On the Development of a New Nonequilibrium Chemistry Model for Mars Entry

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Motivation

- NASA has been embarked on a program of scientific exploration of Mars by landing increasingly larger and heavier payloads
  - Prediction of thermal load used to determine TPS requirements
  - Testing in ground facilities and CFD simulations play critical roles

Nonequilibrium chemistry model currently in use is 20+ years old and based on mostly 35+ year old experiments

We are critically examining this “legacy” model and developing a new model based on computational chemistry and physics

Our objective is to reduce the uncertainty in predictions of thermal loads for Mars entry
• Legacy nonequilibrium chemistry model
• Computational approach for developing a new model
• Rate Coefficients
  - Chemical reactions for Mars entry
  - Uncertainty Quantification
  - CO dissociation
• Comparison with other models
  - Convective heating
  - Radiative Flux
• Next steps in developing the nonequilibrium chemistry model
• Conclusions
Legacy Mars Chemistry Model

• Nonequilibrium between translational and internal energy modes of the flowfield species in the bow shock layer
  - After shock wave gas is compressed and heated
  - Two temperatures (T = T_r and T_v = T_{el-st})
  - First order relaxation equation describes evolution of T_v from the shock to thermal equilibrium (T_v = T); governed by relaxation time τ_v
  - Dissociation reactions modeled by Arrhenius rate expression using an average temperature T_{av} = (T \cdot T_v)^{1/2}
  - Rate coefficient parameters originally taken from 1960’s-70’s shock tube experiments, but subjected to empirical adjustment

• Developed by Chul Park at NASA Ames 1986-1992 (Park et al, JTHT 8, 9-23 (1994))

• Recent modification of parameters by Johnston and Brandis (JSQRT 149, 303-317 (2014))
Mars Entry: What Collisional Processes are Important?

- Mars atmosphere is ~96% CO$_2$, ~2% N$_2$ ~2% Ar
- Dissociation
  - CO$_2$ (5eV) very fast and nearly complete
  - CO (11 eV) slow, rate determining process
- Heterogeneous exchange reactions provide lower energy (i.e. faster) routes for CO$_2$ and CO dissociation
  - CO$_2$ + O → CO + O$_2$
  - CO + O → C + O$_2$
  - CO + N → O + CN
  - CO + C → O + C$_2$

For Mars entry at 6-8 km/s, the rate of CO dissociation is critical because CO 4$^\text{th}$ positive emission is the dominant source of radiative heating
New Paradigm for a Nonequilibrium Chemistry Model

• **Accurate** quantum mechanics calculations to quantify interaction energy between atoms and molecules
  - Potential Energy Surface (PES) obtained from solution of Schrödinger equation
  - Repeated for many geometric arrangements of the atoms (for \( n \) atoms there are \( 3n-6 \) degrees of freedom)
  - Goal is \( \leq \pm 5 \) kJ/mol relative accuracy (~0.05 eV, ~400 cm\(^{-1}\))

• Classical mechanics simulations of heavy particle collisions to compute collision cross sections and rate coefficients
  - Compute trajectories of many individual collisions (Quasi-Classical Trajectory or QCT calculation)
  - Monte Carlo sampling used to reproduce random or thermal collisional distributions

*This strategy should yield rate coefficients accurate to \( \pm 20\% \)*

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Experiment</th>
<th>PES</th>
<th>QCT rate coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>D1</strong> CO₂ + M → CO + O + M M = CO₂, N₂, CO, O</td>
<td>Shocktube expts 1968-74 &amp; 1984</td>
<td></td>
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<tr>
<td>※D4 O₂ + M → O + O + M M = N₂, CO, O</td>
<td>Expts 1960s, 84 Hanson 2016</td>
<td>Varandas 1988</td>
<td>Andrienko 2016</td>
</tr>
<tr>
<td>E1 CO₂ + O → CO + O₂</td>
<td>Ibragimova 1991</td>
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<tr>
<td>※E4 NO + O → O₂ + N</td>
<td>Fontijn 1998</td>
<td>Sayos 2002</td>
<td>Sayos 2003</td>
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<tr>
<td>E5 CO + N → CN + O</td>
<td>Nyman 2000-2008</td>
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<tr>
<td>E6 CO + N → NO + C</td>
<td>Nyman 2000-2008</td>
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<tr>
<td>E7 CN + O → NO + C</td>
<td>Roth 1990</td>
<td>Nyman 2000-2008</td>
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<tr>
<td>E8 CO + C → C₂ + O</td>
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Uncertainty Quantification (UQ)

- UQ used to identify critical reactions
  - Monte Carlo sensitivity analysis
  - 96% CO₂/4% N₂ (free stream at 0.25 torr and 300 K)
  - 1-d shock at 7.75 km/s
  - Random sampling of rate coefficient and vibrational relaxation parameters
  - Two criteria considered: sensitivity to CO 4th positive radiative intensity and sensitivity to attaining chemical equilibrium ($T/T_{eq} = 1.05$)
- Repeated many times for statistical analysis
- Key reactions:

<table>
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<tr>
<th>Reaction</th>
<th>Sensitivity to Radiative Flux</th>
<th>Sensitivity to Equilibration Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + O → C + O + O</td>
<td>55%</td>
<td>48%</td>
</tr>
<tr>
<td>CO + CO → C + O + CO</td>
<td>25%</td>
<td>10%</td>
</tr>
<tr>
<td>CN + O → C + NO</td>
<td>9%</td>
<td>24%</td>
</tr>
<tr>
<td>CO + O → C + O₂</td>
<td>4%</td>
<td>8%</td>
</tr>
</tbody>
</table>
• The radiative heat flux experienced by spacecraft entering the Martian atmosphere at 5-8 km/s is mostly due to the CO 4th positive band system (\(\lambda < 200\) nm)
  - Radiative heating is therefore proportional to the mole fraction of CO in the bow shock layer
  - CFD-Radiative transport calculations using the T-T\textsubscript{V} model (legacy Mars chemistry model) predict greater radiance than observed in tests run in the Electric Arc Shock Tube (EAST) at Ames
  - Johnston and Brandis (JQSRT, 2014) scaled some of the rate coefficient parameters to force agreement between CFD and EAST for CO 4th positive

• Ab initio PESs have been computed for CO + Ar and CO + O and used in QCT calculations of CO dissociation rate coefficients (Schwenke et al., J Chem. Phys. submitted)
  - Experimental data for CO + Ar seem more reliable than for CO + O
  - Efficiency of different collision partners (M) for promoting dissociation has been expressed as ratio \(k(\text{CO+M})/k(\text{CO+Ar})\)
Rate Coefficient Ratios for CO Dissociation

• Early experimental values (Baulch, based on pre-1972 shock tube experiments)
  - \( \frac{k_{CO+CO}}{k_{CO+Ar}} = 1-2 \quad \frac{k_{CO+O}}{k_{CO+Ar}} = 15 \)

• Park (1994) T-T_v model
  - \( \frac{k_{CO+CO}}{k_{CO+Ar}} = 10 \quad \frac{k_{CO+O}}{k_{CO+Ar}} = 15 \)

• Johnston and Brandis (2014)
  - \( \frac{k_{CO+CO}}{k_{CO+Ar}} = 10 \quad \frac{k_{CO+O}}{k_{CO+Ar}} = 15 \)
  - \( \frac{k_{CO+Ar(JB)}}{k_{CO+Ar(Park)}} = 5 \)

• Objectives of our QCT rate coefficient calculations:
  - Evaluate the accuracy of the experimental data used in the legacy model
  - Determine these rate coefficient ratios as a function of temperature
  - Study the importance of the exchange reactions in the shock layer
After nearly all of the CO$_2$ is dissociated, CO and O are the major species (with equal mole fraction)

Experimental data
- Davies (1964) CO + Ar, CO, O
- Appleton (1970) CO + Ar, CO, O
- Hanson (1974) CO + CO, O
- Mick & Roth (1993) CO + Ar, CO
- Park (1994) T-T$_v$ model


- Scatter in experimental data is small
- Very good agreement between QCT and Appleton and Mick and Roth expt.
- Fair to good agreement between QCT and Davies and Park (94)
• Three triplet PESs with equal statistical weight govern CO + O (\(^3\)P) collisions
  - Lead to different non-linear CO\(_2\) triplet electronic states (\(1\ ^3A',\ 1\ ^3A''\) and \(2\ ^3A''\)) with O-C-O angle \(\sim 120^\circ\)
  - \(1\ ^3A'\) has well depth \(\sim 75\ \text{kJ/mol} \ (\sim 0.8\ \text{eV})\); other states are more weakly bound

• Heterogeneous exchange reaction forming O\(_2\) + C also possible on these PESs
  - Reaction is endothermic by 6.1 eV (low in comparison to the 11.2 eV dissociation energy of CO)

• All three PESs used for QCT calculations of CO dissociation and exchange reactions
The CO + O Rate Coefficients (experiment)

- Considerable scatter in the Appleton data
- Fairly good agreement between Appleton (8,000-15,000 K) and Hanson (5500-9000 K) data
- Hanson 3-parameter fit is not suitable for extrapolation
- Park and Johnston recommendations bracket the experimental results
CO + O Rate Coefficients (only dissociation)

- Good agreement between QCT dissociation rate coefficient and Park model
- Agreement between QCT dissociation rate coefficient and expt is poor
- \( k_{CO+O}/k_{CO+Ar} \sim 3-5 \) for QCT not 15 as in Park model
CO + O Rate Coefficients (dissoc. + exchange)

- Addition of hetero exchange rate coeff to dissociation greatly improves agreement with expt (especially at lower temperatures)
- Good agreement with Johnston scaled value ~8,000 K, but temperature dependence is quite different
- Exchange is the dominant CO removal process for T< 8000K

This exchange reaction was not previously thought to be important
Key Points for CO Dissociation

• Experimental data look quite good!
  - However, it is advantageous to use experimental data points (if available), not just Arrhenius expressions

• Heterogeneous exchange reaction provides an important pathway for CO removal, especially for T < 10,000 K
  - Converts CO to O$_2$, which is readily dissociated at these temperatures
  - Experimental CO dissociation rate coefficients implicitly include this reaction by having spuriously large dissociation rates and larger temperature exponents
  - When combined with dissociation, agreement between QCT and experimental results is excellent

• QCT rate coefficients needed for CO + CO to complete work on this set of reactions
Use in CFD Simulations

- Used new rate coefficient data in simulations of convective heating for LENS XX shock tunnel tests
  - Pure CO\textsubscript{2} flow impinging on 12” diameter model
  - Flow enthalpies up to 43 MJ/kg
  - Compared Park94 model with new CO rate coefficients from present work to the Johnston modification of the original Park model in DPLR simulations
Moderate enthalpy (14.3 MJ/kg):
- Convective heat flux predictions for the models are barely distinguishable
- CFD and test data in good agreement
- This condition applicable to Mars entry

High enthalpy (43 MJ/kg):
- Heat flux prediction lower for new rate coefficients
- Agreement between CFD and test data is not good
- This condition is applicable to Venus entry
Use in CFD Simulations

• Used new rate coefficient data in simulations of CO $4^{th}$ positive and CN violet integrated intensities from EAST tests
  - 96% CO$_2$/4% N$_2$ in Electric Arc Shock Tube at NASA Ames
  - Flow enthalpy up to 43 MJ/kg
  - Compared Park94 with new CO rate coefficients from present work with Johnston modification and the original Park model in LAURA-HARA simulations
Simulation vs EAST Test Data

$P_0 = 0.25$ torr and shockspeed $= 6.43$ km/s
Simulation vs EAST Test Data

$P_0 = 0.1$ torr and shockspeed = 7.98 km/s
On-going Work

• Potential energy surfaces:
  - PES for CO + CO collisions to enable determination of rate coefficients for CO dissociation by CO + CO collisions

• Rate coefficients:
  - QCT calculations for CO + N reactions forming CN + O and NO + C
  - QCT calculations for O$_2$ dissociation and Zel’dovich reactions (N$_2$ + O and NO + O) using published PESs

• Analysis of quasi-steady state (QSS) models and internal energy relaxation ($\tau_v$, $\tau_{int}$) using coarse-grained QCT methods developed by Prof. Panesi at U. Illinois at Urbana-Champaign

• Examination of alternative multi-temperature models and other approaches to describing nonequilibrium flows
Conclusions

• The effort to create a new physics-based model for describing nonequilibrium phenomena in Mars entry flowfields is bearing fruit.

• Potential energy surfaces and thermal rate coefficients for dissociation and exchange reactions have been computed for many of the important chemical reactions:
  - Independent calculations for $N_2$ dissociation from two research groups show remarkable agreement.
  - Rate coefficients for different dissociation reactions show limitations and successes in the older data from shock tube experiments.

• Work is progressing toward creation of a data base of QCT rate coefficients for the complete set of heavy particle reactions for modeling Earth and Mars entry:
  - Relaxation parameters ($\tau_v$) and thermochemical data (specific heats, enthalpies and entropies) are also being computed.

• We are also examining alternatives to the $T-T_v$ model using coarse-grained QCT calculations.
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  - Simone Venturi
  - Robyn Mcdonald

Mars tourism is coming!