Student Laboratory Module: The Kinetics of NH_3 Cracking

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Presentation Outline

- Laboratory work in traditional lecture courses
- Ammonia decomposition as a model reaction
- Kinetics lab hardware
- Data collection
  - Detector details
  - Experimental concerns/considerations
- Data analysis
  - Development of kinetic rate law
  - Rate limiting step?
  - Reactor design methodology

Laboratory Modules in CBE

- Hands-on work with foundational undergraduate courses is a rarity for most curricula
  - Cost of lab development and instruction
  - Limitation on material covered in lectures
- CBE Department at CSM makes them a priority
  - Kinetics laboratory
  - Transport laboratory
  - Process and bioprocess design labs
  - Thermodynamics and process principles laboratories
- Senior labs (kinetics, transport) administered at end of Fall semester

Kinetics Laboratories

- **Previous kinetics labs**
  - **Mutarotation of D-glucose (dextrose)**
    - **Reversible reaction, no chemical hazards**
    - **Complicated, boring, messy**
    - **Hard on equipment**
  - **Food coloring / bleach**
    - **Irreversible, fairly safe chemicals**
    - **Uses lots of water**
    - **Difficult to create robust absorbance detector**
- **Present effort:**

heterogeneous catalytic gas reactions

Heterogeneous Catalysis

- **Dominant reaction type in process industries that hire our graduates**
  - **Hydrodesulfurization (hydrotreating)**
  - **Catalytic cracking of hydrocarbons**
  - **Steam reforming**
- **Advantages of this lab experiment type**
  - **No waste clean-up**
  - **Long-lasting, easy to procure reactant gases**
  - **High detector reliability**
- **Concerns**
  - **Special safety considerations (chemical, thermal, fire)**
  - **Limited selection of reactions**

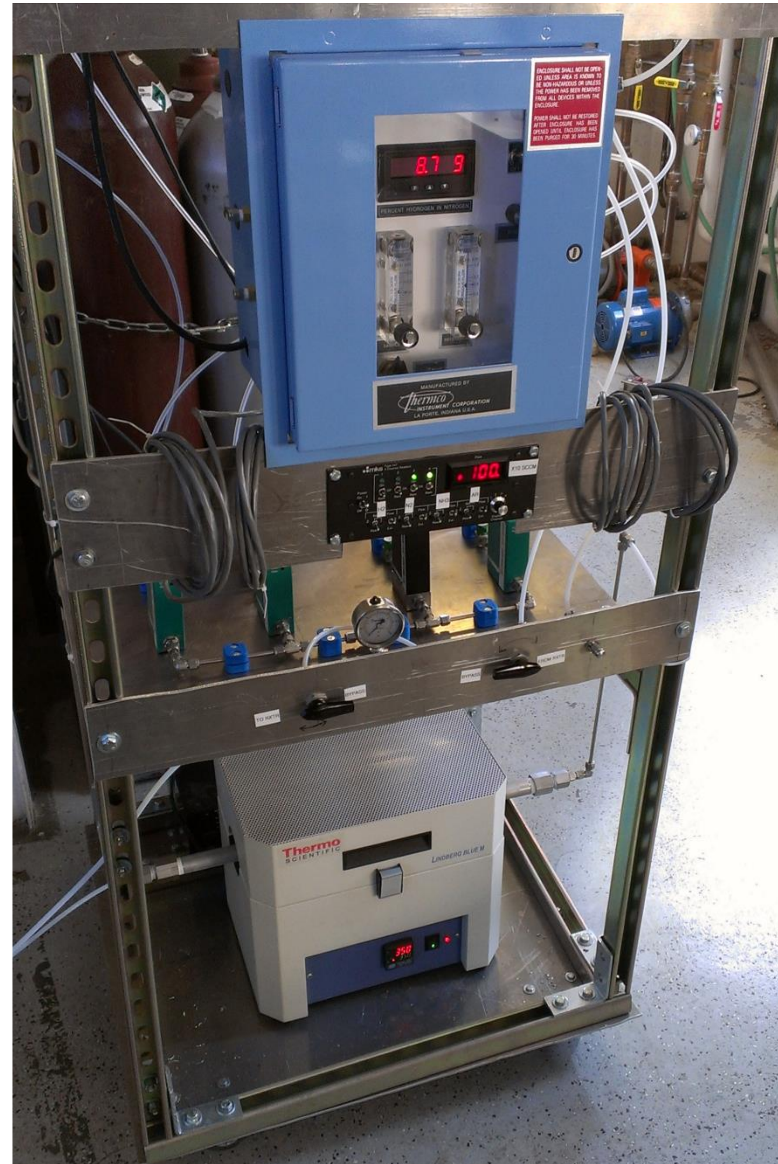
Ammonia Decomposition

$$2\ NH_3 \longrightarrow 3\ H_2 + N_2 \qquad \Delta H^\circ = 46\ kJ/mol$$

- **Reversible reaction, but nearly irreversible at low reactor pressures (a desired condition)**
- **Small heat of reaction, but is also endothermic**
- **Nearly ideal chemistry for student investigation**
  - **No side reactions or products**
  - **Large thermal conductivity change with reaction**
  - **Large stoichiometric coefficient for hydrogen**
- **Long-lasting store of reactant (NH_3)!**

Experimental Setup

- **Fixed- or packed-bed reactor in tube furnace**
- **Calibrated mass flow controllers for gases**
- **Thermal conductivity detector (0-100% H_2 in N_2)**
- **Reactor bypass available**
- **Rolling cart holds all instruments**
  - **Portability**
  - **Remove to storage in Spring**



Experimental Setup, cont'd.

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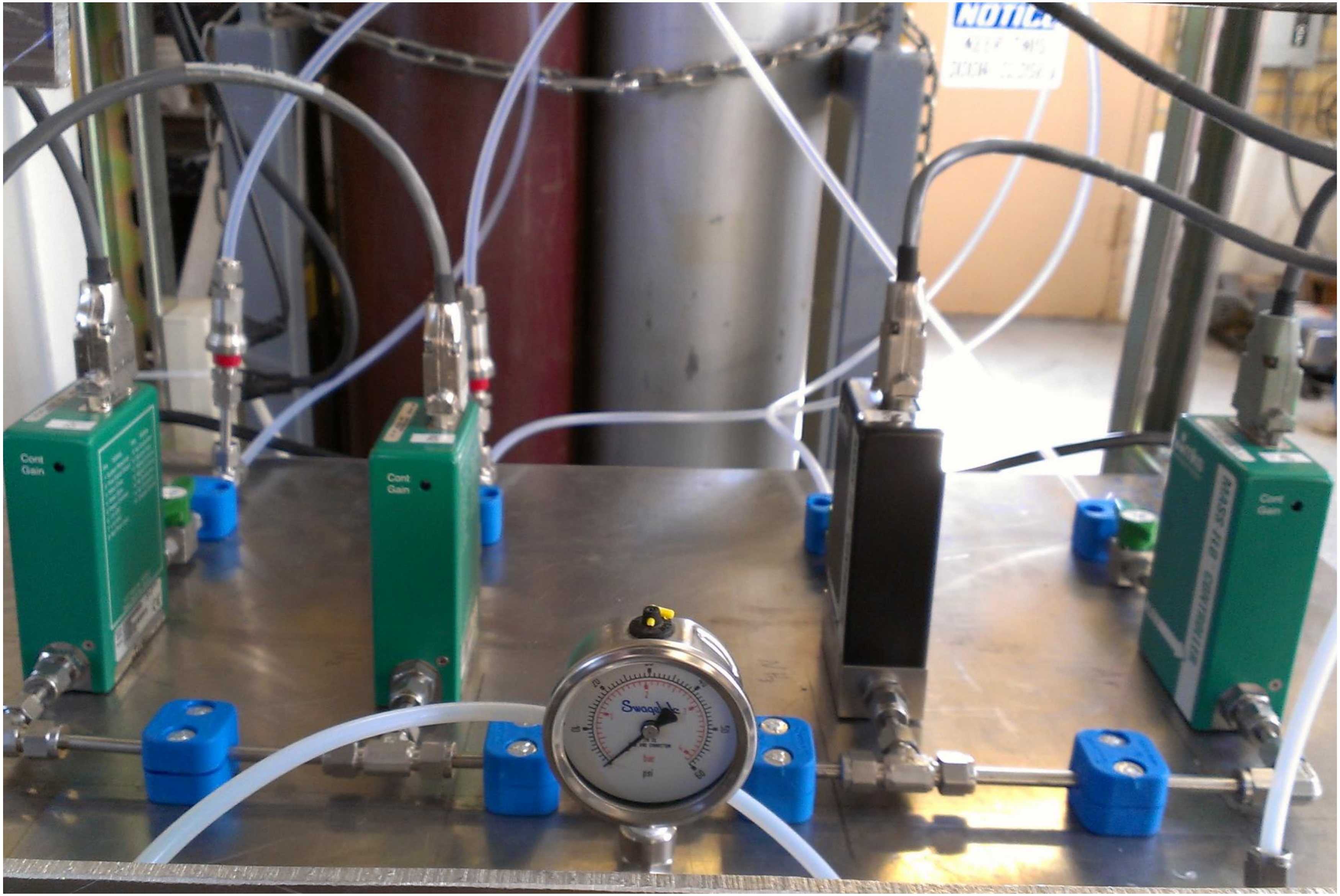
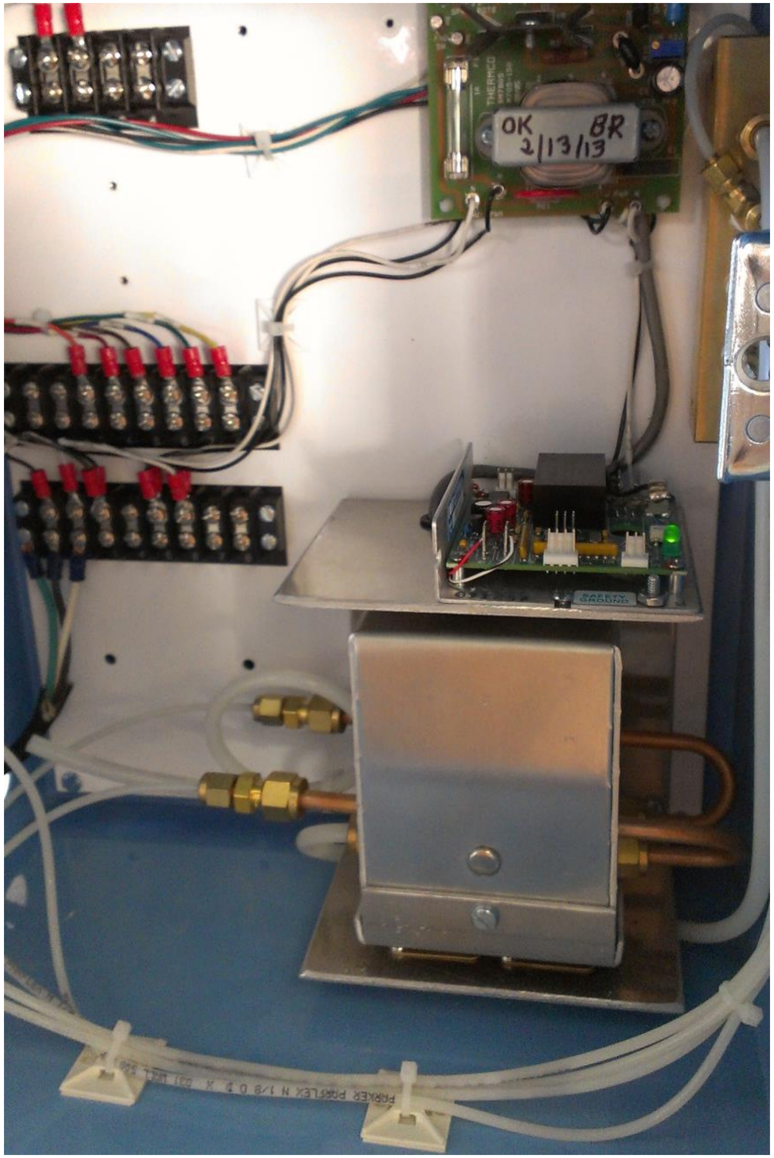


Experimental Setup, cont'd.

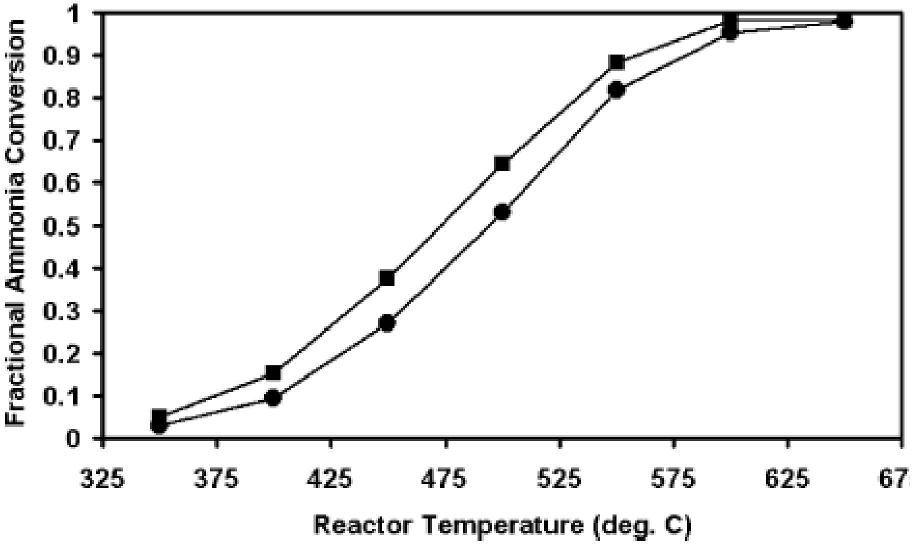


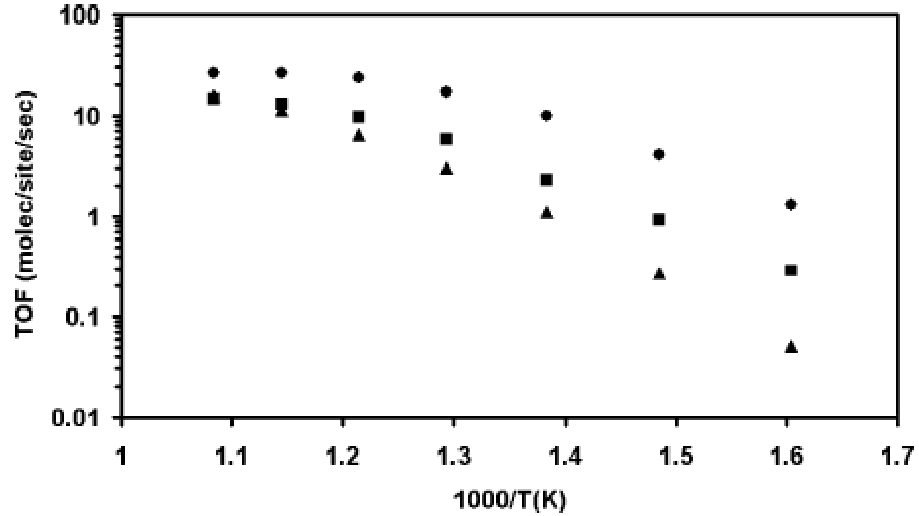
Catalyst Details

- 2 wt% Ruthenium on ¼" gamma alumina rings
- Total surface area ~ 100 m^2 per gram
- Metal dispersion ~ 40%
- Common NH_3 use:
  - Ammonia cracking
  - Low P synthesis
- Chosen system causes little to no catalyst poisoning or deactivation

Gathering Data

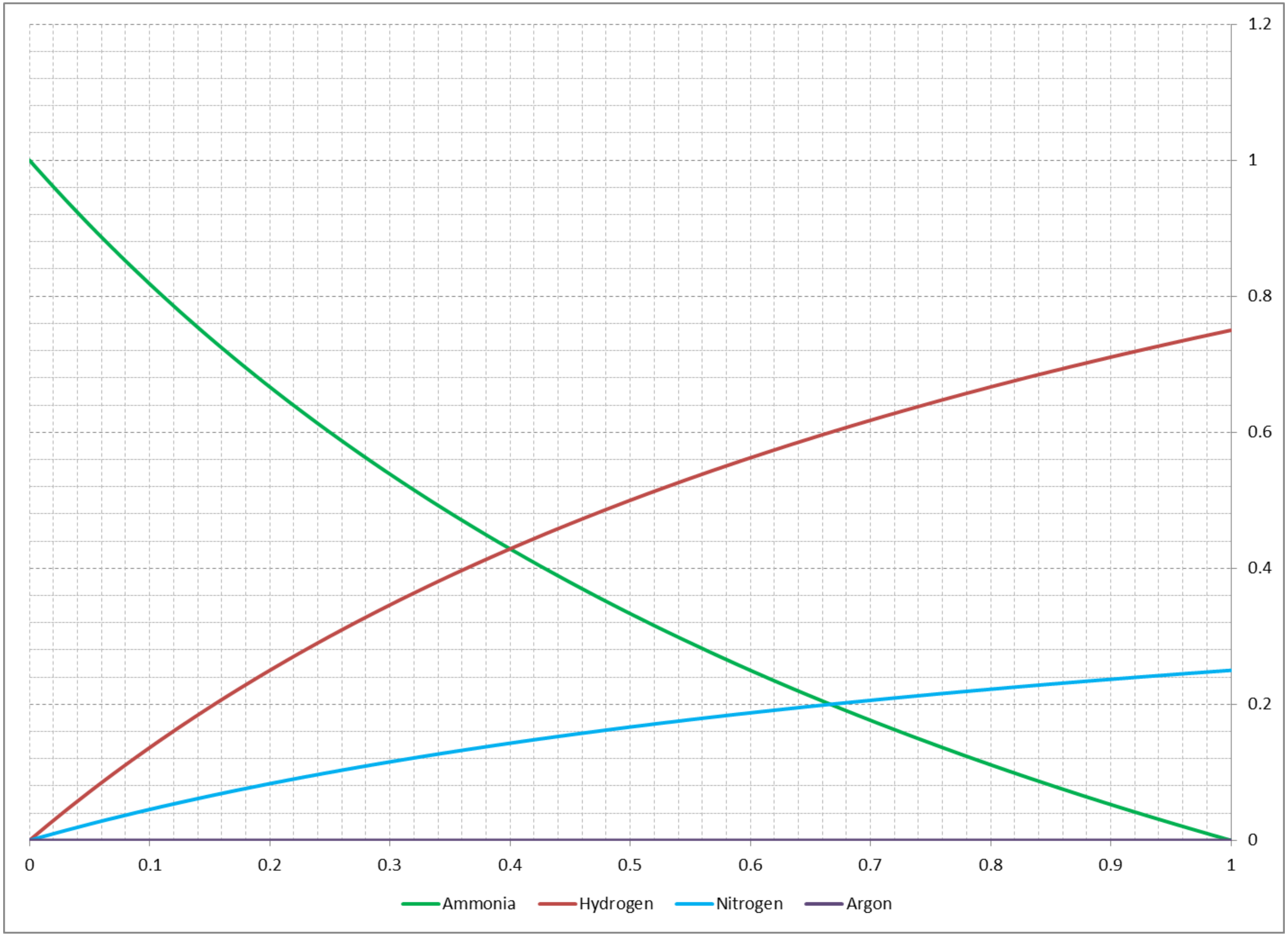
- "Differential" reaction rate data required
  - Products generated may influence reaction rate
  - Extent of reaction must be small, but measurable
- Guide: previous work on ammonia decomposition





J.C. Ganley, J. of Catalysis vol. 227 (2004)

Composition vs. Conversion



Gathering Data

- Initial gas mixtures chosen to isolate individual reactant and product effects on reaction rate
- Argon used as a diluent only

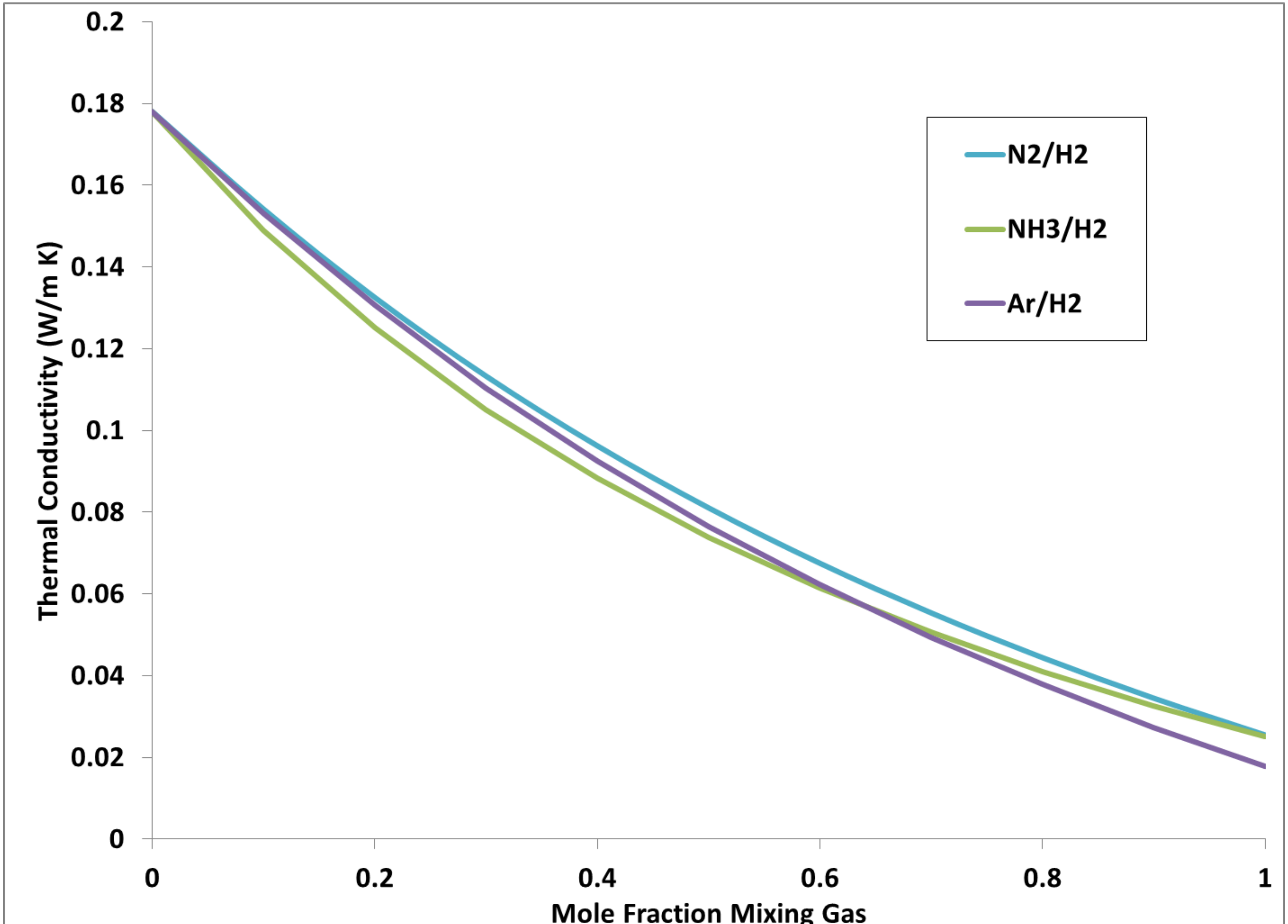
Data: 350°C, 95 g catalyst

H_2 (sccm)	N_2 (sccm)	NH_3 (sccm)	Ar (sccm)
0	0	1000	0
0	0	1000	500
0	0	1000	1000
0	0	1000	1500
250	0	1000	750
500	0	1000	500
1000	0	1000	0
0	500	1000	500
0	750	1000	250
0	1000	1000	0

Reactor Effluent Analysis

- **Must proceed carefully with the thermal conductivity detector!**
  - **Factory calibrated, 0-100% H_2 in N_2**
  - **Thermal conductivity of gas mixtures are typically nonlinear with composition.**
- **H_2: High thermal conductivity [186 mW / (m K)]**
- **N_2, NH_3, Ar much lower & close to each other, but not exactly the same…**
  - **N_2 : 25.8 mW / (m K)**
  - **NH_3 : 25.1 mW / (m K) (-2.7%)**
  - **Ar : 18.0 mW / (m K) (-30%)**

Varying Thermal Conductivity

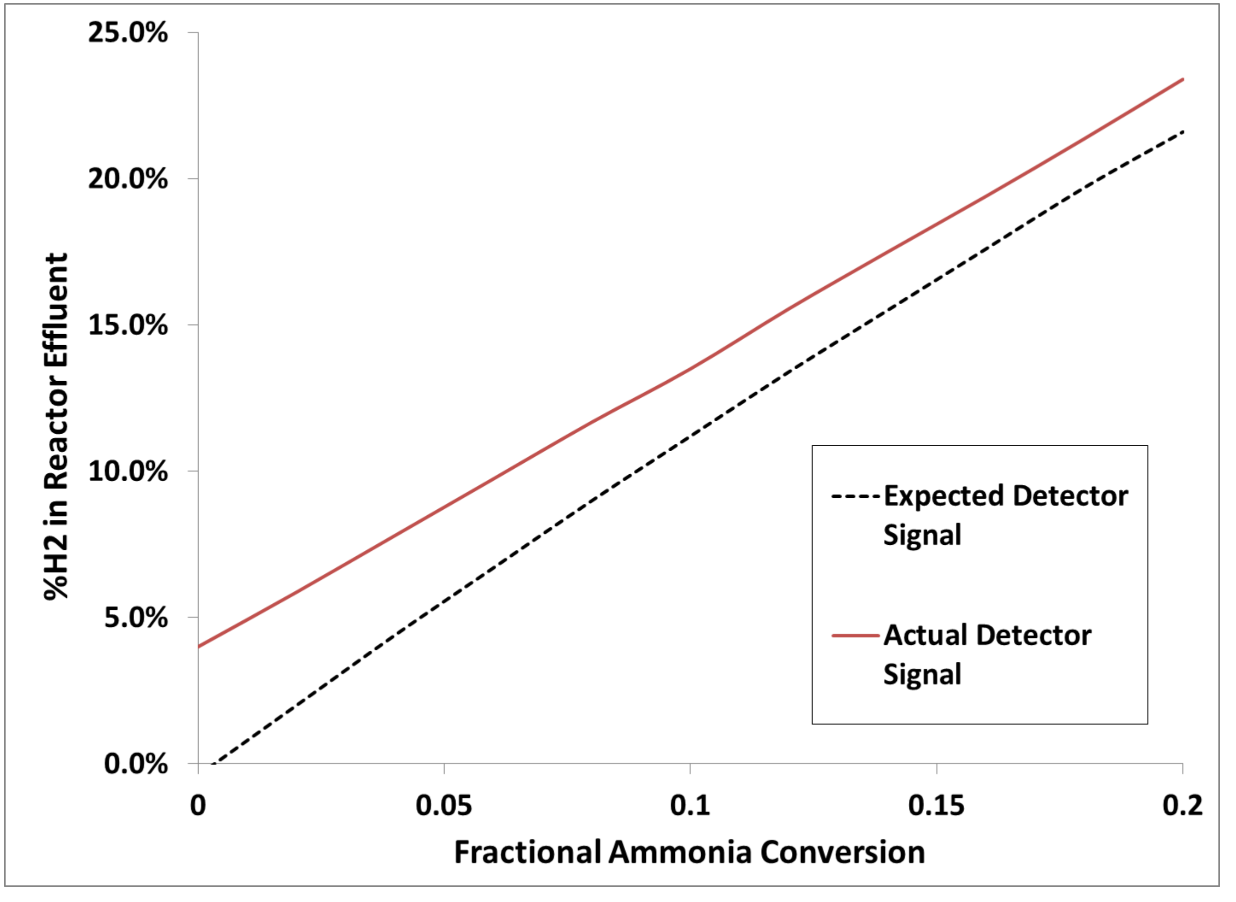


Dilution of N_2 with Argon

H_2 (sccm)	N_2 (sccm)	Ar (sccm)	Bypass Signal
20	180	0	10.0%
20	160	20	8.7%
20	140	40	7.5%
20	120	60	6.4%
20	100	80	5.3%
20	80	100	4.3%
20	60	120	3.3%
20	40	140	2.4%
20	20	160	1.5%
20	0	180	0.6%

Mixtures w/Small H_2 Variance

- **Good news: differential reactor conditions reduce nonlinearity with conversion of ammonia**
- **Condition-specific calibration & detector reading interpretation is still necessary**



(Unverified!) Results with Rate Data

H_2 (sccm)	N_2 (sccm)	NH_3 (sccm)	Ar (sccm)	Rate (mol NH_3/kg cat/h)
0	0	1000	0	3.24
0	0	1000	500	3.08
0	0	1000	1000	2.71
0	0	1000	1500	1.87
250	0	1000	750	1.05
500	0	1000	500	0.37
1000	0	1000	0	< 0.01
0	500	1000	500	2.69
0	750	1000	250	2.62
0	1000	1000	0	2.60

Rate Law: Surface Reaction Rate Limit

$$-r_A = \frac{kP_AP_B \ldots}{1 + K_AP_A + K_BP_B + \cdots}$$

- **Use this form to generate a qualitative rate law that follows kinetic data**
- **Rate of disappearance of reactant "A" will be increased by terms in numerator, decreased by denominator terms, and mixed effect when terms appear in both**
- **Look at partial pressures, or concentrations, of involved species alongside rate effects.**

Dependence on N_2

H_2 (sccm)	N_2 (sccm)	NH_3 (sccm)	Ar (sccm)	Rate (mol NH_3/kg cat/h)
0	0	1000	1000	2.71
0	500	1000	500	2.69
0	750	1000	250	2.62
0	1000	1000	0	2.60

- **What's going on here? Not much.**
- **Fairly constant rate of ammonia disappearance regardless of nitrogen presence.**
- **Note: Equivalent partial pressure of ammonia in each experimental run.**

Dependence on NH_3

H_2 (sccm)	N_2 (sccm)	NH_3 (sccm)	Ar (sccm)	Rate (mol NH_3/kg cat/h)
0	0	1000	0	3.24
0	0	1000	500	3.08
0	0	1000	1000	2.71
0	0	1000	1500	1.87

- **What's going on here? It's complicated.**
- **Rate of ammonia disappearance increases with initial ammonia concentration, then levels off.**
- **Note: Partial pressure of ammonia varies from 0.4 up to 1 by variation of argon content of mix.**

Dependence on H_2

H_2 (sccm)	N_2 (sccm)	NH_3 (sccm)	Ar (sccm)	Rate (mol NH_3/kg cat/h)
0	0	1000	1000	2.71
250	0	1000	750	1.05
500	0	1000	500	0.37
1000	0	1000	0	< 0.01

- What's going on here? H_2 has a big effect.
- Rate of ammonia disappearance drops quickly as initial hydrogen content rises.
- Note: Equivalent partial pressure of ammonia in each experimental run.

Rate Law & Parameter Estimation

- **Ammonia increases rate at low concentrations, less effect at higher concentrations**
- **Hydrogen strongly inhibits reaction rate**
- **Nitrogen has little (if any) effect**
- **Rate law that qualitatively agrees:**

$$-r_A = \frac{kP_A}{1 + K_A P_A + K_H P_H}$$

- **Rate law parameters (k, K_A, K_H) determined by linearization of rate law, performing nonlinear regression of rate data**

Reactor Design

- **Simple process, but tedious**
- **Using packed-bed reactor design equation in differential form…**
  - **Express all concentrations of gases as partial pressures**
  - **Recast the partial pressures as functions of ammonia conversion**
  - **Integrate the design equation**
- **Allows reactor design for desired conversion or reactor pressures (including integral reactors… those with larger conversions than the rate data here was allowed)**

Questions?

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