Screening binary redox pairs for solar thermochemical ammonia synthesis using machine learned predictions of the Gibbs formation energies at finite temperatures

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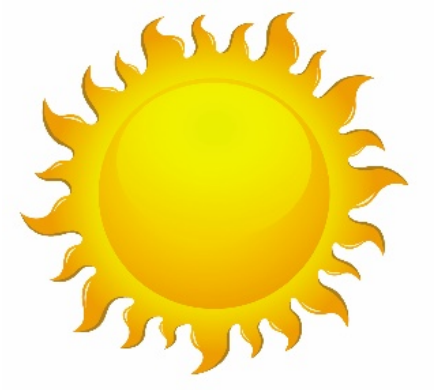
Solar thermochemical NH_3 synthesis (STAS)

$$\frac{1}{b}M_aN_b + \frac{ad}{bc}H_2O \rightarrow \frac{a}{bc}M_cO_d + NH_3 + \left(\frac{ad}{bc} - \frac{3}{2}\right)H_2$$



$$\frac{a}{bc}M_cO_d + \frac{ad}{bc}R \rightarrow \frac{a}{b}M + \frac{ad}{bc}RO$$

Reduction/oxidation of metal oxide/metal nitride pair driven by concentrated solar radiation

$$\frac{a}{b}M + \frac{1}{2}N_2 \rightarrow \frac{1}{b}M_aN_b$$

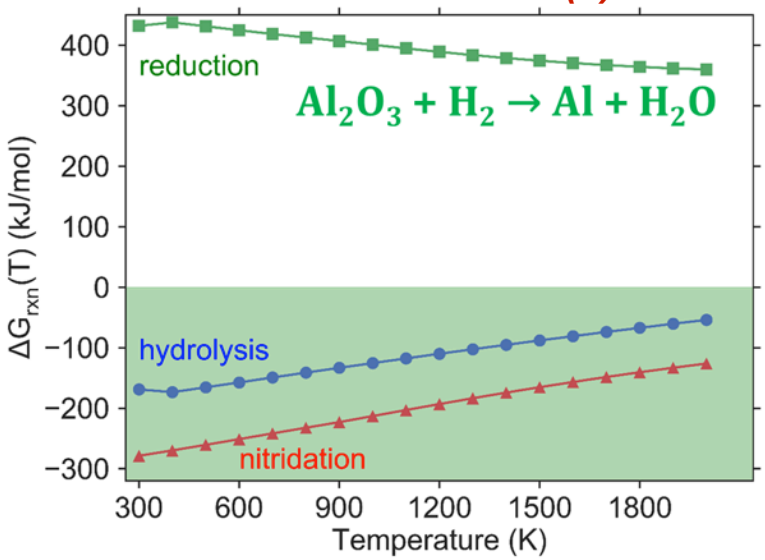
AlN/Al_2O_3 the first proposed redox pair

Galvez et al., *Ind. Eng. Chem. Res.* 2007

Michalsky and Pfromm, *AIChE Journal,* 2011

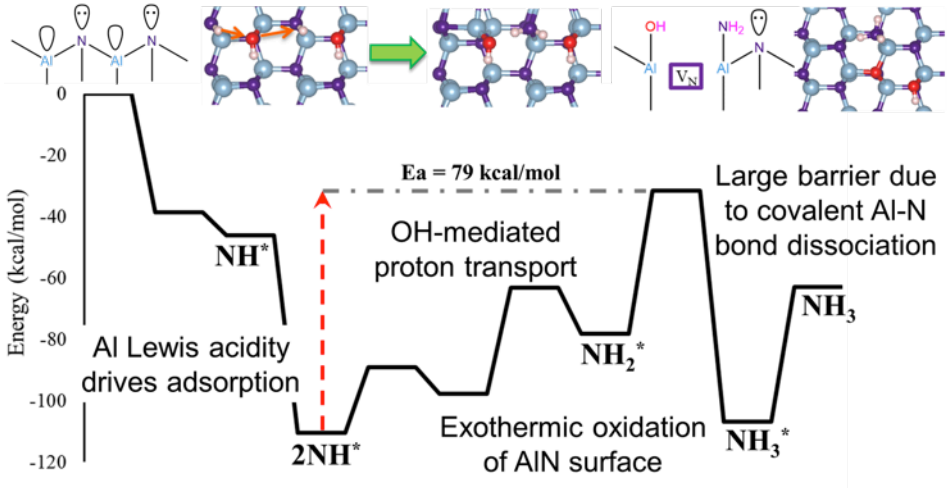
AlN/Al_2O_3 not the ideal redox pair

Reduction of Al_2O_3 requires $C_{(s)}$



Data from FactSage

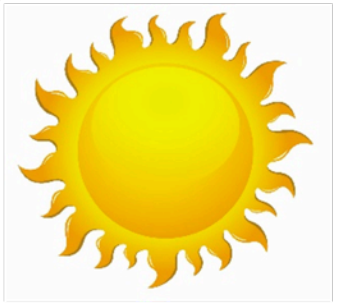
Kinetics of hydrolysis are challenging



Bartel et al., *ACS App. Mater. Interfaces* 2016

Identifying viable pairs (MN/MO)

$$\frac{1}{b}M_aN_b + \frac{ad}{bc}H_2O \rightarrow \frac{a}{bc}M_cO_d + NH_3 + \left(\frac{ad}{bc} - \frac{3}{2}\right)H_2$$



$$\frac{a}{bc}M_cO_d + \frac{ad}{bc}R \rightarrow \frac{a}{b}M + \frac{ad}{bc}RO$$

What about other materials?!

$$\frac{a}{b}M + \frac{1}{2}N_2 \rightarrow \frac{1}{b}M_aN_b$$

Reduction/oxidation of metal oxide/metal nitride pair driven by concentrated solar radiation

What makes a good pair (based on thermo)?

- Rxns are spontaneous and high yield
- MN and MO are thermodynamically stable

Michalsky and Pfromm, *AIChE Journal,* 2011

Identifying viable pairs (MN/MO)

What makes a good pair?

- Rxns are spontaneous and high yield
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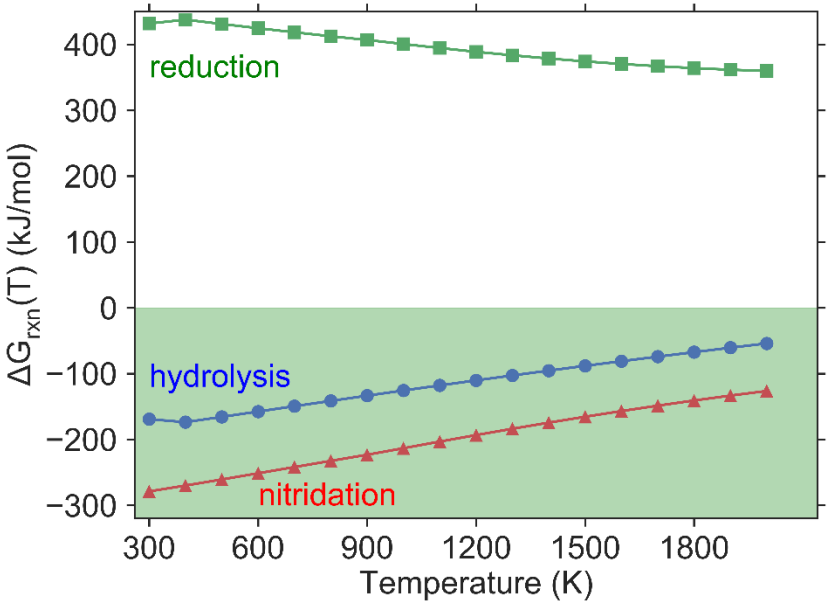
$$\Delta G_f(T)$$

$$\Delta G_{rxn}(T) < 0$$



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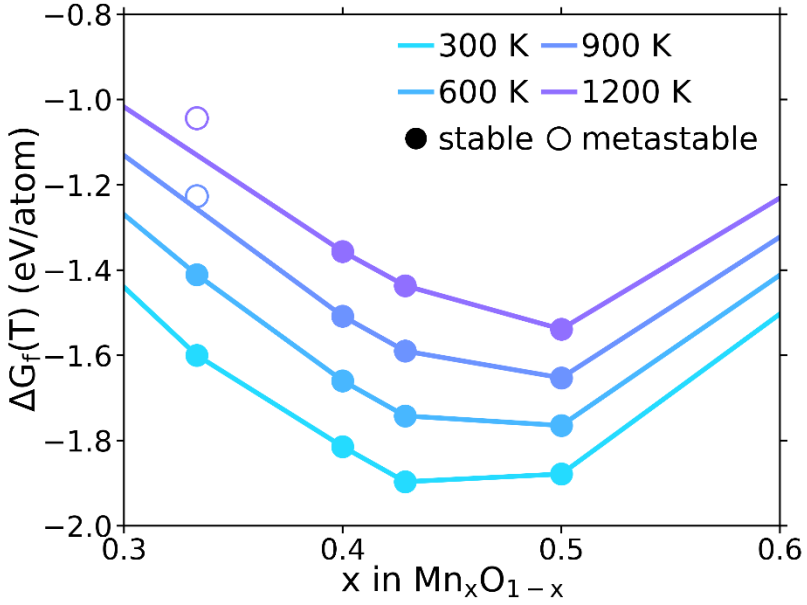


Acquiring Gibbs formation energies

Experimental data is incomplete (and difficult)

National Institute of Standards and Technology
U.S. Department of Commerce

~100s of experimental $\Delta G_f(T)$ (~20 MN)

Aluminum Oxide, Alpha (Al_2O_3) Al_2O_3(cr)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K^{-1} mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	-10.020	-1663.608	-1663.608	INFINITE
100	12.855	4.295	101.230	-9.693	-1668.606	-1641.642	857.506
200	51.120	24.880	57.381	-6.500	-1673.383	-1612.656	421.183
298.15	79.015	50.950	50.950	0.	-1675.692	-1582.275	277.208
300	79.416	51.440	50.951	0.147	-1675.717	-1581.696	275.398
400	96.086	76.779	54.293	8.995	-1676.342	-1550.226	202.439
500	106.131	99.388	61.098	19.145	-1676.045	-1518.718	158.659

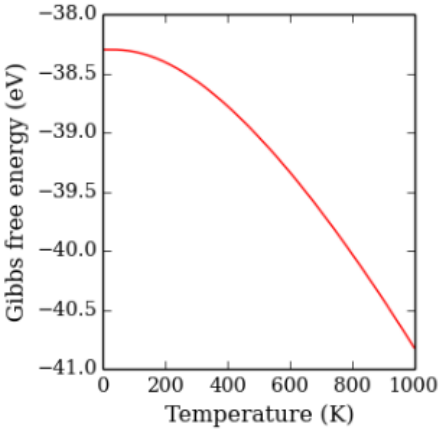
Chase et al., 1998

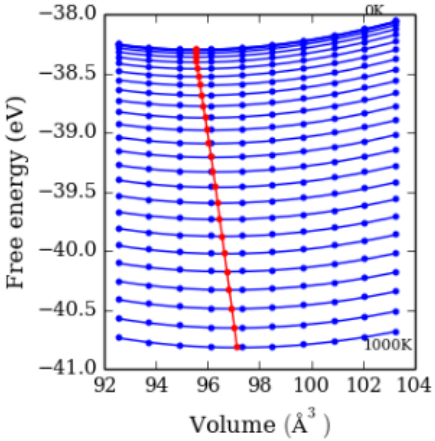
Calculation data is incomplete (and difficult)

KYOTO UNIVERSITY FOUNDED 1897 KYOTO JAPAN

phonondb

~100s of calculated G(T)





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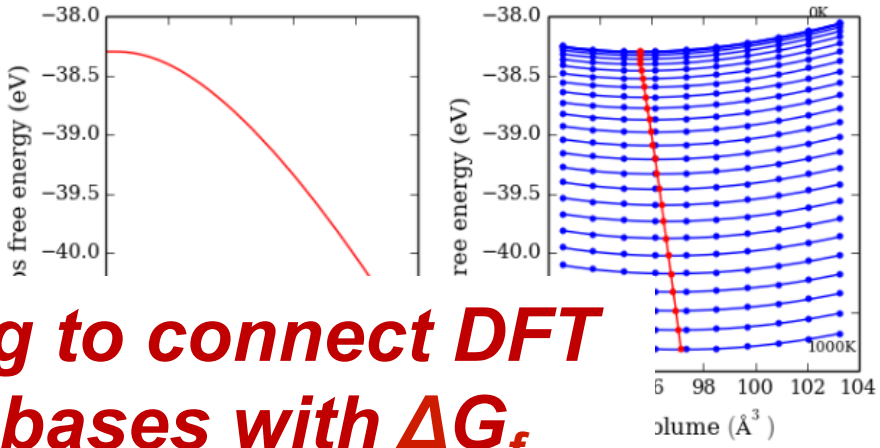

Machine learning to connect DFT materials databases with ΔG_f

Chase et al., 1998

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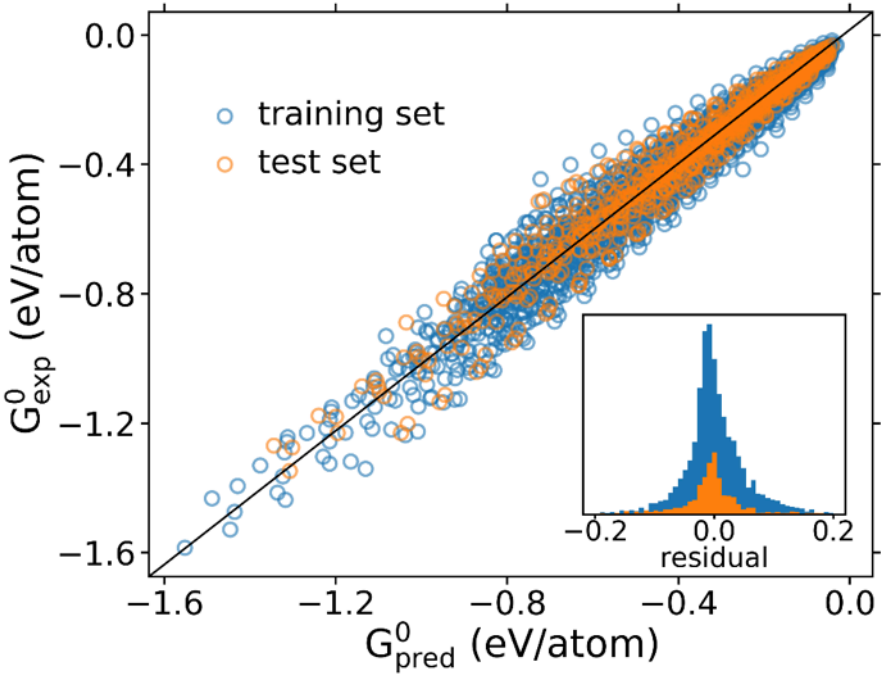
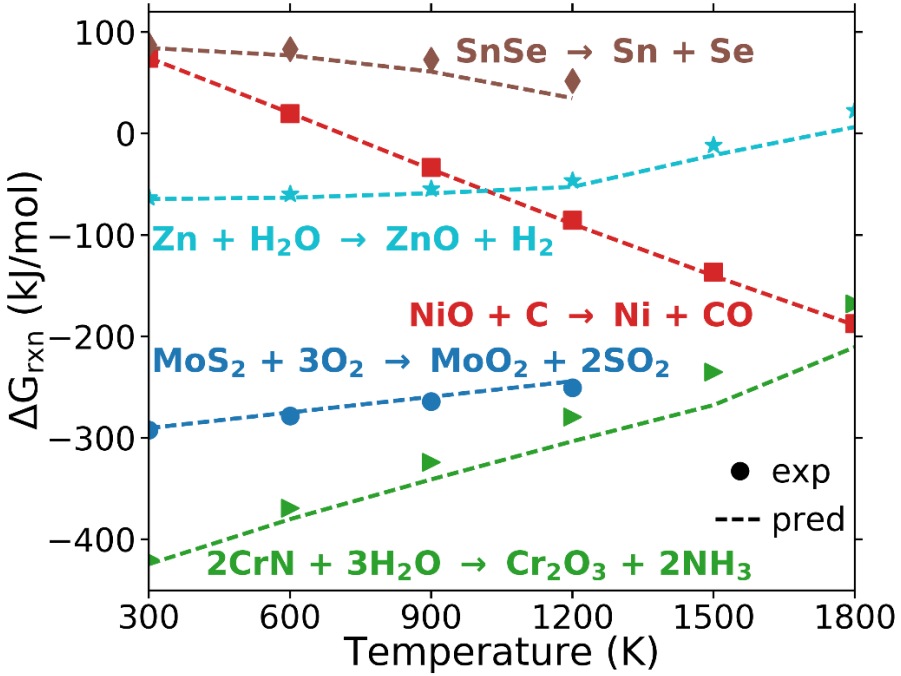
Some evidence that ML model works

ML model performs similarly on training and test sets



ML model captures reaction energetics well



Bartel et al., *Submitted*

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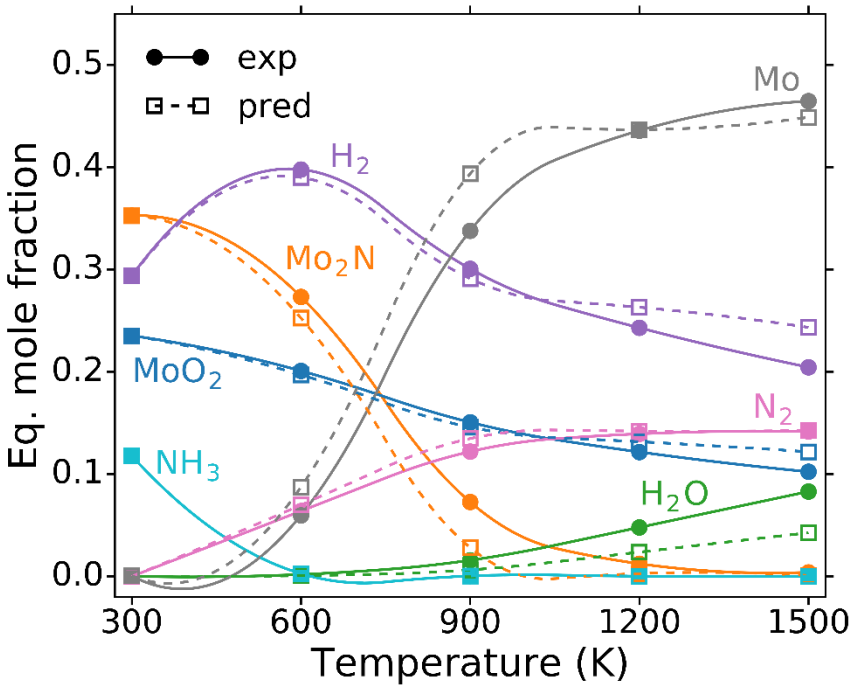
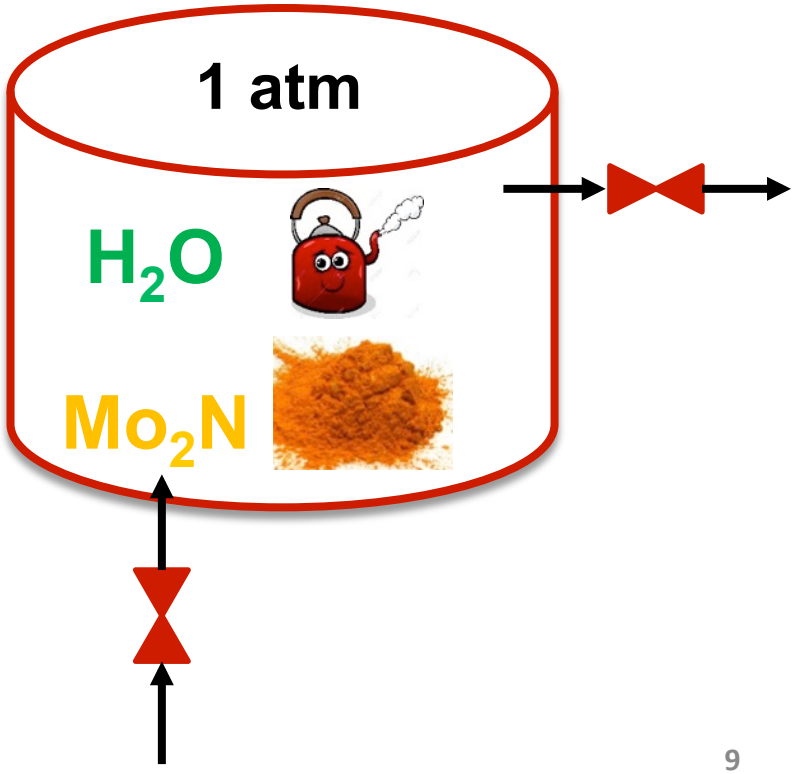
$$2Mo + 0.5N_2 \leftrightarrow Mo_2N$$

$$NH_3 \leftrightarrow 0.5N_2 + 1.5H_2$$

$$MoO_2 + 2H_2 \leftrightarrow Mo + 2H_2O$$

Complex thermodynamic equilibrium well predicted





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What makes a good pair?

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$\Delta G_f(T)$

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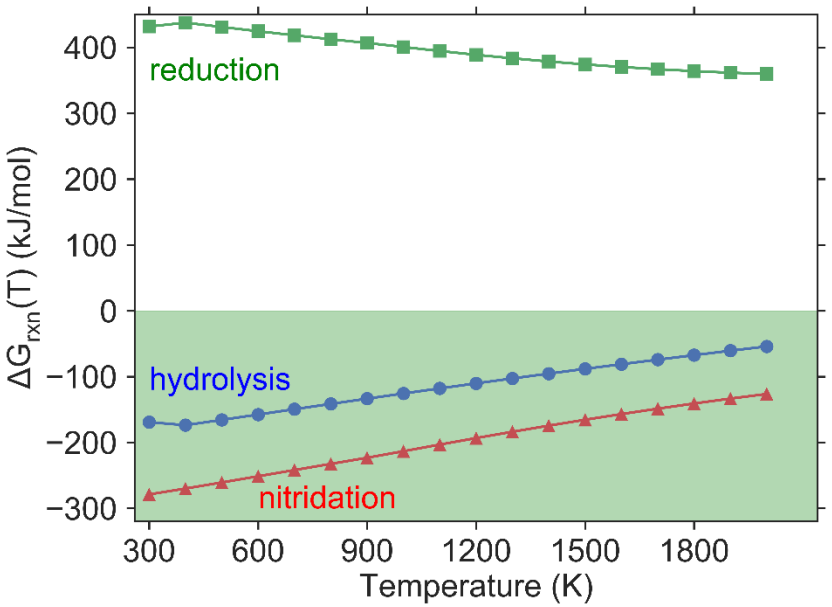

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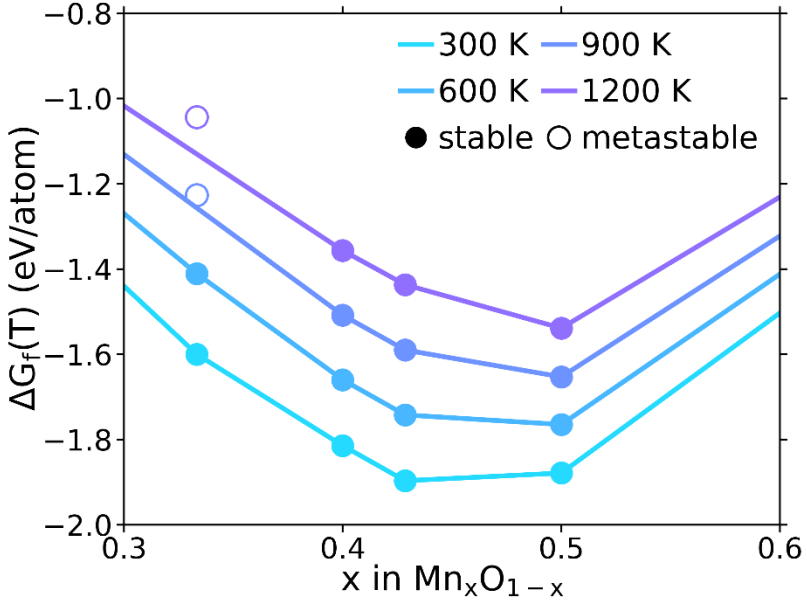


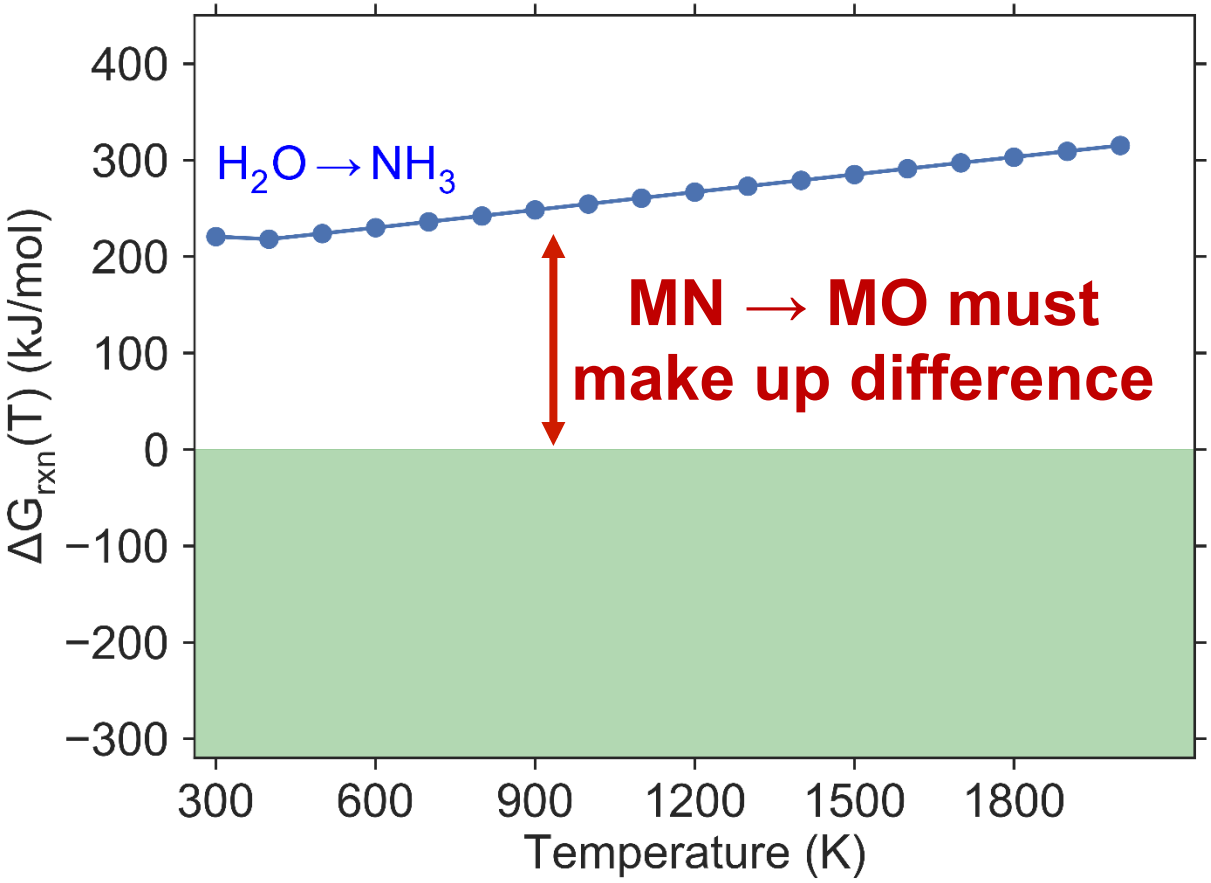
MATERIALS PROJECT

$\Delta H + ML \rightarrow \Delta G$

Viability of pairs for NH_3 generation

$$\frac{1}{b}M_aN_b + \frac{ad}{bc}H_2O \rightarrow \frac{a}{bc}M_cO_d + NH_3 + \left(\frac{ad}{bc} - \frac{3}{2}\right)H_2$$

$$1.5H_2O \rightarrow NH_3$$



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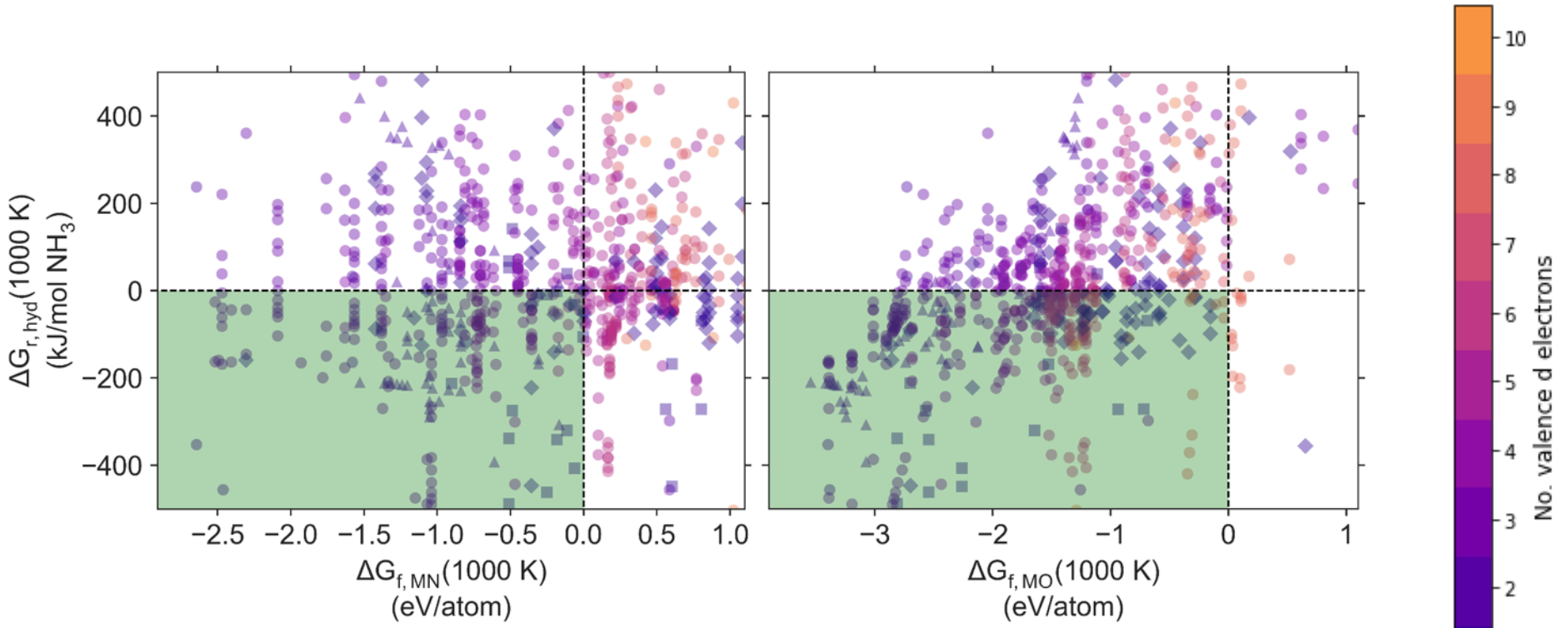
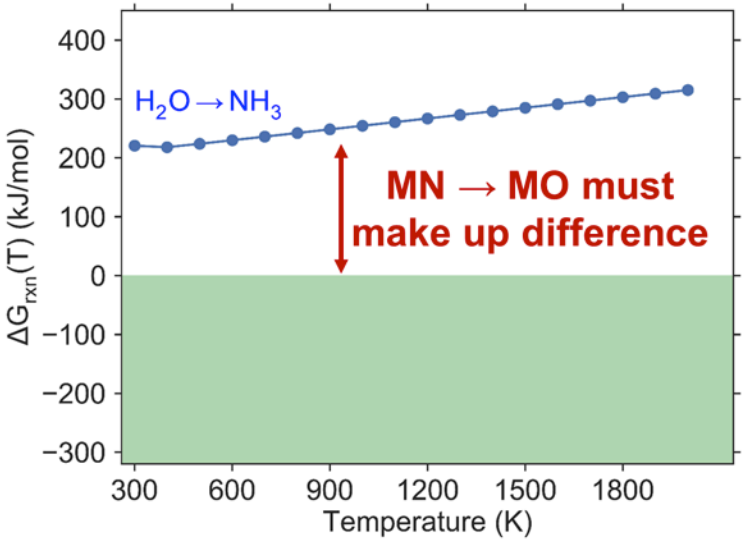
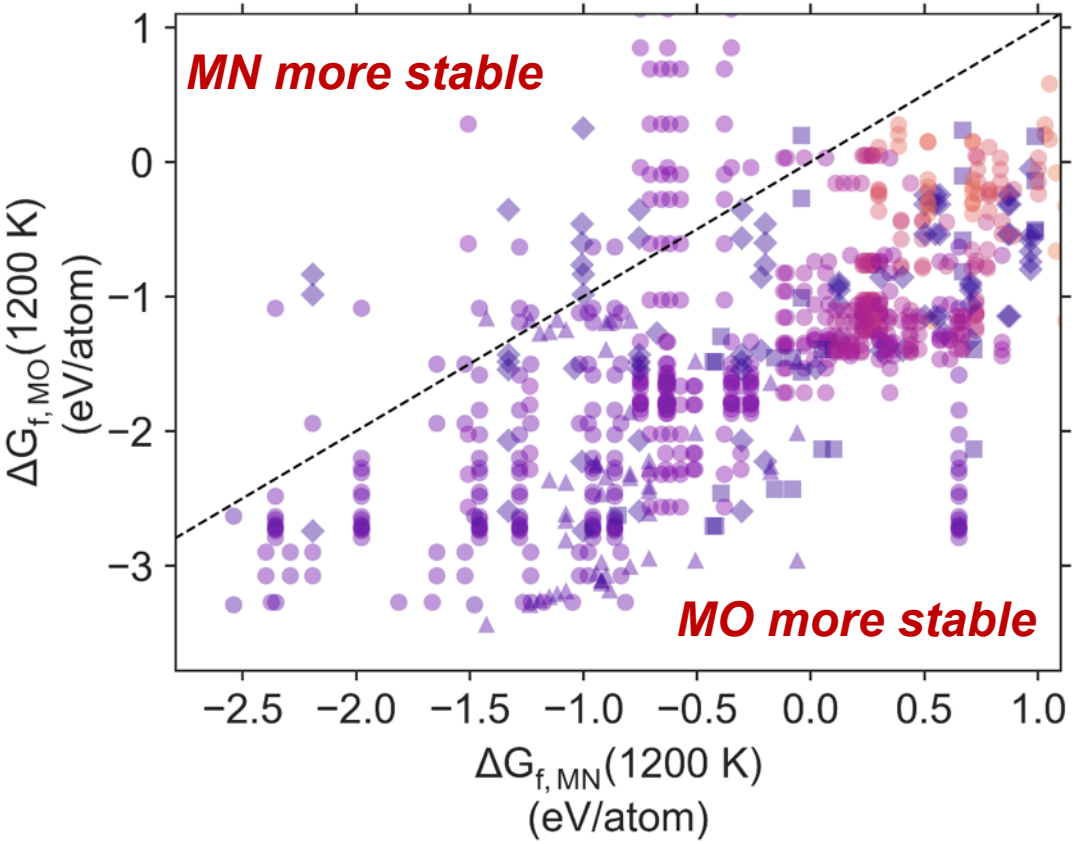


Plenty of pairs viable for the hydrolysis step

Viability of pairs for NH_3 generation

$$\frac{1}{b}M_aN_b + \frac{ad}{bc}H_2O \rightarrow \frac{a}{bc}M_cO_d + NH_3 + \left(\frac{ad}{bc} - \frac{3}{2}\right)H_2$$





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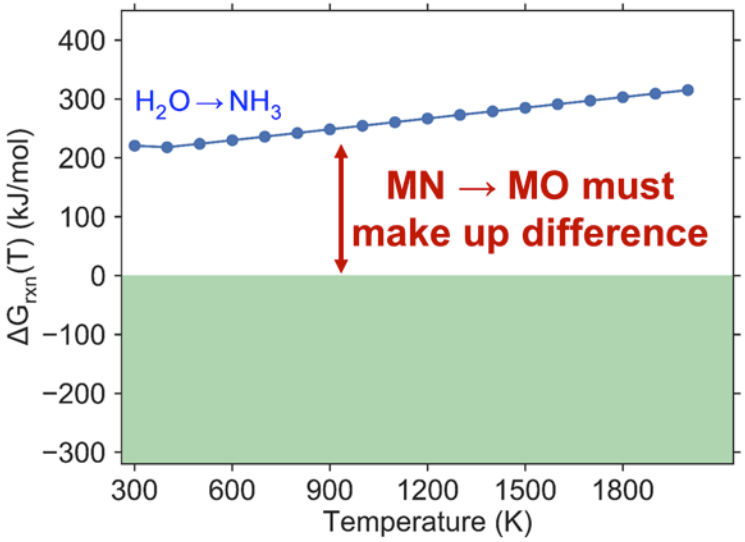
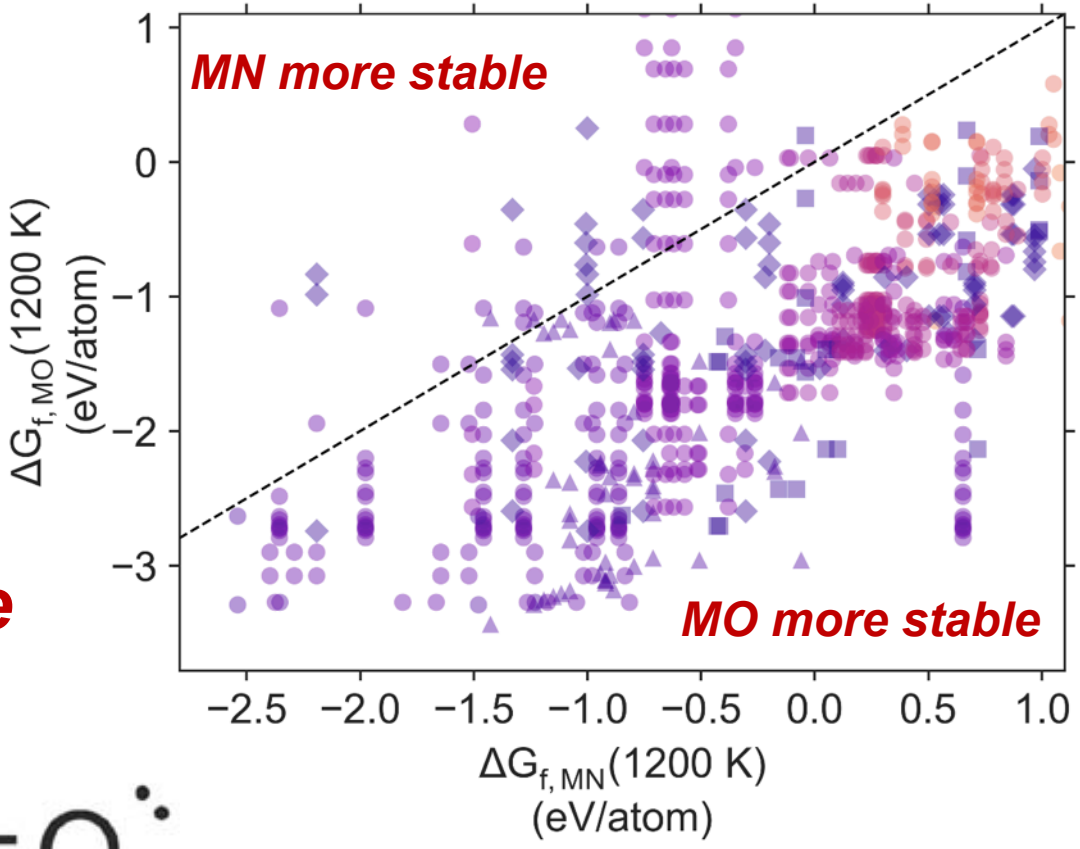
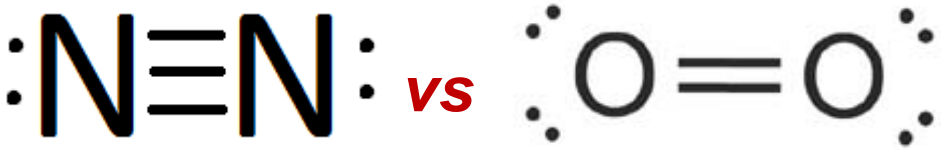
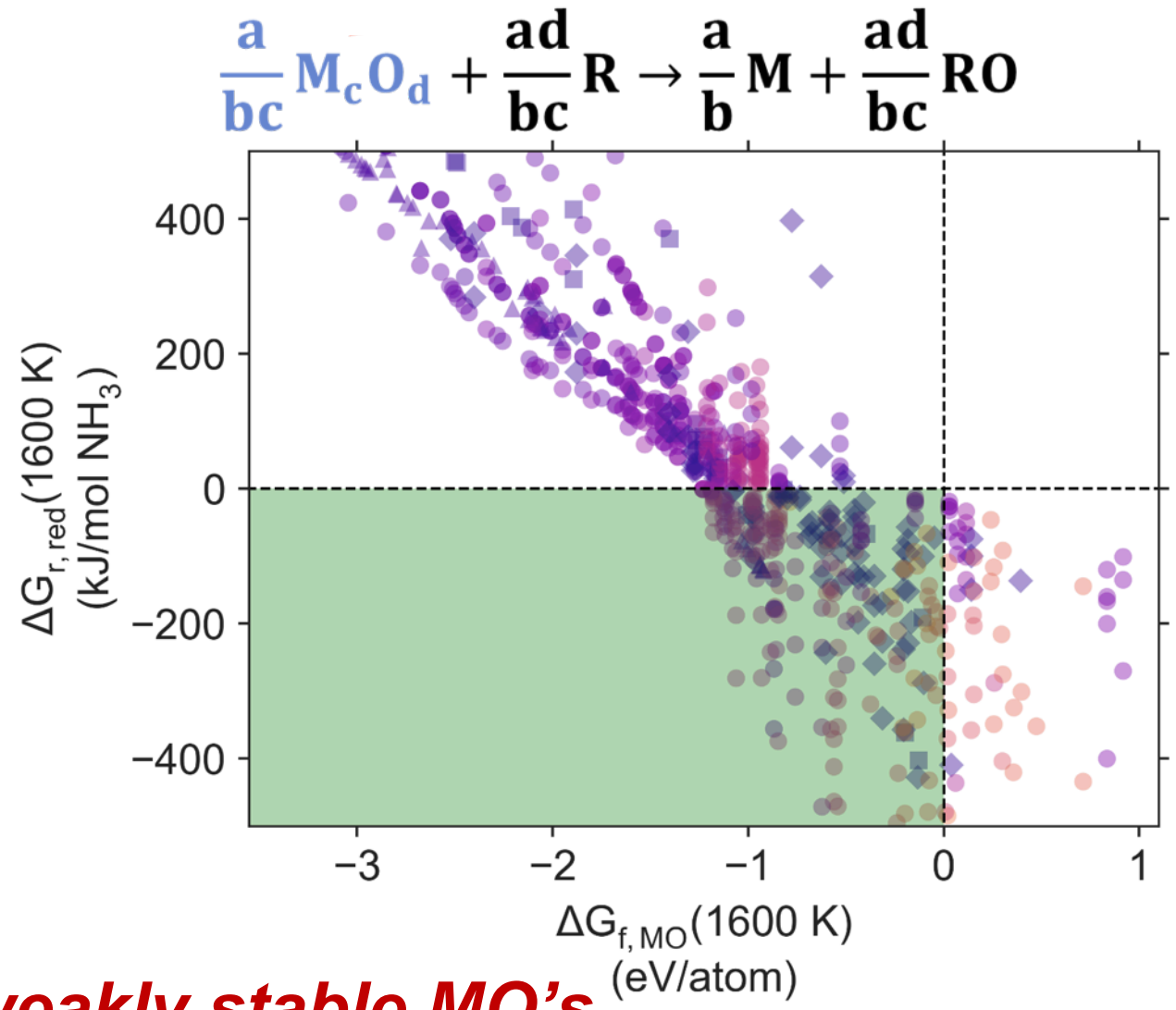




In general, MO more stable than MN



Viability of pairs for MO reduction by H_2

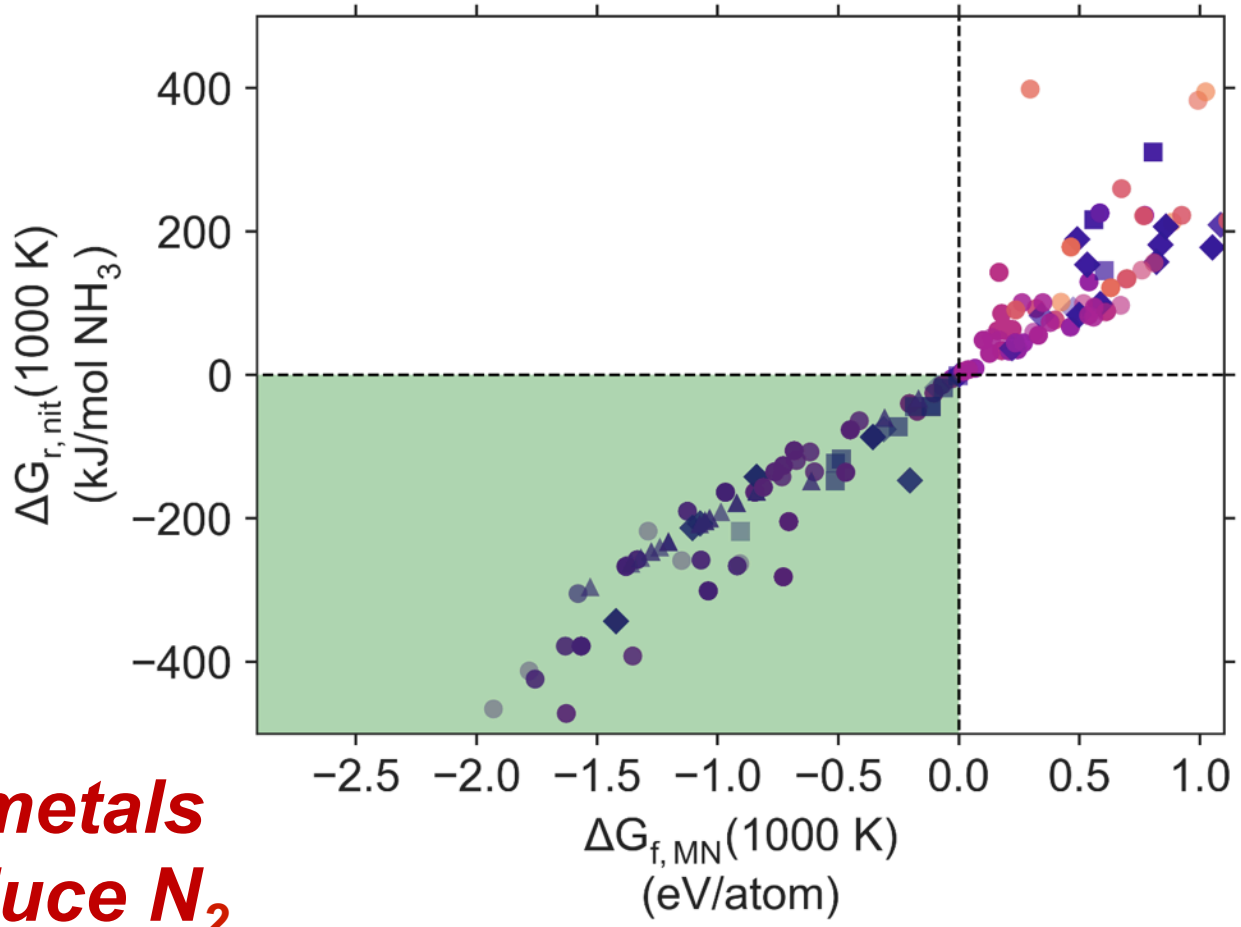


Many weakly stable MO's are reducible at 1600 K

Viability of pairs for N fixation

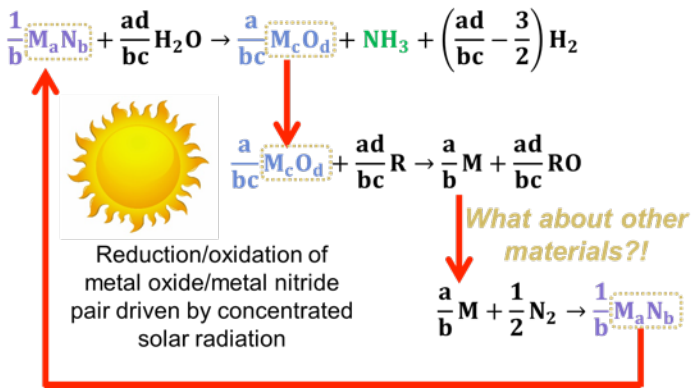
$$\frac{a}{b}M + \frac{1}{2}N_2 \rightarrow \frac{1}{b}M_aN_b$$

$$\Delta G_{f,MN} < 0$$

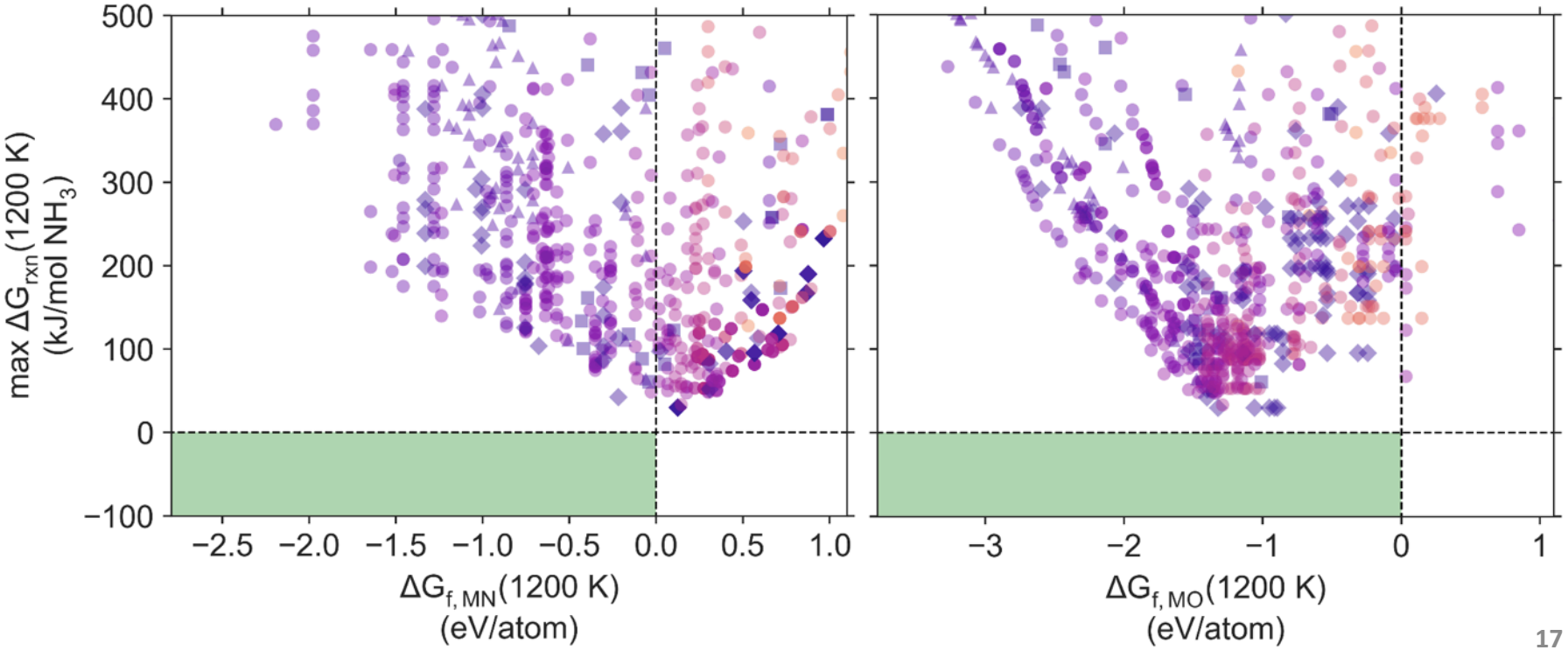


Many metals can reduce N_2

But what about the full cycle?



Correlated stability of MN/ MO limits viability



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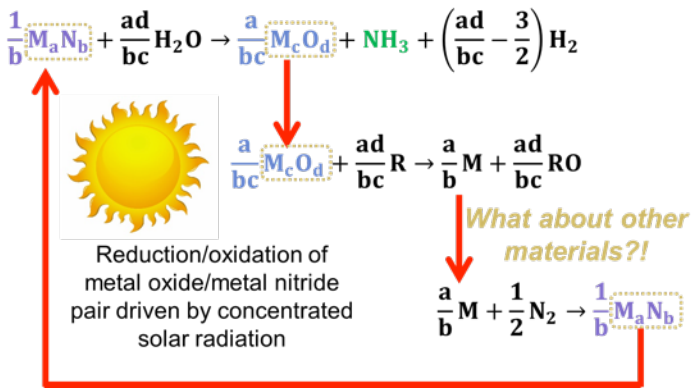

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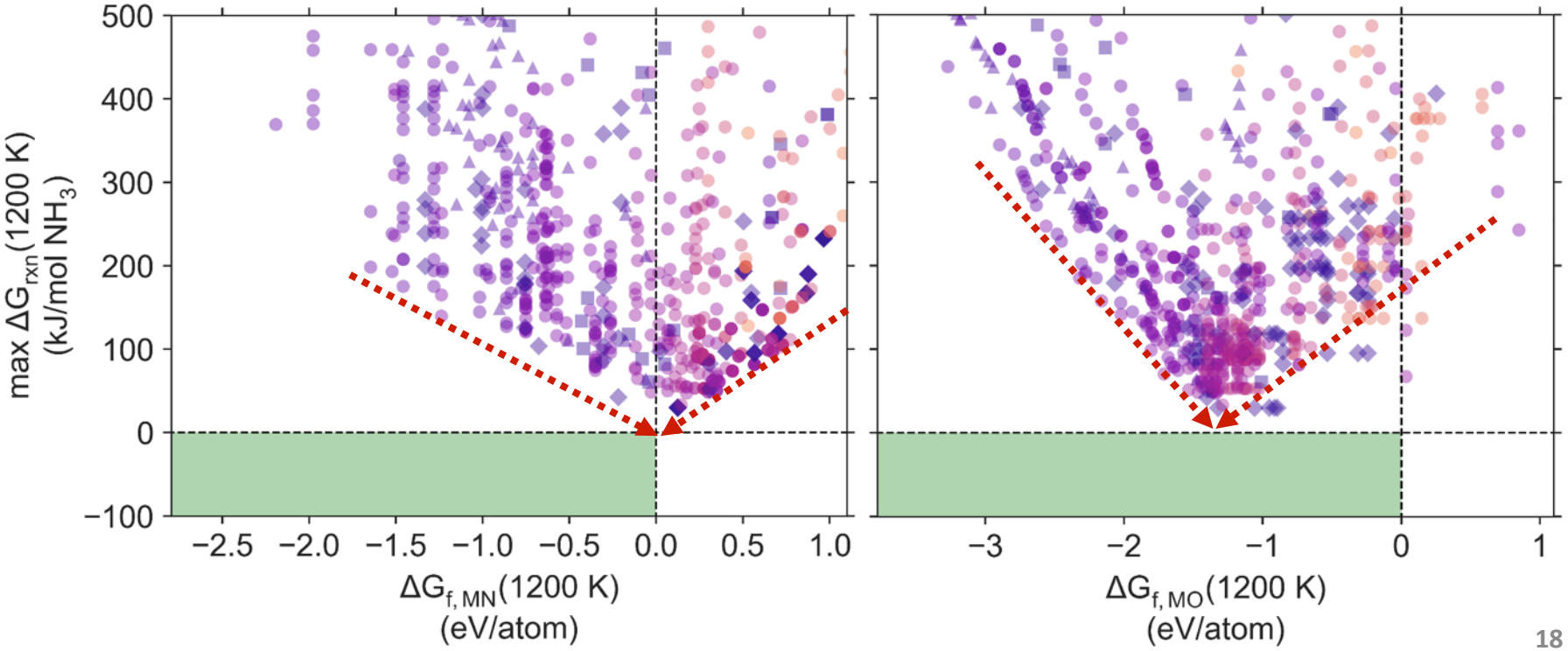

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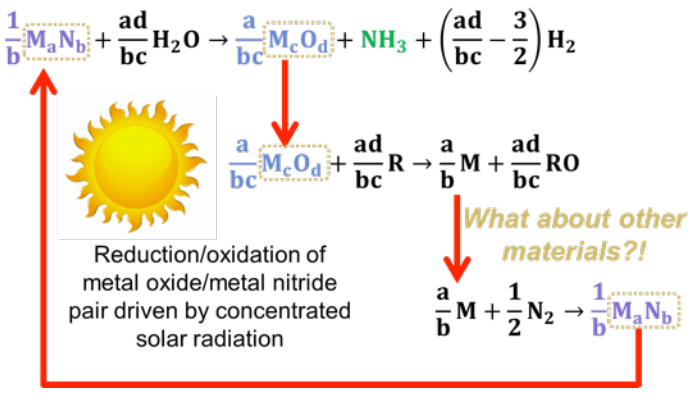

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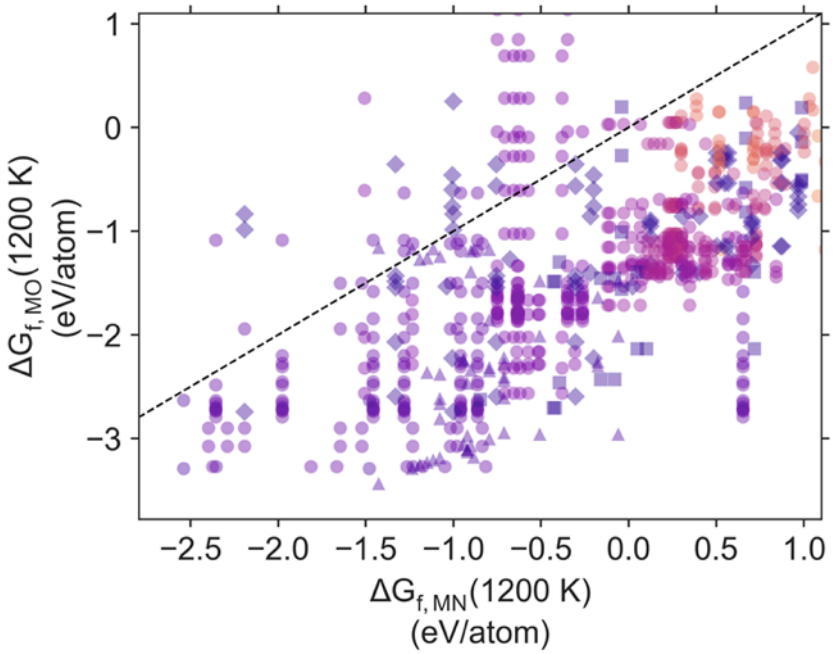

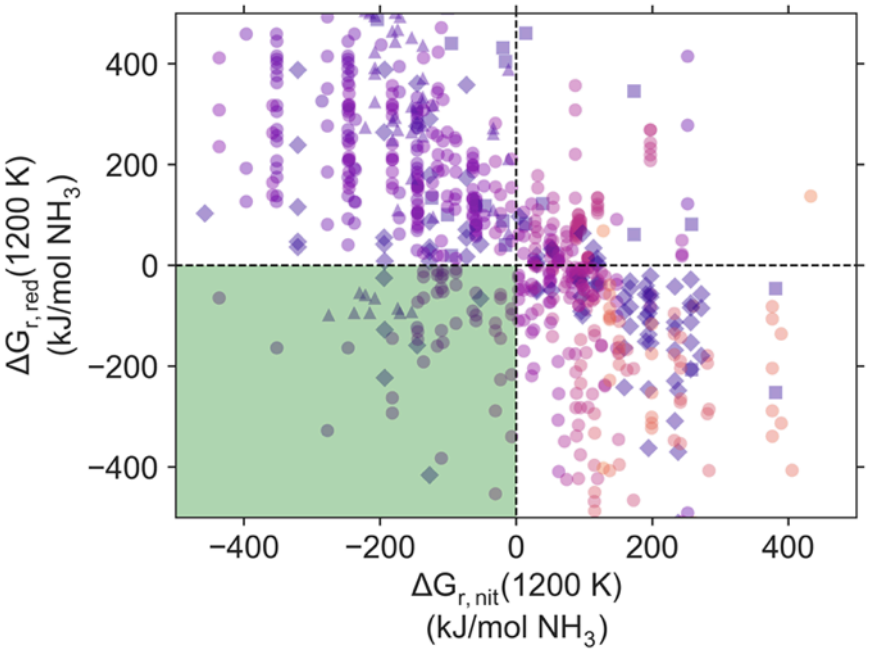

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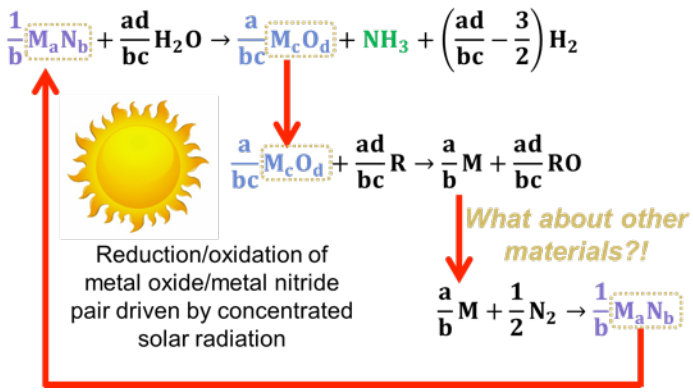

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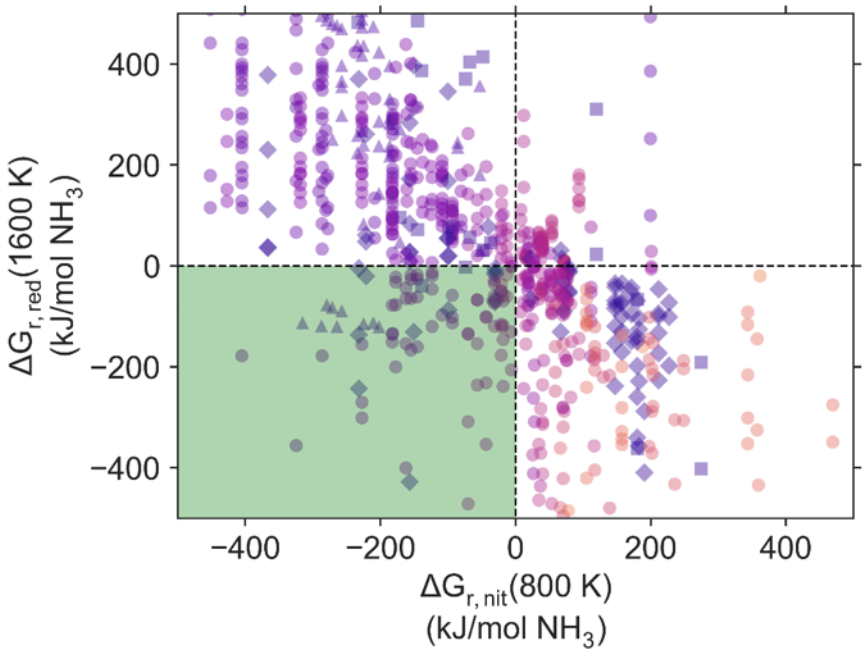

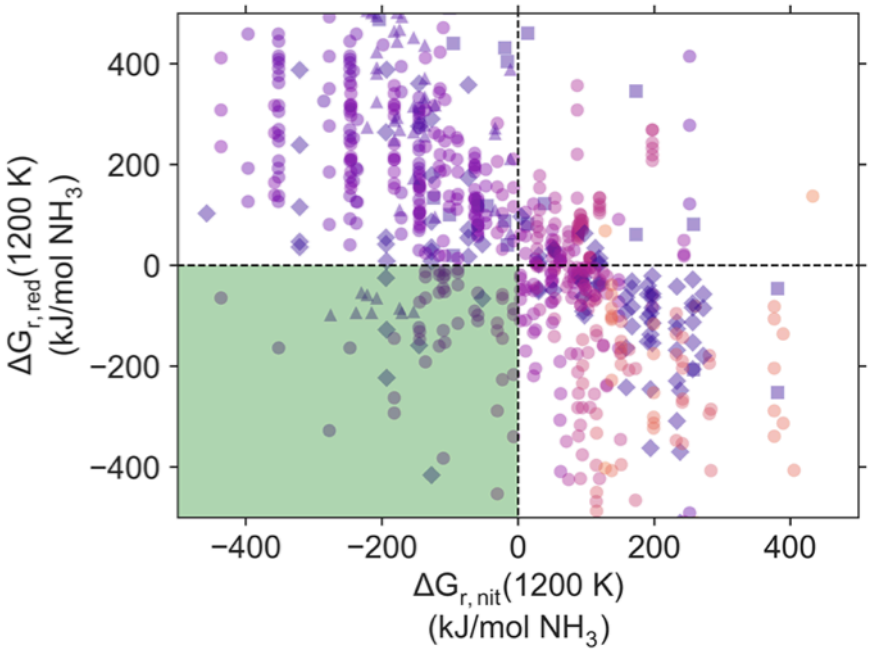

What about going beyond reaction energetics?

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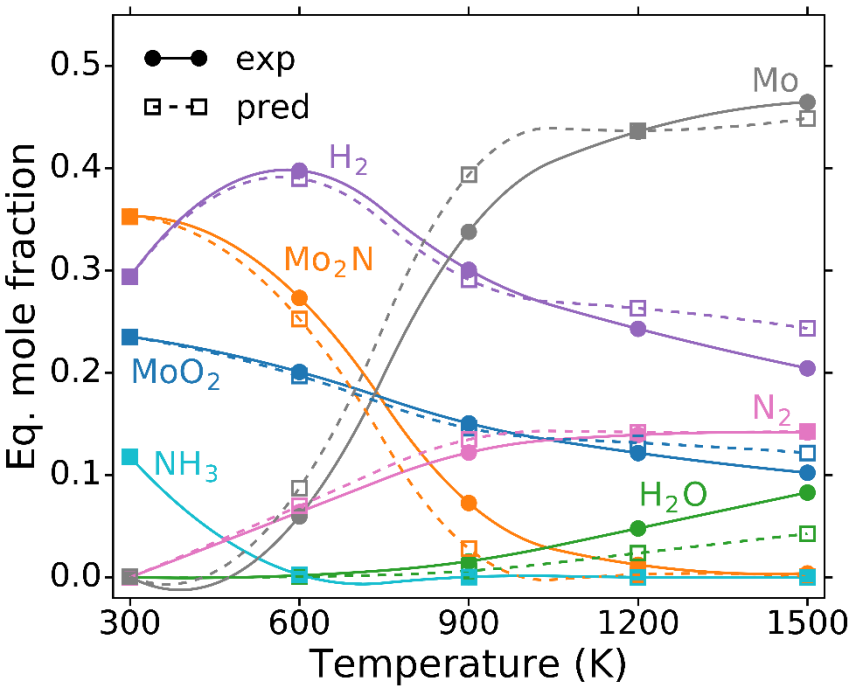

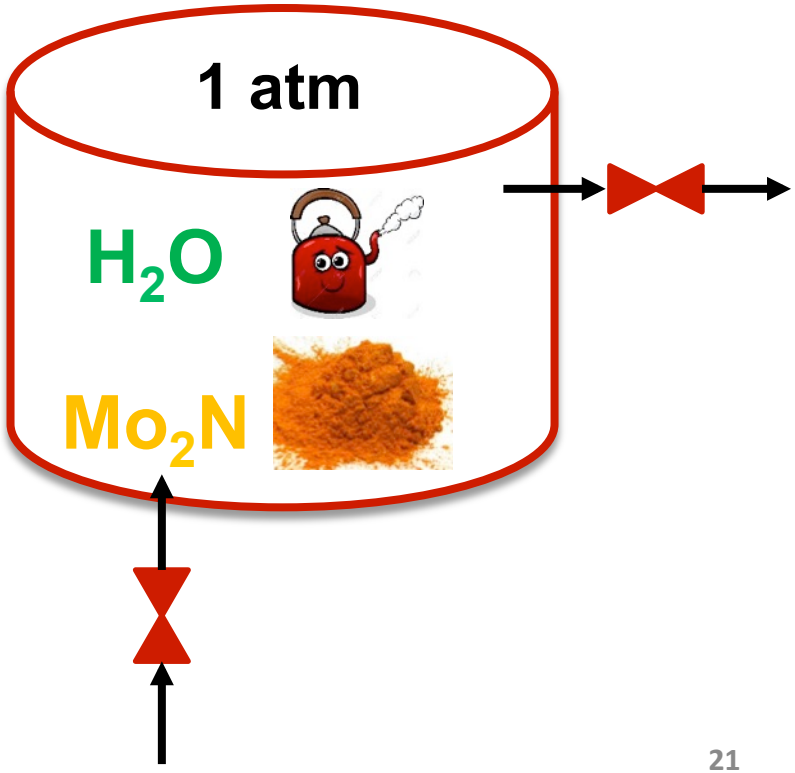

Implicitly considers stability in addition to reaction energetics

Bartel et al., *Submitted*

Benchmarking equilibrium analysis

Cr

- $Cr + N_2 \rightarrow Cr_2N$ shown at 1000°C
- $Cr_2N + H_2O \rightarrow Cr_2O_3$ shown at 1000°C
- $Cr_2O_3 + H_2 \rightarrow Cr$ failed at 1600°C

Michalsky et al., *Solar Energy* 2011

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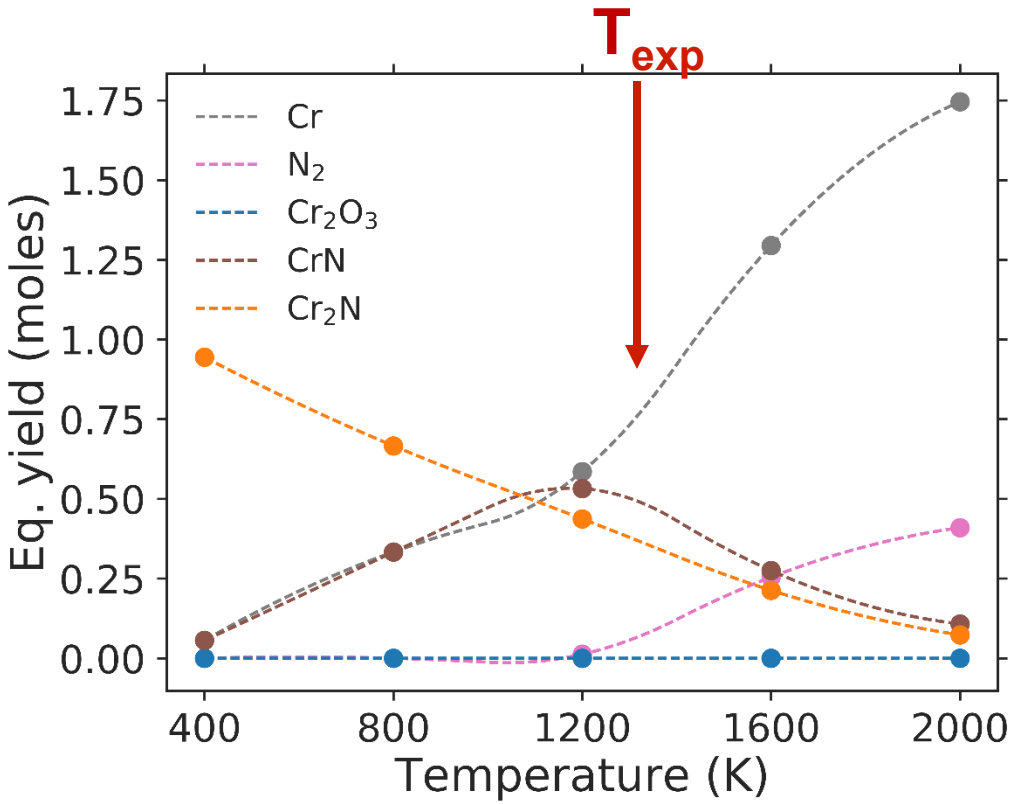

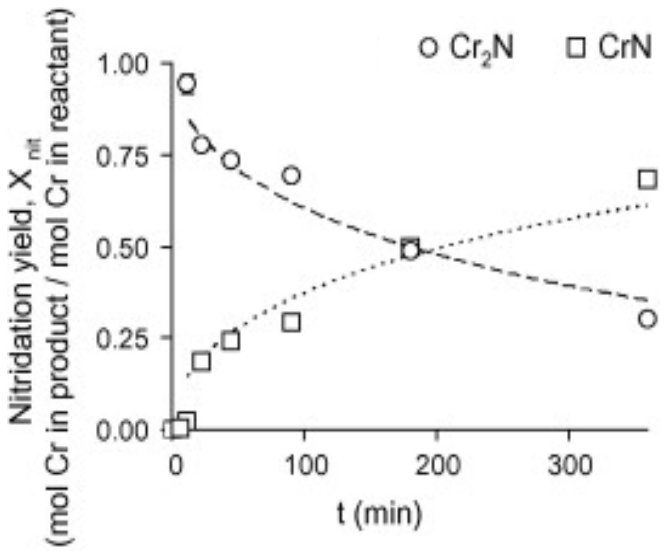

Mix of CrN/Cr_2N predicted and observed

Michalsky et al., *Solar Energy* 2011

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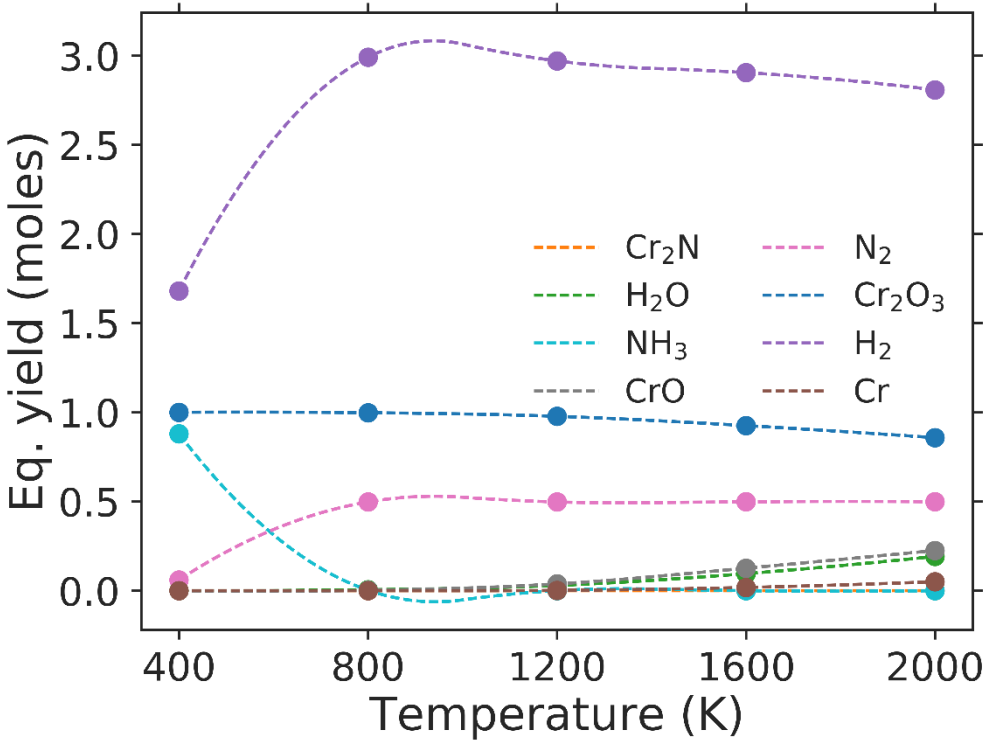

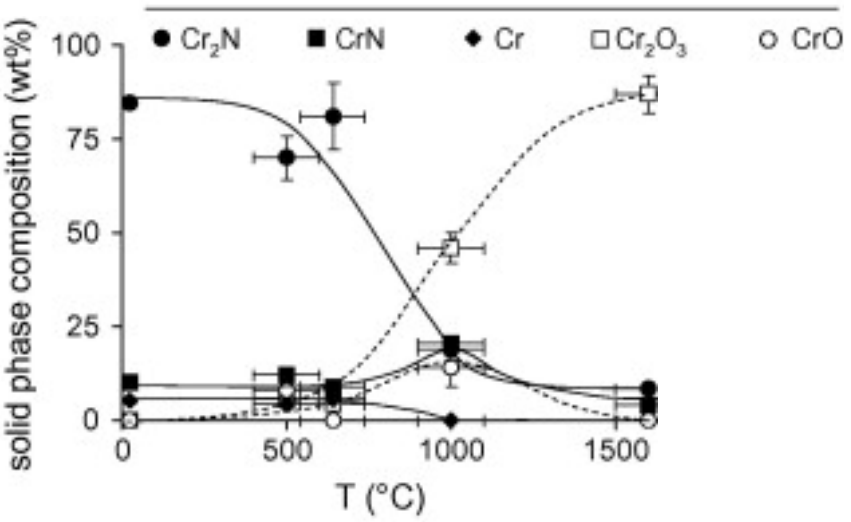

Nitride corrosion predicted and observed

Michalsky et al., *Solar Energy* 2011

Benchmarking equilibrium analysis

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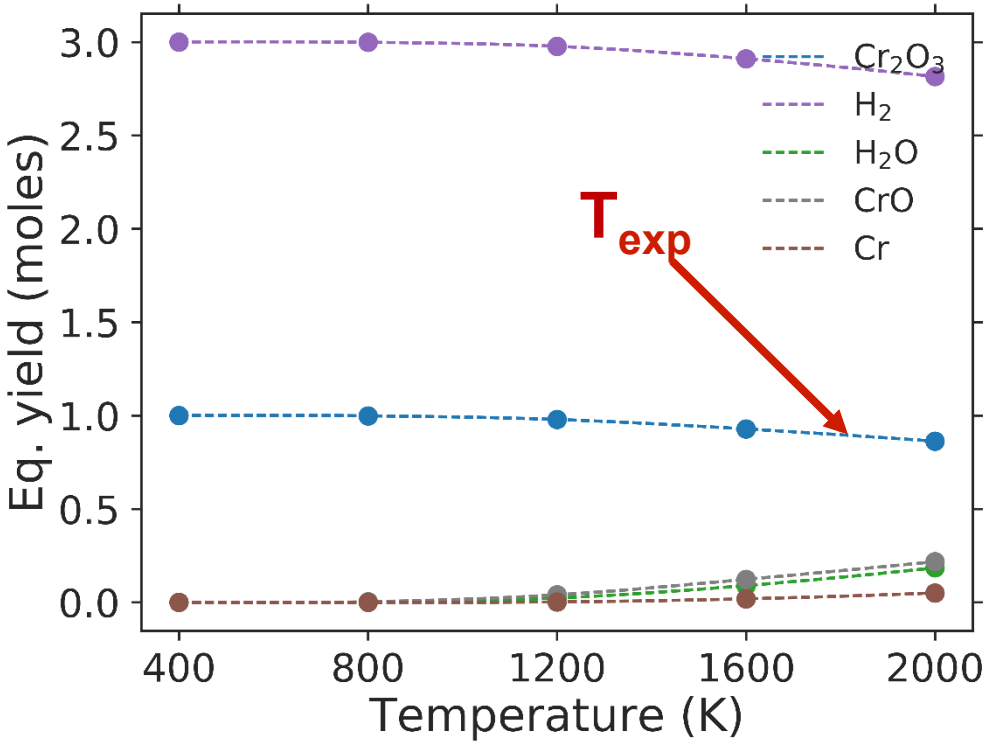
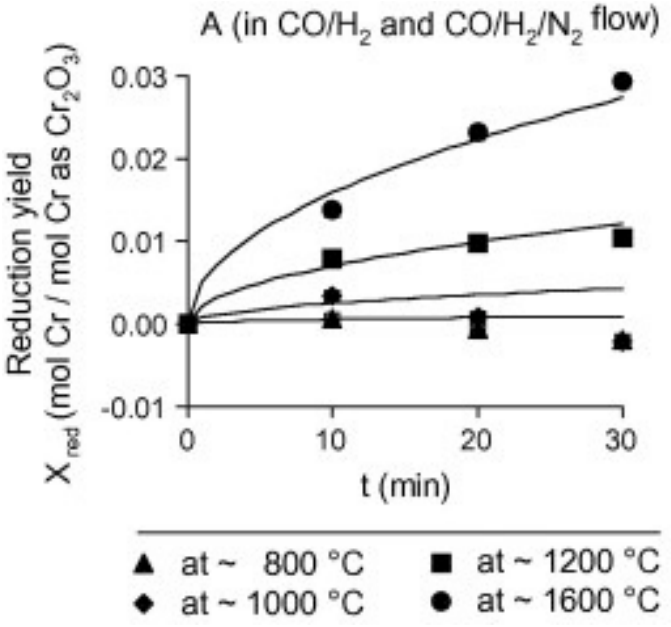
- $Cr_2N + H_2O \rightarrow Cr_2O_3$ shown at 1000°C
- **$Cr_2O_3 + H_2 \rightarrow Cr$** failed at 1600°C



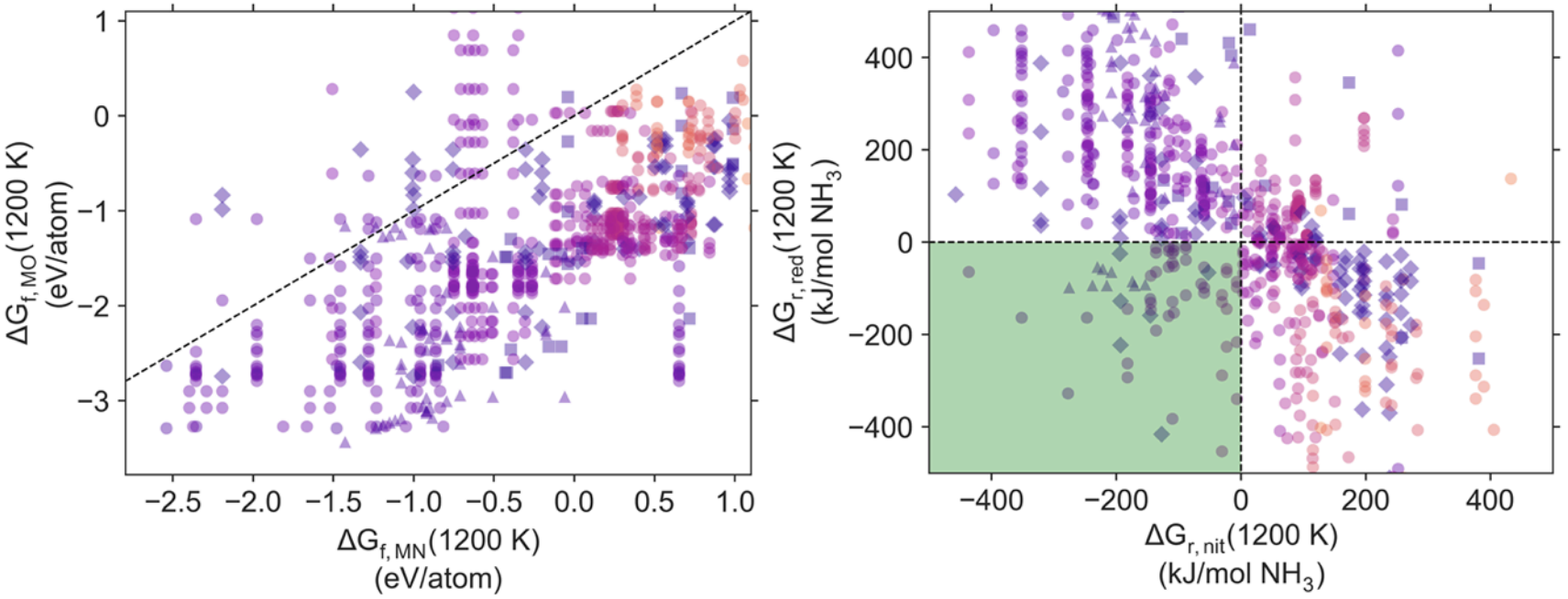


Minimal reduction yield predicted and observed

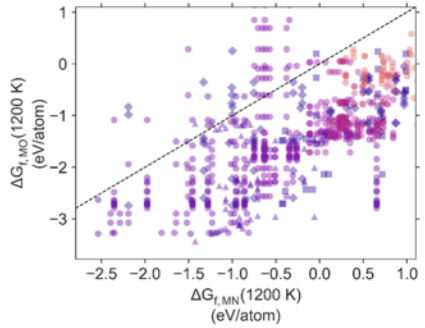
Michalsky et al., *Solar Energy* 2011

Systematic thermodynamic screening of MN/MO

- ✓ **STAS limited by correlated MO/MN stability**

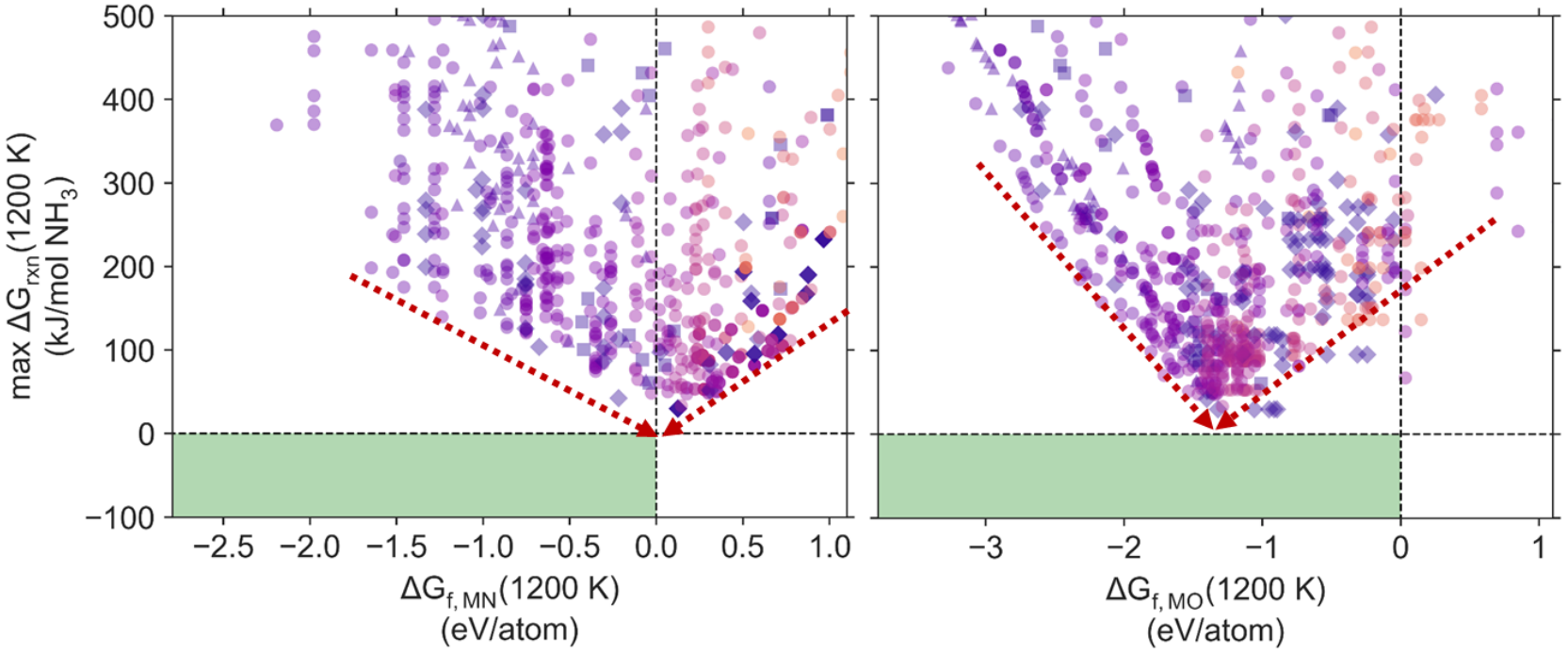


Systematic thermodynamic screening of MN/MO



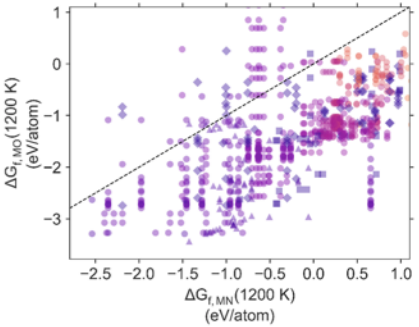
✓ STAS limited by correlated MO/MN stability

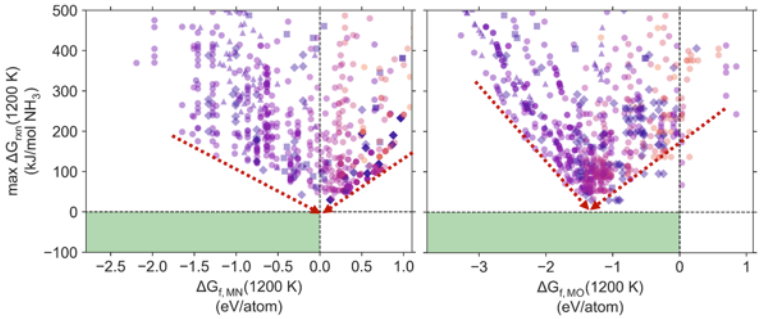
✓ **Nature of the redox cycle leads to volcano-like dependence upon ΔG**

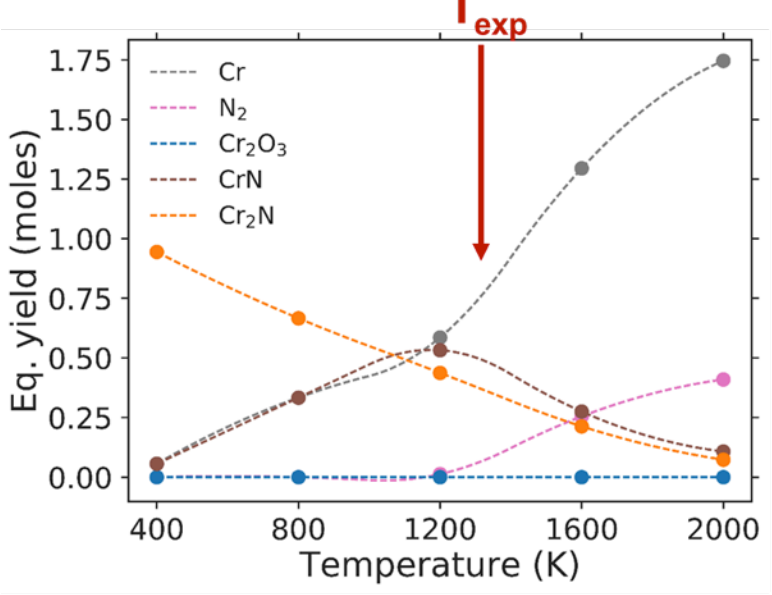


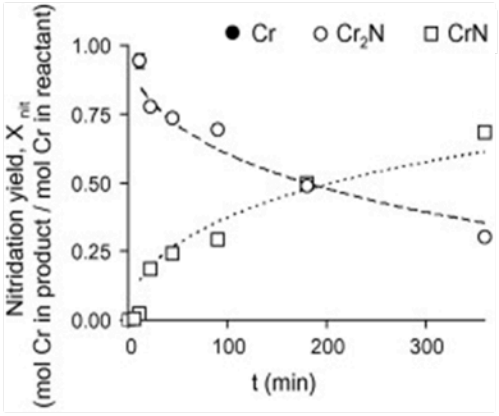
Systematic thermodynamic screening of MN/MO

- ✓ STAS limited by correlated MO/MN stability
- ✓ Nature of the redox cycle leads to volcano-like dependence upon ΔG
- ✓ **Machine-learned eq analysis compares well with experiment**





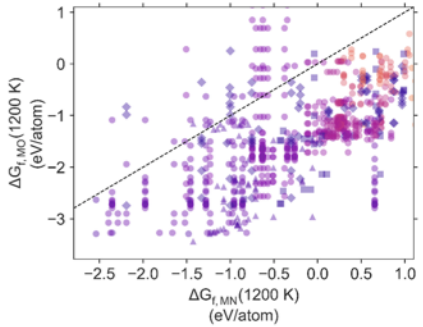


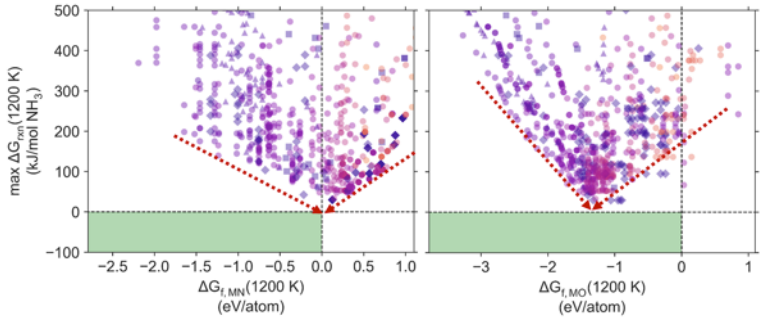


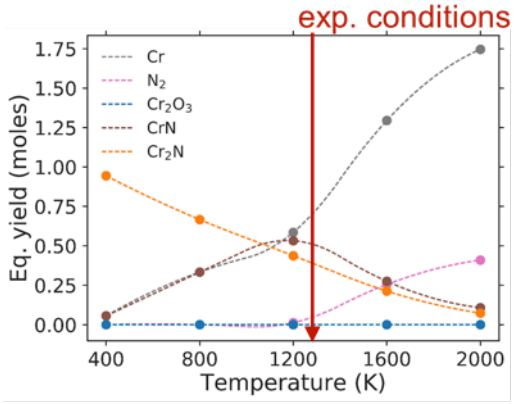
Mix of CrN/Cr_2N predicted and observed

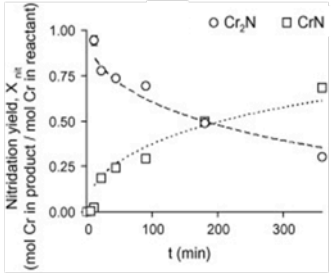
Systematic thermodynamic screening of MN/MO

- ✓ STAS limited by correlated MO/MN stability
- ✓ Nature of the redox cycle leads to volcano-like dependence upon ΔG
- ✓ Machine-learned eq analysis compares well with experiment









Mix of CrN/Cr_2N predicted and observed

QUESTIONS?