

# **N<sub>2</sub>O Abatement: Reaction Mechanisms and Methods for Improving Destruction Efficiency:**

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# Objectives

- Demonstrate value and applicability of kinetic modeling as applied to the specific problem of N<sub>2</sub>O abatement in semiconductor manufacturing processes.
- Evaluate value of kinetic modeling as a *general purpose tool* to allow fabs to estimate and identify *potential* emissions arising from thermal treatment of a range of process exhausts containing a range of various species.

# ESH Metrics and Impact

The primary ESH metric addressed through judicious application of kinetic modeling is

- Reduction in emission of ESH-problematic material to environment

Specifically, kinetic modeling is used for

- *Identification of potential* emission species prior to new process being implemented or new chemicals being employed.
- *Suggestions* for methods of pollutant emission abatement.

Kinetic modeling alone, without an accurate mixing model, is NOT used for

- *Quantitative* predictions of pollutant emissions from a *specific* device.
- *Quantitative* predictions of performance of a *specific* burner or thermal treatment system
- Integrating an accurate detailed kinetic model into an accurate CFD code to describe mixing is currently outside the capabilities of most simulation codes.
- Methods that approximate either the kinetics or the mixing fluid mechanics can provide additional insight into specific POU devices.

# What is kinetic modeling?

- Allows prediction of concentration behavior of many species ( $\sim 100$ 's) interacting with each other through many reactions ( $\sim 1000$ 's).
  - Particularly useful for estimation of trace species concentrations in combustion processes
- Requires an accurate kinetic mechanism –see following slide
- Requirements for a mechanism
  - Specified environment (e.g. heat loss, initial condition, initial temperature.
  - Specified idealized reactor configurations
    - Plug flow reactor (no back mixing)
    - Well stirred reactor (perfectly back-mixed)
    - Plug flow reactor with admixing of reactants along length
    - Combinations of the above

# What is required for a useful kinetic mechanism

1. List of stable and unstable species that are of interest.
  1. Usually requires some expert judgment.
2. Thermodynamic properties of these species – heats of formation, entropy of formation, specific heat as a function of temperature.
  1. Much is available in the literature
  2. Missing data can be calculated from first principles – molecular theory and some expert judgment.
  3. Required (needed) for thermodynamic consistency.
  4. Required for calculation of reverse reaction constants.
  5. Required for equilibria concentrations at a given T and P

# What is required for a useful kinetic mechanism (Continued)

- List of important (elementary) chemical reactions between these species
  - Usually requires some judgment, although it can be automatically generated.
- Chemical reaction rate coefficients for each reaction
  - Much is available in the literature for C, H, N, O, S, Cl, F, Hg.....  
Systems up to species involving 2 or 3 carbon atoms.
  - Can be estimated using molecular theory, similarity rules, and expert judgment
    - Up to C<sub>2</sub> hydrocarbon species.
    - Probably not yet possible for reactions involving complex molecules.

We shall comment on currently available mechanisms later

# Example: Using kinetic modeling to explore N<sub>2</sub>O abatement

- Issue: when and how does N<sub>2</sub>O entering a combustion chamber leave as NO or NO<sub>2</sub>?
- Approach
  - Use existing (and validated) kinetic mechanism: GRIMech 3.0
    - Optimized mechanism describing NO formation and destruction during the combustion of natural gas (CH<sub>4</sub>/Air)
    - Developed by the University of California at Berkeley [Smith, *et al.*, 2000, [http://www.me.berkeley.edu/gri\\_mech](http://www.me.berkeley.edu/gri_mech)]
    - 53 species, 325 reactions.
    - Input designed for CHEMKIN II software, NASA Thermodynamics Format
    - Validated by 77 comparisons with experimental data (“Targets”)
      - Ignition delay data from shock tubes
      - Flame speed data
      - Species profiles in flames and reactors

# Example: Using kinetic modeling to explore $\text{N}_2\text{O}$ abatement (continued)

- Approach (continued)
  - Explore behavior in isothermal plug flow reactor
    - 3 Temperatures - 1700K, 2000K, 2200K
    - 2 Stoichiometries – Fuel rich SR=0.7; Fuel lean SR=1.1
    - $\text{N}_2\text{O}$  injected a) with fuel b) into post flame
  - Extend to complex (mixed) reactor configurations
- Results showed
  - NO *was* formed from  $\text{N}_2\text{O}$
  - Conversion to NO depended on stoichiometry and temperature
  - Conversion to NO can be minimized through judicious mixing arrangements of fuel and air.

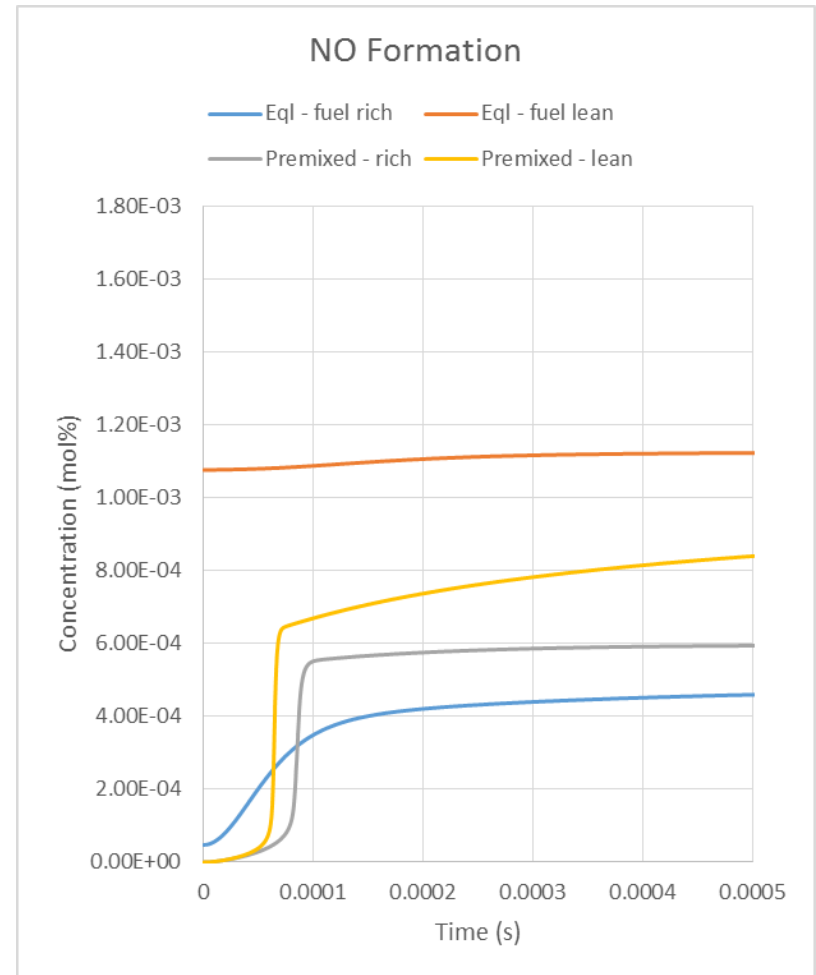


# N<sub>2</sub>O reactions in GRImech

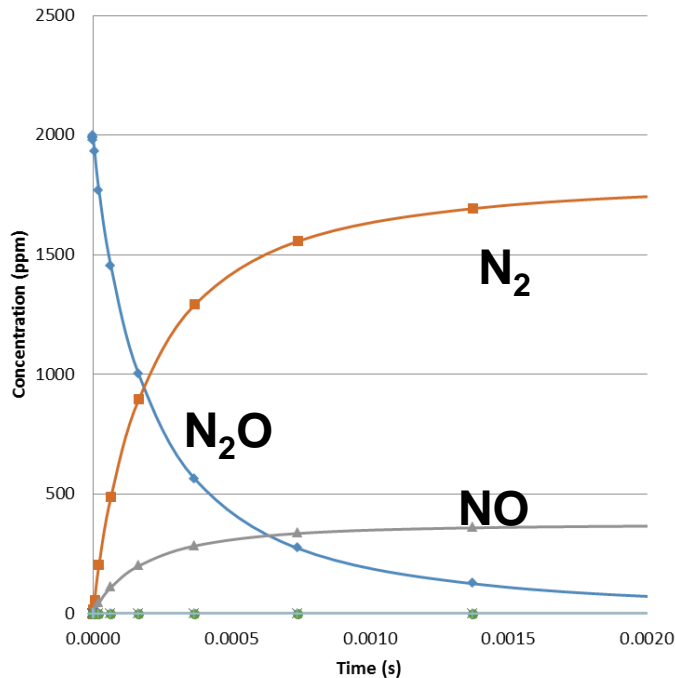
Reaction	A (cgs)	B (K)	E <sub>A</sub> (cal/mol K)	Source
N <sub>2</sub> O + OH ↔ N <sub>2</sub> + HO <sub>2</sub>	0.200E+13	0.000	10000.000	JAM 9/87
N <sub>2</sub> O + O ↔ 2 NO	0.100E+15	0.000	28200.000	PG
N <sub>2</sub> O + M ↔ N <sub>2</sub> + M + O	6.900E+23	-2.500	64760.000	Bowman 1991
N <sub>2</sub> O + H ↔ N <sub>2</sub> + OH	0.760E+14	0.000	15200.000	NH3 CST
N <sub>2</sub> O + O ↔ N <sub>2</sub> + O <sub>2</sub>	0.100E+15	0.000	28200.000	PG
CN + N <sub>2</sub> O ↔ NCO + NO	0.100E+14	0.000	0.000	JAM
NCO + NO ↔ N <sub>2</sub> O + CO	0.100E+14	0.000	-390.000	PEERY
NH + NO ↔ N <sub>2</sub> O + H	1.400E+14	0.000	12700.000	Bowman 1991
NNH + O ↔ N <sub>2</sub> O + H	0.100E+15	0.000	0.000	

# Kinetic Calculations for N<sub>2</sub>O to NO – NO<sub>x</sub> Formation

- NO<sub>x</sub> formation results show trends consistent with results found in the literature:
  - Fuel lean conditions → increased NO<sub>x</sub> production
  - Higher temperatures → increased NO<sub>x</sub> production
  - Premixing the N<sub>2</sub>O and fuel → increased NO<sub>x</sub> production in fuel lean conditions

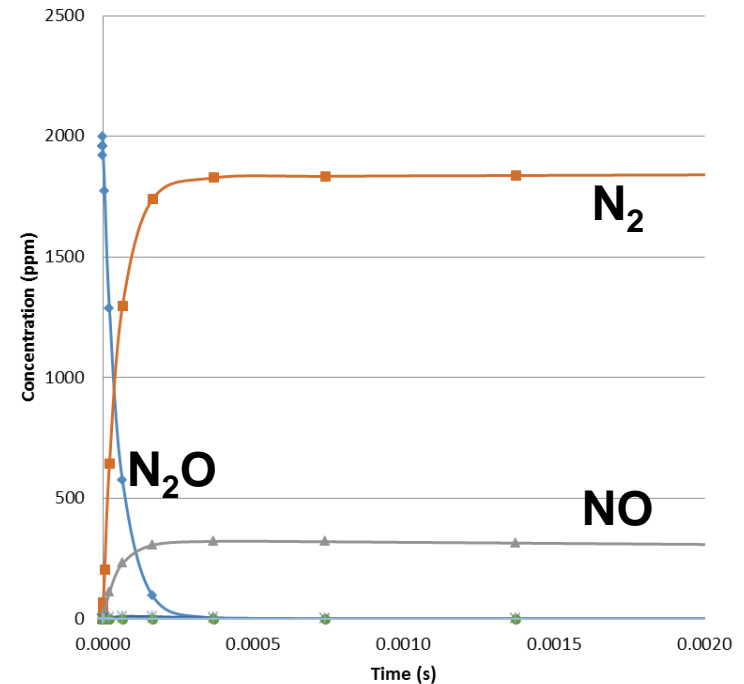


# N<sub>2</sub>O conversion in (premixed) CH<sub>4</sub>/O<sub>2</sub>/Ar flames (N<sub>2</sub> from N<sub>2</sub>O only – no air)



SR = 1.1, T = 1700K

>80% of the N<sub>2</sub>O reacted to become N<sub>2</sub>, remainder became NO<sub>x</sub>

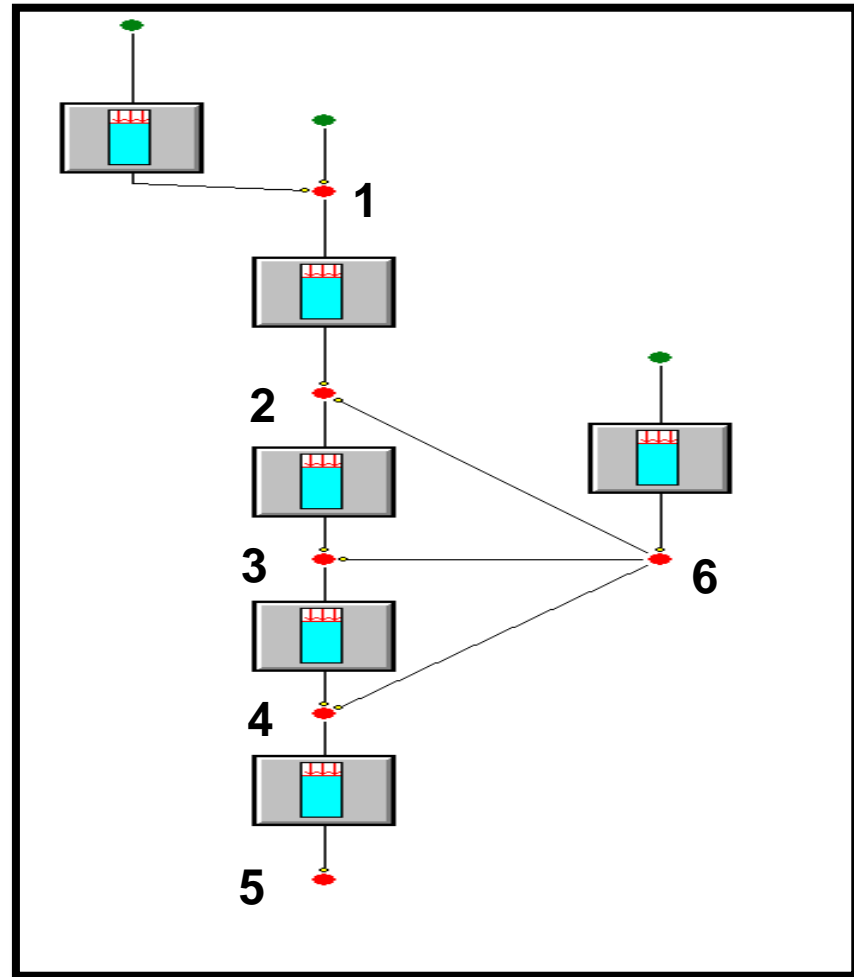


SR = 0.7, T = 1700K

>95% of the N<sub>2</sub>O reacted to become N<sub>2</sub>, remainder became NO<sub>x</sub>

# Modlink Process Model: Combinations of Reactor Types

- The model was constructed as a series of plug flow reactors (PFR) in REI's process flow software, Modlink.
- Grey boxes represent PFRs, colored nodes represent streams.
- Additional PFR at the top represents fuel/N<sub>2</sub>O mixing
- Composition can be obtained from any of the nodes and major species concentrations tabulated. Detailed time, temperature, and composition history can be obtained from each PFR.



# Example Node Compositions

Species	Node 1	Node 2	Node 3	Node 4	Node 5
CH <sub>4</sub>	0.397	0.032	0.000	0.000	0.000
CO	--	0.000	0.001	2 ppm	< 1 ppm
CO <sub>2</sub>	--	0.080	0.100	0.096	0.096
H <sub>2</sub>	--	0.000	0.001	0.000	0.000
H <sub>2</sub> O	--	0.161	0.200	0.193	0.193
N <sub>2</sub>	--	0.662	0.690	0.700	0.700
N <sub>2</sub> O	0.034	0.003	< 1 ppm	< 1 ppm	< 1 ppm
NO	--	7 ppm	106 ppm	74 ppm	74 ppm
O <sub>2</sub>	0.564	0.062	0.008	0.011	0.011
OH	--	0.000	0.000	0.000	0.000
SR	0.73	0.99	1.04	1.06	1.06

# Possible Future work – Two Approaches

1. Develop stand alone tools for fab personnel to explore potential issues by themselves
  - Software provided to fab.
  - Fab personnel must first specify which elements, or species are of interest
  - Individual kinetic mechanism sets (similar to GRI Mech 3.0) can then be established – one set for one application - and provided to customer.
    - Requires literature search or
    - Theoretical calculations for kinetic rate coefficients
      - Should be possible for simple hydrocarbons and F, Si, Hg and some other elements.
      - Example: current theoretical work (Bozzelli lab, 2014) has shown that poly-fluorinated compounds are more stable (i.e more difficult to react) than singly-fluorinated compounds.
2. Explore specific problems requested by fab personnel
  - Contractor rather than fab personnel conducts calculations
  - Transmits results, not the enabling software, to customer

BUT work is needed on mechanism development (see next slide)

# Current status of chemical kinetic mechanisms available for chemical kinetic modeling.

1. Mature and validated mechanisms (can be used by non experts)
  - a) C<sub>1</sub> hydrocarbon combustion with NO formation and destruction
  - b) NH<sub>3</sub>, HCN, N<sub>2</sub>O formation and destruction with C<sub>1</sub> hydrocarbon combustion.
  
2. Established mechanisms with limited validation (to be used at your own risk)
  - a) Expansion of 1a and 1b to include C<sub>2</sub> and (some) C<sub>3</sub> hydrocarbons.
  - b) Expansion to include chlorine and chlorinated compounds including chlorinated hydrocarbons (C<sub>1</sub> – C<sub>2</sub>).
  - c) Expansion to include reactions involving sulfur, and mercury
  
3. Work in progress (needs development before use, although prediction methods exist – molecular simulation etc.)
  - a) Expansion to include reactions involving fluorine and fluorinated hydrocarbons (incomplete mechanism with no validation might be available).
  - b) Expansion to include reactions involving silicon, arsenic and trace metals at high temperature (?).
  - c) Expansion to higher hydrocarbons, C<sub>4</sub> and above.

# Conclusion

Chemical kinetic modelling is a useful tool *today* to predict the fate of N<sub>2</sub>O in POU combustion systems, and has the potential, with additional work, to be a useful tool *tomorrow* to predict the fate of other compounds containing additional elements, such as chlorine, fluorine, silicon and arsenic.



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