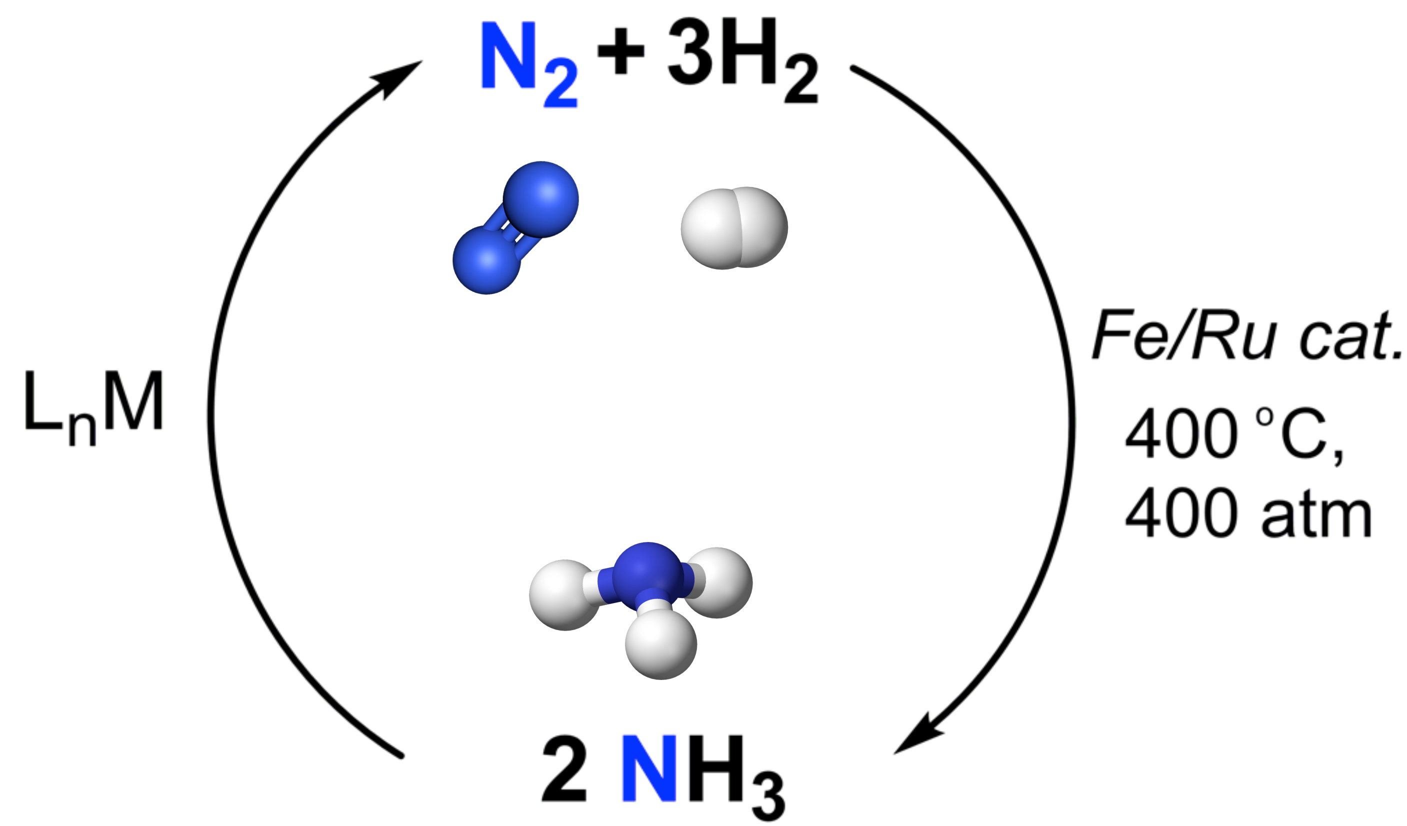

The Interconversion of Ammonia with Its Elements

2018 Annual Meeting of the Andlinger Center

Paul J. Chirik and Robert R. Knowles
Department of Chemistry
Princeton University

PRINCETON UNIVERSITY
DEPARTMENT OF CHEMISTRY

andlinger center
for energy+the environment

According to Nature, who are the most influential scientists of the 20th century?

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1918 - Nobel Prize

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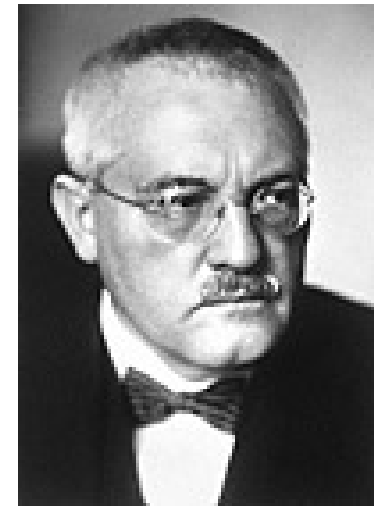

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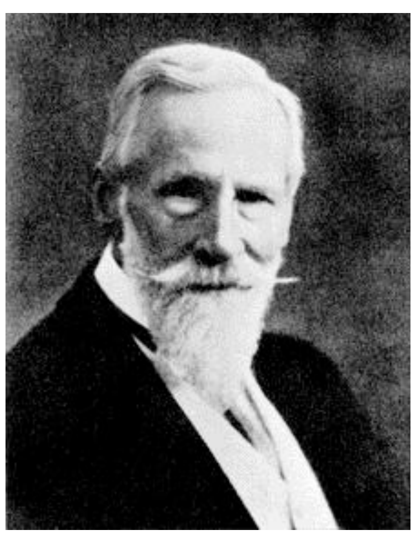

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(1898)

"England and all civilized nations stand in deadly peril."

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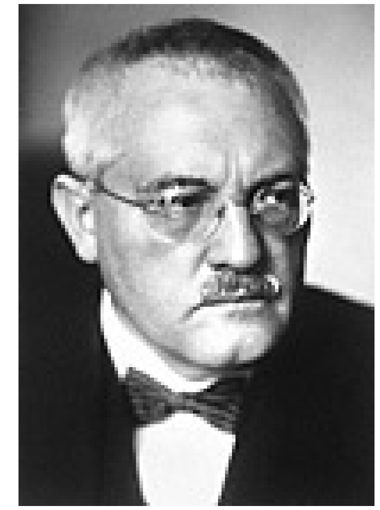

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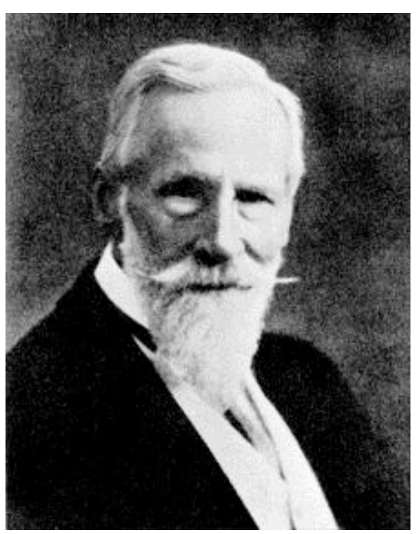

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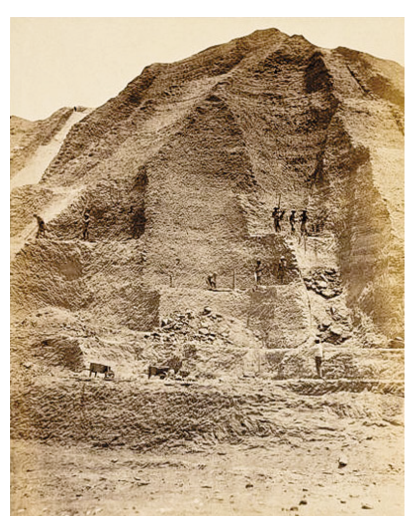
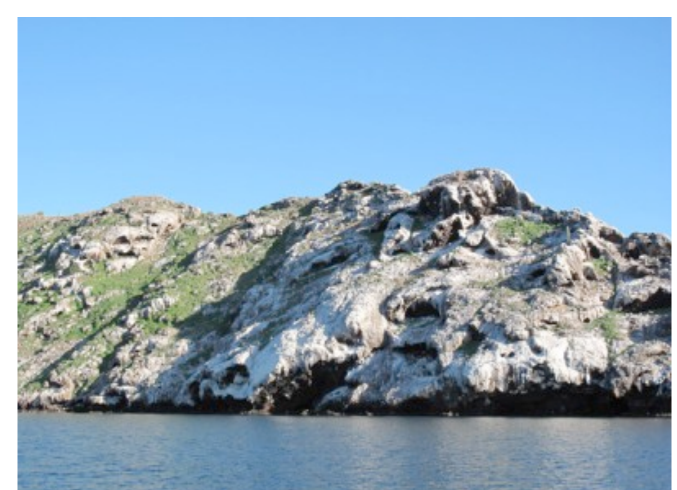
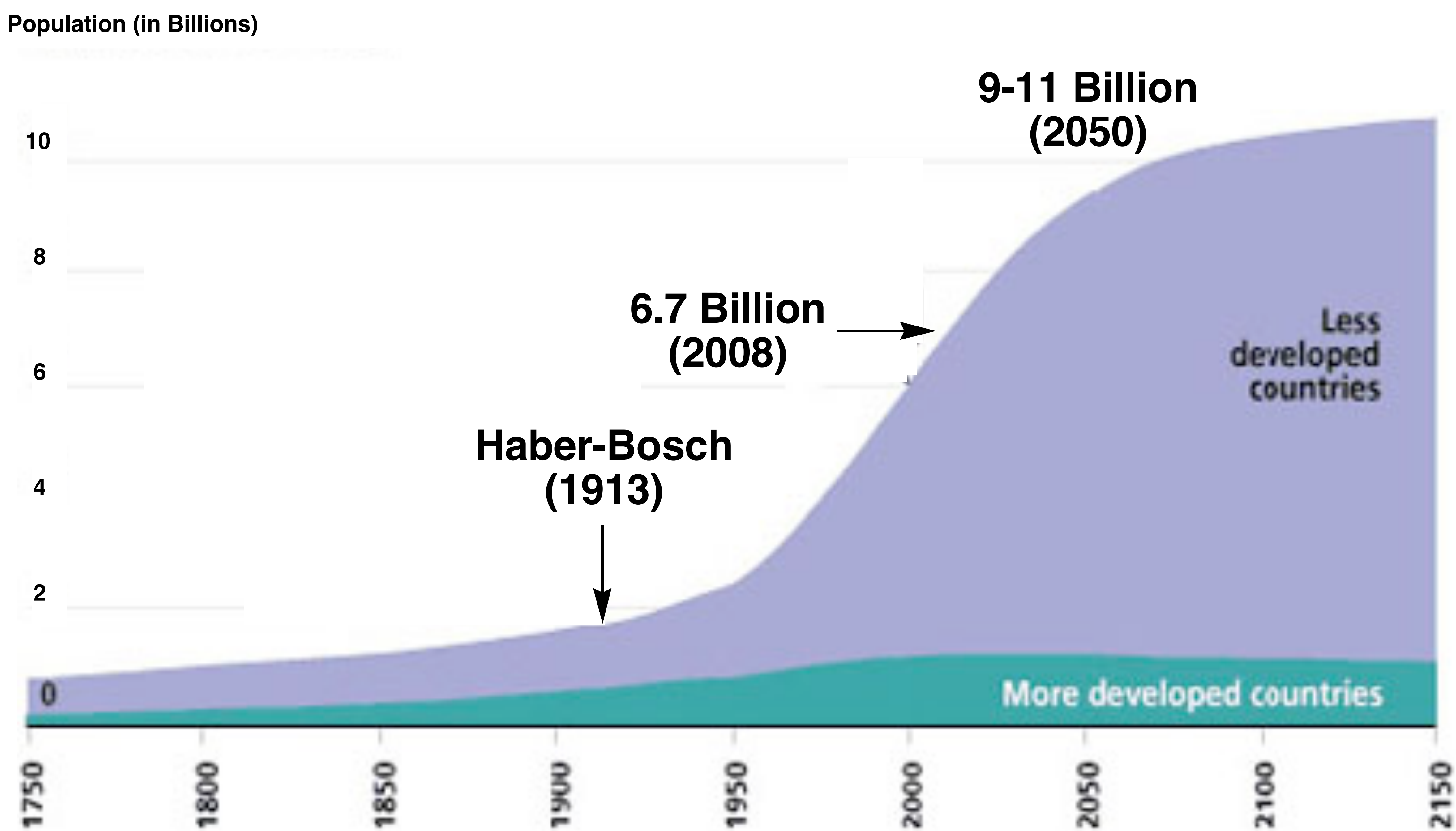
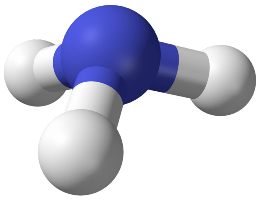




Population Explosion

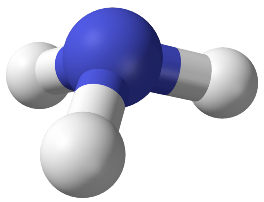


Chemistry eradicated world hunger, starvation is mostly political, economic…



Ammonia: A Most Important Molecule

Calibration: One Haber-Bosch plant makes 1 ton NH_3 per minute!



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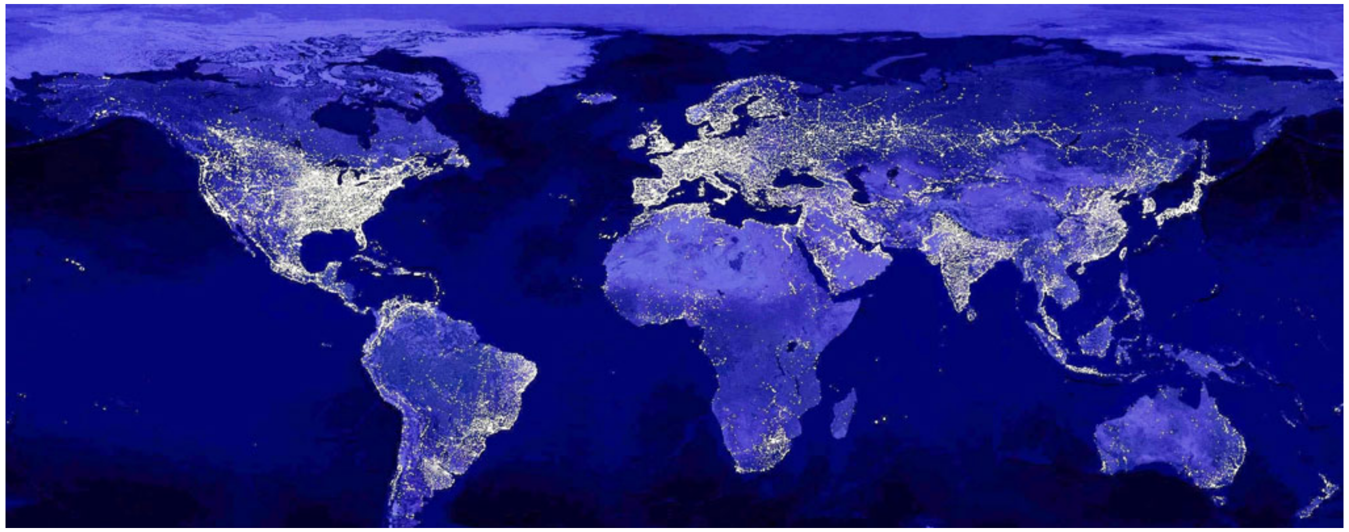
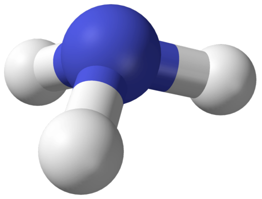


- **2-3% of the world's energy supply**



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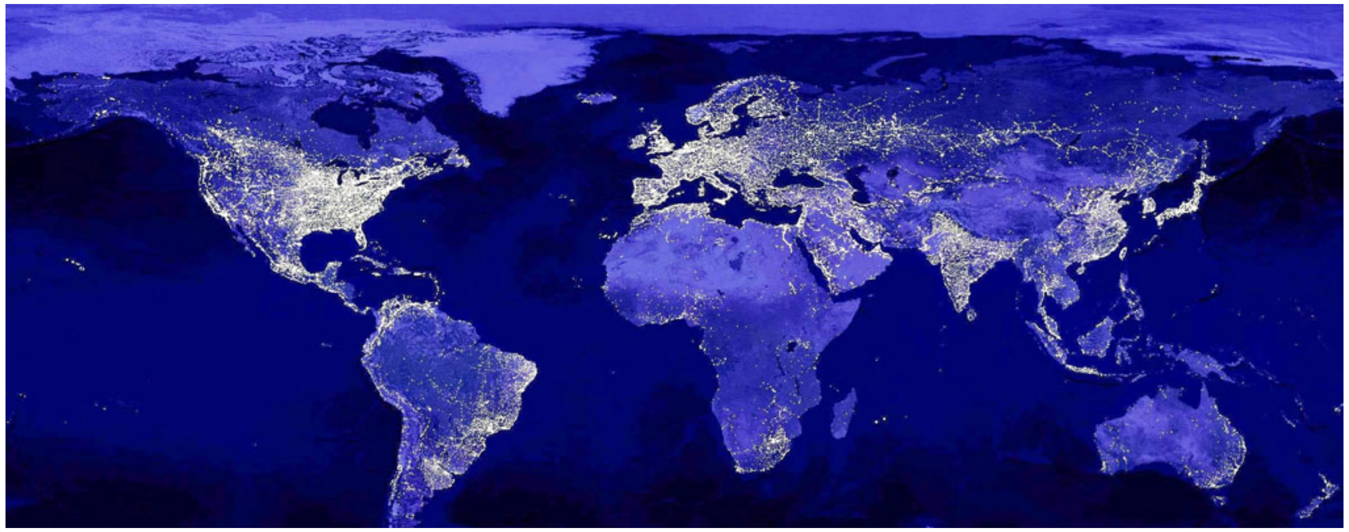

- **2-3% of the world's energy supply**
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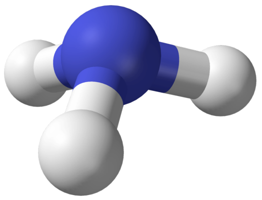
- **Distillation: 10-13%**



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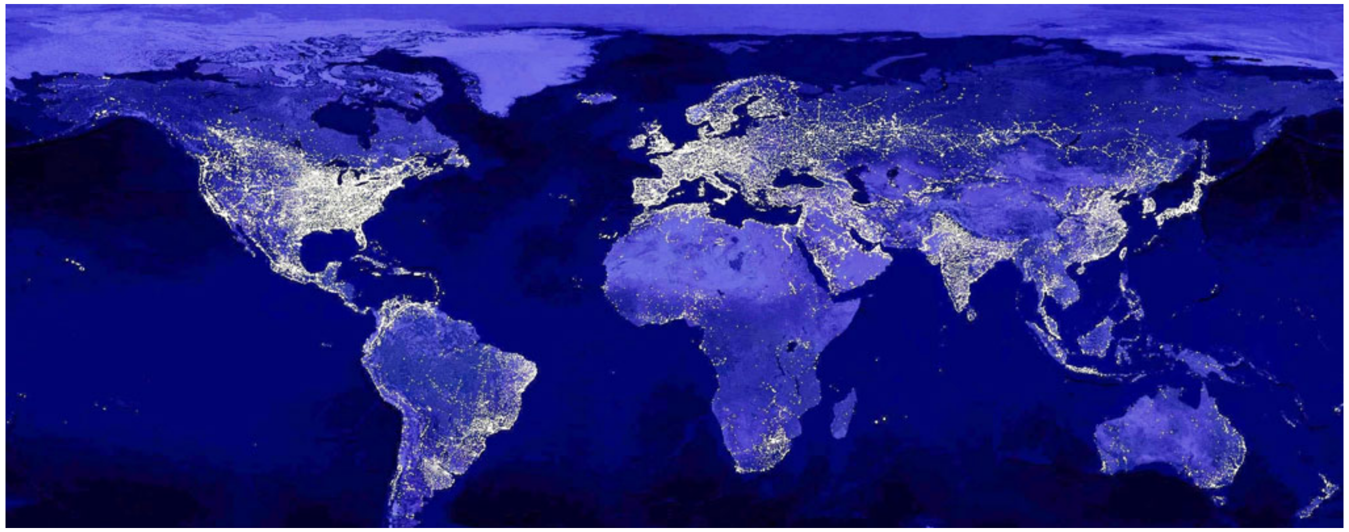

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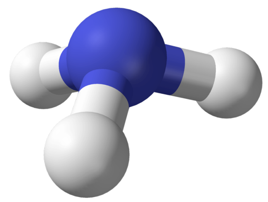

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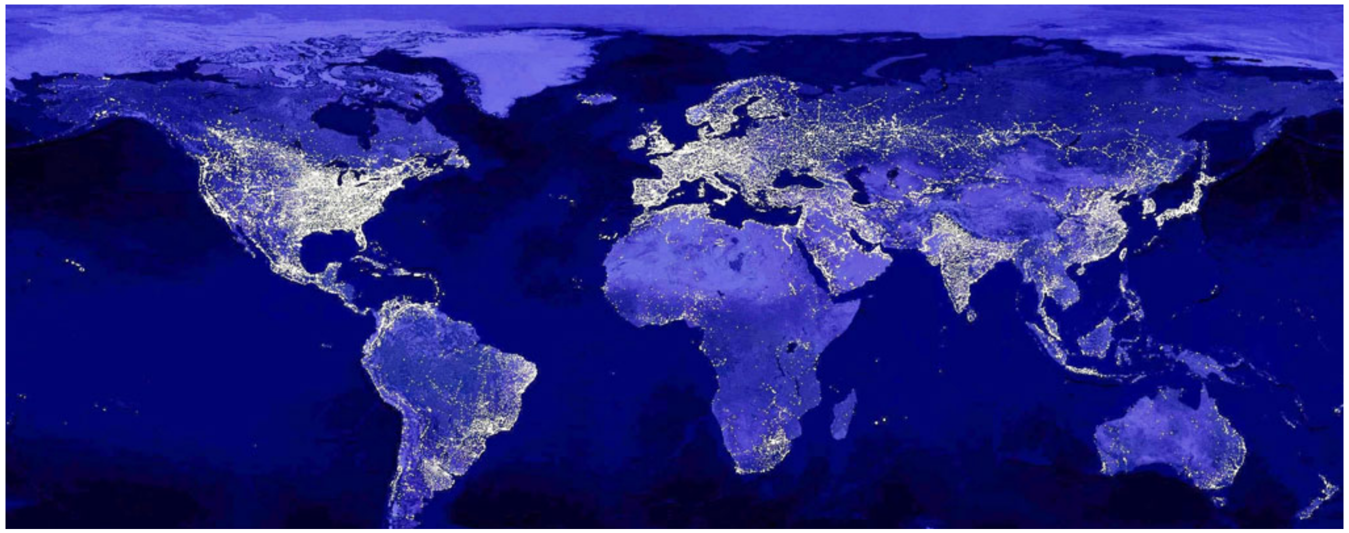

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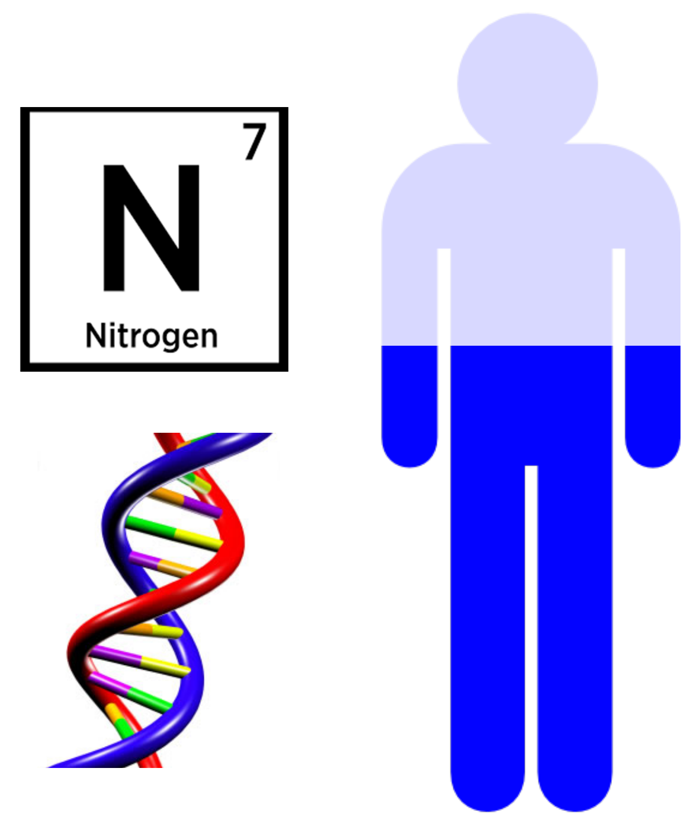


60% of the N atoms in the human body

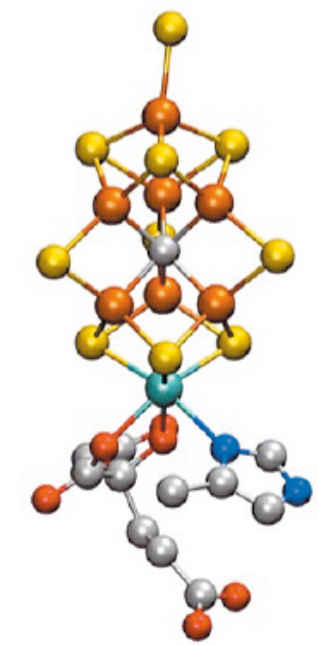
Industry versus Nature

What is more energy efficient?

Nitrogenase Enzymes

$$N_2 + 8e^- + 8\,H^+ \xrightarrow[\text{16 ATP} \rightarrow \text{16 ADP}]{\text{enzyme}} 2\,NH_3 + H_2 + 16\,P_i$$

23 ºC, 1 atm



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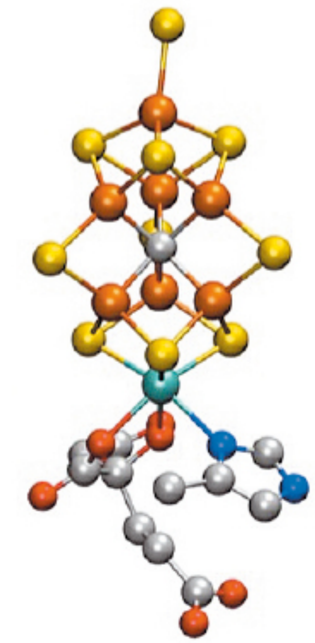

Chemical Overpotential = 1.2 V!

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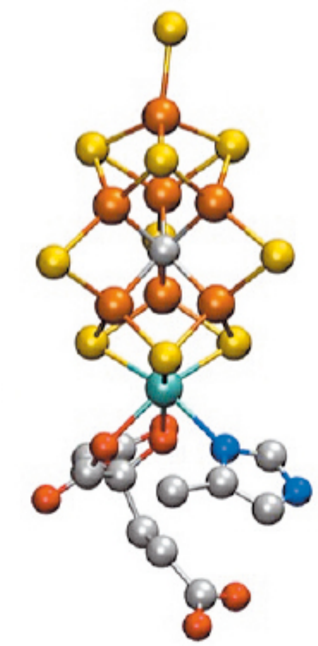

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Haber-Bosch Process

$$N_2 + 3\,H_2 \underset{\text{400 °C, 400 atm}}{\overset{\text{Fe/Ru on } Al_2O_3}{\rightleftharpoons}} 2\,NH_3$$

BASF, Ludwigshafen

Chemical Overpotential = 0.55 V

A Closer Look at Haber-Bosch

Bosch (1932): "Improvements to the catalyst will have minimal impact" (still true today).

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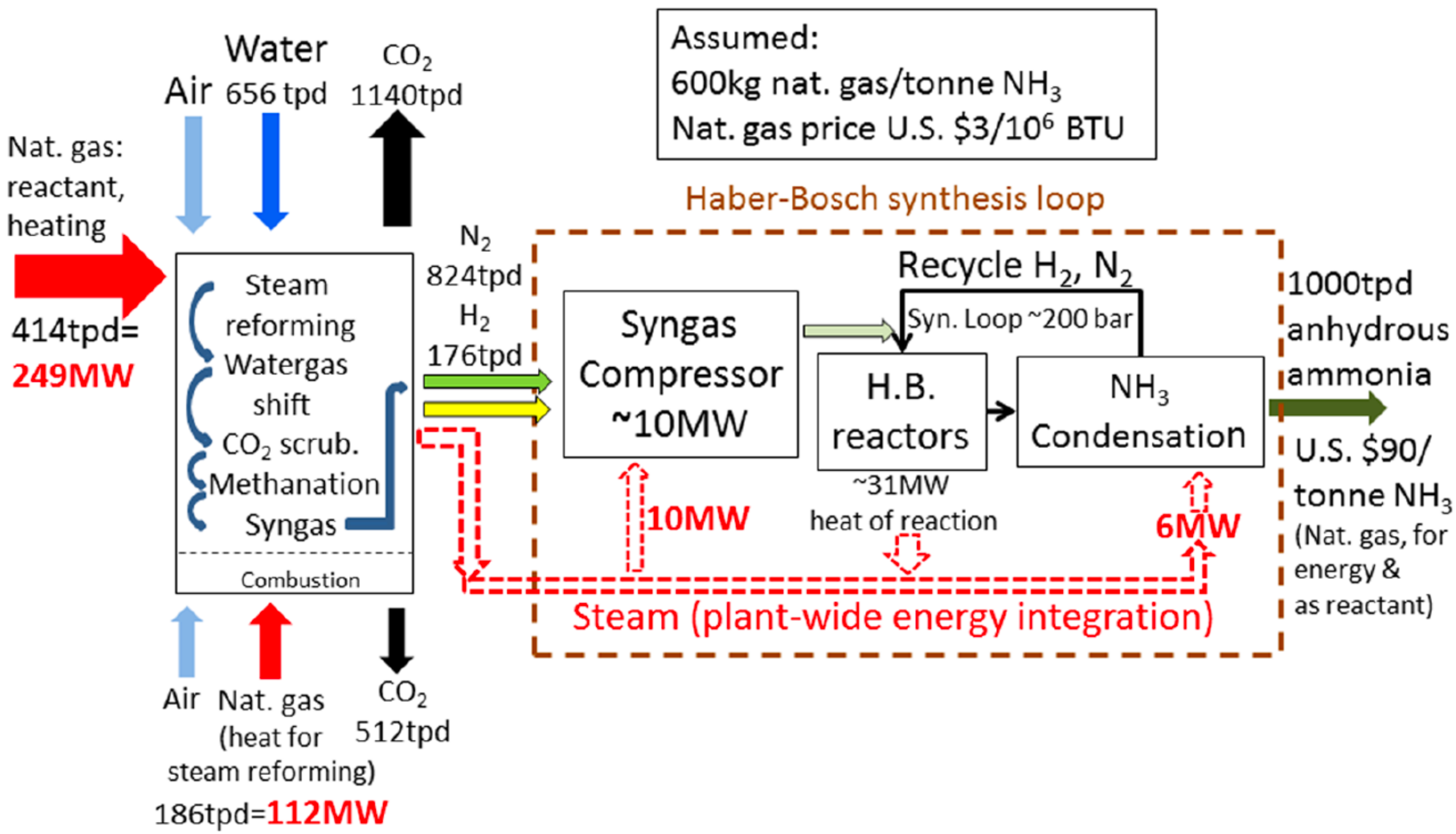

■ **H-B Catalyst is only ~8% of the energy! Most in the H_2 synthesis.**

Pfromm, P. H. *J. Renew. Sus. Energy* **2017**, *9*, 034702.

Why Study Ammonia Synthesis?

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It Has a Carbon Footprint!

$$N_2 + 3\,H_2 \underset{400\ ^\circ C,\ 400\ atm}{\overset{Fe/Ru\ on\ Al_2O_3}{\rightleftharpoons}} 2\,NH_3$$

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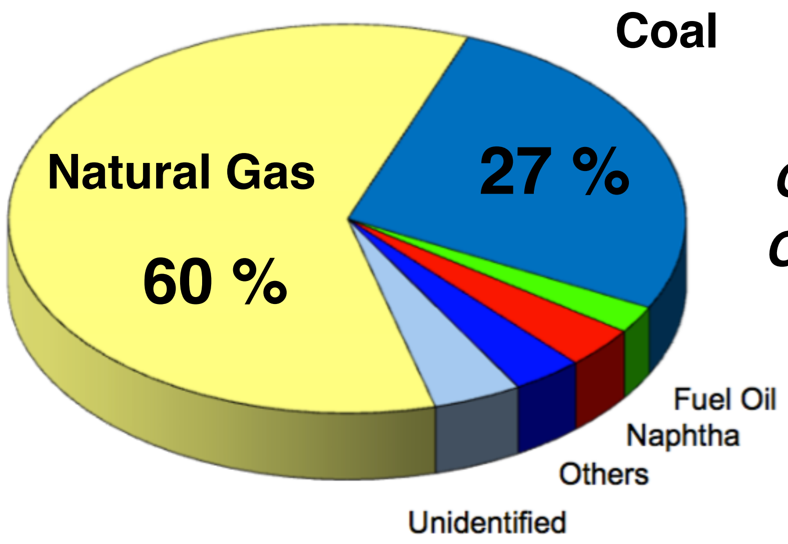

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Coal: 3.3 t CO_2 / t NH_3

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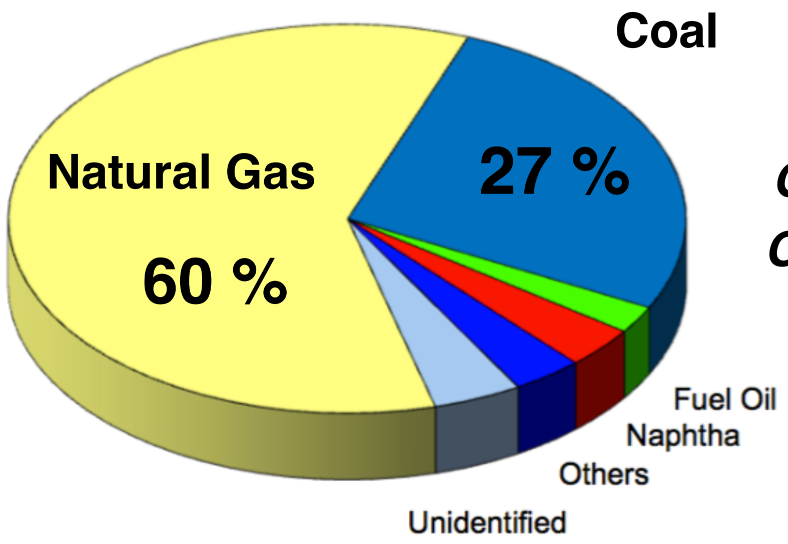

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- **Capital Investment: ~$1B + infrastructure**
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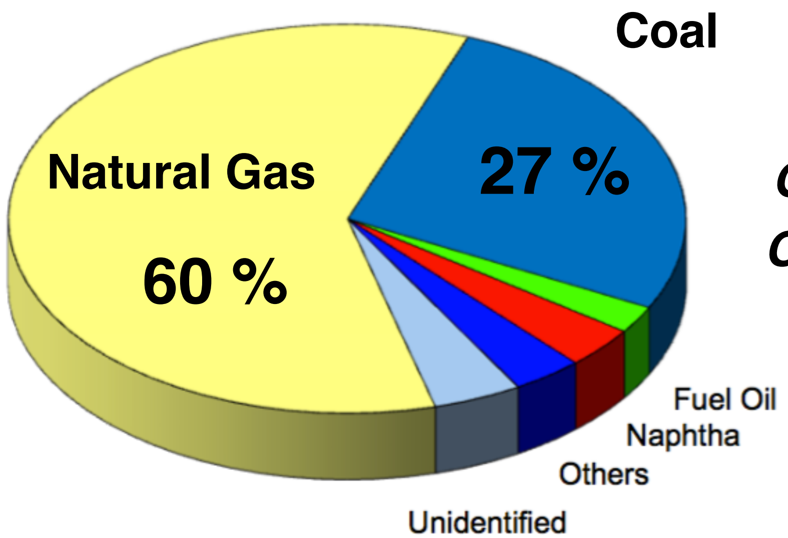

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H-B for the Developing World

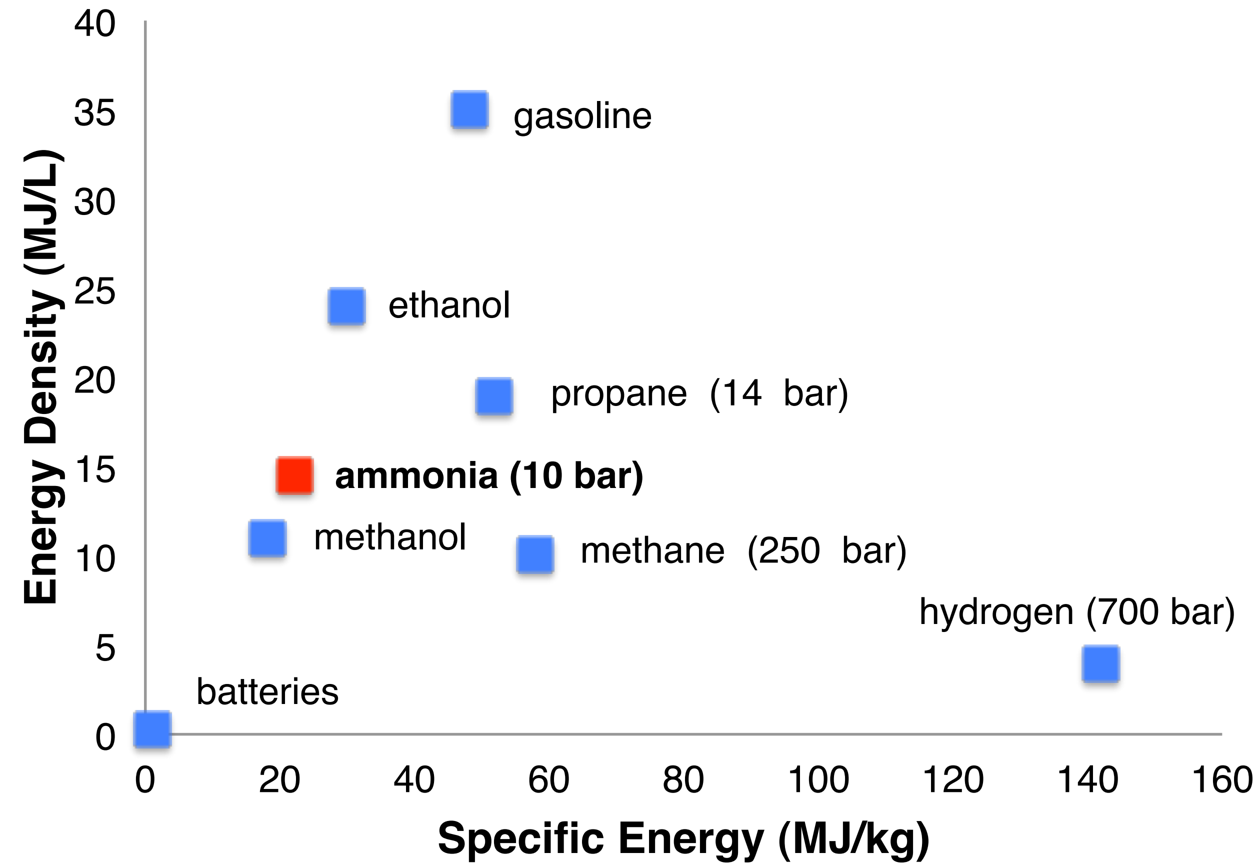
- Batch (not flow) synthesis.
- Intermittent (renewable) H_2.
- New catalysts are needed!

The Case for Ammonia as a Fuel

NH_3 as a Hydrogen Carrier

$$2\,NH_3 \longrightarrow N_2 + \boxed{3\,H_2}$$

Low ED/V



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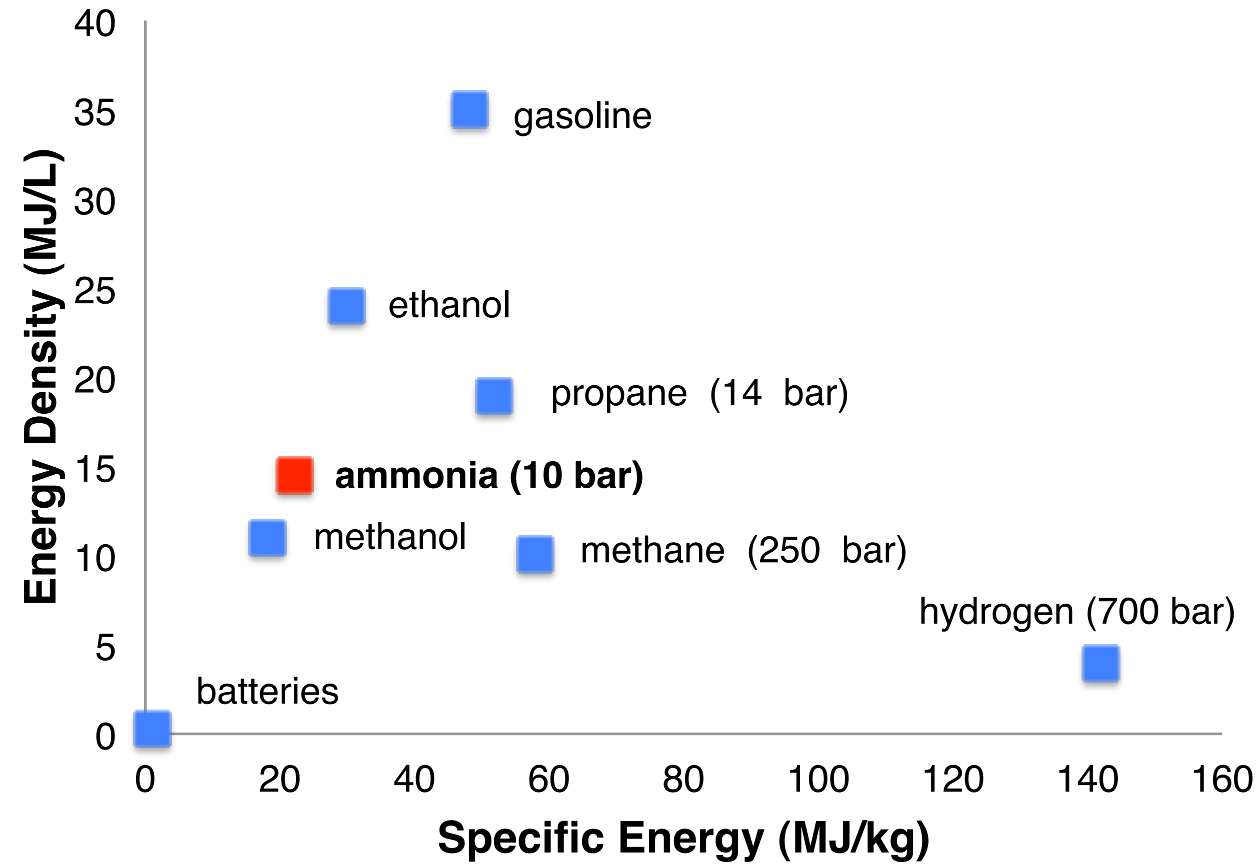


NH_3 as a Fuel

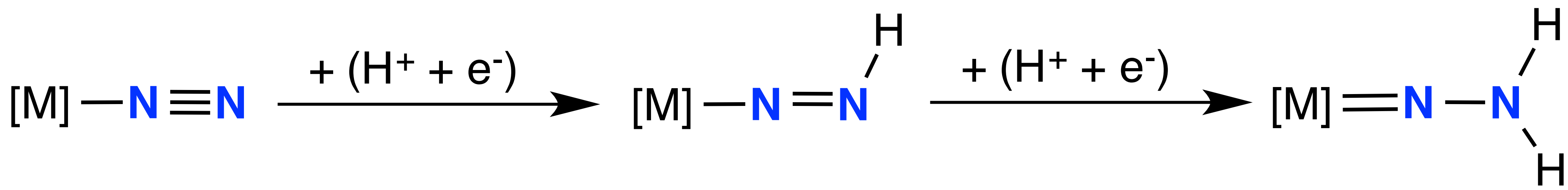
$$4\,NH_3 + 3\,O_2 \longrightarrow 2\,N_2 + 6\,H_2O$$

X-15 Aircraft (Supersonic)

Belgian Buses (WWII)

Overview of Today's Talk: PCET for N-H Formation and Breaking

Ammonia Synthesis



What are N-H bond strengths?

What are the optimal reagents for promoting efficient N-H bond formation?

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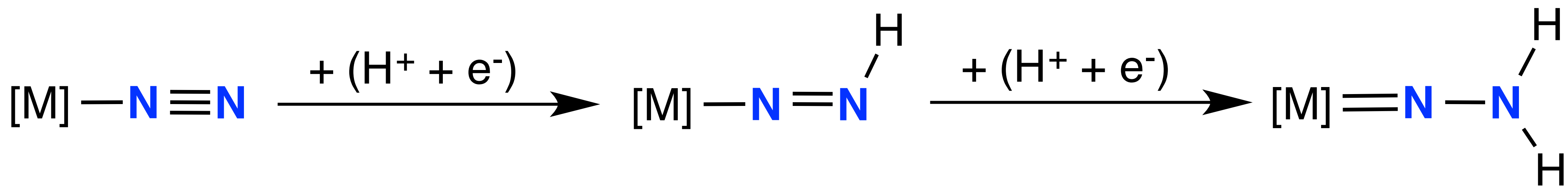

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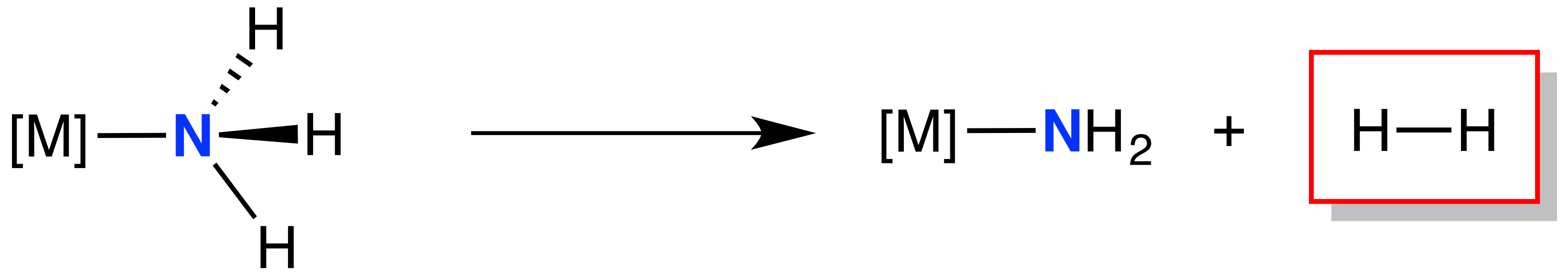
Hydrogen Evolution

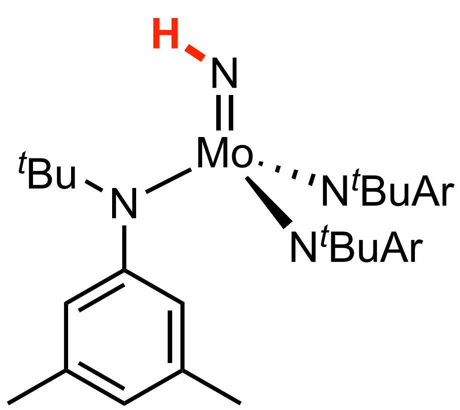


What does this value need to be for H_2 loss?

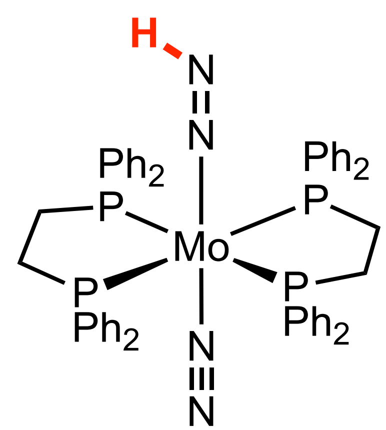
How do we enable "bond weakening by coordination"?

A Fundamental Chemical Challenge

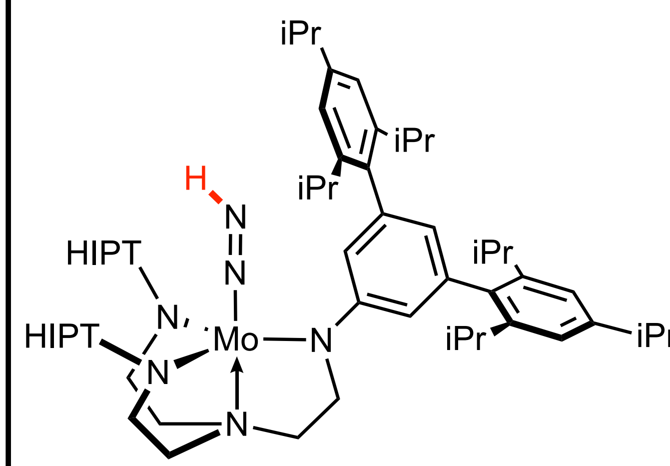
Many N-H bonds are <49 kcal/mol (weak!). How do we overcome thermodynamic limitations?



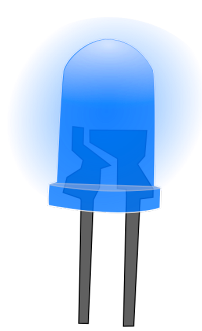
BDFE = 41 kcal/mol



BDFE = 23 kcal/mol



BDFE = 43 kcal/mol



Blue light: ~ 55 kcal/mol

Proton Coupled Electron Transfer

Protons and electrons are exchanged together in a concerted elementary step

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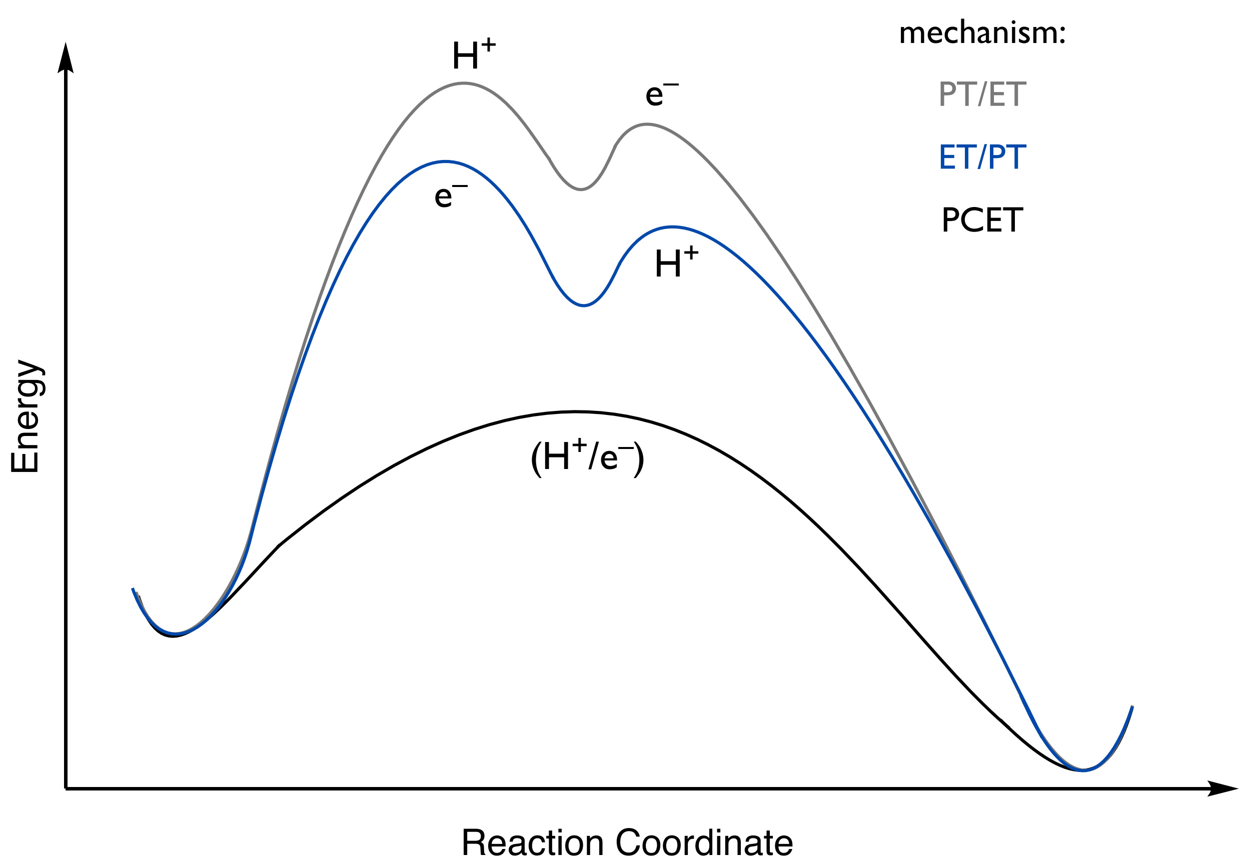
Improved Kinetics



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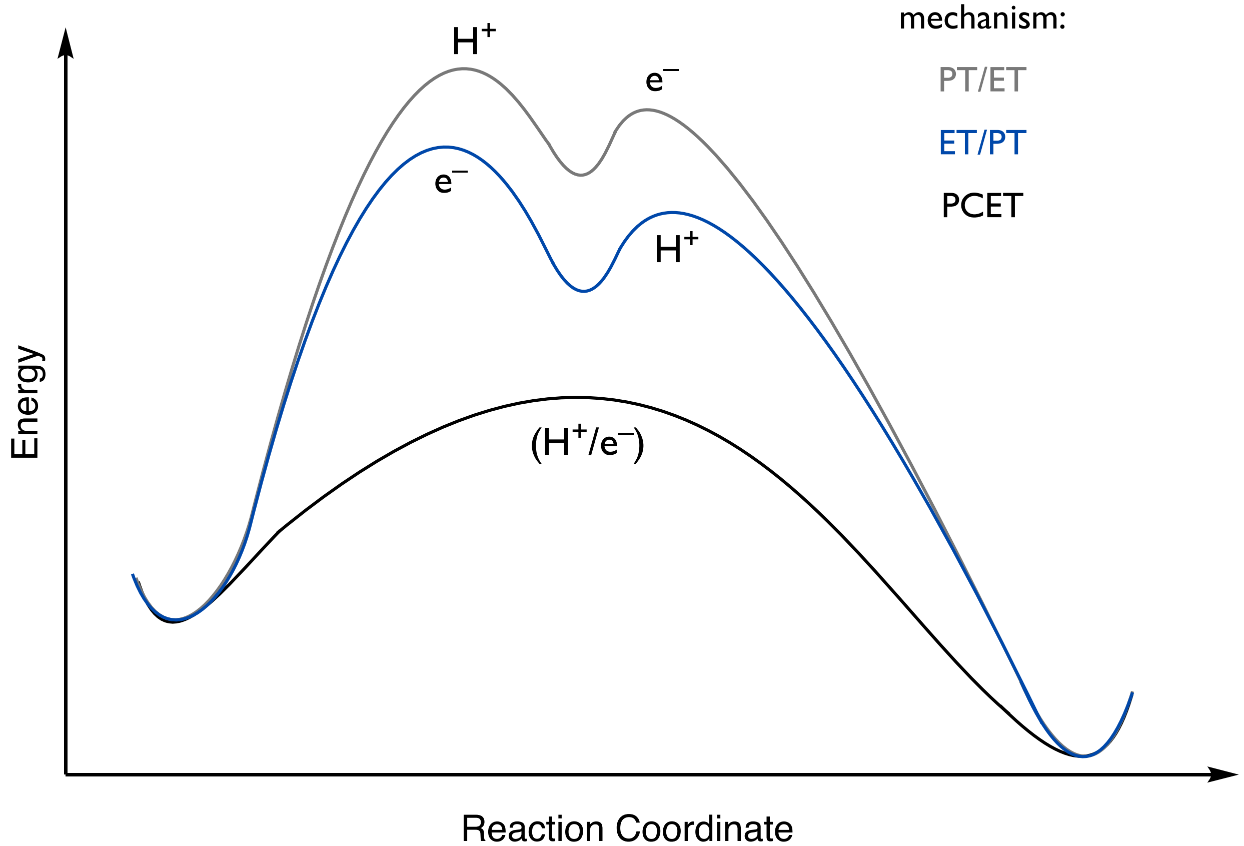
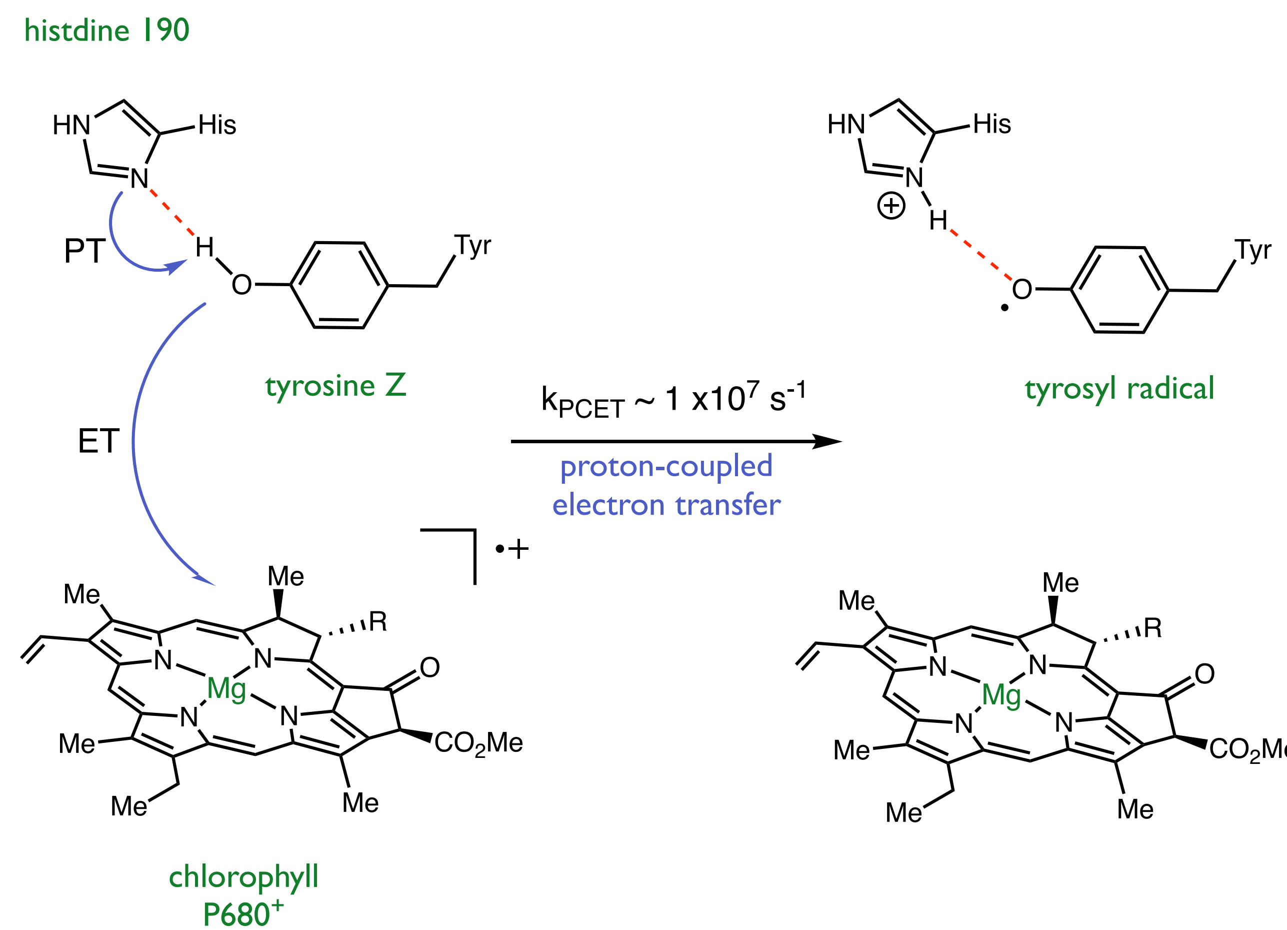
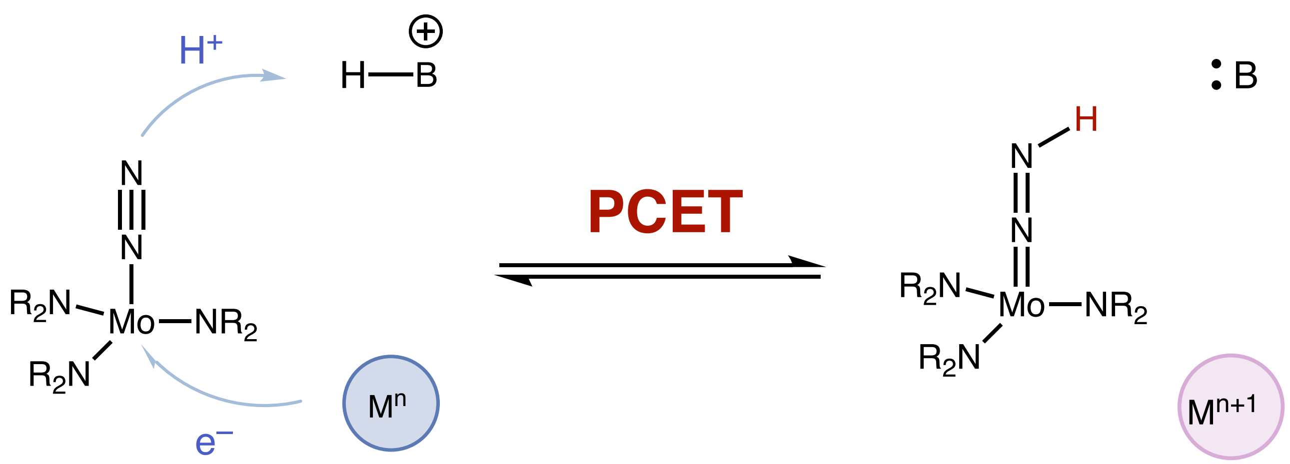


Prevalent in Biology (PSII, RNR, lipoxygenases, etc)



- H-bonding lowers the potential of the phenol by ~ 450 mV
- Removal of His190 renders PSII completely inactive

Light Driven, Multi-Site Reduction PCET



$\Delta G° =$ N-H BDFE – PCET 'BDFE'

Hydrogen Atom Donor Pairs

Reductant	Acid	$E_{1/2}$ (V)	pK_a	'BDFE'
Cp_2Co	$PhCO_2H$	-1.34	21.5	54
Cp^*_2Co	lutidinium	-1.47	14.1	40
$Ru^{I}(bpy)_3$	pyridinium	-1.71	12.5	33
$Ru^{I}(bpy)_3$	*p*TSA	-1.71	8.6	27
$^*Ir(ppy)_3$	$(PhO)_2PO_2H$	-2.11	13	24

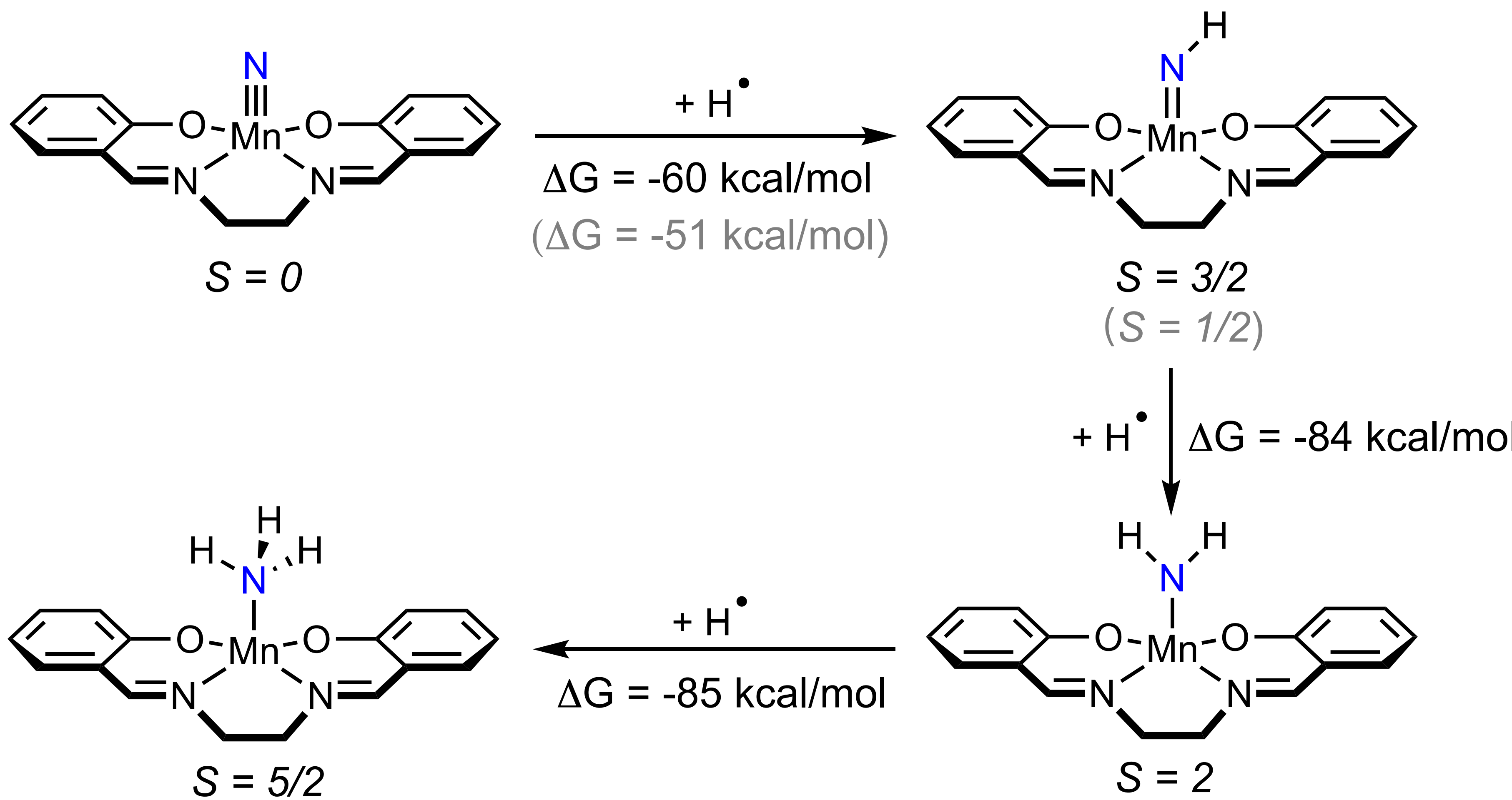
Challenging N-H bonds can be achieved by choice of reductant and acid.

We will rely on photocatalyst to convert light energy to redox potential.

Bordwell, F. G.; Zhang, X.-M. *Acc. Chem. Res.* **1993**, *26*, 510-517.
Warren, J. J. Tronic, T. A. Mayer, J. M. *Chem. Rev.* **2010**, *110*, 6961-7701.

Wang, Knowles, Chirik *unpublished*

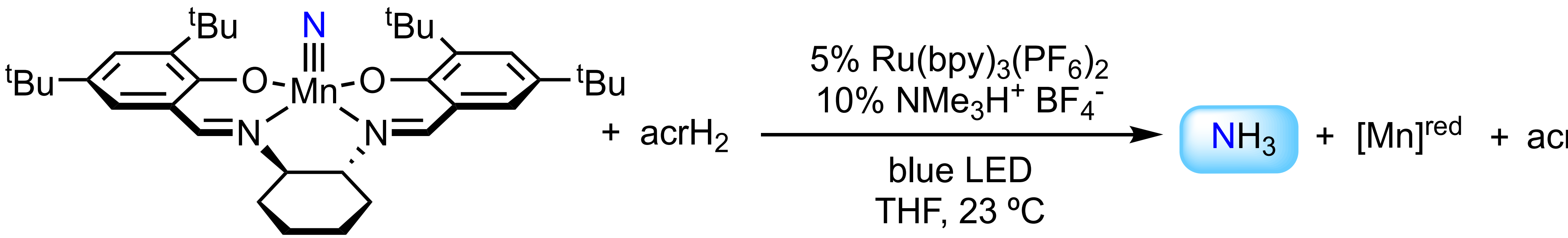
Targeting a More Robust Complex

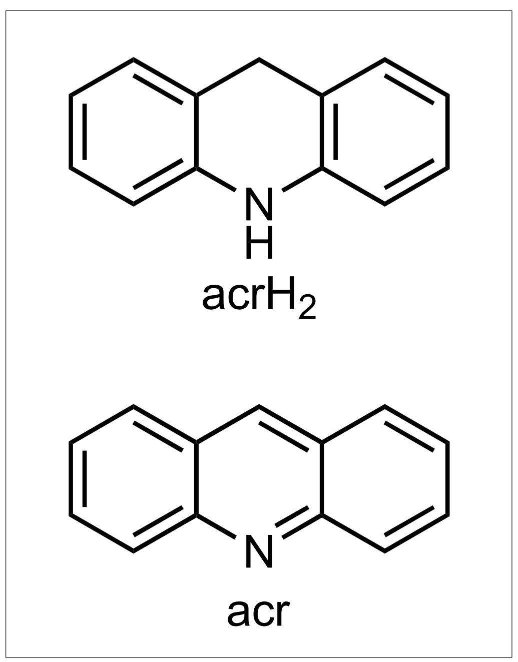


First N-H bond formation transfer is the most challenging in N-H formations step.

Wang, Knowles, Chirik *unpublished*

Successful Ammonia Synthesis



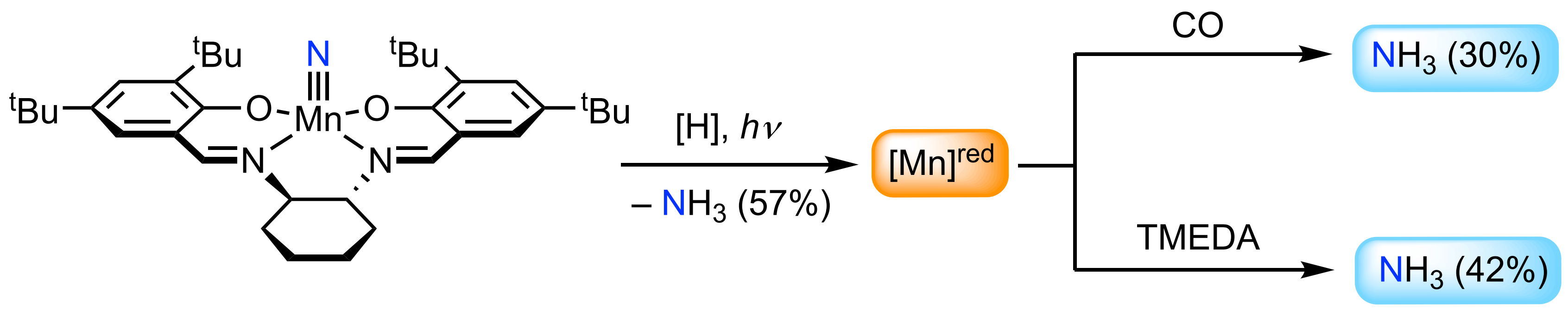


	Change to Reaction Condition	NH_3%
1	-	44
2	dark	0
3	no Ru, no NMe_3H BF_4	3
4	no NMe_3H BF_4	5
5	no Ru	15
6	Hantzsch ester instead of $acrH_2$	10
7	CH_2Cl_2 as solvent	**57**

Light, acid, reductant and photocatalyst are all required for NH_3 synthesis.

Wang, Knowles, Chirik *unpublished*

Why 57% Yield and Where is the Manganese Going?



Total NH_3: 57% (free) + 42% (bound) = 99%

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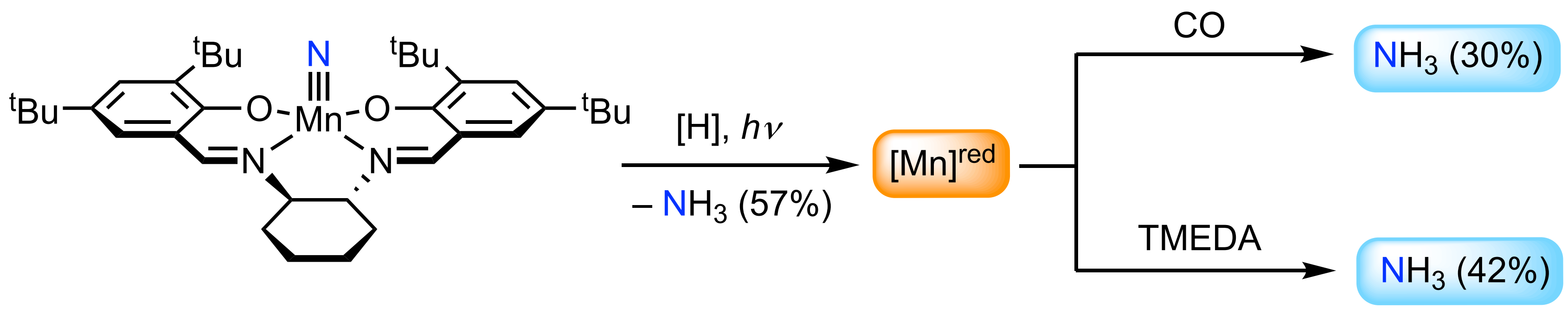

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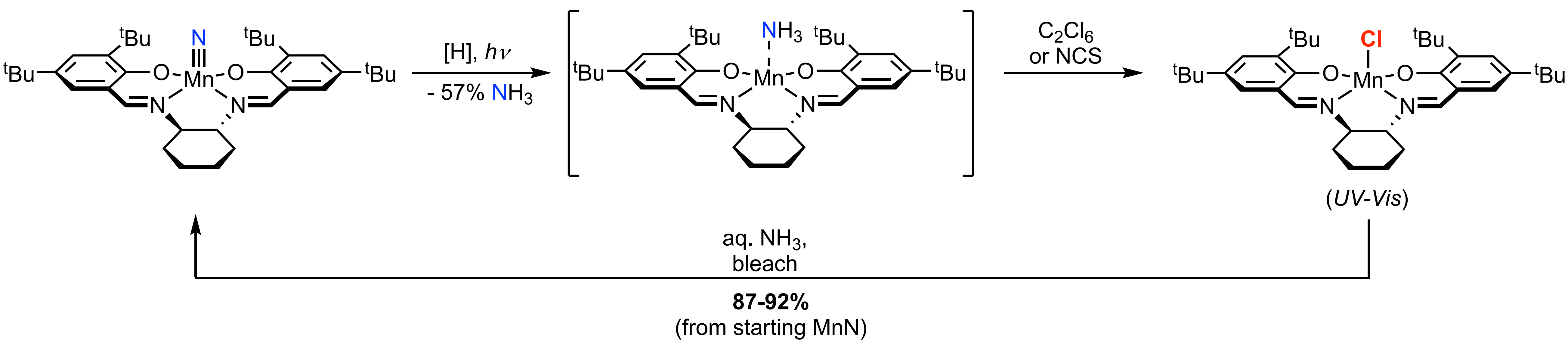
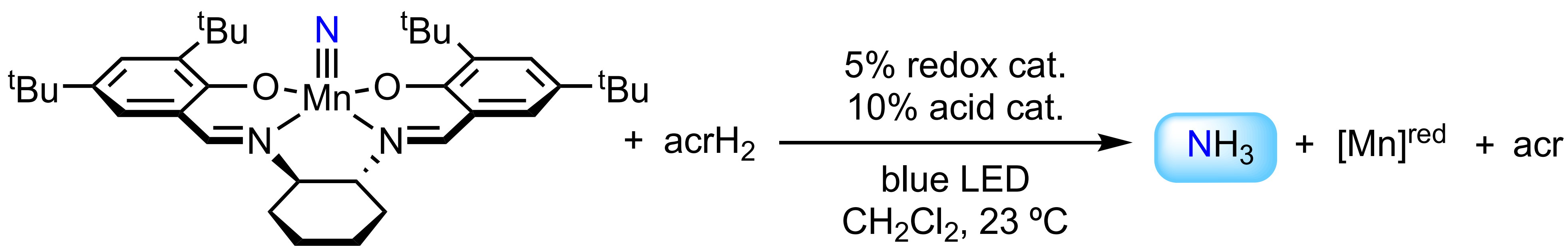
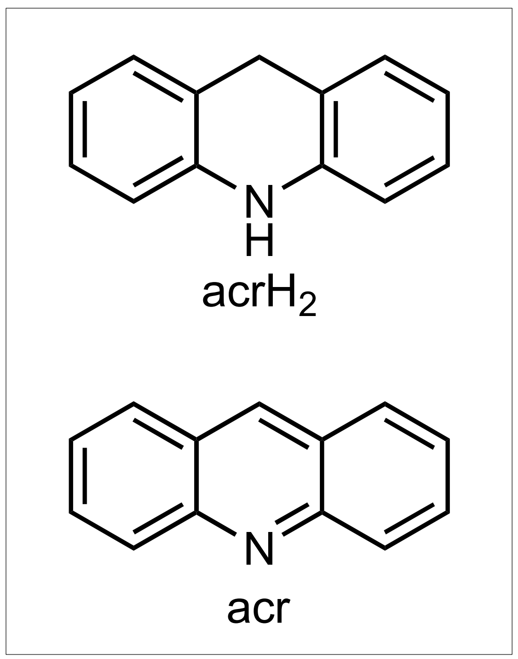
Fate of the Mn:



Mass balance: NH_3 (99%) + Mn (~90%)

Comparison of Catalyst Pairs with Varied BDFEs

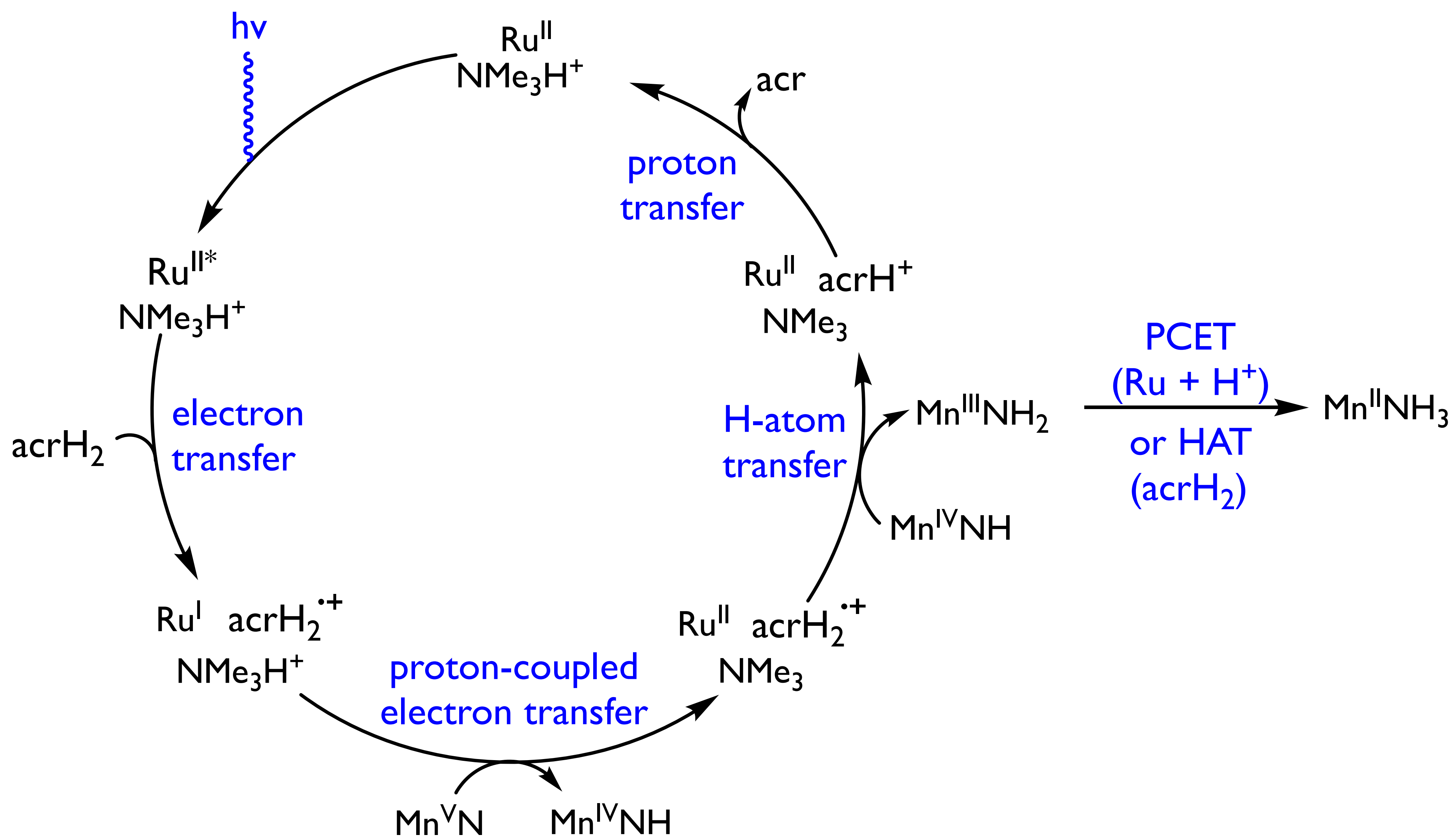




	redox cat.	acid cat.	'BDFE'	NH_3%
1	Ir(ppy)2(dtbpy)(PF_6)	NMe_3H^+ BF_4^-	35	50
2	$Ru(bpy)_3(PF_6)_2$	NMe_3H^+ BF_4^-	40	57
3	$Ru(bpy)_3(PF_6)_2$	$PhCO_2H$	45	55
4	Ir(ppy)2(dtbpy)(PF_6)	$^tBuC_6H_4SO_2NH_2$	46	50
5	$Ru(bpy)_3(PF_6)_2$	HOAc	48	20
6	$Ru(bpm)_3(PF_6)_2$	$PhCO_2H$	55	19
7	$Ru(bpm)_3(PF_6)_2$	$^tBuC_6H_4SO_2NH_2$	59	24
8	-	-	-	15

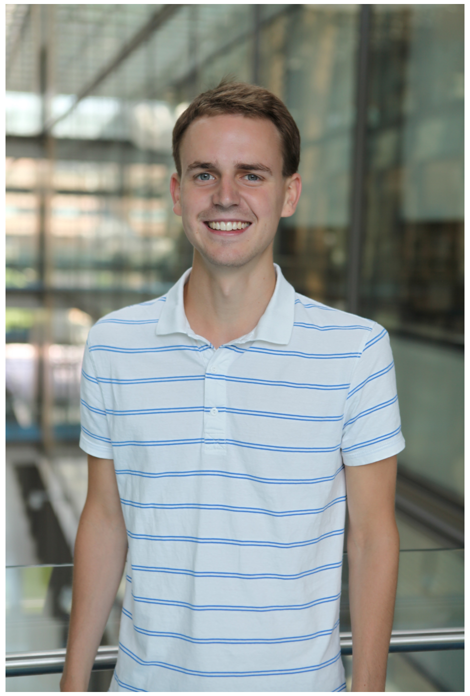
Wang, Knowles, Chirik *unpublished*

Proposed Mechanism for Ammonia Synthesis

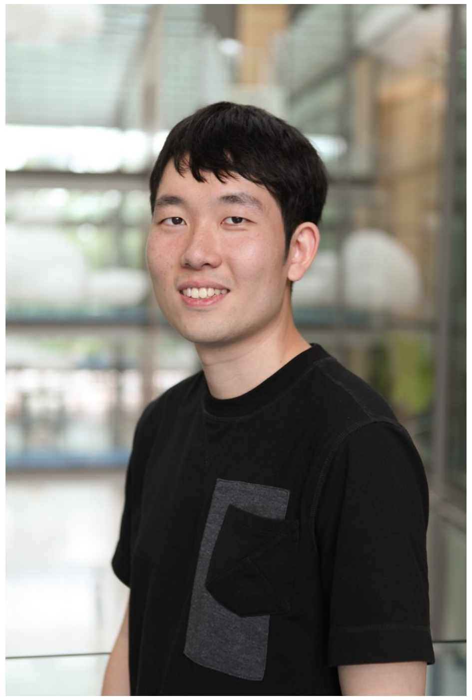


Wang, Knowles, Chirik *unpublished*

Team Ammonia

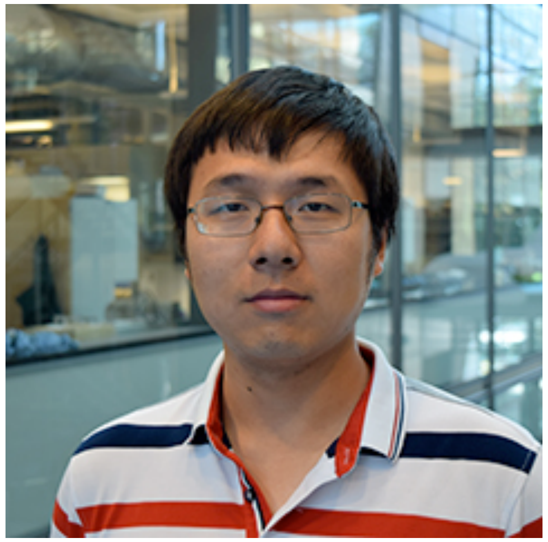


Máté Bezdek



Sangmin Kim

Dr. Florian Loose

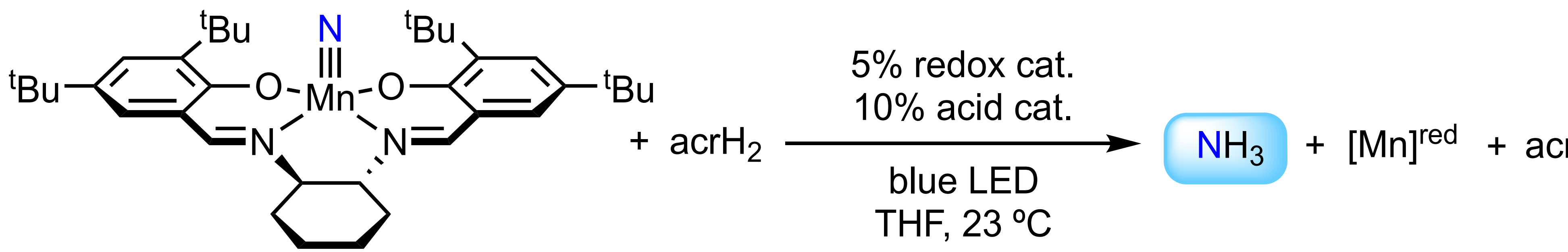


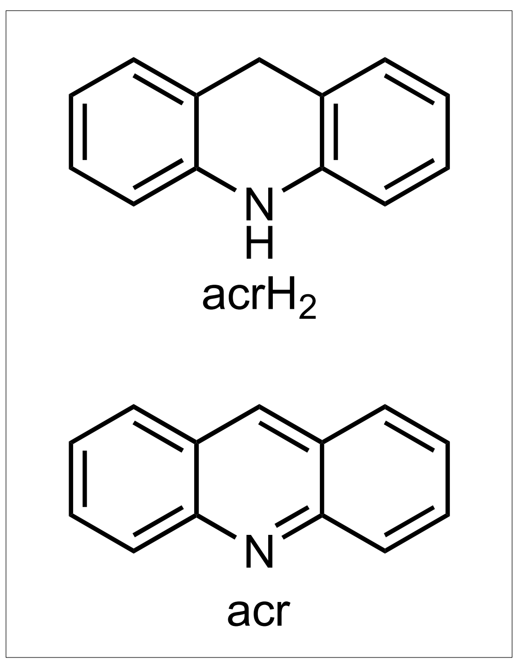
Dian Wang

(w/ Rob Knowles)

andlinger center
for energy+the environment

Comparison of Catalyst Pairs with Varied BDFEs (in THF)





	redox cat.	acid cat.	'BDFE'	NH_3%
1	$Ir(ppy)_2(dtbpy)(PF_6)$	NEt_3HBF_4	41	69
2	$Ru(bpy)_3(PF_6)_2$	NEt_3HBF_4	45	44
3	$Ir(ppy)_2(dtbpy)(PF_6)$	*p*$CNC_6H_4CO_2H$	52	30
4	$Ru(bpy)_3(PF_6)_2$	$TBDH^+Cl^-$	53	13
5	$Ru(bpy)_3(PF_6)_2$	*m*$NO_2C_6H_4CO_2H$	56	3
6	$Ru(bpy)_3(PF_6)_2$	$PhCO_2H$	61	8
7	$Ru(bpm)_3(PF_6)_2$	$TBDH^+Cl^-$	63	5
8	$Ru(bpy)_3(PF_6)_2$	${}^tBuC_6H_4SO_2NH_2$	68	2

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