Uncertainty Analysis of Reaction Rates in a Finite-Rate Gas-Surface Model

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AFOSR MURI Fundamental Processes in High Temp. Gas-Surface Interactions

5th Ablation Workshop (2/29/12)
Dr. Ioana Cozmuta (Co-PI on catalysis work)
Prof. Adri van Duin

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- Dr. Paolo Valentini
- Paul Norman
- Cory Sorensen
- Savio Poovathingal

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AFOSR MURI Fundamental Processes in High Temp. Gas-Surface Interactions
1) Finite-Rate Catalytic (FRC) wall boundary condition implemented in US3D CFD code. Uncertainty analysis performed.

2) Computational Chemistry simulations and the development of a FRC model for oxygen-silica catalysis under hypersonic conditions.

3) Preliminary results for oxidation of carbon-based surface ablators.
Finite-Rate Catalytic (FRC) Boundary Condition

- Finite-rate chemistry in the gas-phase and at the wall
- Modifies diffusion/chemistry in the boundary layer (coupled problem)
  - Ex. 2.7 km/s CO$_2$ flow ($T_w=500$ K)
Finite-Rate Model and Parameters

Example: Air-silica catalysis model

1. \( O + [s] \rightarrow O_s \) \hspace{1cm} \textit{Adsorption Reaction}
2. \( N + [s] \rightarrow N_s \) \hspace{1cm} \textit{Adsorption Reaction}
3. \( O + O_s \rightarrow O_2 + [s] \) \hspace{1cm} \textit{E – R Reaction}
4. \( N + N_s \rightarrow N_2 + [s] \) \hspace{1cm} \textit{E – R Reaction}
5. \( O + N_s \rightarrow NO + [s] \) \hspace{1cm} \textit{E – R Reaction}
6. \( N + O_s \rightarrow NO + [s] \) \hspace{1cm} \textit{E – R Reaction}
7. \( O_{sm} + O_s \rightarrow O_2 + 2[s] \) \hspace{1cm} \textit{L – H Reaction}
8. \( N_{sm} + N_s \rightarrow N_2 + 2[s] \) \hspace{1cm} \textit{L – H Reaction}
9. \( O_{sm} + N_s \rightarrow NO + 2[s] \) \hspace{1cm} \textit{L – H Reaction}
10. \( N_{sm} + O_s \rightarrow NO + 2[s] \) \hspace{1cm} \textit{L – H Reaction}
11. \( O_s \rightarrow O + [s] \) \hspace{1cm} \textit{Desorption Reaction}
12. \( N_s \rightarrow N + [s] \) \hspace{1cm} \textit{Desorption Reaction}
Finite-Rate Model and Parameters

Example: Air-silica catalysis model

\begin{align*}
(1) \quad O + [s] & \rightarrow O_s & \textit{Adsorption Reaction} \\
(2) \quad N + [s] & \rightarrow N_s & \textit{Adsorption Reaction} \\
(3) \quad O + O_s & \rightarrow O_2 + [s] & \textit{E – R Reaction} \\
(4) \quad N + N_s & \rightarrow N_2 + [s] & \textit{E – R Reaction} \\
(5) \quad O + N_s & \rightarrow NO + [s] & \textit{E – R Reaction} \\
(6) \quad N + O_s & \rightarrow NO + [s] & \textit{E – R Reaction} \\
(7) \quad O_{s,m} + O_s & \rightarrow O_2 + 2[s] & \textit{L – H Reaction} \\
(8) \quad N_{s,m} + N_s & \rightarrow N_2 + 2[s] & \textit{L – H Reaction} \\
(9) \quad O_{s,m} + N_s & \rightarrow NO + 2[s] & \textit{L – H Reaction} \\
(10) \quad N_{s,m} + O_s & \rightarrow NO + 2[s] & \textit{L – H Reaction} \\
(11) \quad O_s & \rightarrow O + [s] & \textit{Desorption Reaction} \\
(12) \quad N_s & \rightarrow N + [s] & \textit{Desorption Reaction}
\end{align*}

1 Halpern and Rosner, *Journal of the Chemical Society*, 1978
5 Marschall, MacLean, and Barnhardt, “A Finite Rate Surface Reaction Model for DPLR”, NASA 2011
Finite-Rate Model and Parameters

Example: Air-silica catalysis model

1. $O + [s] \rightarrow O_s$ \textit{Adsorption Reaction}
2. $N + [s] \rightarrow N_s$ \textit{Adsorption Reaction}
3. $O + O_s \rightarrow O_2 + [s]$ \textit{E – R Reaction}
4. $N + N_s \rightarrow N_2 + [s]$ \textit{E – R Reaction}
5. $O + N_s \rightarrow NO + [s]$ \textit{E – R Reaction}
6. $N + O_s \rightarrow NO + [s]$ \textit{E – R Reaction}
7. $O_{sm} + O_s \rightarrow O_2 + 2[s]$ \textit{L – H Reaction}
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$k_f = \left( \frac{\nu}{4\Phi_{total}} \right) \gamma_o T^\beta \exp\left( -\frac{E_{er}}{RT} \right)$

\textit{Eley – Rideal}

$\gamma_{er,O} = \gamma_{er,N} = 0.001$
$\beta_O = \beta_N = 0$
$E_{er,O} = E_{er,N} = 9000 J / mol$

$(\Phi_{total}) \text{ is set to } 7.5 \times 10^{-6} \text{ mol/m}^2$

Elementary atomistic quantities

5. Marschall, MacLean, and Barnhardt, “A Finite Rate Surface Reaction Model for DPLR”, NASA 2011
Excellent agreement despite completely different implementation procedures
- Ex. 6 km/s air flow over 1m radius cylinder ($T_w=2250$ K)

MacLean, Marschall, and Driver, AIAA Paper 2011-3784, Honolulu, HI.
Sorensen, Valentini, and Schwartzentruber, AIAA Paper 2011-3643, Honolulu, HI.
5th Ablation Workshop (2/29/12)
Natural result of FRC model is that $\gamma = f(\text{surface coverage}) \sim f(\text{pressure})$
- $\gamma$ increases by 4x between $\theta=0^\circ$ and $\theta=90^\circ$ despite constant $T_{wall}$

MacLean, Marschall, and Driver, AIAA Paper 2011-3784, Honolulu, HI.
Sorensen, Valentini, and Schwartzentruber, AIAA Paper 2011-3643, Honolulu, HI.

5th Ablation Workshop (2/29/12)
Specifying Consistent Backwards Rates

Certain backwards rates must be set consistent with the gas-phase thermodynamics:

Park 90 model for air:

\[
\begin{align*}
N_2 & \xrightleftharpoons[k_{eq}^{d1}]{k_{eq}^{d1}} N + N , \\
O_2 & \xrightleftharpoons[k_{eq}^{d2}]{k_{eq}^{d2}} O + O , \\
NO & \xrightleftharpoons[k_{eq}^{d3}]{k_{eq}^{d3}} N + O , \\
NO + O & \xrightleftharpoons[k_{eq}^{ex1}]{k_{eq}^{ex1}} N + O_2 , \\
NO + N & \xrightleftharpoons[k_{eq}^{ex2}]{k_{eq}^{ex2}} O + N_2 ,
\end{align*}
\]

\[
\begin{align*}
k_{eq}^{d1} &= \frac{[N]^2}{[N_2]} \\
k_{eq}^{d2} &= \frac{[O]^2}{[O_2]} \\
k_{eq}^{d3} &= \frac{[N][O]}{[NO]} \\
k_{eq}^{ex1} &= \frac{k_{eq}^{d3}}{k_{eq}^{d2}} \\
k_{eq}^{ex2} &= \frac{k_{eq}^{d3}}{k_{eq}^{d1}}
\end{align*}
\]

\[
\begin{align*}
&O + (s) \xleftrightharpoons[k_{b}^{1}]{k_{f}^{1}} O(s) \\
&O + O(s) \xrightleftharpoons[k_{f}^{3}]{k_{b}^{3}} O_2 + (s)
\end{align*}
\]

\[
\begin{align*}
k_{eq}^{1} &= \frac{k_{f}^{1}}{k_{b}^{1}} = \frac{[O(s)]}{[O][s]} \\
k_{eq}^{3} &= \frac{k_{f}^{3}}{k_{b}^{3}} = \frac{[O_2][s]}{[O][O(s)]}
\end{align*}
\]

\[
k_{b}^{3} = k_{f}^{3} k_{eq}^{1} k_{eq}^{d2}
\]

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Uncertainty Analysis (applied to rates)

- Off-nominal rate sets determined by sampling each rate from a log-normal distribution centered at nominal value (~1 order of magnitude variation)
- 2000 US3D simulations (different rate sets) per wall temperature
- Chemical heat flux variation directly proportional to rate uncertainty (no unexpected non-linear coupling)
- However, magnitude of $q_c$ variation diminishes as $T_w$ increases as recombination becomes diffusion-limited
• Linear regression is used to determine the reactions’ correlation to chemical heat flux

• E-R recombination is highly correlated to the heat flux at 1750K while reaction L-H oxygen shows no trend

• Adsorption of oxygen and L-H oxygen are both correlated to the heat flux at 2750K
- E-R is most correlated to heat flux at temperatures below 2000K
- Above 2000K, L-H becomes most correlated
- Around 2750K, adsorption of oxygen becomes most correlated
- All reactions which are most correlated involve oxygen only
Conductive, Chemical, and Total Heat Flux

- Total heat flux is the sum of trans-rot and vibrational conductive terms plus chemical contribution

- An increase in chemical heat flux (due to rate uncertainty) does not lead to the same increase in total heat flux

- Due to an altered boundary layer state (more diatomic molecules), which lowers the conduction heat flux
  - Note: We assume full energy accommodation

\[
q_w = \left( \kappa \frac{\partial T}{\partial n} \right)_w + \left( \kappa_v \frac{\partial T_v}{\partial n} \right)_w + \rho_w \sum_i D_i h_i \left( \frac{\partial c_i}{\partial n} \right)
\]

\[
\Delta q_{conductive} = -(1 - \text{slope}) \Delta q_{chem}
\]
Conclusions Regarding Finite-Rate Model

1) Backwards surface reaction rates should be determined in a consistent manner with adsorption/desorption/gas-phase equilibrium constants.

2) $\gamma_O = \text{fcn}(T_w, \text{and } \textit{coverage})$, possibly parameterized by partial pressure of oxygen.

3) Uncertainty in chemical heat flux is directly linked to the dominant mechanism at that wall temperature and its associated uncertainty.

4) Uncertainty in chemical heat flux decreases (for same rate variation) as wall temperature increases due to diffusion-limited chemistry.

5) An increase in chemical heat flux due to rate uncertainty leads to only a fraction of that increase in total heat flux (reactivity alters the boundary layer and therefore the conductive heat flux).

In general, uncertainty in heat flux is ‘well-behaved’ for a given set of mechanisms. The problem lies in omitting mechanisms and/or applying in diffusion limited situations (heat flux insensitive to rates).
Silica is a significant component in both ablative and non-ablative thermal protection systems because of its good insulating properties.

Many TPS materials, including Space Shuttle Tiles, SiC, and Ultra High Temperature Ceramics (UHTCs) form layers of primarily SiO$_2$ (stoichiometric) when exposed to atomic oxygen[1-3].

There is little experimental evidence as to the structure of a silica surface exposed to high T due to the difficulties of in situ measurements.

**Goals:**

1) What are the in-situ surface structures for silica surfaces?
2) What are the dominant catalytic mechanisms for dissociated oxygen interacting with such surfaces? (for example, we observe no high-T LH reactions…)
3) What are the associated rates?

Prior Oxygen-Silica Research

• Assume that oxide layers formed on SiC are $\beta$-Cristobalite ($\text{SiO}_2$ polymorph)

• Furthermore, cleave this bulk material to form a surface and place adsorbed atoms arbitrarily on surface

(b) Oxygen Terminated (001) $\beta$-Cristobalite Surface (side). Topmost layer of oxygen highlighted in blue.
Prior Oxygen-Silica Research

- Assume that oxide layers formed on SiC are $\beta$-Cristobalite ($\text{SiO}_2$ polymorph)

- Furthermore, cleave this bulk material to form a surface and place adsorbed atoms arbitrarily on surface

- Such surfaces are highly unphysical (high energy dangling bonds)

- Stable (non-catalytic) reconstructions observed in our MD simulations and experimentally
Surface Coverage on High-T Amorphous SiO$_2$

![Visualization of annealed amorphous SiO2 after exposure to dissociated oxygen at high pressure. Defects are highlighted. Blue = (≡Si - O·). Green = (≡Si - O$_2$).](image)

- There is experimental and computational evidence for the existence of the ≡Si-O defect [1-3], and the stable/non-catalytic (Si-O-Si) reconstructions [4]


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Surface Coverage on High-T Amorphous SiO$_2$

- There is experimental and computational evidence for the existence of the $\equiv$Si-O defect [1-3], and the stable/non-catalytic (Si-O-Si) reconstructions [4]

Individual Collision-Defect Simulations

• Isolate each defect and compute average **activation energies** and **steric factors** for reactions due to gas-phase collisions

• $T_{\text{wall}} = T_{\text{gas}}$ (Maxwell-Boltzmann velocities at random angle)
Finite-Rate Model via Computational Chemistry

\begin{align*}
O + E_c & \rightleftharpoons O_c & \text{Atomic Oxygen Adsorption} & (1) \\
O + O_c & \rightleftharpoons O_2 + E_c & \text{Eley Rideal Recombination} & (2) \\
O + O_c & \rightleftharpoons O_2 & \text{Molecular Oxygen Formation} & (3) \\
O + O_2c & \rightleftharpoons O_2 + O_c & \text{Molecular Oxygen Replacement} & (4) \\
O_2c & \rightleftharpoons O_2 + E_c & \text{Molecular Oxygen Desorption} & (5) \\
O + E_f & \rightleftharpoons O_f & \text{Atomic Oxygen Physisorption} & (6) \\
O_f + E_c & \rightleftharpoons E_f + O_c & \text{Physisorbed to Chemisorbed} & (7) \\
O_f + O_c & \rightleftharpoons E_f + E_c + O_2 & \text{Langmuir Hinshelwood Recombination} & (8)
\end{align*}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Rate & Rate Equation & Functional Form & $A$ & $E_a$ (eV) \\
\hline
$r_1^f$ & $k_1^f[O][E_s]$ & $(\bar{c}_O/4) \times (2\pi r_s^2) \times (A_1^f e^{-E_1^f/(k_B T)})$ & 1.0 & 0.0 \\
$r_2^f$ & $k_1^f[O]$ & $\Lambda_1^f e^{-E_1^f/(k_B T)}$ & $10^{-15}$ (s$^{-1}$) & 4.25 \\
$r_3^f$ & $k_2^f[O][O_s]$ & $(\bar{c}_O/4) \times (2\pi r_s^2) \times (A_2^f e^{-E_2^f/(k_B T)})$ & 0.169 & 0.401 \\
$r_4^f$ & $k_2^f[O_2][E_s]$ & $(\bar{c}_O/4) \times (2\pi r_s^2) \times (A_2^f e^{-E_2^f/(k_B T)})$ & 0.663 & 1.27 \\
$r_5^f$ & $k_3^f[O][O_s]$ & $(\bar{c}_O/4) \times (2\pi r_s^2) \times (A_3^f e^{-E_3^f/(k_B T)})$ & 1.13 & 0.253 \\
$r_6^f$ & $k_3^f[O_2][O_s]$ & $\Lambda_3^f e^{-E_3^f/(k_B T)}$ & $10^{-15}$ (s$^{-1}$) & 4.14 \\
$r_7^f$ & $k_4^f[O][O_2s]$ & $(\bar{c}_O/4) \times (2\pi r_s^2) \times (A_4^f e^{-E_4^f/(k_B T)})$ & 0.172 & 0.303 \\
$r_8^f$ & $k_4^f[O_2][O_s]$ & $(\bar{c}_O/4) \times (2\pi r_s^2) \times (A_4^f e^{-E_4^f/(k_B T)})$ & 0.716 & 1.18 \\
$r_9^f$ & $k_5^f[O_2]$ & $A_5^f e^{-E_5^f/(k_B T)}$ & $1.20 \times 10^{14}$ (s$^{-1}$) & 2.71 \\
$r_10^f$ & $k_5^f[O_2][E_s]$ & $(\bar{c}_O/4) \times (2\pi r_s^2) \times (A_5^f e^{-E_5^f/(k_B T)})$ & 1.0 & 0.0 \\
$r_11^f$ & $k_6^f[O][E_f]$ & $(\bar{c}_O/4) \times (2\pi r_s^2) \times (A_6^f e^{-E_6^f/(k_B T)})$ & 1.0 & 0.0 \\
$r_12^f$ & $k_7^f[O][O_f][E_c]$ & $(2\pi r_s A_D) \times (\bar{c}_O/4) \times P_{rc} \times (A_7^f e^{-E_7^f/(k_B T)})$ & 1.0 & 0.130 \\
$r_13^f$ & $k_8^f[O][O_f][O_c]$ & $(2\pi r_s A_D) \times (\bar{c}_O/4) \times P_{rc} \times (A_8^f e^{-E_8^f/(k_B T)})$ & 1.0 & 0.2 \\
\hline
\end{tabular}
\caption{Rate Equations and Functional Forms}
\end{table}
Finite-Rate Model vs. Experiment

- Exponential trend of $\gamma(T)$ in general agreement with experiment
  - a direct result of dominant defects/mechanisms/activation energies

- Magnitude of $\gamma$ influenced by surface roughness (currently fit to experiment)

Waiting for final results based on new DFT data specific to these reactions.

5th Ablation Workshop (2/29/12)
Carbon-based Surface Ablators

- Molecular beam experiments on Highly-Oriented Pyrolytic Graphite

Exp: Prof. Minton – Montana State

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