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

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Motivation

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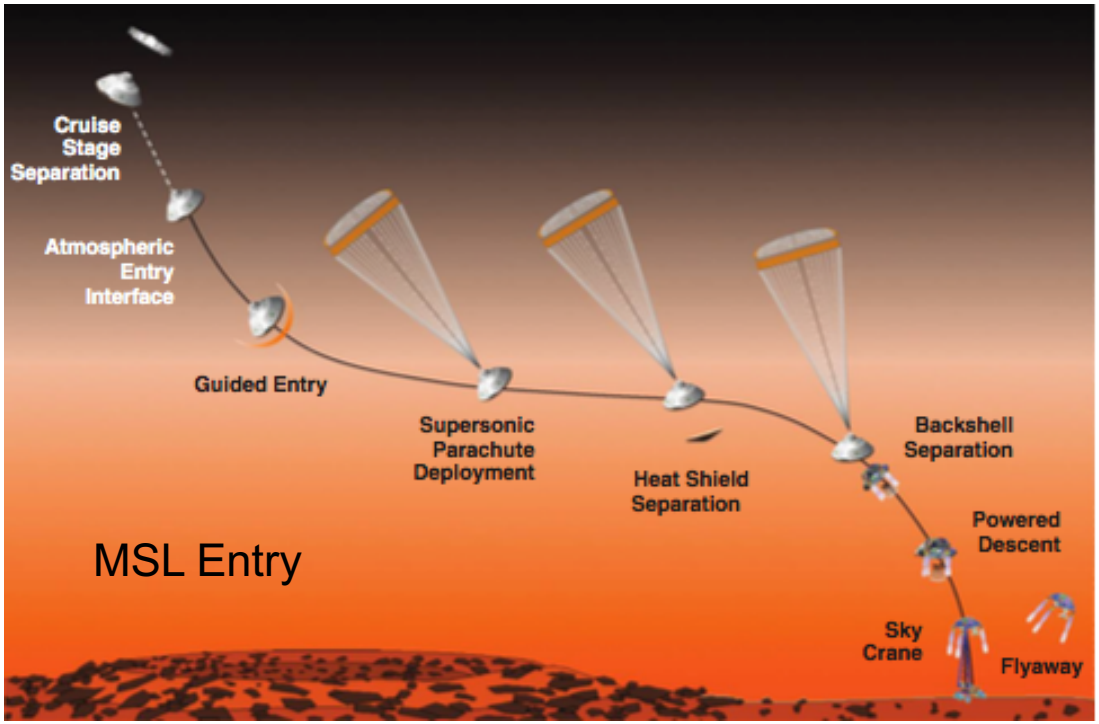
- NASA has been embarked on a program of scientific exploration of Mars by landing increasingly larger and heavier payloads
  - Prediction of thermal load used to determine TPS requirements
  - Testing in ground facilities and CFD simulations play critical roles



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

Outline

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- Legacy nonequilibrium chemistry model
- Computational approach for developing a new model
- Rate Coefficients
  - Chemical rections 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

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- 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 $T_v = T_{el\text{-}st}$)
  - 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?

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- 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
  - $CO_2 + O \rightarrow CO + O_2$
  - $CO + O \rightarrow C + O_2$
  - $CO + N \rightarrow O + CN$
  - $CO + C \rightarrow O + C_2$

For Mars entry at 6-8 km/s, the rate of CO dissociation is critical because CO 4th positive emission is the dominant source of radiative heating

New Paradigm for a Nonequilibrium Chemistry Model

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- ***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 ≤ ± 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 reproduce random or thermal collisional distributions

This strategy should yield rate coefficients accurate to ±20%

(Ref: Jaffe et al. "First principles calculation of heavy particle rate coefficients" in "Hypersonic nonequilibrium Flows: Fundamentals and Recent Advances", E. Josyula, ed, AIAA 2015)

Important Chemical Reactions for Mars Entry

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	Reaction	Experiment	PES	QCT rate coeff.
D1	CO_2+ M → **CO** + O + M M = CO_2, N_2, CO, O	Shocktube expts 1968-74 & 1984		
D2	*CO + M → C + O + M* *M = CO, O*	*Shocktube expts 1968-74 & 1984*	*NASA Ames 2016*	*NASA Ames 2016*
❊D3	N_2 + M → N + N + M M = N_2, N	Shocktube expts 1964-74 & 1993	NASA Ames 2010 U. Minnesota 2013	NASA Ames 2010-16 U. Minn. 2013-16
❊D4	O_2 + M → O + O + M M = N_2, CO, O	Expts 1960s, 84 Hanson 2016	Varandas 1988 Dawes 2011-13	Andrienko 2016
E1	CO_2 + O → **CO** + O_2	Ibragimova 1991		
E2	*CO + O → C + O_2*	*Hanson 1991*	*NASA Ames 2016*	*NASA Ames 2016*
❊E3	N_2 + O → NO + N	Michael 1992 Roth 1985	Sayos 2003-16	Sayos 2010-12 U. Minn 2016
❊E4	NO + O → O_2 + N	Fontijn 1998	Sayos 2002	Sayos 2003
E5	CO + N → **CN** + O		Nyman 2000-2008	
E6	CO + N → NO + C		Nyman 2000-2008	
E7	CN + O → NO + C	Roth 1990	Nyman 2000-2008	
E8	CO + C → **C_2** + O			

Uncertainty Quantification (UQ)

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- UQ used to identify critical reactions
  - Monte Carlo sensitivity analysis
    - 96 % CO_2/4% N_2 (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 4^{th} positive radiative intensity and sensitivity to attaining chemical equilibrium (T/T_{eq} = 1.05)
- Repeated many times for statistical analysis
- Key reactions:

Reaction	Sensitivity to Radiative Flux	Sensitivity to Equilibration Time
$CO + O \rightarrow C + O + O$	55%	48%
$CO + CO \rightarrow C + O + CO$	25%	10%
$CN + O \rightarrow C + NO$	9%	24%
$CO + O \rightarrow C + O_2$	4%	8%

CO Dissociation

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- 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 (λ < 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_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(CO+M)/k(CO+Ar)

Rate Coefficient Ratios for CO Dissociation

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- Early experimental values (Baulch, based on pre-1972 shock tube experiments)
  - k_{CO+CO}/k_{CO+Ar} = 1-2 k_{CO+O}/k_{CO+Ar} = 15
- Park (1994) T-T_v model
  - k_{CO+CO}/k_{CO+Ar} = 10 k_{CO+O}/k_{CO+Ar} = 15
- Johnston and Brandis (2014)
  - k_{CO+CO}/k_{CO+Ar} = 10 k_{CO+O}/k_{CO+Ar} = 15
  - $k_{CO+Ar(JB)}/k_{CO+Ar(Park)}$ = 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

CO + Ar

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After nearly all of the CO_2 is dissociated, CO and O are the major species (with equal mole fraction)

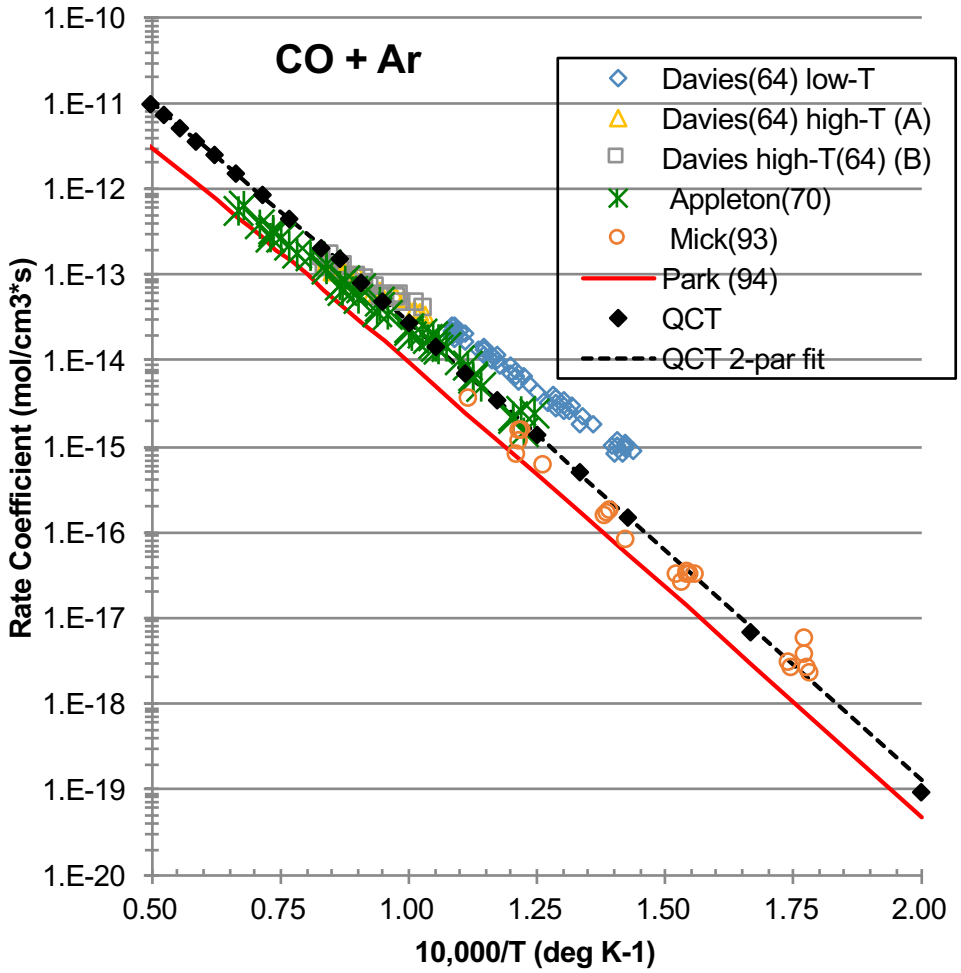
Experimental data

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

NASA Ames (2014-2015) QCT

- 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)



CO + O (^{3}P)

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- Three triplet PESs with equal statistical weight govern CO + O (^{3}P) collisions
  - Lead to different non-linear CO_2 triplet electronic states (1 ^{3}A', 1 ^{3}A" and 2 ^{3}A") with O-C-O angle ~120^o
  - 1 ^{3}A' has well depth ~75 kJ/mol (~0.8 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

CO + O Rate Coefficients (experiment)

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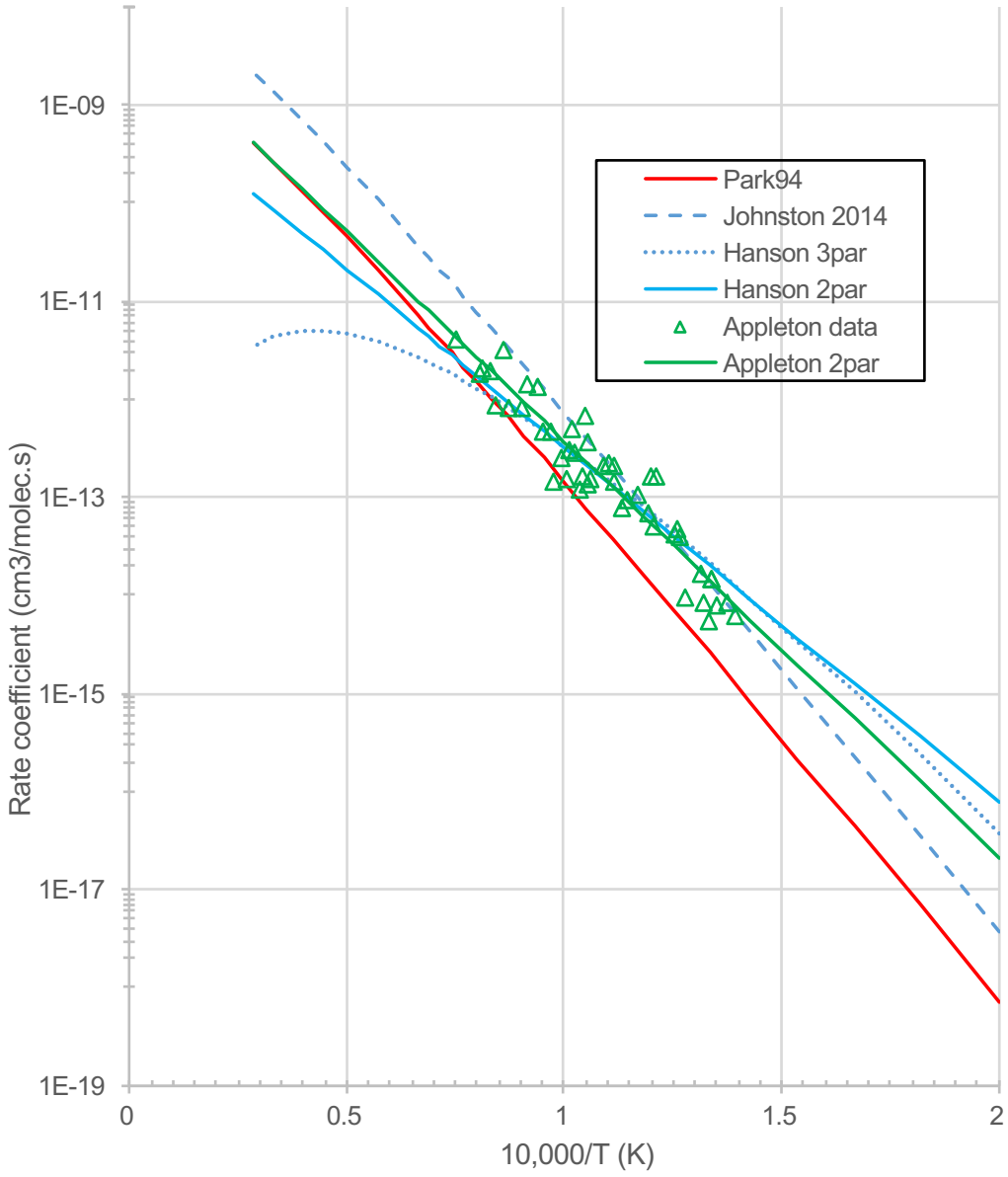

- Considerable scatter in the Appleton data
- Fairly good agreement between Appleton (8,000-15,000 K) and Hanson (5500-9000 K) data
- Hanson 3-parameter fit is not suitable for exptrapolation
- Park and Johnston recommendations bracket the experimental results

CO + O Rate Coefficients (only dissociation)

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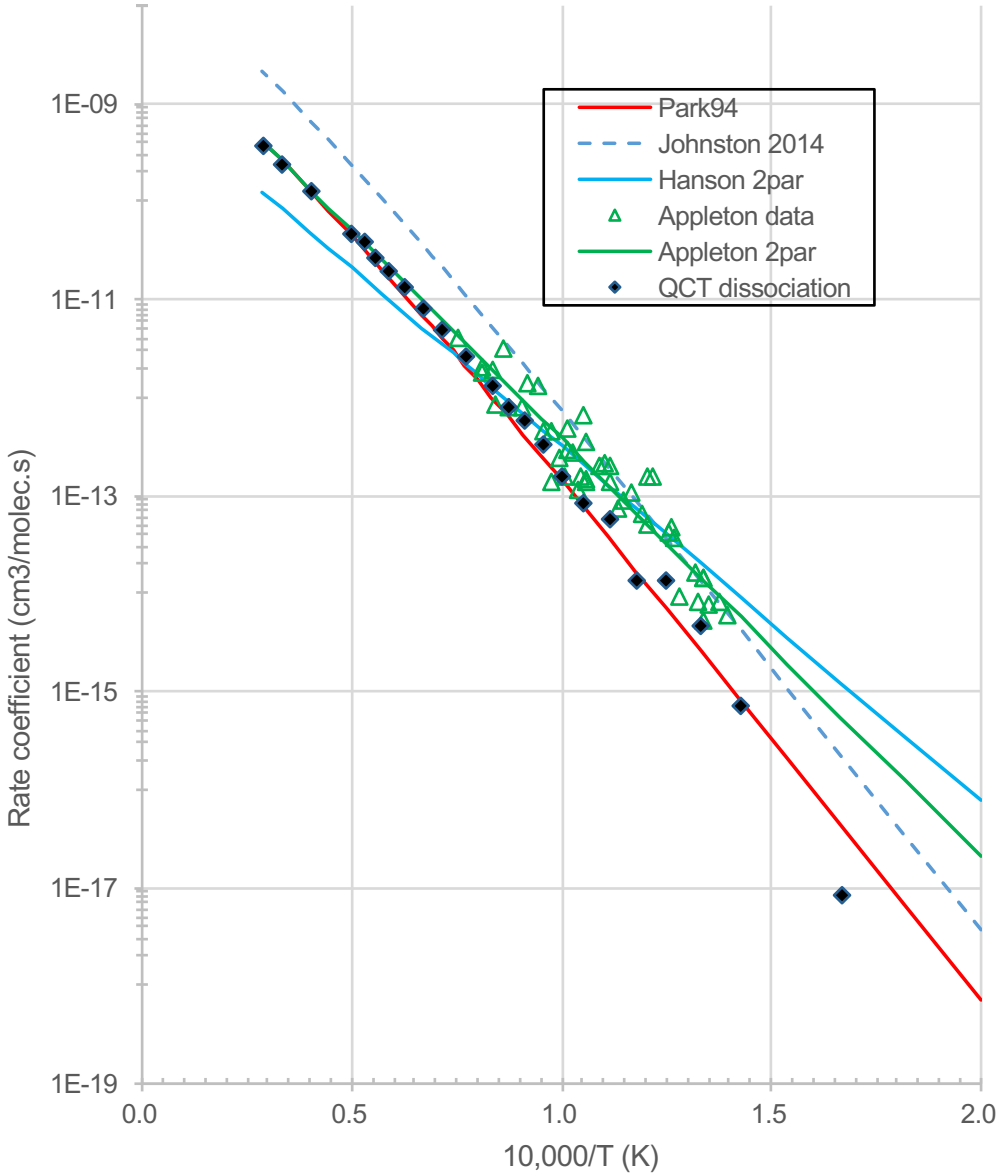
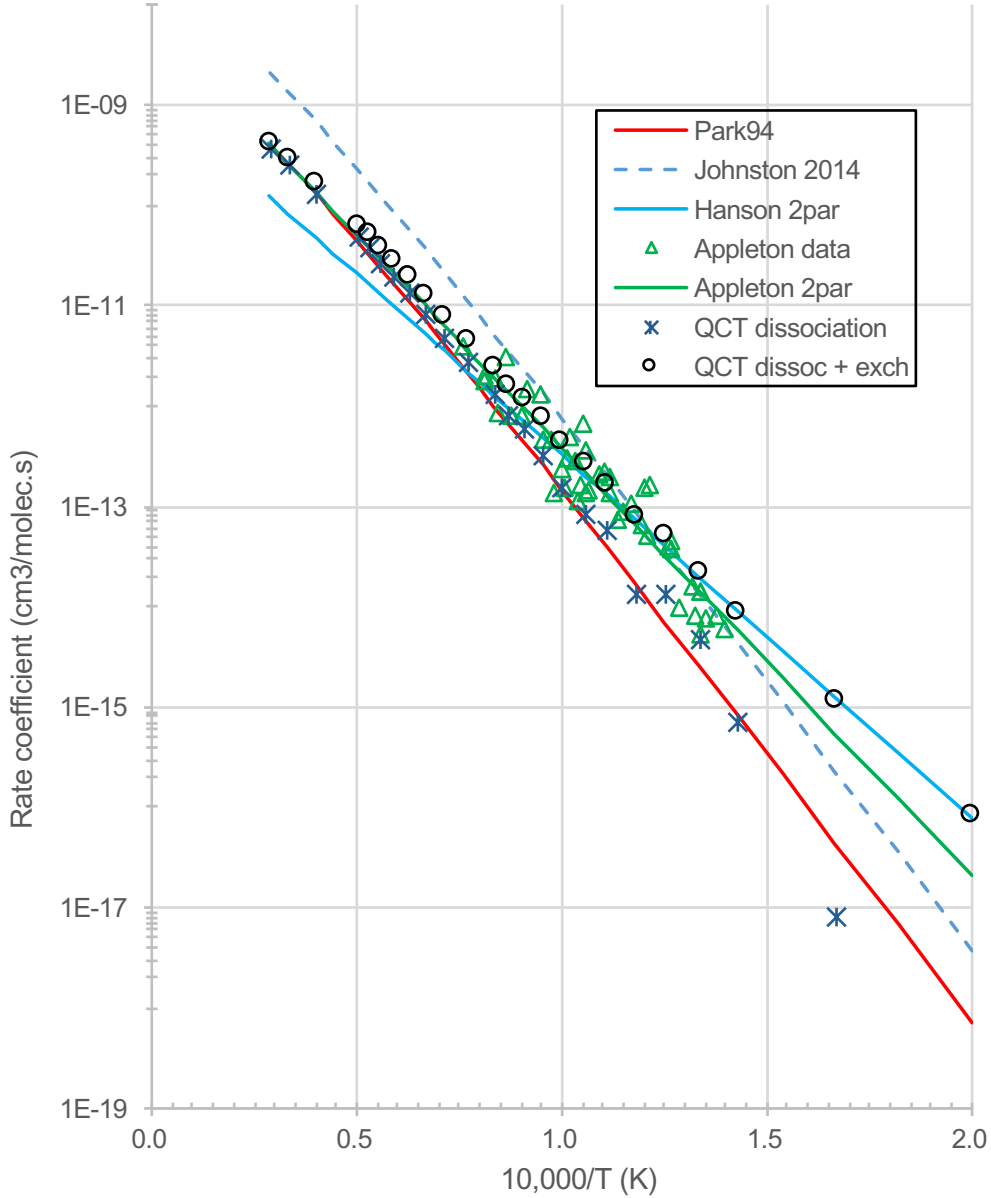


- Good agreement between QCT dissociation rate coefficient and Park model
- Agreement between QCT dissociation rate coefficient and expt is poor
- k_{CO+O}/k_{CO}+Ar ~3-5 for QCT not 15 as in Park model

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

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- 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 betwee 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

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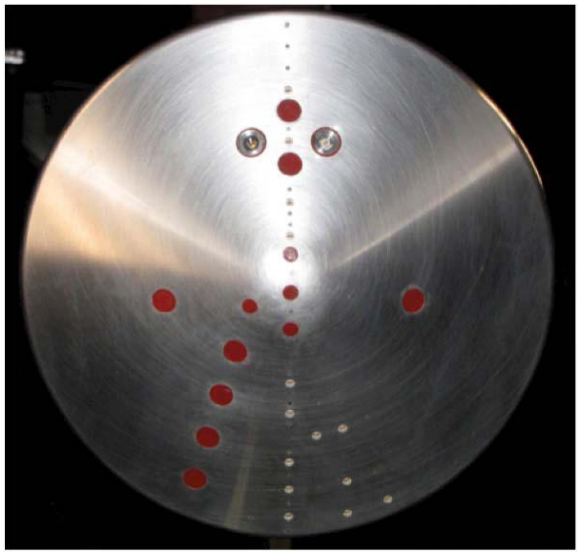
- Used new rate coefficient data in simulations of convective heating for LENS XX shock tunnel tests
  - Pure CO_2 flow impinging on 12” diameter model
  - Flow enthalpies up to 43 MJ/kg
  - Compared Park94 model with new CO rate coefficients from present work to the Johnston modification of the original Park model in DPLR simulations



Simulation vs LENS XX Test Data

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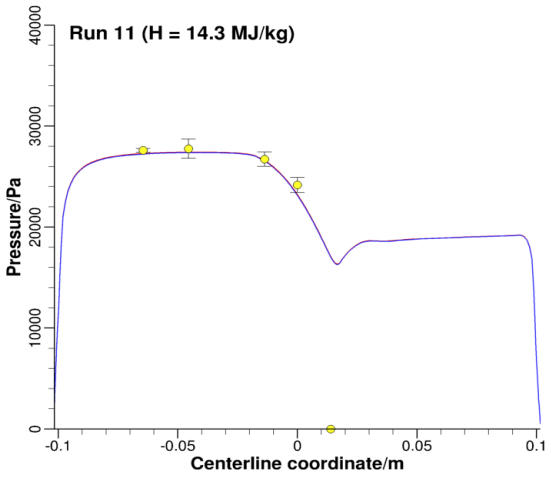
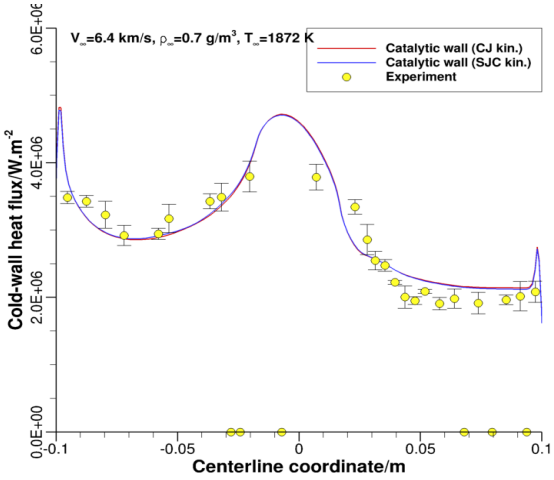
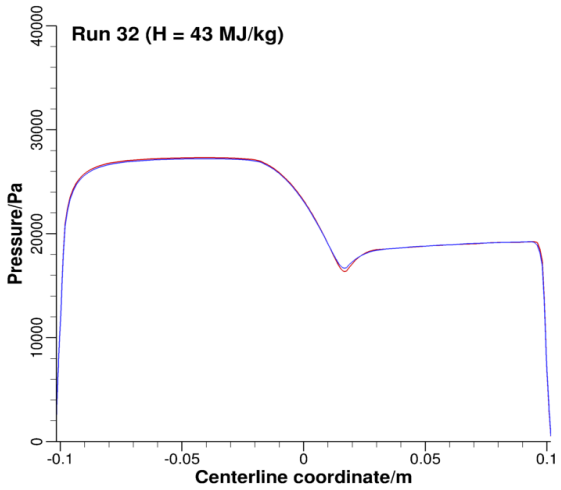
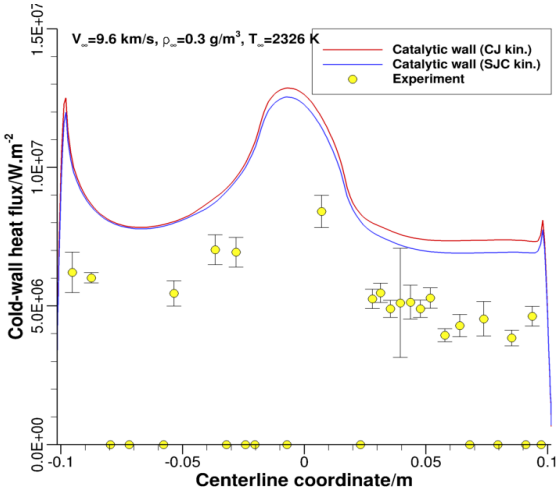
Moderate enthalpy (14.3 MJ/kg):

- 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

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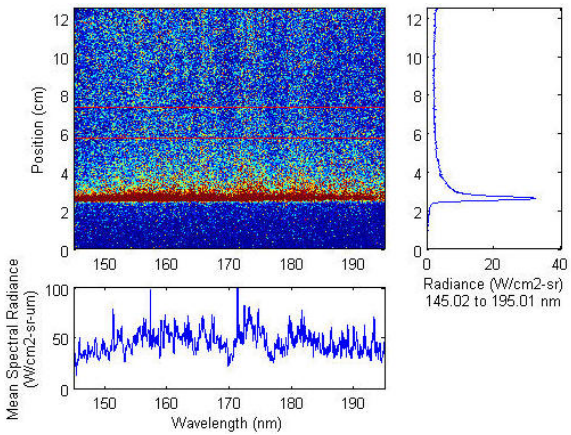
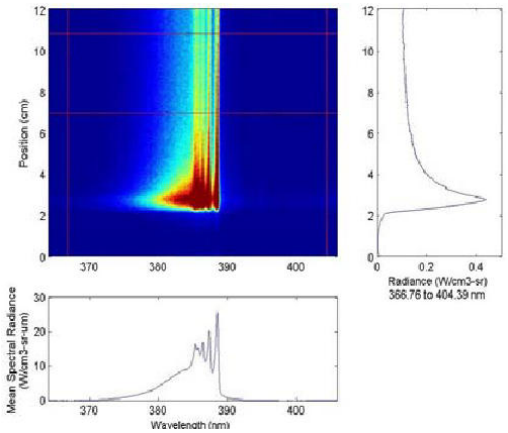
- Used new rate coefficient data in simulations of CO 4th positive and CN violet integrated intensities from EAST tests
  - 96% CO_2/4% N_2 in Electric Arc Shock Tube at NASA Ames
  - Flow enthalpy up to 43 MJ/kg
  - Compared Park94 with new CO rate coefficients from present work with Johnston modification and the original Park model in LAURA-HARA simulations



CN violet ⏩
⏪ CO 4th+



Simulation vs EAST Test Data

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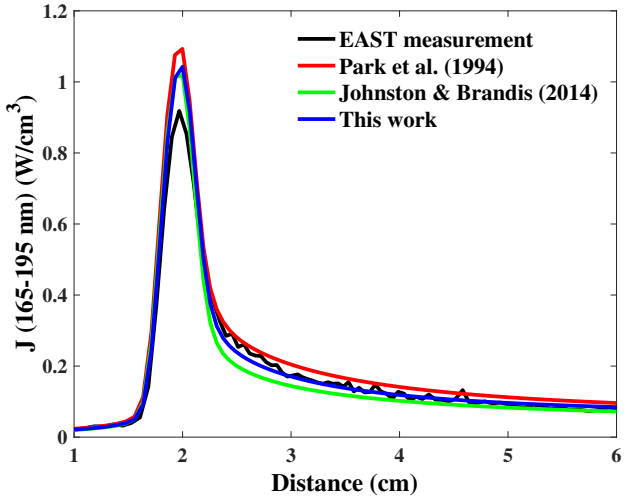
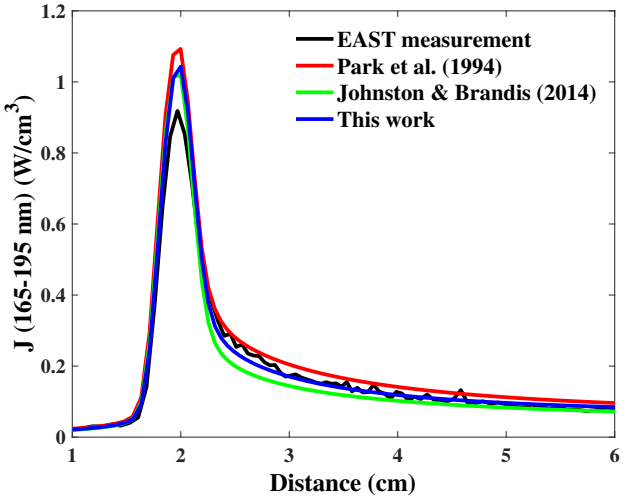
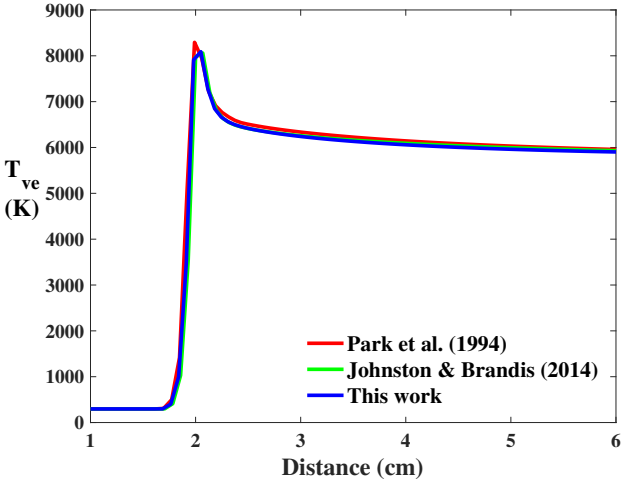
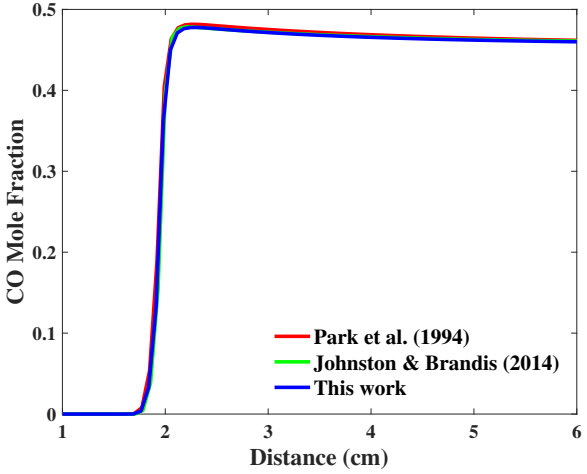
P_0 = 0.25 torr and shockspeed = 6.43 km/s









Simulation vs EAST Test Data

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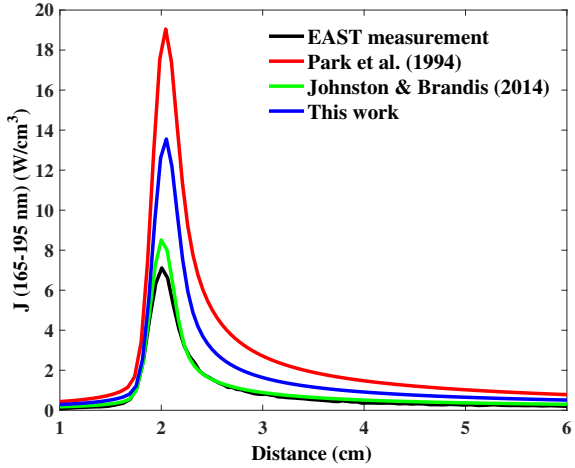
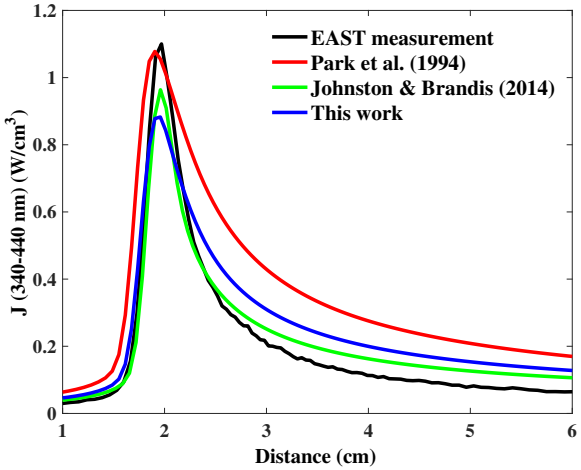
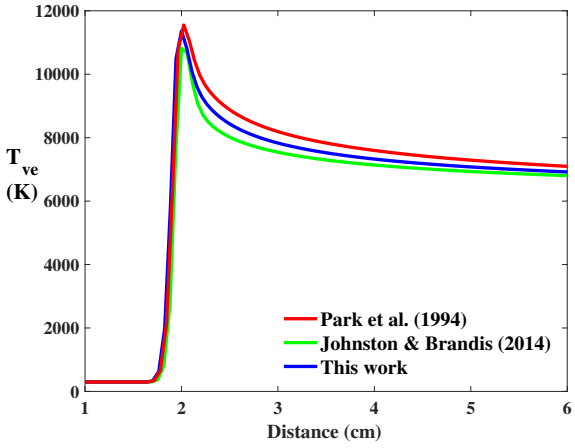
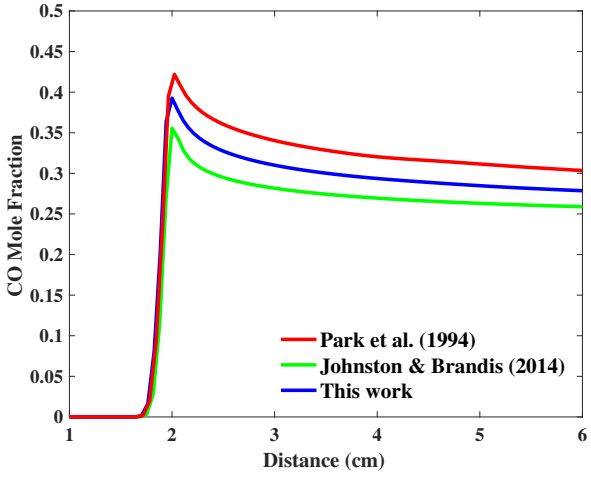
P_0 = 0.1 torr and shockspeed = 7.98 km/s









On-going Work

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- 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 (τ_v, τ_{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

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- 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 (τ_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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  - Lu Xu
- U. Illinois Collaborators
  - (Prof) Marco Panesi
  - Simone Venturi
  - Robyn Mcdonald

Mars tourism is coming!