Investigations of Surface-Catalyzed Recombination Reactions in the Mars Atmosphere

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In the design of a thermal protection system (TPS) for atmospheric reentry, aerothermodynamic heating presents the biggest challenge owing to large uncertainties in chemical reactions taking place at the surface. Supercatalycity, the assumption that all dissociated species recombine to the freestream composition, is the most conservative approach and leads to an increased TPS mass. Computational and experimental work is underway to better characterize the mechanism of surface catalycity in the plasma boundary layer with the goal of designing more efficient means of thermal protection, specifically for entry into the Mars atmosphere. Measurements of recombining species above a catalytic surface are performed using laser diagnostics and a new 30 kW inductively coupled plasma torch facility.

I. Introduction

Aerothermodynamic heating poses the largest challenge in the design of a thermal protection system for atmospheric reentry. Surface catalyzed recombination reactions must be considered in any heat flux analysis of a candidate TPS due to the significant chemical energy produced during recombination.¹ There are four primary simplifying assumptions made when performing calculations. These are (in order of predicted heat flux level): a) supercatalytic, in which it is assumed all dissociated species recombine to their freestream values; b) fully-catalytic, in which surface catalytic reactions occur; c) partially catalytic, used when catalytic properties of the surface material are known; and d) non-catalytic, in which it is assumed no surface recombination reactions occur. Depending on the gas composition and reentry velocity, the difference in predicted heat flux between non-catalytic and fully catalytic can be a factor of two. Figure 1 shows a comparison of computed heat flux values for different surface recombination models. The extreme difference in heating between non-catalytic and supercatalytic is readily apparent.

Owing to high interest in scientific missions to Mars, surface catalysis in the Mars atmosphere is a topic that must be better understood. The Martian atmosphere contains approximately 97% CO₂ and 3% N₂ and trace amounts of other species (Ar, O₂, et cetera). During entry into this atmosphere, CO₂ molecules readily dissociate into CO and O when a shockwave is encountered. The major species of interest are CO, O, C, N, and NO. The Mitcheltree model² considers the following reactions:

\[ O + (s) \rightarrow O_s; \ CO + O_s \rightarrow CO_2; \]
\[ CO + (s) \rightarrow CO_s; \ O + CO_s \rightarrow CO_2; \]

where (s) represents an adsorption site. These reactions assume an Eley-Rideal (ER) recombination mechanism. Because it produces the dominant freestream molecule, it closely resembles the supercatalytic assumption. This model ignores the competing reaction:

\[ O + O \rightarrow O_2 \]

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It has been found\textsuperscript{1} that the oxygen recombination occurs more readily than carbon dioxide recombination and as a result, it is likely that the supercatalytic assumption is overly conservative.

Surface catalyzed reactions in the Mars atmosphere are being studied using laser spectroscopic techniques in a new 30 kW Inductively Coupled Plasma (ICP) Torch Facility. Despite its normally subsonic operation, an ICP facility has two main benefits over arc-jet facilities: 1) plasma is generated using radio-frequency coupling, without electrodes, and therefore is free of contaminants; and 2) the composition of the test gas can be varied quickly and accurately. Scaling of the stagnation point heat flux between an ICP facility arc-jets is understood, as both facilities must match the same set of flight parameters: total enthalpy, post-shock pressure, and velocity gradient. In principle, the boundary layer of such a facility is very similar to that found in a flight condition at the stagnation point.

The goal of the current work is to characterize surface catalyzed reactions in the Martian atmosphere by measuring the major species in the boundary layer, including the arriving species flux rates. It is expected that the results of these experiments will show which reactions are most relevant for a Mars entry flight condition and provide a basis from which to create more accurate surface recombination models for CO\textsubscript{2} and N\textsubscript{2} plasmas.

II. Computational approach

Two numerical codes are being used to complement the experimental investigation in the ICP facility. These codes were developed at the von Karman Institute and are the NEBOULA (Non-Equilibrium Boundary LAyer) code\textsuperscript{4} and MUTATION (MUlti-component Transport And Thermodynamic properties/chemistry properties for IONized gases) library.\textsuperscript{5} NEBOULA is used to predict the boundary layer properties for a given set of freestream and surface boundary conditions for any gas mixture. NEBOULA relies on the PEGASE (PErfect GAS Equation) library to compute high temperature gas mixture thermodynamic and transport properties. MUTATION is used to calculate equilibrium mixtures to aid in defining freestream conditions in flight and for the ICP torch.

III. Facility description

The plasma diagnostics lab at the University of Vermont is built around a 30 kilowatt ICP Torch. The torch itself is comprised of three main systems: the radio frequency (RF) power supply, the injector block...
assembly, and the test chamber. The power supply can generate 30 kilowatts at frequencies from 2.5 to 5 megahertz. The plasma is generated within a quartz tube connected to the injector block. Quartz is used because it is regarded as being a non-reacting material and thus will not contaminate the flow. Surrounding the quartz tube is a water-cooled copper coil through which current is run from the power supply, inducing an RF magnetic field within the quartz tube and thus creating the plasma. A table of the plasma torch parameters is seen in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inductive heater power [kW]</td>
<td>30</td>
</tr>
<tr>
<td>Enthalpy range [MJ kg⁻¹]</td>
<td>10 - 40 (for air)</td>
</tr>
<tr>
<td>Mach range</td>
<td>&lt; 0.3 to 1</td>
</tr>
<tr>
<td>( q_{stag} ), [W cm⁻¹]</td>
<td>10-290</td>
</tr>
<tr>
<td>( P_{stag} ), [atm]</td>
<td>0.05 - 1.0</td>
</tr>
<tr>
<td>Plasma jet diameter [mm]</td>
<td>30</td>
</tr>
<tr>
<td>Test gas</td>
<td>air, Ar, N₂, CO₂, variable mixture fractions</td>
</tr>
</tbody>
</table>

Table 1. Plasma torch parameters

Sample surface temperature is measured with a two-color pyrometer. A two-color pyrometer is ideal for conditions in which a surface may be partially obscured or when subject to a changing atmosphere, both of which apply to the conditions inside the test chamber. Heat flux measurements are taken with a slug calorimeter before the sample is placed in the plasma flow. Temperature measurements for the calorimeter are obtained from a thermocouple attached to the back of the copper slug. Total pressure measurements will be obtained from a pitot probe in the stagnation point location in the plasma flow. Test chamber static pressure measurements are obtained from a port on the chamber. Table 2 shows a list of the current capabilities of the ICP facility. Figure 2 shows a picture of the test chamber and the power supply.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum run time [min]</td>
<td>8</td>
</tr>
<tr>
<td>Maximum recorded heat flux [W cm⁻²]</td>
<td>81</td>
</tr>
<tr>
<td>Maximum operating pressure [torr]</td>
<td>180</td>
</tr>
</tbody>
</table>

Table 2. Current ICP capabilities

Figure 2. Picture of the test chamber and power supply

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Figure 3 shows a schematic representation of the plasma diagnostics facility and the laser system. The dye laser system will operate near 678 nm and frequency tripling produces tunable laser energy from 226 nm to 230 nm. UV photons for two-photon laser induced fluorescence (LIF) come from a Nd:YAG pumped dye laser system with frequency doubling and tripling. A microwave discharge flow reactor is used to calibrate measurements taken in the ICP. This is done by creating well-characterized populations of the target species in the plasma. Simultaneous excitation of the transition in the ICP and the flow reactor allow for calculation of the concentration of the target species in the ICP. In addition, diode laser absorption spectroscopy will be used to attempt to quantify any CO$_2$ production from surface recombination. A spectrometer is used to quantify emission in the boundary layer of test samples. Figure 4 shows the excitation wavelengths for CO and O. The excitation for O atoms occurs at 226 nm and the excitation for CO occurs at 230 nm. These similar excitations are beneficial for two-photon LIF techniques.

IV. Current and future work

NEBOULA and MUTATION are being used to predict properties for various gas mixtures used in the ICP. Since at present certain gases require a component of argon to run in the ICP in a stable configuration, these custom mixtures must be investigated accordingly.
Figure 5 shows two-photon LIF measurements from the ICP torch with measurements from the flow reactor. The gas mixture used for these measurements was 60% CO$_2$ and 40% Ar. It shows a fit temperature of 4497 K.

![Graph showing LIF measurements](image)

Figure 5. Measured signal from two-photon LIF of O atoms in ICP freestream

The ICP facility is fully functional and surface catalycity measurements are due to begin soon. Measurements will be taken on known catalytic (copper, platinum) and non-catalytic (quartz) samples in order to determine the concentrations of species in the stagnation point boundary layer. It is expected that these measurements will provide data to reinforce the concept that the supercatalytic assumption is overly conservative and that future physical models should account for a partially catalytic wall.

The full paper will include the boundary layer measurements over different surfaces and analysis of these measurements.

References


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