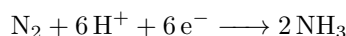


Unit 4

???

4.1 Lecture 15: Nitrogen Fixation

5/3: • General form:



- Alternatively, it could be $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$.
- A simple reaction on paper, but in practice and mechanistically, very difficult.

- Nitrogen is one of the essential elements for life (CHNOPS), but we can't absorb it from the air in its elemental form as $\text{N}\equiv\text{N}$ gas. Indeed, we need it to be **fixed** before we can incorporate it (i.e., through food sources).

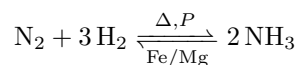
- Main pathways:

- Lightning.



- 4-10 million tons per year.
- Nitrate can be used by organisms; converted into useful nitrogen.
- Natural enzymatic fixation.
 - 100-300 million tons per year (probably closer to the 100 side).
 - 40/60 ocean/land ratio.
 - Done by the enzyme nitrogenase, with $\text{FeMoCO}^{[1]}$ as a cofactor.
- Mankind.
 - About 190 million tons per year.
 - Thus, mankind is currently fixing more nitrogen than all natural sources combined by a fair amount right now. This is what allows us to feed the planet at its current population.
 - Accomplished by the **Haber-Bosch process**.

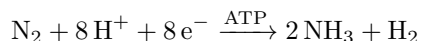
- **Haber-Bosch process:** Humanity's primary method of fixing nitrogen.



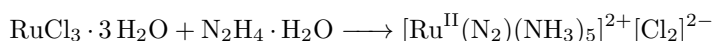
- -92 kcal/mol (thermodynamically favored but kinetically difficult).
- 200 atm of pressure (pushes the equilibrium to the right via Le Châtelier's principle).

¹Literally pronounced as its written, i.e., "fih-MOH-koh."

- 400 °C (required for the rate).
- Potassium is an activator.
- 2 Nobel prizes for this: Fritz Haber (1918) and Carl Bosch (1931).
 - Controversial at the time because the process facilitated the explosives industry and Haber was a Nazi.
 - World War I and II would not have been sustainable for Germany without this process.
- Mechanism:
 - On the surface of the iron catalyst, the pressure binds H₂ gas as hydrides and N₂ gas as bridging nitrides (between various iron atoms at the surface). It follows in a statistical and thermodynamic manner that amine ligands will be formed on the surface attached to the iron. These can then break off into ammonia gas.
 - A solid state heterogeneous process.
 - Nobel Prize (2007) to Gerhard Ertl for this mechanism.
- This process is highly efficient, but very energy intensive as well.
 - As such, there is a race to find a less energy-intensive catalytic alternative.
- Molecular systems: The nitrogenase enzyme.

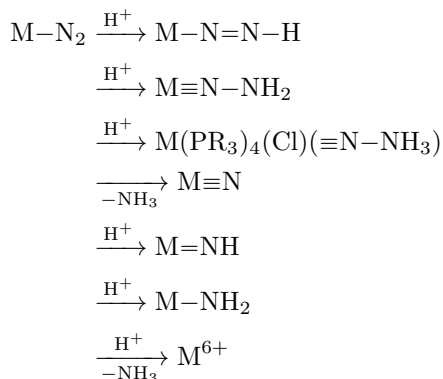


- Other extant cofactors include FeVCO and FeFeCO, but they are less common.
- Since ATP is used, this is still a very energy-intensive process.
- N₂ bonds to metal centers in many ways:
 - Linear, bent, side-on, bridging linear, bridging side-on, multi-metal center bridging, etc.
- N₂ complexes are much less common than CO complexes since N₂ is a terrible ligand.
 - The HOMO in N₂ makes it a σ donor, but CO's negative formal charge on the carbon makes it a better σ donor.
 - Additionally, CO is a much better π acid due to its polarization.
- Allen and Senoff (in 1965) reported the first dinitrogen complex.



- N₂H₄ is hydrazine (rocket fuel), and is much more stable as a hydrate.
- The product is d^6 with 18 e[−] and has $\mu_{\text{N}_2} = 2170\text{--}2115 \text{ cm}^{-1}$ (the range depends on the anion).
- For reference, free N₂ has a stretching frequency of 2331 cm^{−1}.
- Yamamoto gives the first example of a dinitrogen complex formed from free N₂ (HCo(PPh₃)₃(N₂)).
- Joe Chatz, George Leigh, and Dilworth in Sussex (of the British/American camp), and Hidai and Nishibayashi (of the Japanese camp) became interested in nitrogen fixation following Yamamoto's work.
 - Second and third row Group 6 complexes such as molybdenum were the focus.
 - Example: $\text{MoX}_4\text{L}_2 \xrightarrow[\text{Na/Hg}]{\text{N}_2, \text{L}} \text{Mo}(\text{N}_2)_2\text{L}_4$.
 - L is typically a phosphine.
 - With various phosphine ligands, you can get different geometries.

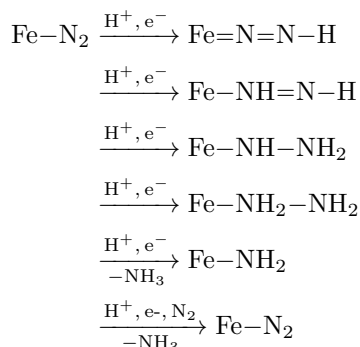
- Another example: $\text{cis-W(N}_2)_2(\text{PMe}_2\text{Ph})_4 \xrightarrow[\text{MeOH}]{\text{H}_2\text{SO}_4} 2\text{NH}_3 + \text{N}_2 + \text{W}^{\text{VI}}(\text{oxo})$.
 - Works with molybdenum, too, but tungsten gives a better yield.
 - The overall reaction is $\text{W}^0 + 6\text{H}^+ + \text{N}_2 \longrightarrow 2\text{NH}_3 + \text{W}^{\text{VI}}$.
 - Some important subreactions/steps are $\text{N}_2 + 4\text{e}^- \longrightarrow \text{N}_2\text{H}_4$ and $\text{N}_2 + 2\text{e}^- \longrightarrow \text{N}_2\text{H}_2$.
- Mechanism (by Chatt):



- Very few compounds in the form of the first intermediate (diazene) are known. These compounds are very susceptible to β -H elimination from water, though.
- The second intermediate has a hydrazido ligand.
- The fourth intermediate has a nitride.
- The fifth intermediate has an imide.
- The sixth intermediate has an amide ligand.
- Hidai uses silanes: $\text{M(N}_2)_2(\text{PR}_3)_4 \xrightarrow{\text{TMSI}} \text{TMS-N=N-MI(PR}_3)_4 \xrightarrow[\text{N}_2]{\text{Na, THF}} \text{M(N}_2)_2(\text{PR}_3)_4 + \text{NH(TMS)}_2 + \text{NH}_3 + \text{NaNH}_2 + \text{NaNH(TMS)}$, etc.
- Yandulov and Schrock (2003) creates a well-defined catalyst for nitrogen fixation.
 - The catalyst is molybdenum bound to dinitrogen and a tridentate TREN scaffold anion (with hexaisopropyl *tert*-phenyl (HIPT) aryl groups).
 - They add eight equivalents of cobaltocene (CoCp_2), seven equivalents of lutidinium (a pyridinium acid), and the bulky, noncoordinating counteranion $[\text{BAr}^{\text{F}}_4]^-$.
 - They fish out $\text{Mo-NH}_3 + \text{NH}_3$. Reducing the former product gives $\text{Mo}^{\text{III}}(\text{N}_2)$ with a weak reductant.
 - If you use a slightly stronger reductant (decamethylchromocene; CrCp_2^*) and a slow addition of acid, you get approximately 8 turnovers.
 - This is not a great yield, but the important part is that it exists and they can observe all of the intermediates.
 - Observing said intermediates verified the mechanism proposed by Chatt and Hidai.
 - To reiterate, this is the Chatt/Distal^[2] cycle they observed: $\text{Mo-N}\equiv\text{N} \xrightarrow{\text{H}^+, \text{e}^-} \text{M-N=N-H} \xrightarrow{\text{H}^+, \text{e}^-} \text{M}\equiv\text{N-NH}_2 \xrightarrow{\text{H}^+, \text{e}^-} \text{M}\equiv\text{N} \xrightarrow{\text{H}^+, \text{e}^-} \text{M}\equiv\text{NH} \xrightarrow{\text{H}^+, \text{e}^-} \text{M-NH}_2 \xrightarrow[-\text{NH}_3]{\text{H}^+, \text{e}^-, \text{N}_2} \text{Mo-N}\equiv\text{N}$.
 - Note that molybdenum starts in the 3+ oxidation state at $\text{M-N}\equiv\text{N}$ and goes up to 6+ at $\text{Mo}\equiv\text{N}$ before cycling back down.
- Shilov had a number of systems, but they were poorly defined.

²Note that Chatt and Distal are interchangeable synonyms.

- Other selected examples.
 - Zirconium can do this catalysis in some cases.
 - Laplaza and Cummins (1995) find that molybdenum trisannelides and dinitrogen can go through a kinked transition state to yield two equivalents of $L_3Mo\equiv N$.
- Iron:
 - Present in all enzymatic cofactors that mediate nitrogen fixation.
 - Until 10-15 years ago, they thought it wasn't directly involved though.
 - $(PR_3)_4Fe(N_2) \xrightarrow{XSH^+}$ only trace amounts of NH_3 .
 - Yuki et al. (2012) finds that simple iron salts and even substituted ferrocenes react with a strong reductant, sodium, and TMSCl to make $N(TMS)_3$ (which is catalytic and can be transformed into ammonia). The yield is about 25 equivalents per iron.
 - This shows that iron can do this chemistry.
 - Dr. Anderson's thesis work with Jonas Peters finds that $Fe(N_2)(B(PR_2Ph)_3) \xrightarrow[XSHBAr^F_4]{XSKC_8} NH_3^{[3]}$ (Anderson et al., 2013).
 - Seven equivalents per iron. More recent tinkering has brought it up to nearly 100 equivalents per iron.
 - Mechanism: $L_3FeN_2^- \xrightarrow{2H^+} L_3Fe\equiv N-NH_2^+ \longrightarrow \longrightarrow \longrightarrow NH_3$.
 - Suggests a Chatt/Distal mechanism.
 - Differing mechanistic proposal: Alternating mechanism.



- This doesn't require as many oxidation states as the Chatt mechanism (which favors iron, which doesn't easily form oxidation states other than 2+ and 3+).
- We also don't see a nitride or imide intermediate, but we do see a diazene, hydrazido 1-, and hydrazine adducts.
- Enzyme data supports this mechanism.

4.2 Office Hours (Anderson)

- How much strain is needed for ROMP to proceed?
 - Norbornene is a common one.
 - 4 membered rings.
 - 7- and 8-membered rings are usually not sufficiently strained.

³Note that the reactant is the same compound discussed in problem 3 of Homework 1.

- Cyclopropene does exist, and it does do ROMP, but it polymerizes so quickly that you can't do much with it.
 - If it's cold and you throw in a metathesis catalyst, it will probably work.
 - Recall that it also participates in Diels-Alder reactions.
- ROMP does *not* release ethylene.
 - Ring strain is the driving force.
 - Part (d) is a typo; ethylene gas is the common byproduct of *most* of these reactions. We should still show ROMP as is.
- How do metal d orbitals enable $2 + 2$ cycloaddition?
 - Butadiene plus ethylene requires ethylene to have filled π^* orbitals (these have the appropriate symmetry).
 - Diels-Alder $4 + 2$ cycloaddition is allowed.
 - The symmetry of the metal orbitals (esp. d_{z^2} and d_{xy}) enables $2 + 2$ cycloaddition.
- η and κ bonding?
 - IUPAC likes κ more now, but η is historical.
 - η indicates a contiguous π system while κ simply indicates denticity.
 - Figure 2.23a is κ^2 as well.
 - Bidentate ligands bond in a κ^2 fashion.
 - Numbers on these as well as μ should exclusively be superscripts.
 - A metal bound face-on to a carboxylate would be η^3 , but this is very atypical/nontexistent bonding. Side-on bonding (i.e., to both oxygens) would be κ^2 .