A Surface Kinetic Model for Steady-State Surface Coverage of Nitrogen and Oxygen Atoms

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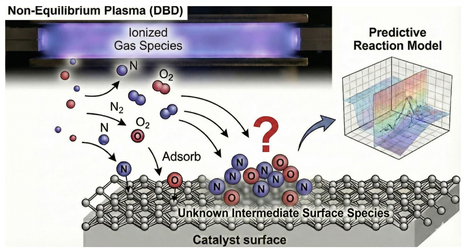
Motivation: Predictive Models in Plasma Catalysis



- Plasma catalysis provides emerging opportunities for electrified manufacturing [1].
- A key chemical pathway is the adsorption of atoms such as N and O on surfaces [2].
- The design of plasma-catalysis systems has largely relied on empirical trial-and-error approaches, highlighting the need for predictive reaction models.
- Purely empirical fits capture pressure dependence but lack mechanistic interpretability regarding surface coverage and reaction pathways.

Governing Equation & Reaction Kinetics

$$n\frac{d\theta_A}{dt} = \dot{\omega}_{a,A} - \dot{\omega}_{er,AA} - 2\dot{\omega}_{LH,AA} - \dot{\omega}_{Des,A} = 0 \quad \text{(A: refers to N and O atoms)}$$

Chemisorption $A+[s] \rightarrow A_s$ Langmuir-Hinshelwood Mechanism $A_{s,m} + A_s \rightarrow A_2 + 2[s]$

$$\dot{\omega}_{a,A} = s_A \theta_f \dot{n}_A \qquad \dot{\omega}_{LH,AA} = P_{ster,lh}\sqrt{\frac{kT}{2\pi m}}\frac{Z_{A(g)}}{Z_v^{Diff,A}}\tilde{n}_0\theta_A^2 e^{-\frac{Q_{lh,AA}}{kT}}$$

Eley-Rideal Mechanism $A + A_s \rightarrow A_2 + [s]$ Desorption $A_s \rightarrow A + [s]$

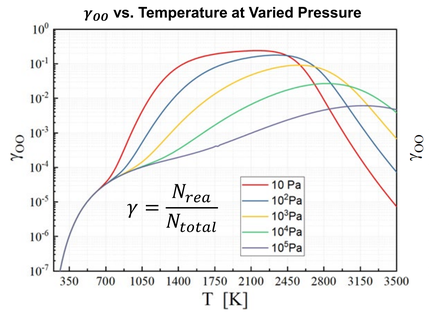
$$\dot{\omega}_{er,AA} = P_{Ster,er,AA}e^{-\frac{Q_{er,AA}}{kT}}\theta_A\dot{n}_A \qquad \dot{\omega}_{Des,A} = P_{Ster,Des,A}s_{Ad}\frac{1}{1-\theta_A}\frac{kT}{h}\frac{1}{Z_{A(a)}(T)}\frac{\tilde{n}_0}{N_A}e^{-\frac{D_{Des}}{kT}}\theta_A$$

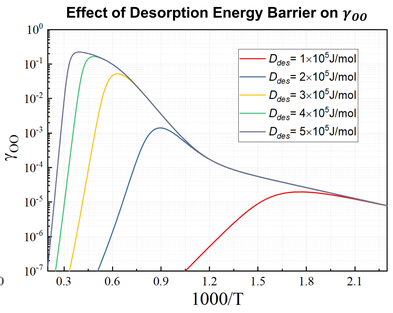
Category	Symbol	Meaning
Surface coverage	θ_A [-]	Fractional surface coverage of species A
Reaction rates	$\dot{\omega}_{a,A}$, $\dot{\omega}_{LH,AA}$, $\dot{\omega}_{er,AA}$, $\dot{\omega}_{Des,A}$ $[atoms/m^3 \cdot s]$	Rates of adsorption(chemisorption) Langmuir–Hinshelwood, Eley–Rideal Desorption reactions
Sticking / reaction coefficients	s_A, $P_{\mathrm{Ster},X}$, γ^*_{AA} [-]	Sticking probability, Steric probability factor Recombination probability
Energies	$Q_{LH,AA}$, $Q_{er,AA}$, D_{Des} $[J/atoms]$	Activation or desorption energies for the corresponding reactions
Constants / parameters	$k\left[\frac{m^2 \cdot kg}{s^2 \cdot K}\right]$, $h[J \cdot s]$, $N_A[mol^{-1}]$, $\tilde{n}_0[m^{-2}]$	Boltzmann constant, Planck constant Avogadro number, Total site density
Partition Function	$Z_{A(g)}$, $Z_{A(a)}$ [-]	(g) gas phase,(a) adsorption

Project Objectives

- Develop an elementary surface-reaction model incorporating nitrogen and oxygen ground state and electronically excited states (e.g., $O(^1D), O(^1S)$).
- Study the pressure/temperature dependence of surface reactions.
- Validated against experimental measurement [5], semi-classical collisional model [6] and Quasi-Classical Trajectory (QCT) calculation [7].

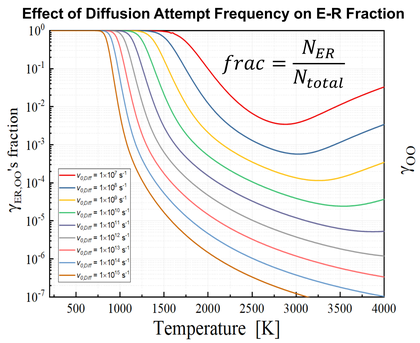
Parametric Studies

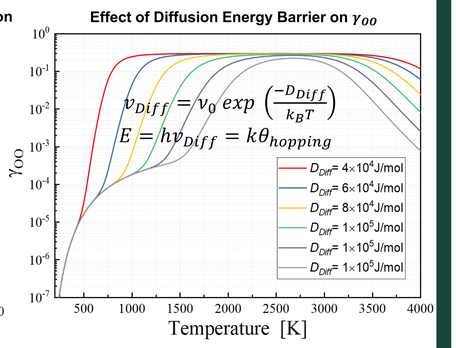




•(Left) At high temperatures, desorption dominates, causing the γ_{OO} to drop sharply.

•(Right) Decreasing the desorption energy shifts the γ_{OO} peak to lower temperatures.

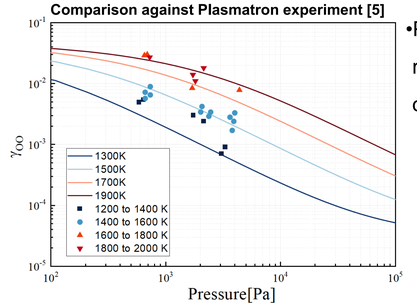




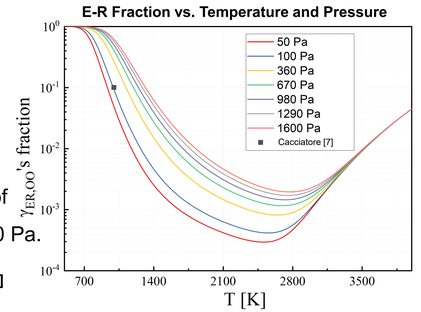
•(Left) **Effect of Frequency**: At low attempt frequency, as temperature rises, the E-R fraction increases because the L-H rate is limited (before desorption dominates).

•(Right) **Effect of Diffusion Barriers:** Lower diffusion barriers enhance adatom surface mobility, shifting the L–H reaction onset to lower temperatures.

Validation against Literature Data



•Plasmatron experiments [5] demonstrate reasonable agreement with model predictions over varied pressures.



•Cacciatore *et al.* [8] report an E–R fraction of 0.1 at 1000 K, matching model output at 100 Pa.

- The model matches collisional (DFT/X3LYP) [6] and QCT [7] results at high temperatures,
- Differences at low temperatures reflect changes in reaction mechanisms and intermediate pathways

Conclusions

- A 0-D model is developed to characterize the surface coverage of N and O atoms.
- Ongoing efforts including modeling H and C atom surface coverage, and integrating with 0-D gas phase models [3] and multi-dimensional fluid models [4].
- The goal is to develop a first-principles-guided predictive model for plasma catalysis modeling.

Reference

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