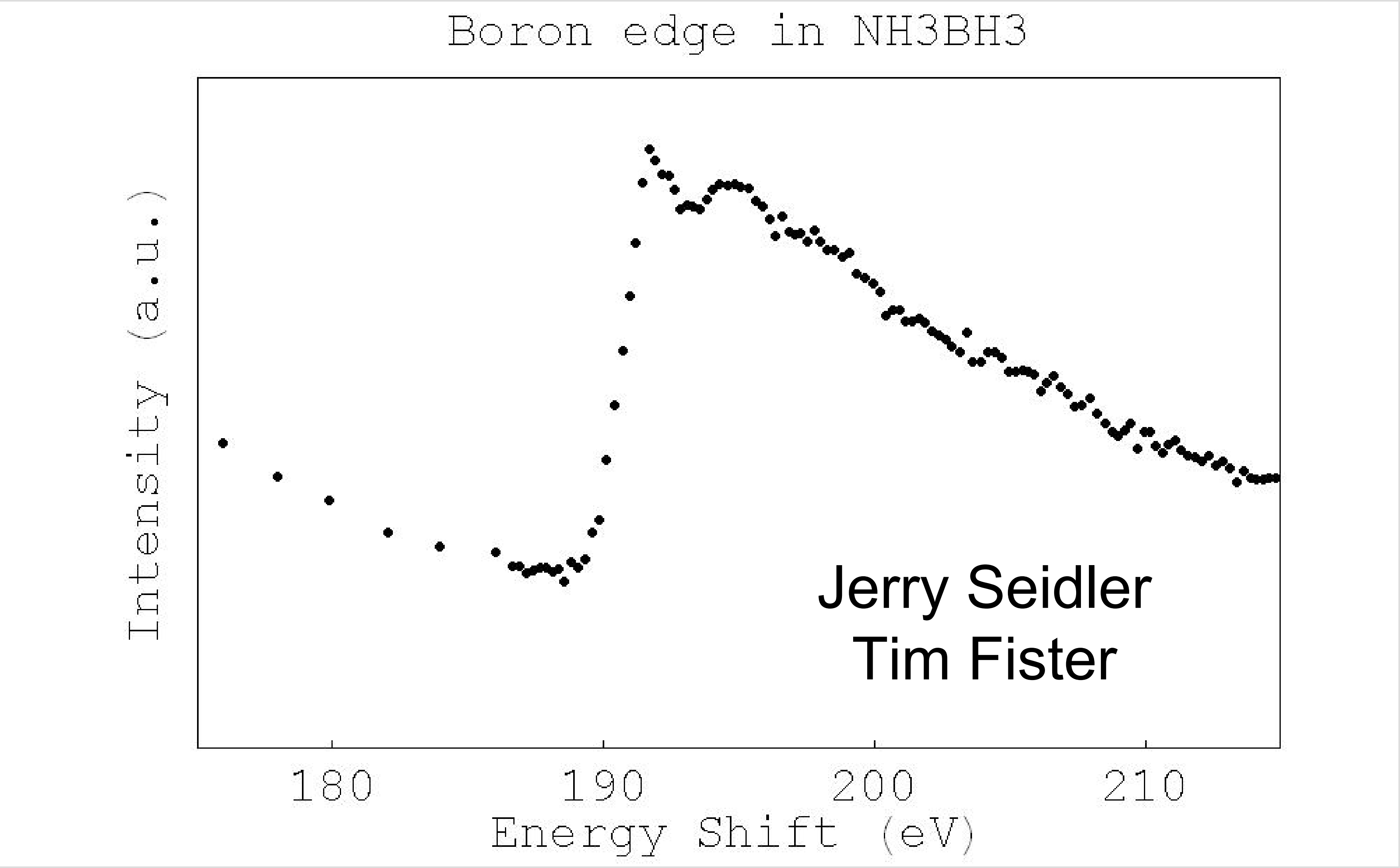
$NH_3(BH_2NH_2BH_2\text{-}NH_2)BH_3)_n$
$\rightarrow NH_3(BH_2NH_2BH{=}NH)_nBH_3 + H_2$



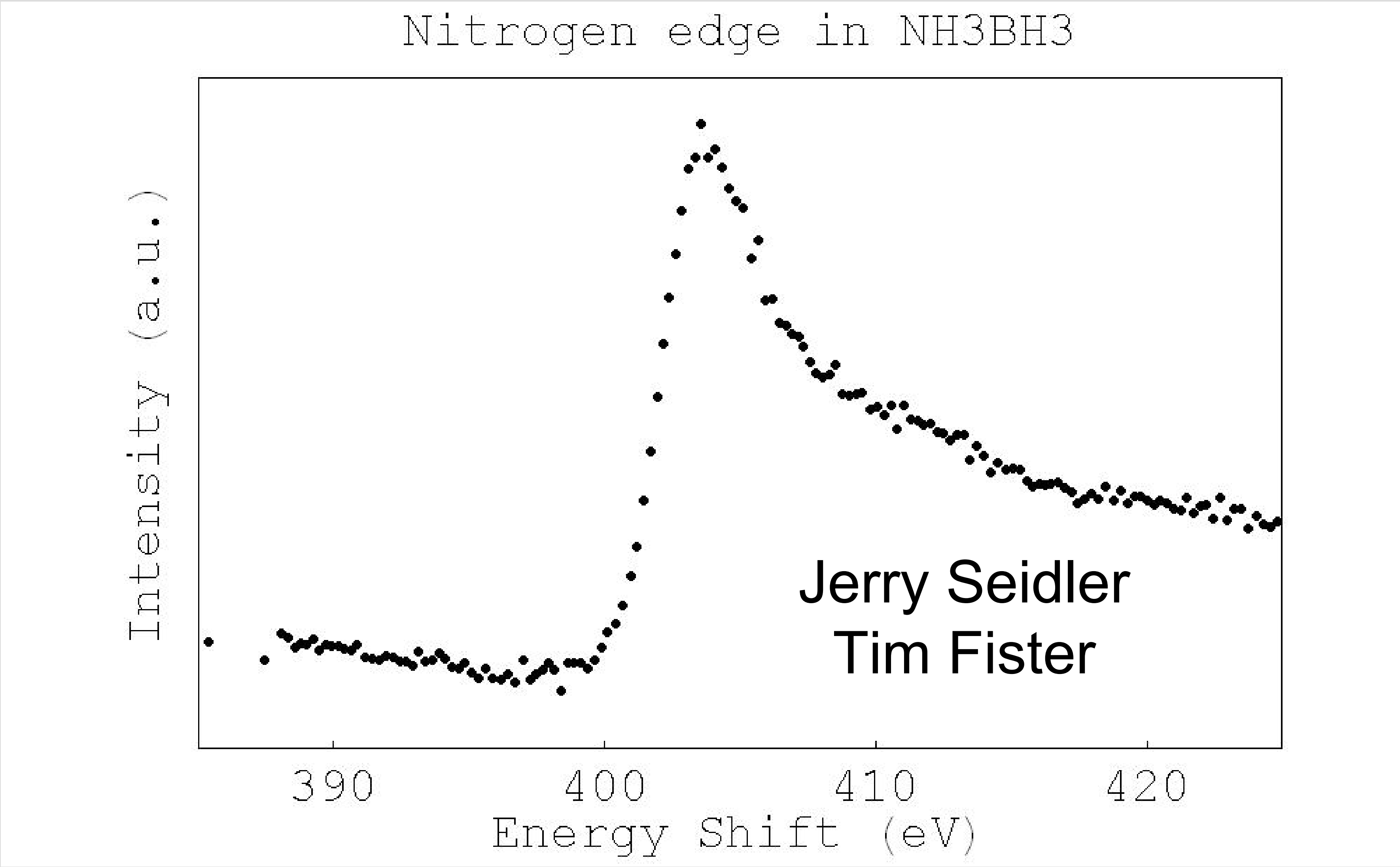
$(NH_3BH_2NH_2BH{=}NHBH_3)_n$
$\rightarrow NH_3(BH{=}NHBH{=}NH)_nBH_3 + H_2$

$NH_3(BH{=}NHBH{=}NH)_nBH_3 \rightarrow$ **borazine** $+ H_2$ FW = 80.47

bp = 55 °C



Boron edge in NH3BH3
Intensity (a.u.)
Jerry Seidler
Tim Fister
180
190
200
210
Energy Shift (eV)


Nitrogen edge in NH3BH3
Intensity (a.u.)
390
400
410
420
Energy Shift (eV)
Jerry Seidler
Tim Fister

Solid State Approaches to H_2 Storage

- Carbon (Single Wall Nano Tubes)
  - Reports vary between 0 to 7% wt% H_2
- Metal Hydrides
  - Up to 2 hydrogen on [MH_2]
  - Up to 4 hydrogen on group IIIB element [MH_4^-]
    - $NaAlH_4$
  - Air sensitive, water sensitive
- ‘Chemical Hydrogen Storage’
  - An attractive alternative?
  - What is feasible?

Hydrogen Storage Challenge

FreedomCAR On-board storage for FC vehicles
Call for "virtual centers" and advanced concepts

Volumetric Density

year	2010	2015
KWh/liter	1.5	2.7
MJ/liter	5.4	9.7
gm/liter	45	81

Gravimetric Density

year	2010	2015
KWh/kg	2	3
MJ/kg	7.2	10.8
gm/kg	60	90

Operational temperature: -20 < ˚C < 80

Material with 9 wt% H_2 that releases H_2 < 80˚ C

Volumetric Storage Challenges
(4 Kg H_2 = 300 miles)

MgH_2 32 liter

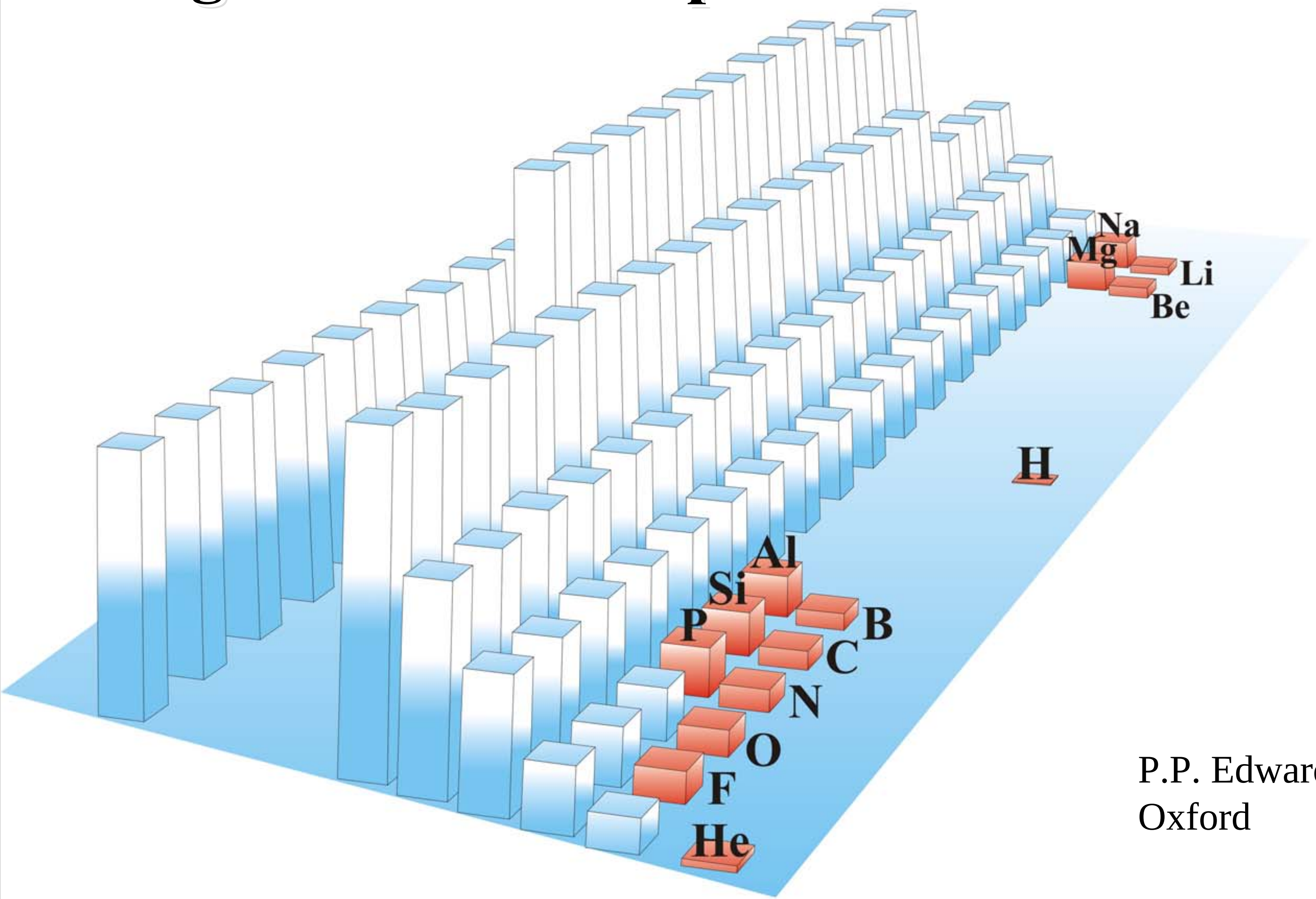
liquid H_2 (-250˚C) 56 liter

$NaAlH_4$ 69 liter

Compressed H_2 (200 bar) 225 liter

Gravimetric Density Challenges

Height of bar corresponds to mass of element

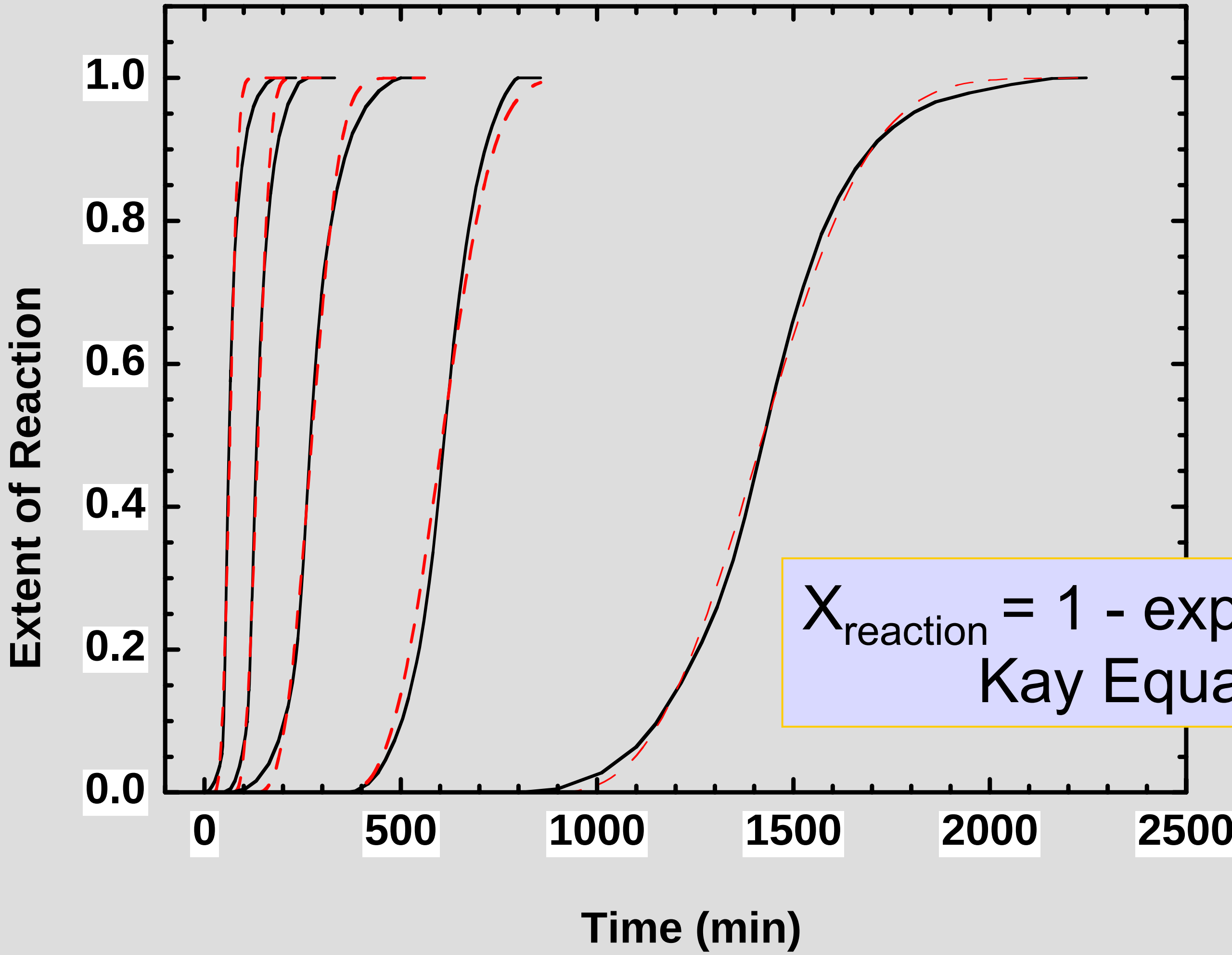


The Periodic Table of the Chemical Elements.
The mass of each element is indicated by its elevation above the plane.

P.P. Edwards
Oxford

March 2004

Nucleation and Growth Kinetics

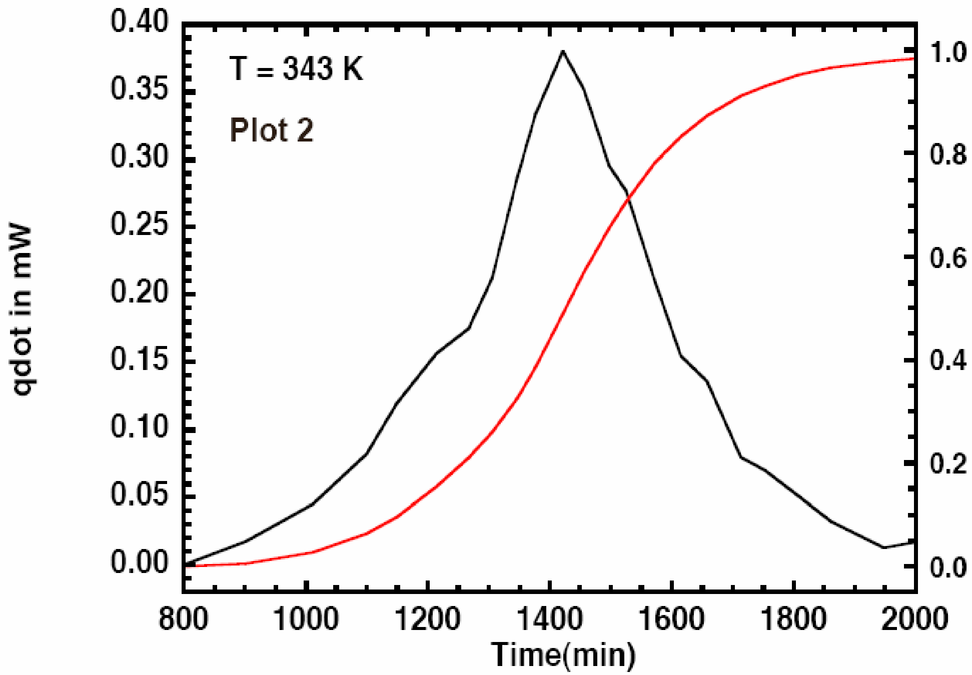


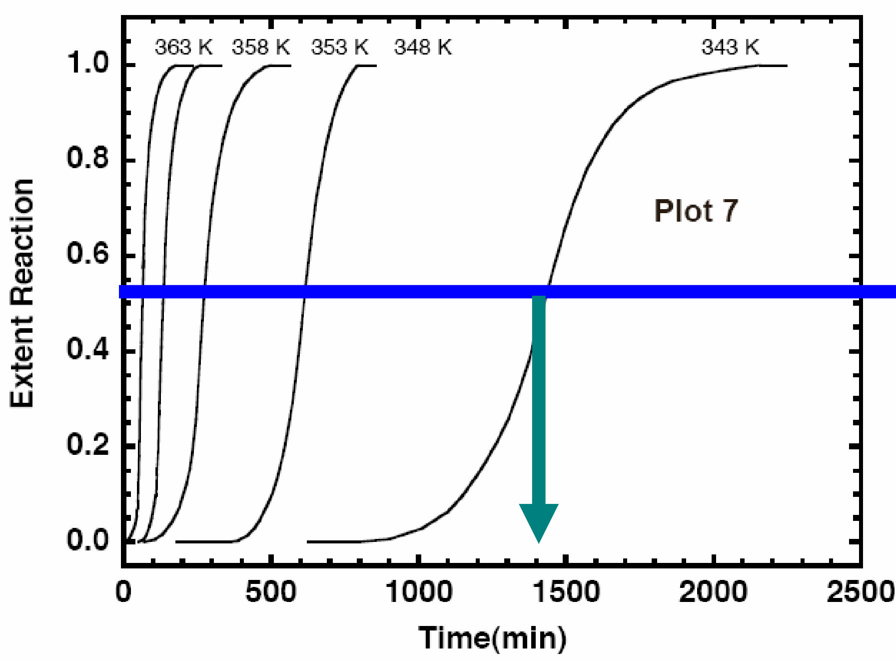
$$X_{reaction} = 1 - \exp\left(-(k(t-\tau))^3\right)$$

Kay Equation

- **Data described well by a modified Avrami Equation**
- **Includes three dimensional growth rate and nucleation rate**

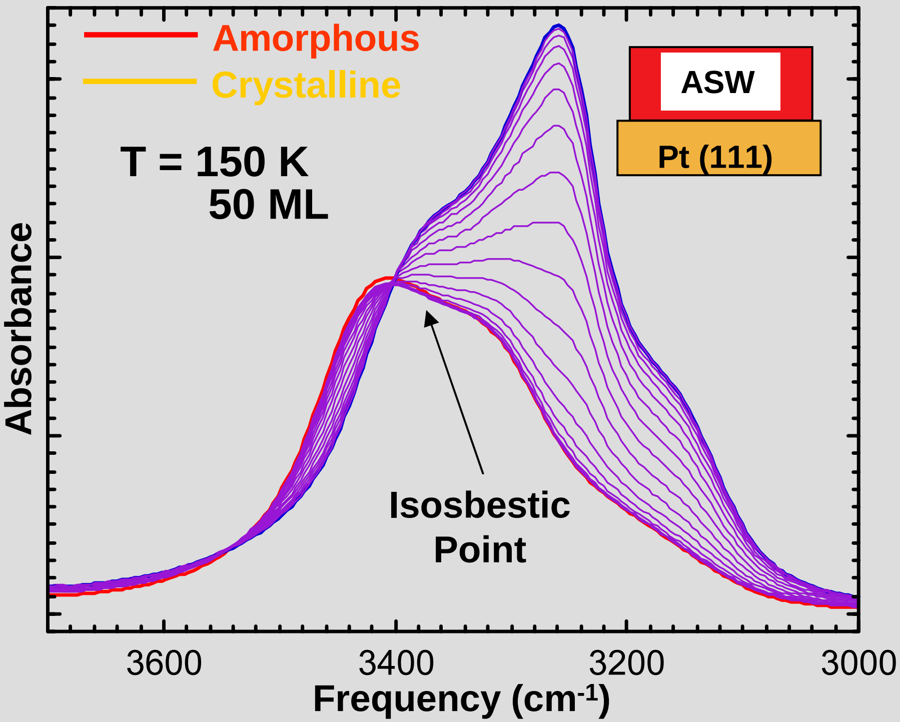
Kinetic Analysis

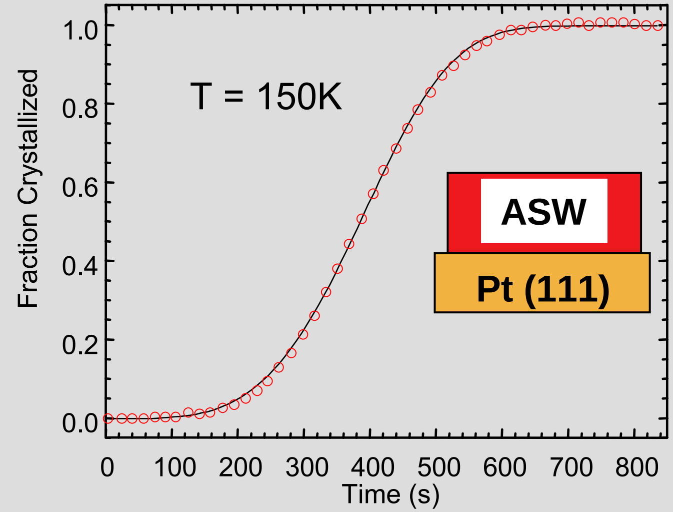




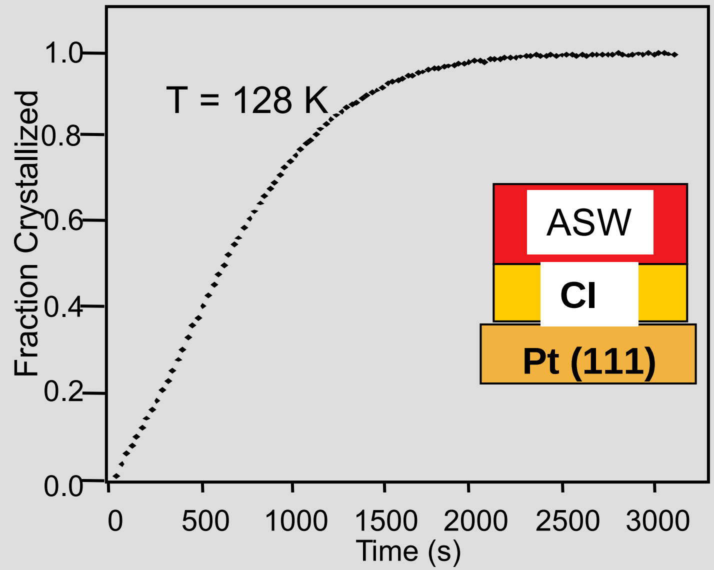
Integrate DSC curves as a function of temperature to get half-life

Time Resolved ASW Crystallization Kinetics Studied via FTIR





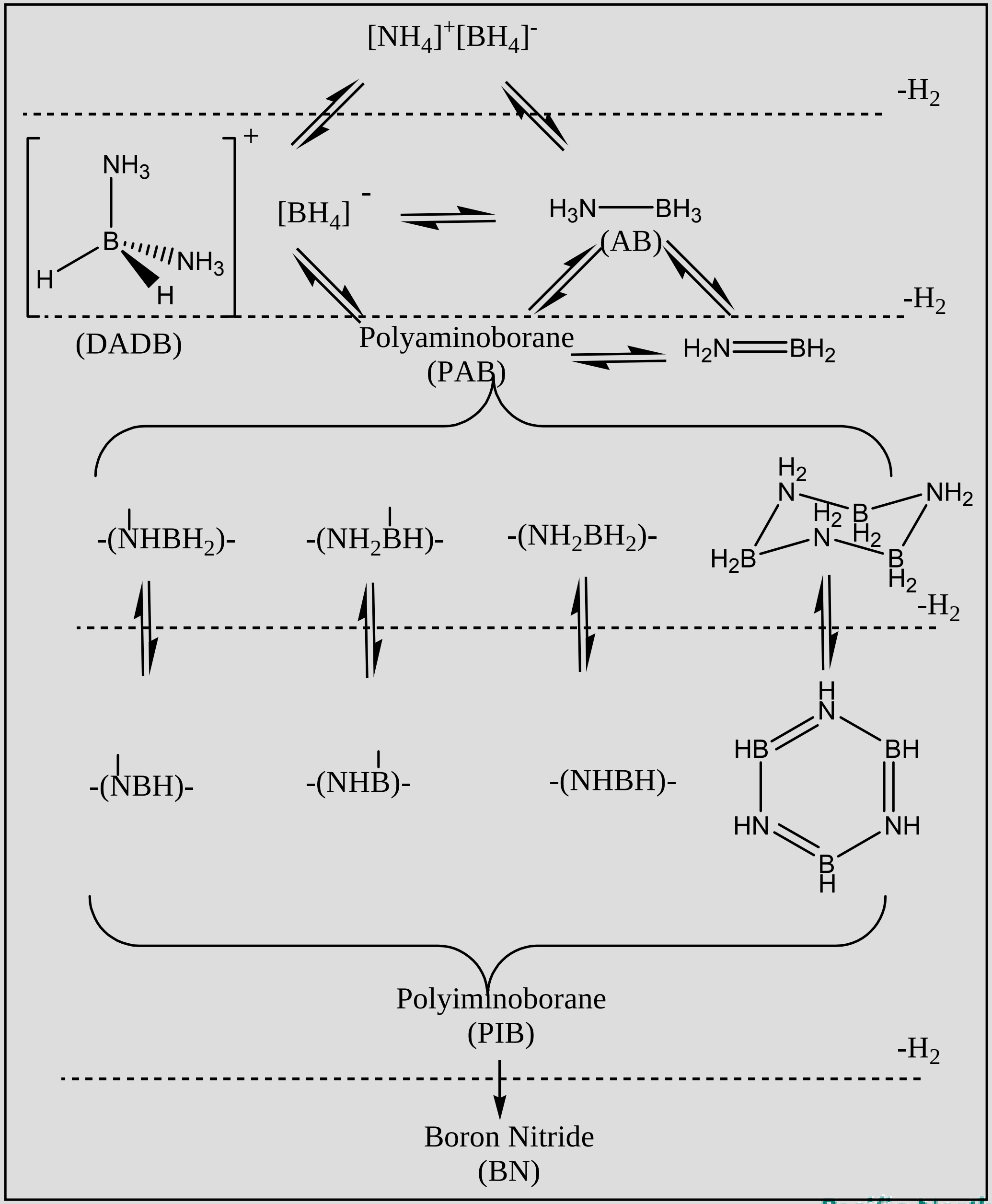
Homogeneous Nucleation and Growth



Linear Growth Front Propagation

- Crystalline template accelerates and alters ASW —> CI phase transition kinetics.

Z Dohnálek, RL Ciolli, GA Kimmel, KP Stevenson, RS Smith, & BD Kay, JCP 110, 5489 (1999)
Z Dohnálek, GA Kimmel, RL Ciolli, KP Stevenson, RS Smith, & BD Kay, JCP 112, 5932 (2000)
RS Smith, Z Dohnalek, GA Kimmel, G Teeter, P Ayotte, JL Daschbach, and BD Kay, in “Water in Confining Geometries”, Chapter 14, (Springer 2003).

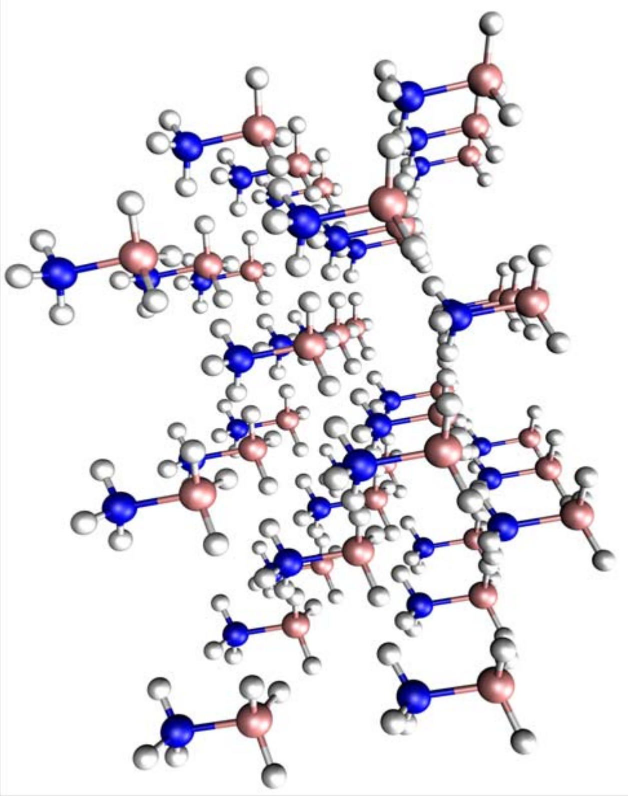

[NH4]+[BH4]-
-H2
NH3
B
H
NH3
H
+
[BH4] -
H3N BH3
(AB)
-H2
(DADB)
Polyaminoborane
(PAB)
H2N BH2
-(NHBH2)-
-(NH2BH)-
-(NH2BH2)-
H2
N
B
NH2
H2
N
H2
H2B
B
H2
-H2
H
N
HB
BH
HN
NH
B
H
-(NBH)-
-(NHB)-
-(NHBH)-
Polyiminoborane
(PIB)
-H2
Boron Nitride
(BN)

NH_xBH_x Store significant quantity of hydrogen (>6 wt%/step)

	Wt% H_2	T (°C)
$NH_4BH_4 \rightarrow NH_3BH_3 + H_2$	6.1	<25
$NH_3BH_3 \rightarrow NH_2BH_2 + H_2$	6.5	<120
$NH_2BH_2 \rightarrow NHBH + H_2$	6.9	>120
$NHBH \rightarrow BN + H_2$	7.3	>500

Two sequential steps > 13 wt% hydrogen

Reaction Pathways to H_2



$NH_3BH_3 \rightarrow NH_2{=}BH_2 + H_2$

$nNH_2{=}BH_2 \rightarrow (NH_2BH_2\text{-}NH_2BH_2)_n$

intramolecular

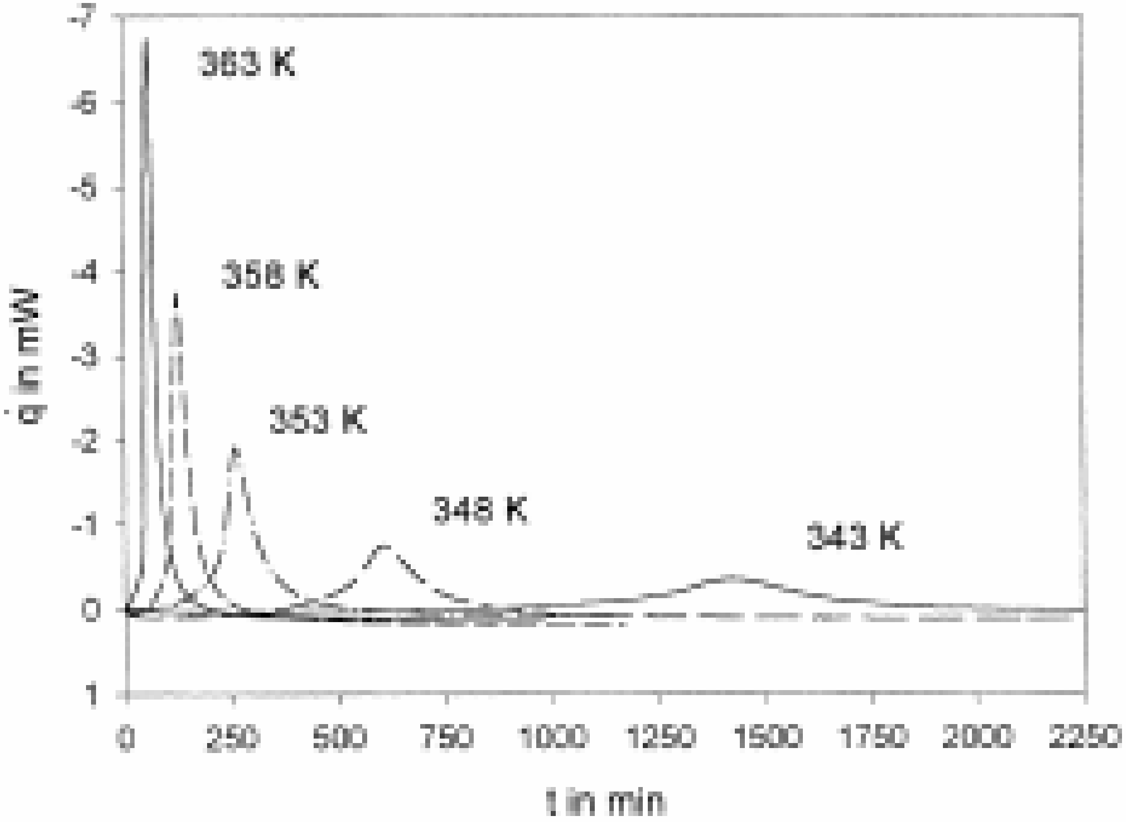
Or

intermolecular

$2\ NH_3BH_3 \rightarrow NH_3BH_2\text{-}NH_2BH_3 + H_2$

$NH_3BH_3(s) \rightarrow (NH_2BH_2)(s) + H_2$

G. Wolf et al. / Thermochimica Acta 343 (2000) 19–25



Thermochim Acta 2000 343, 19. ΔH_r $NH_3BH_3 \rightarrow$ products (-5 kcal/m)

Release hydrogen from the solid state below the melting point

Science"Toward a Hydrogen Economy"

Introduction

- *Not So Simple*

Editorial

- *The Hydrogen Solution*

News

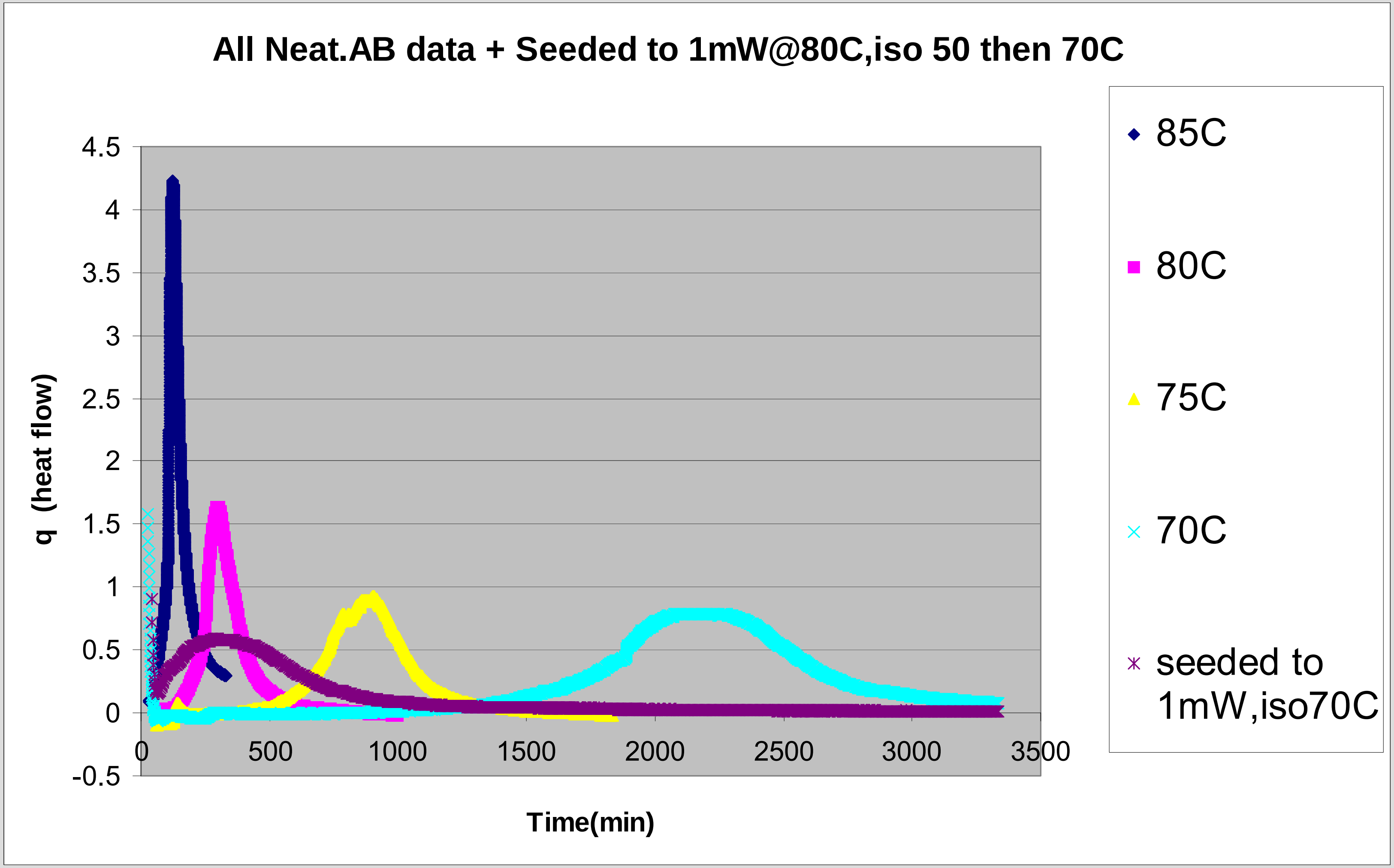
- *The Hydrogen Backlash*

Viewpoints

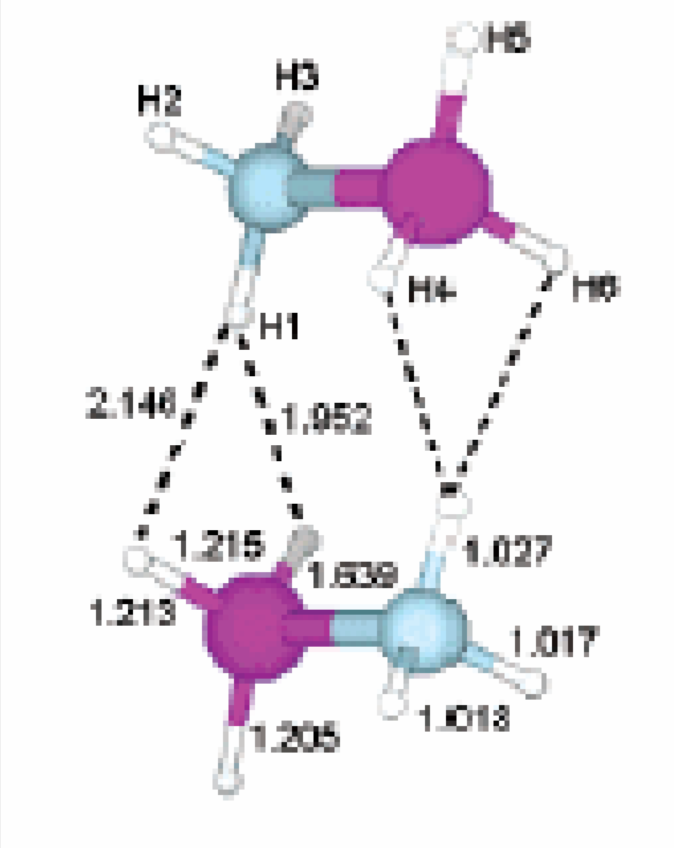
- *Sustainable Hydrogen Production*
- *Hybrid Cars Now, Fuel Cell Cars Later*

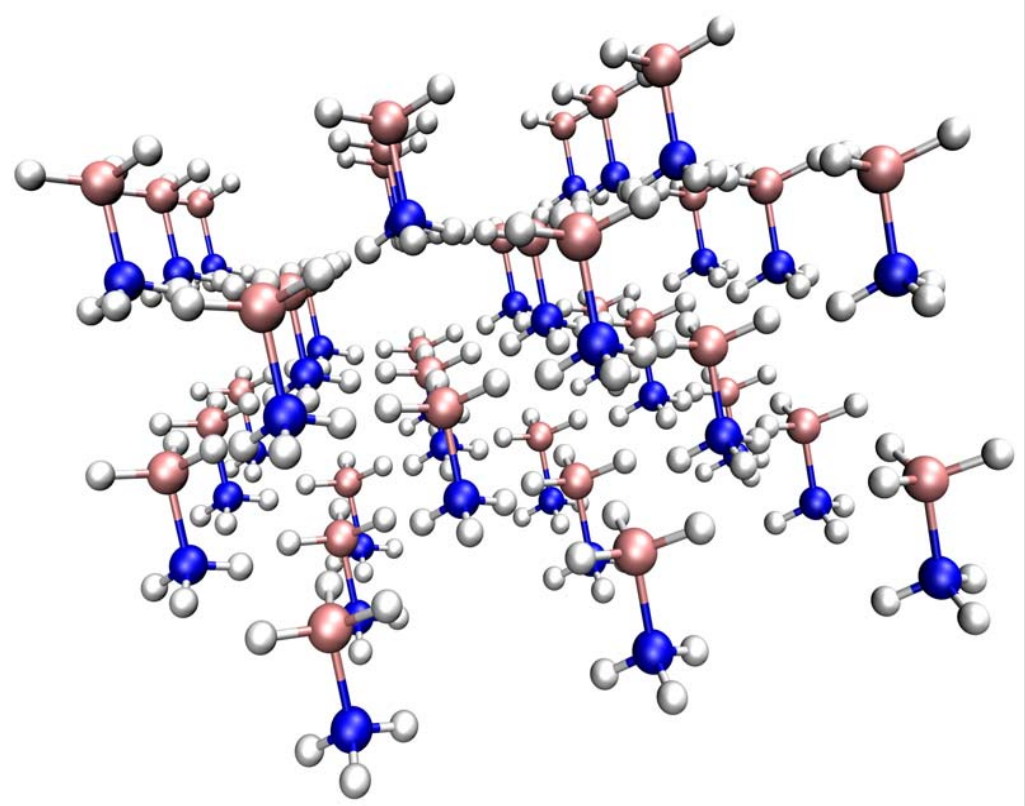
Hydrogen makes up 90% of atoms in the universe (2/3 of it tied up in water, the balance in living organisms and fossil fuels)

Stop & Restart



NH_3BH_3





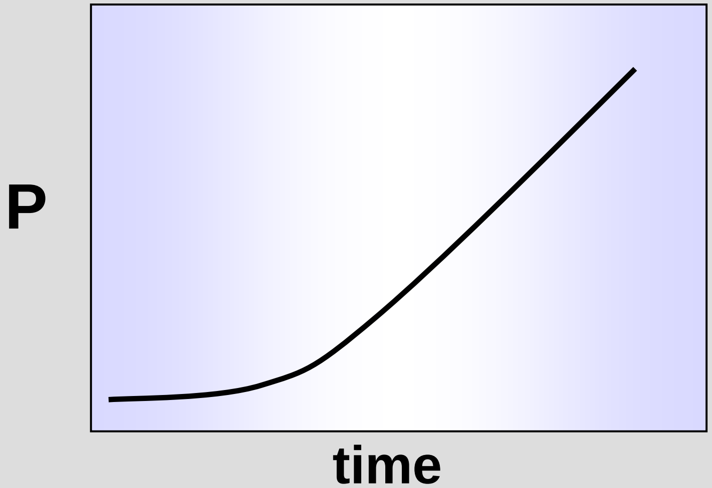
Gabriel Merino, Vladimir I. Bakhmutov, and Alberto Vela
J. Phys. Chem. A, **106** (37), 8491 -8494, 2002

Auto Catalytic Kinetics

Enzyme kinetics

$E + S \rightarrow [ES] \rightarrow P$

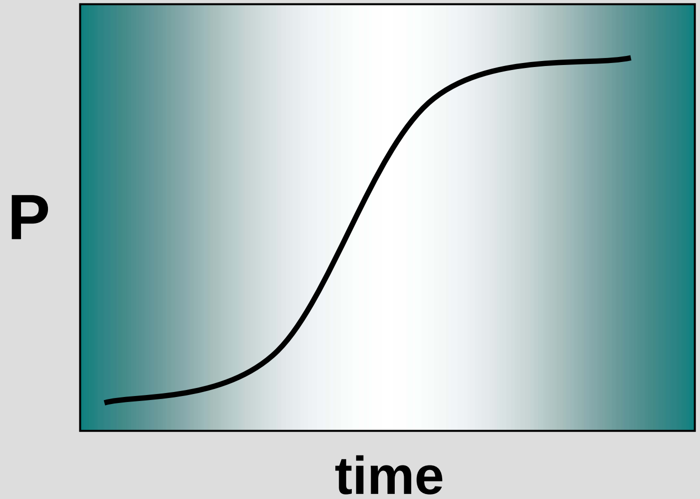
Induction time to build up intermediate



Product Catalyzed Reactions

$A \rightarrow B \qquad -d[A]/dt = k\,[A]\,[B]$

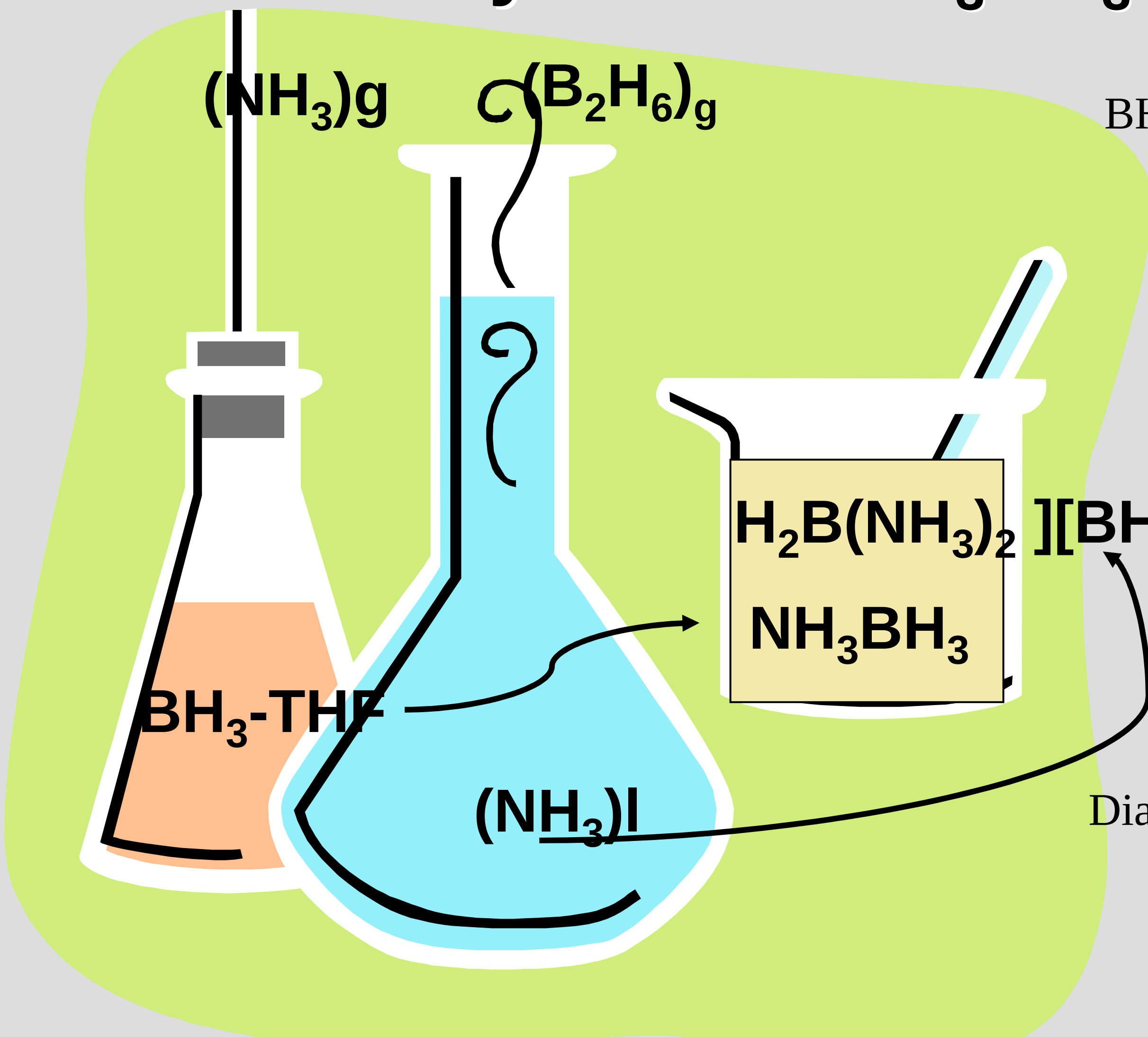
Hydrolysis of esters, acid catalyzed



Phase Transformations

Crystallization, melting, precipitation, condensation

Synthesis NH_3BH_3



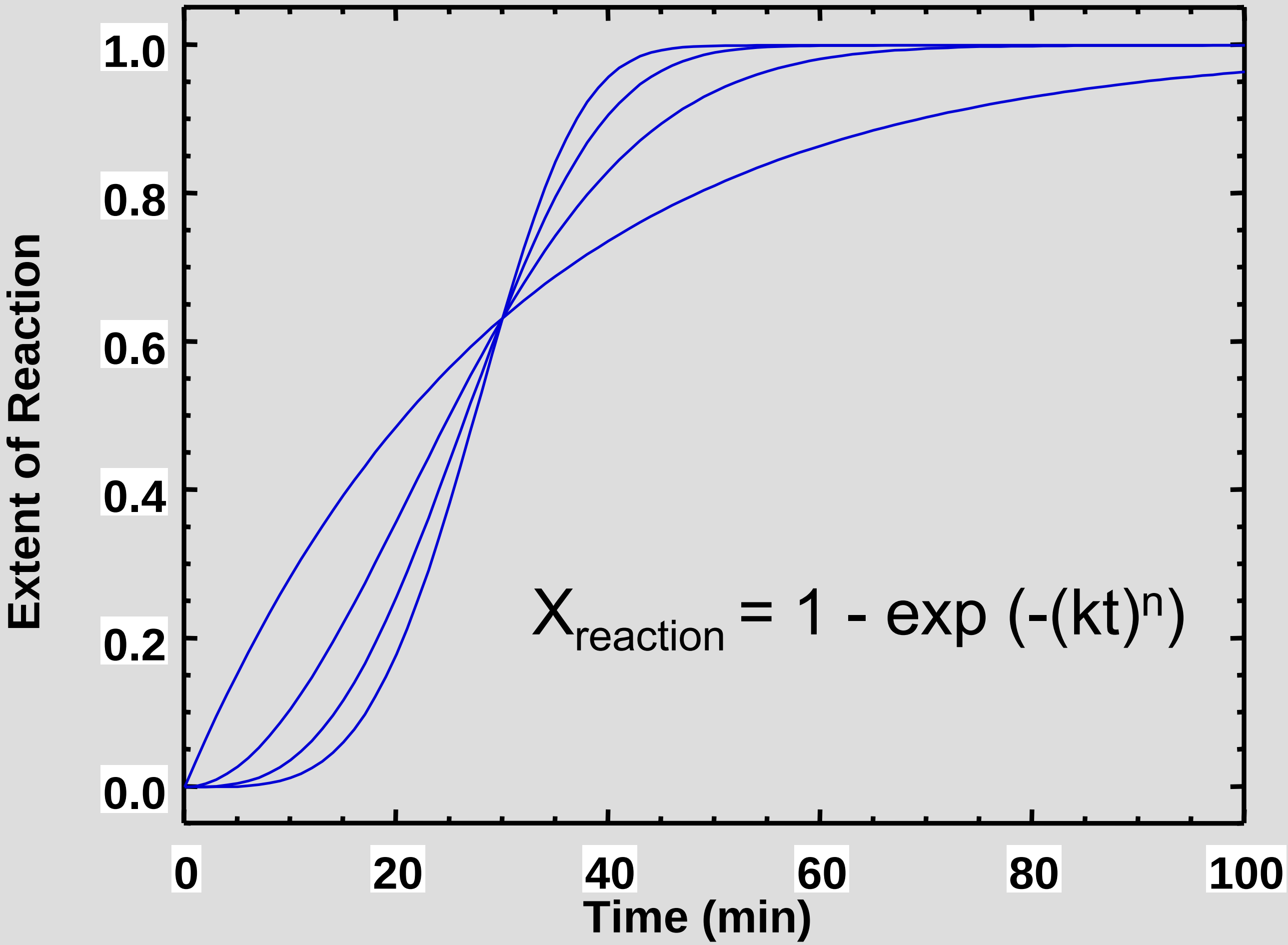
BH_3 – H –BH_2NH_3

NH_3

$[BH_4]^{-}[NH_3BH_2NH_3]^{+}$

Diammoniate of diborane

Avrami Equation with Various Values of n



n = 4
Constant Nucleation + 3D Growth, sphere

n = 3
Nucleation at start + 3D Growth, sphere

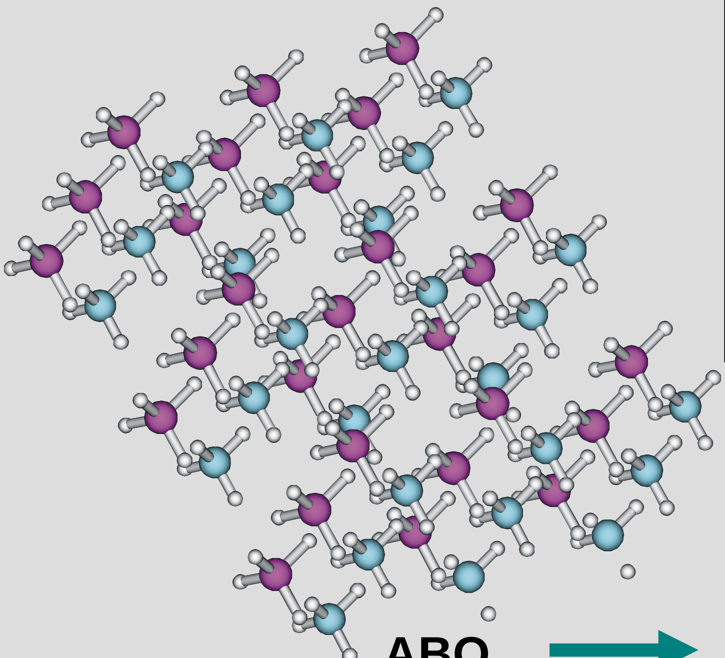
n = 2
Nucleation at start + 2D Growth, cylinder

n = 1
Nucleation at start + 1D Growth, Plate

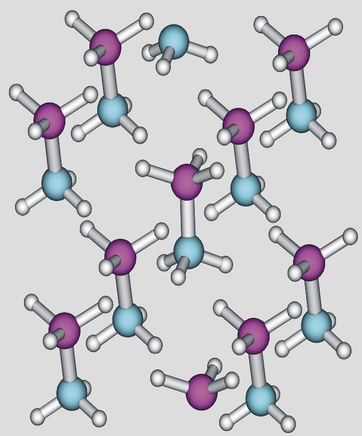
- ***"... it is not possible to determine the nucleation and growth behavior from the time dependence of the transformed volume only, as is often attempted."***
  RH Doremus, Rates of Phase Transformations

Favorable Thermodynamics?

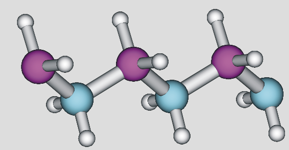
Reactants	Products	ΔE (kcal/mol)
$NH_4BH_4(s)$ $\rightarrow$	$NH_3BH_3(s) + H_2$	-2.3
$NH_3BH_3(s)$ $\rightarrow$	$(NH_2BH_2)_n + H_2$	+8.8
$(NH_2BH_2)_n$ $\rightarrow$	$(NHBH)_n + nH_2$	-3.2
$(NHBH)_n$ $\rightarrow$	$BN(s) + nH_2$	-9.2



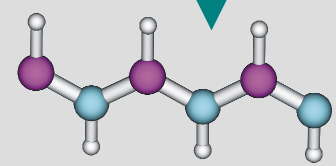
ABO



AB+ H_2



PAB+ H_2



PIB+ H_2

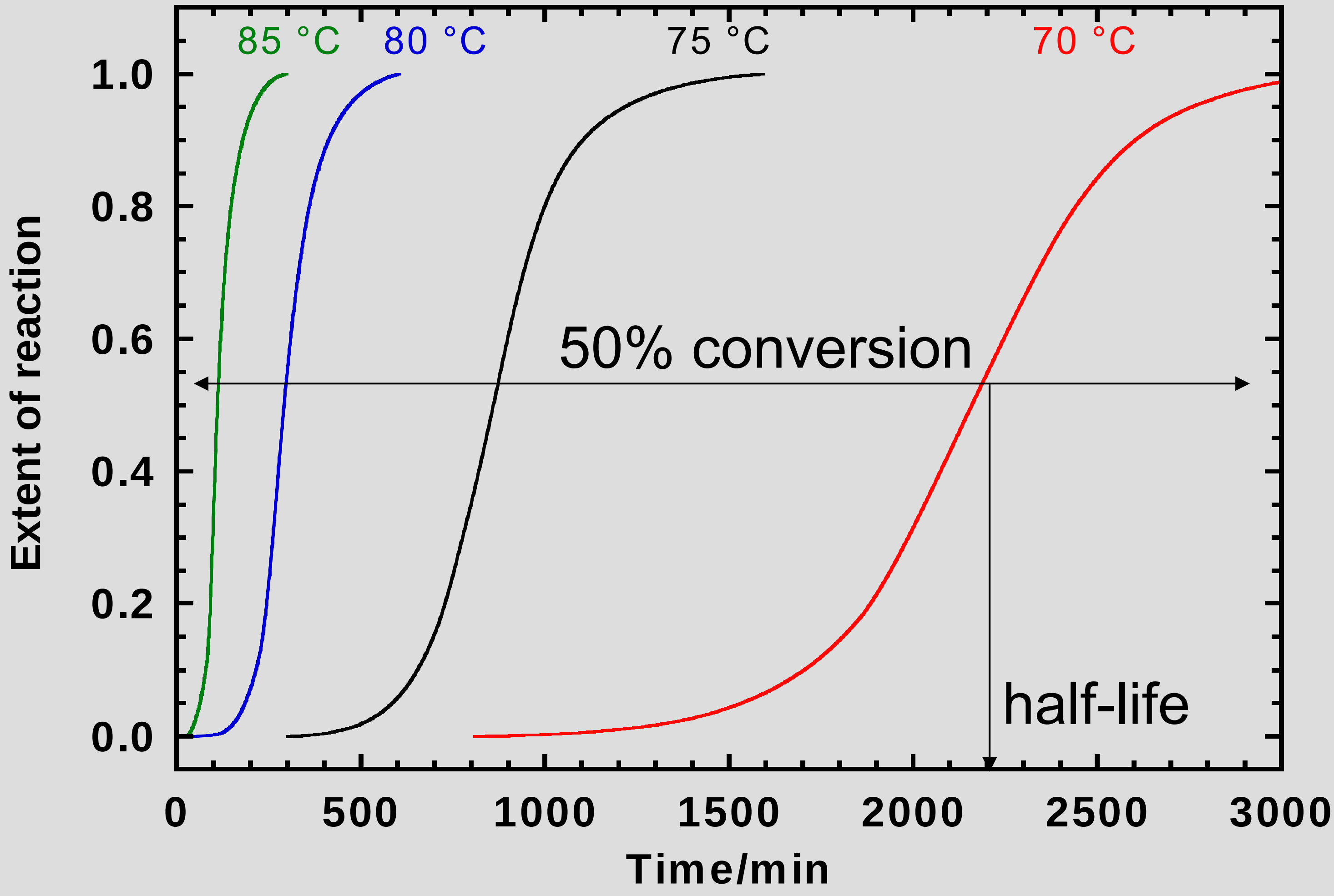
ABO = NH_4BH_4

AB = NH_3BH_3

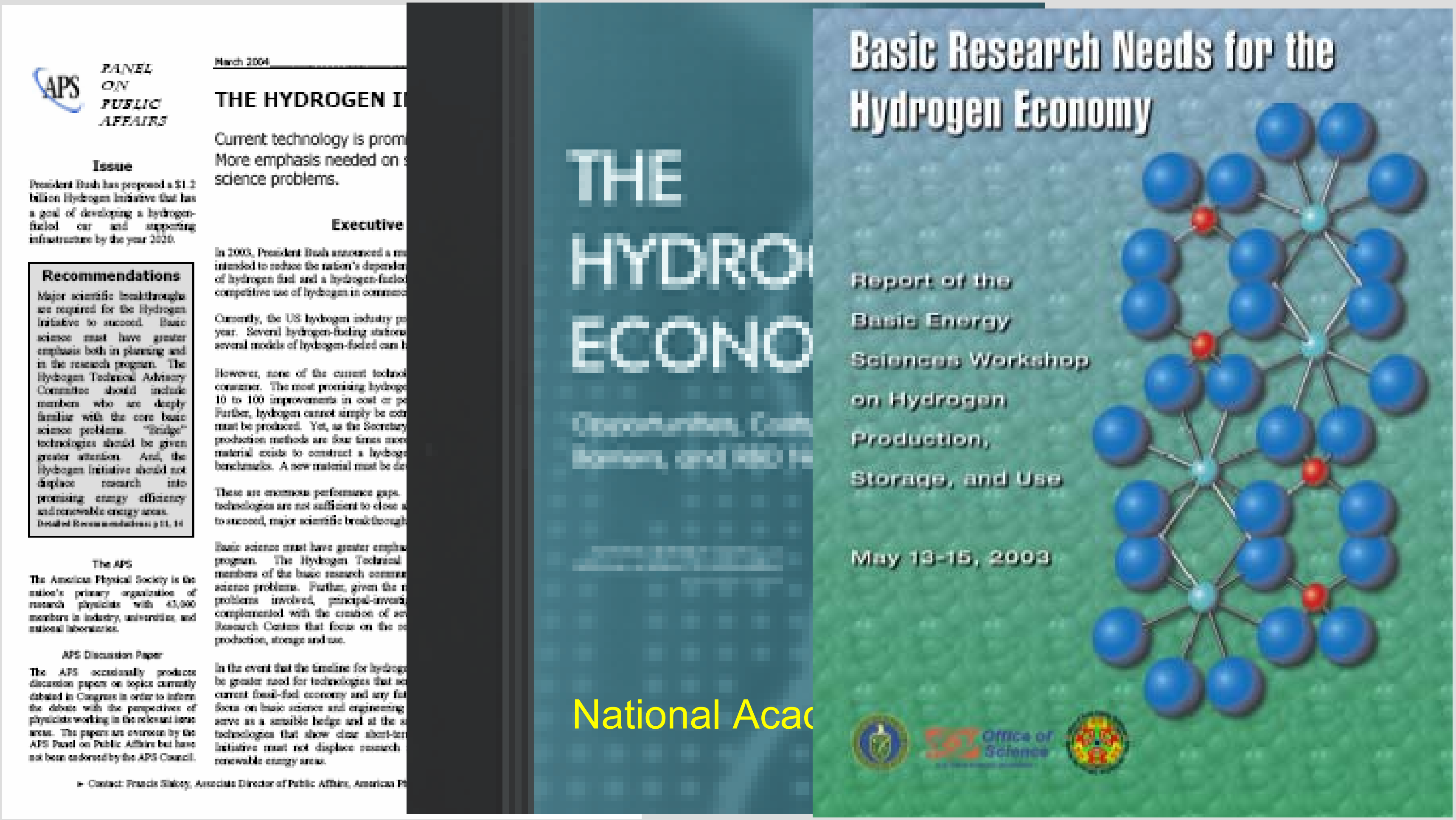
PAB = $(NH_2BH_2)_n$

PIB = $(NHBH)_n$

Kinetic Comparison



Hydrogen Research Needs



One of the Biggest Challenge: ***on-Board Storage***

New ideas, new materials