Abstract for: 35th Annual Conference on Composites, Materials, and Structures
Session: Hypersonic Ablator and Atmospheric Entry Technology

Comparison of Ablation Predictions for Carbonaceous Materials Using CEA and JANAF-Based Species Thermodynamics

Frank S. Milos
NASA Ames Research Center, Moffett Field, CA 94035-1000

In most previous work at NASA Ames Research Center, ablation predictions for carbonaceous materials were obtained using a species thermodynamics database developed by Aerotherm Corporation. This database is derived mostly from the JANAF thermochemical tables. However, the CEA thermodynamics database, also used by NASA, is considered more up to date. In this work, the FIAT code was modified to use CEA-based curve fits for species thermodynamics, then analyses using both the JANAF and CEA thermodynamics were performed for carbon and carbon phenolic materials over a range of test conditions. The ablation predictions are comparable at lower heat fluxes where the dominant mechanism is carbon oxidation. However, the predictions begin to diverge in the sublimation regime, with the CEA model predicting lower recession. The disagreement is more significant for carbon phenolic than for carbon, and this difference is attributed to hydrocarbon species that may contribute to the ablation rate.

Comparison of Ablation Predictions for Carbonaceous Materials Using CEA and JANAF-Based Species Thermodynamics

Frank S. Milos
Thermal Protection Materials Branch
NASA Ames Research Center
Moffett Field, CA 94035-1000

35th Annual Conference on Composites, Materials, and Structures
Cocoa Beach / Cape Canaveral, Florida
24 – 27 January 2011

Outline

- Introduction
- Species thermodynamics
- Model comparisons
- Summary

In previous work at NASA Ames Research Center, ablation predictions were obtained using a species thermodynamics database developed by Aerotherm Corporation. This database is derived primarily from the JANAF thermochemical data tables. However, the CEA thermodynamics database, also used by NASA, is considered more up to date. In this work, the MAT and FIAT codes were modified to use CEA-based curve fits for species thermodynamics, then ablation analyses using both Aerotherm and CEA-based thermodynamics were performed for carbon and carbon phenolic materials. The ablation predictions are comparable at moderate heat fluxes where the dominant mechanism is carbon oxidation. However, the predictions begin to diverge in the sublimation regime, with the CEA model predicting a lower ablation rate. The disagreement is much more significant for carbon phenolic than for carbon, and this difference is attributed to hydrocarbon species that may contribute to the ablation rate.

- This work was funded by the Hypersonics element of the Fundamental Aeronautics Program and by the Entry, Descent, and Landing Technology Development Project
- We also acknowledge NASA-SCAP for their critical financial support of the arcjet operational capability at Ames Research Center

Introduction

- The thermodynamic properties of gas mixtures are used in both hypersonic CFD codes and thermochemical ablation codes, such as DPLR and FIAT, respectively
- Typically, thermodynamics quantities are computed for each species, then mixing rules are applied to obtain the bulk values for the gas mixture
- Properties for the individual species are measured and/or calculated on a theoretical basis, and then tabulated
  - These tables may be interpolated by other codes
  - More commonly, the tabular data are approximated by curve fits that provide smooth functionality with less input

Thermodynamic Curve Fits

- The “data” typically are *calculated* (not measured) tables of C_P–vs–T with additional reference values for enthalpy and entropy
- Three different curve fits are often used by NASA
  - Aerotherm/Sandia
    - Data mostly from JANAF data tables calculated in the 1960s and 1970s
    - Most species fit from 500 to 6000 K, with two temperature ranges
  - Gurvich
    - Data recalculated for many species, up to 20000 K
    - Fit over two or three temperature ranges
  - CEA
    - Data collected from several sources, including Gurvich and JANAF
    - Re-fit using more parameters, over two or three temperature ranges
- Note: these sources do not contain the same set of species
  - Aerotherm and Gurvich have the largest and smallest species sets, respectively

Species Thermodynamics

Specific Heat

- Nondimensionalize using the gas constant
- Approximate by polynomial function

$$\frac{C_p}{R} = \frac{a_1}{z^2} + \frac{a_2}{z} + a_3 + a_4 z + a_5 z^2 + a_6 z^3 + a_7 z^4 \qquad \text{where} \quad z = T/(1000\,°\mathrm{K})$$

- Use multiple temperature (z) ranges, as needed for accuracy

Source	a_1	a_2	a_3	a_4	a_5	a_6	a_7
Aerotherm	✔		✔	✔			
Gurvich	✔		✔	✔	✔	✔	
CEA	✔	✔	✔	✔	✔	✔	✔

Species Thermodynamics – slide 2

Entropy and Enthalpy

- Enthalpy $dH/dT = C_p$ and entropy $dS/dT = C_p/T$
- Integrate the previous equation to get

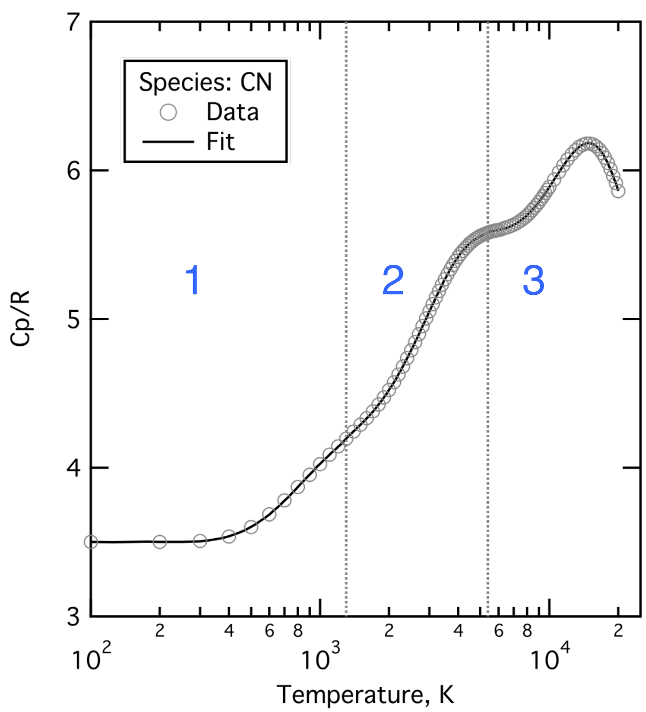
$$\frac{(H/R)}{1000\,^\circ\mathrm{K}} = a_h - \frac{a_1}{z} + a_2 \ln z + a_3 z + \frac{a_4 z^2}{2} + \frac{a_5 z^3}{3} + \frac{a_6 z^4}{4} + \frac{a_7 z^5}{5}$$

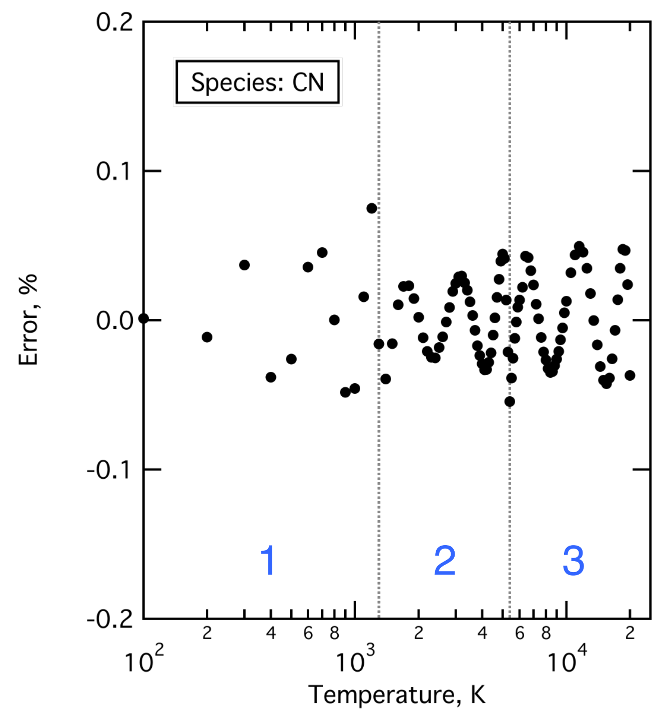
$$\frac{S}{R} = a_s - \frac{a_1}{2z^2} - \frac{a_2}{z} + a_3 \ln z + a_4 z + \frac{a_5 z^2}{2} + \frac{a_6 z^3}{3} + \frac{a_7 z^4}{4}$$

- The integration constants (a_h and a_s) are determined by matching a reference enthalpy and entropy at some reference temperature
  - Aerotherm (JANAF) and CEA use the same reference state, specifically elements in the most prevalent form at standard temperature and pressure
  - The curve fits match the standard enthalpy and entropy of formation (ΔH^0_{298} and S^0_{298}) for each species

Fitting Example 1, Species CN

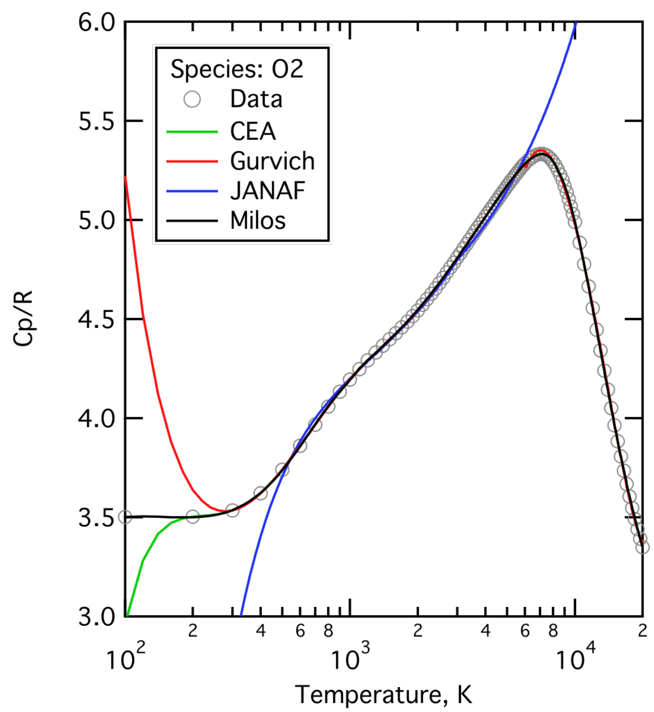
- “Data” of Gurvich from 100 to 20,000 K
- Curve fits generated over three temperature ranges
- C_p is continuous at junctions between curve-fit ranges
- Fractional error was minimized, to below 0.1%

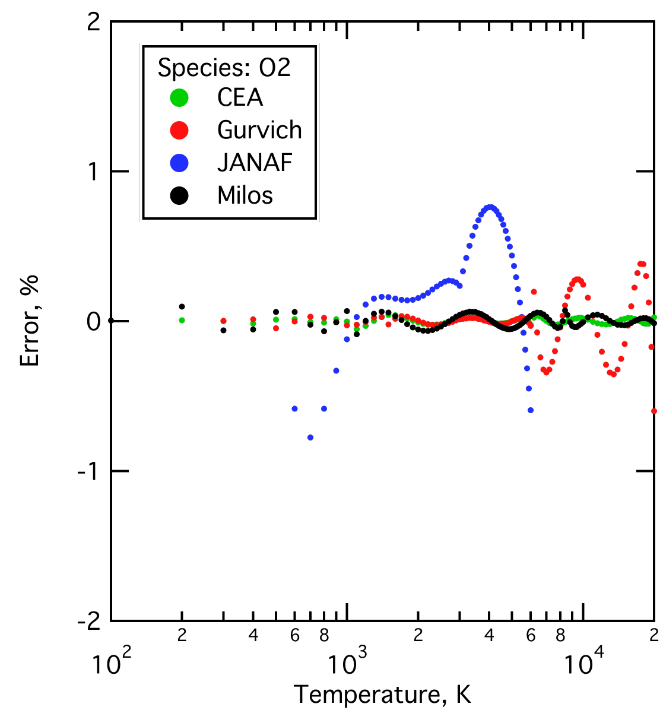




Fitting Example 2, Species O_2

- Plotted "data" of Gurvich from 100 to 20,000 K
  - JANAF data differ slightly
- Fractional error decreases as the number of parameters is increased
- Curve fits are bad outside the applicable temperature range





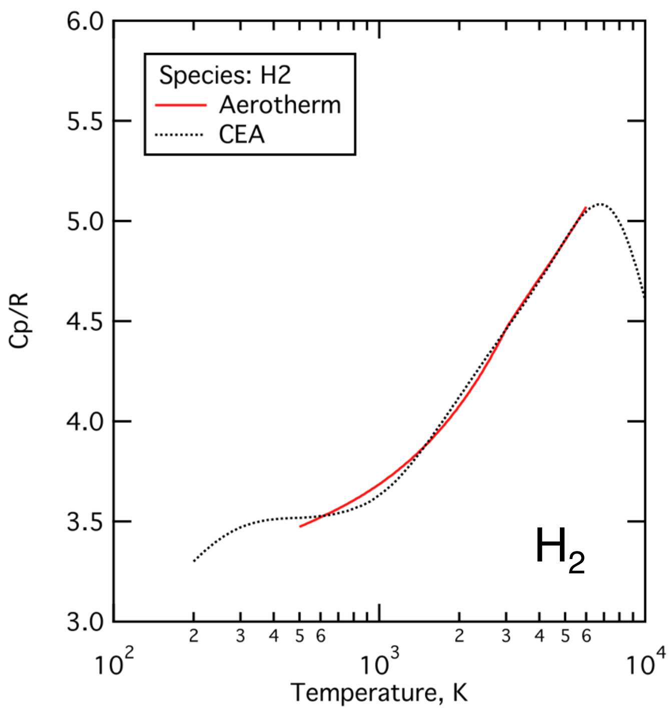
Aerotherm vs CEA Models

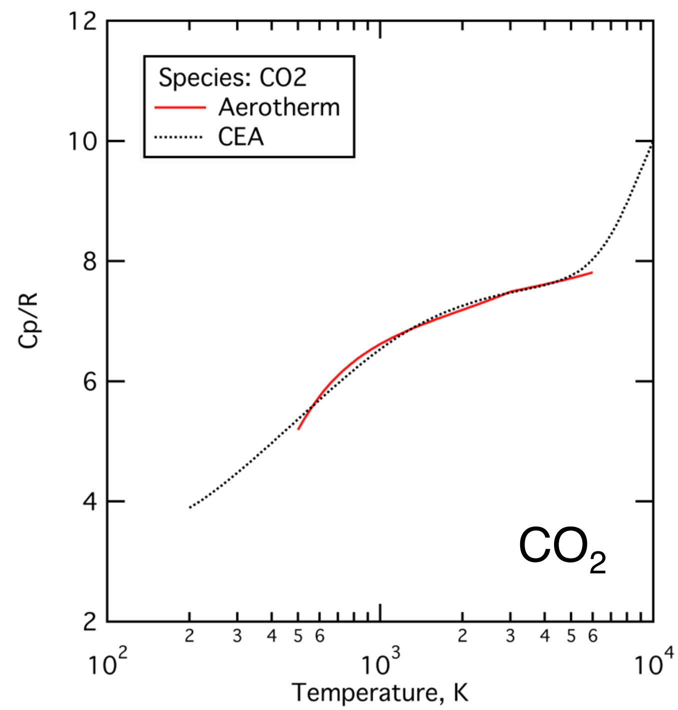
- The CEA model is more up-to-date, but the Aerotherm model contains a more comprehensive set of ablative species
- How to compare these models? We will look at:
  - Data/fits for major ablative species
  - Nondimensional ablation rate for carbonaceous materials
  - Predictions and data for arcjet tests
- FIAT and MAT codes were modified to read CEA-type curve fits
  - Variable number of fitting ranges (1 to 3)
  - Nine parameters per fitting range, with more digits

```
Old style

  1  6  1  8  0  0  0  0  0  0  0  0  0  0JANAF 9-30-65                CO
-264169+5 223569+5 808732+1 281527-3-332124+6 653699+2   500  30001   -0CO
-264169+5 223569+5 885923+1 582009-4-124951+7 653699+2  3000  60001   -0CO

New style

  6  1  8  1                   CEA Gurvich,1979 pt1 p25 pt2 p29                                       200. 3 CO
-15049962+2 31684391+2 14890453-1-29222859+0 57245272+1-81762351+1 14569034+2-10877463+2 30279418+1  1000. 1 CO
-15899806+2 26997082+2 46191972+0-19447048+1 59167142+1-56642828+0 13988145+0-17876803-1 96209356-3  6000. 1 CO
 52034367+3-33689174+3 88686630+3-75003779+3 24954750+3-39563511+2 32977721+1-13184099+0 19989379-2 20000. 1 CO
```

Comparison of Aerotherm and CEA Fits

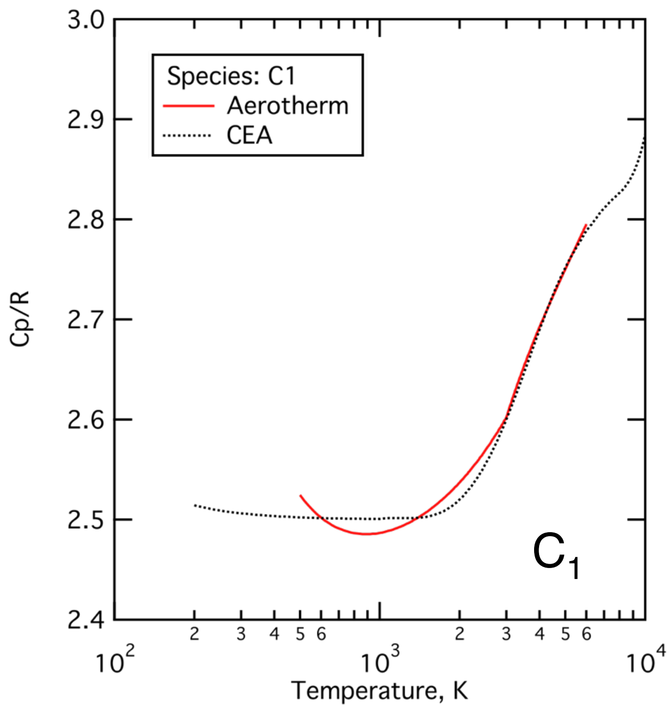
- For some species, the fits are comparable in the common temperature range

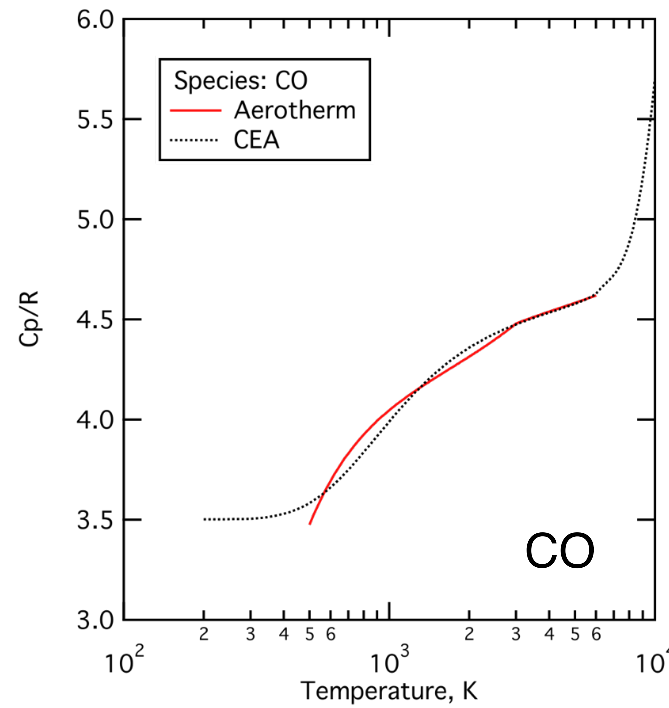




Comparison … - slide 2

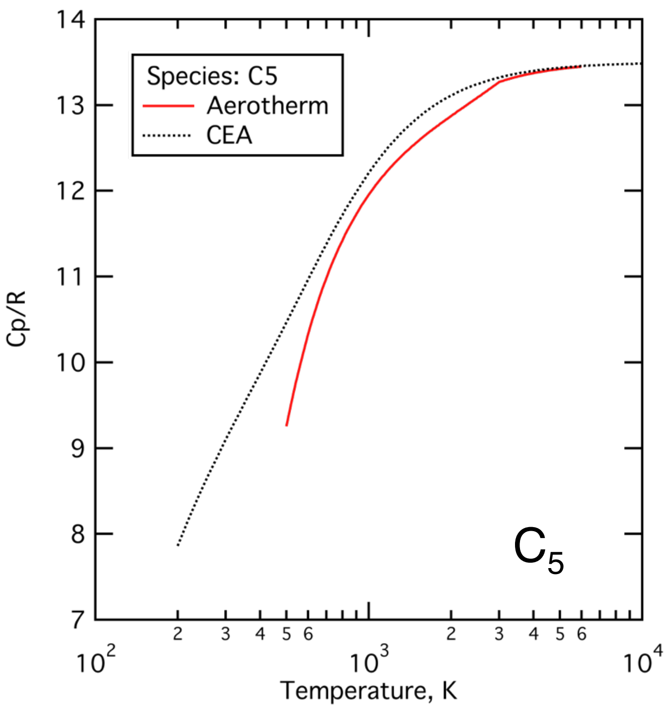
- For others, the comparison is (visually) not as good

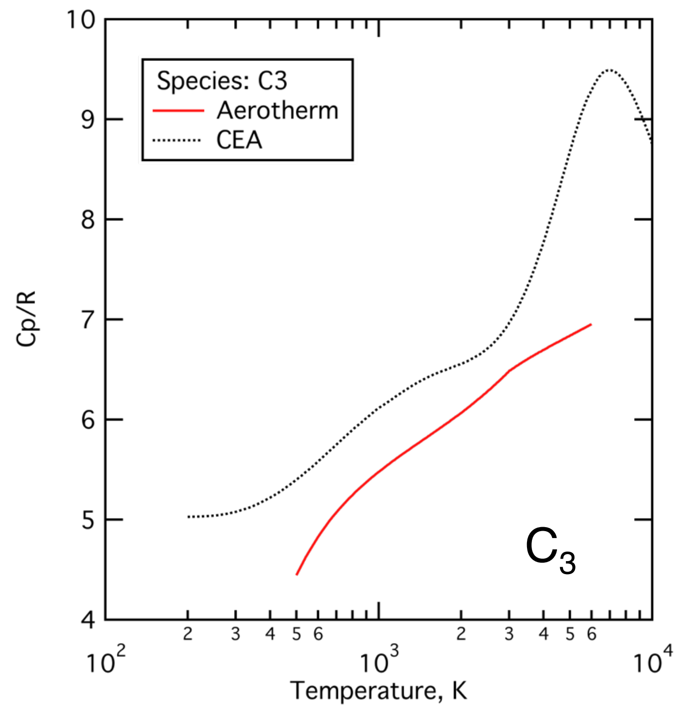




Comparison … - slide 3

- And some are poor

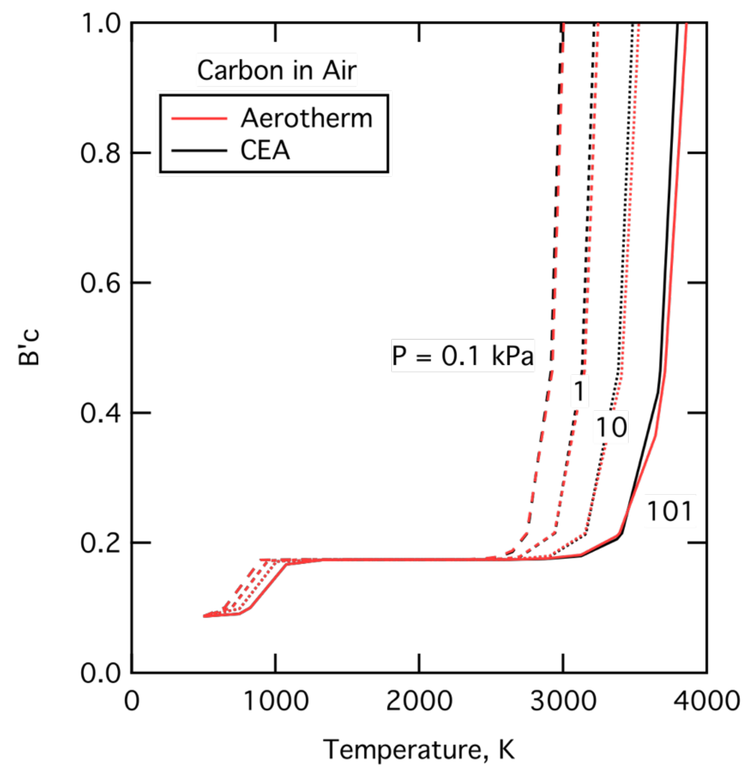




For C_3, Gurvich says "In the JANAF Tables, the contribution of the bending vibration was calculated by direct summation over the first six levels, and then along the equidistant levels with the interval 650 cm^{-1}. This arbitrary model and also disregard of the excited electronic states …"

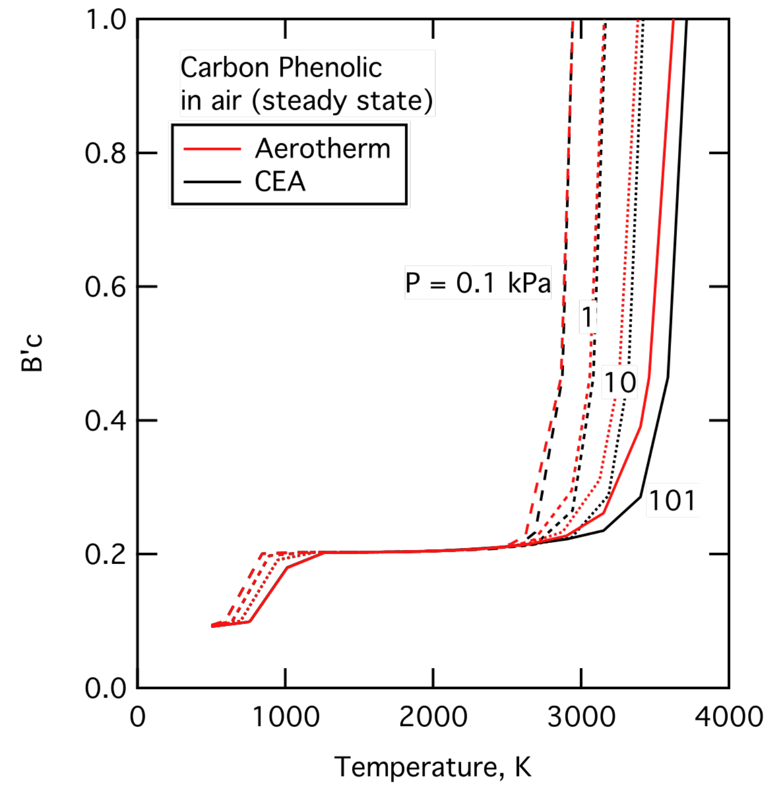
Nondimensional Ablation Rate of Carbon

- The Multicomponent Ablation Thermochemistry (MAT) code was used to calculate the non-dimensional ablation rate (*B’*)
  - Aerotherm and CEA models (red and black curves)
  - Four pressures (different line types)
- Results are comparable throughout the oxidation regime, and partially into the sublimation regime, up to 3500 K
  - Slight differences seen for *B’* > 0.3 and P = 101 kPa



Nondimensional Ablation Rate - slide 2

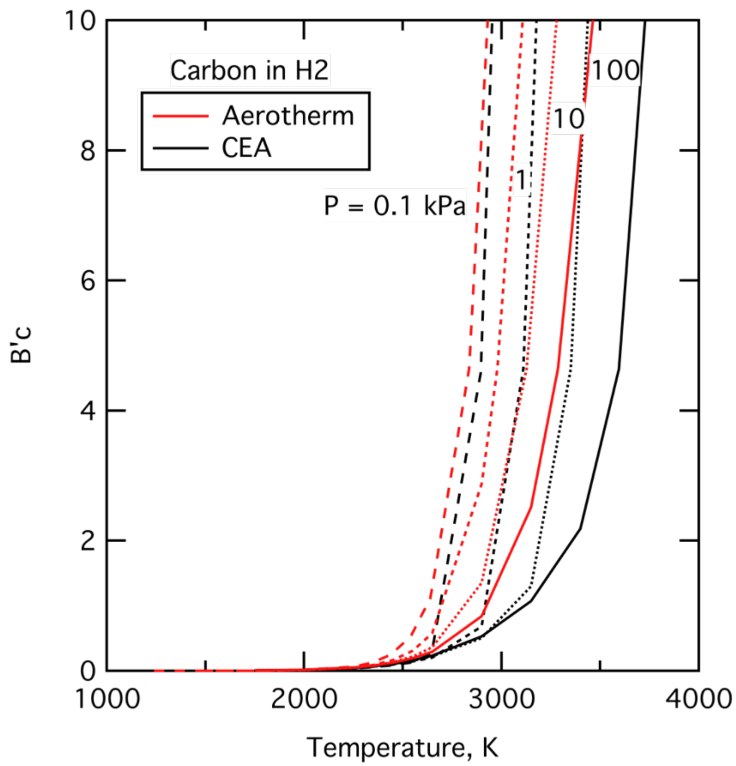
- Ablation of carbon phenolic in air
  - Try steady-state ablation,* then we can compare the models without considering many different values of $B'g$
- Results are comparable only in the oxidation regime up to 2500 K
- Significant differences as sublimation becomes important, especially at the higher pressures

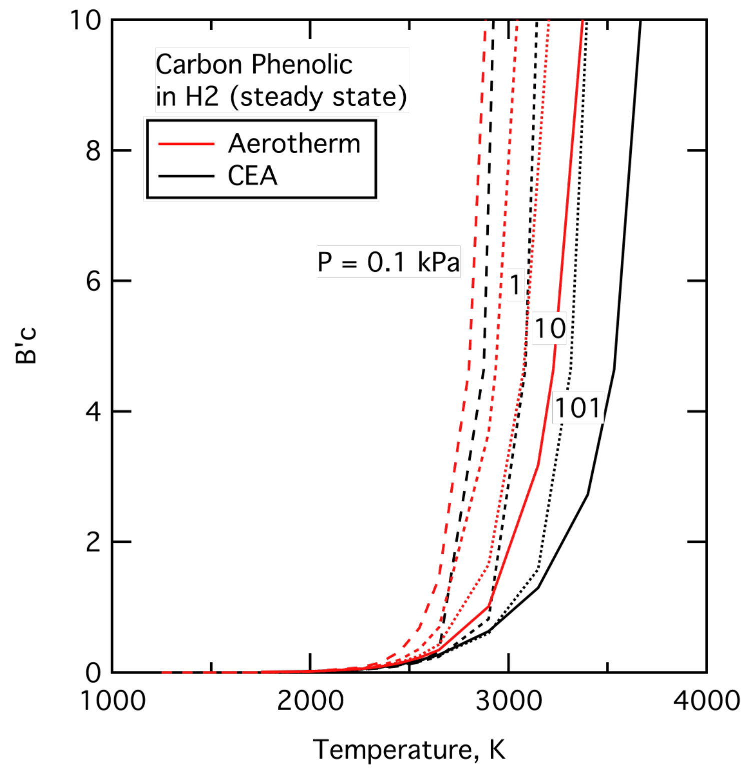


* For a pyrolyzing ablator, steady state provides a better approximation for ablation rate than for elements or species. The approximation improves if the heat flux is very high.

Nondimensional Ablation Rate - slide 3

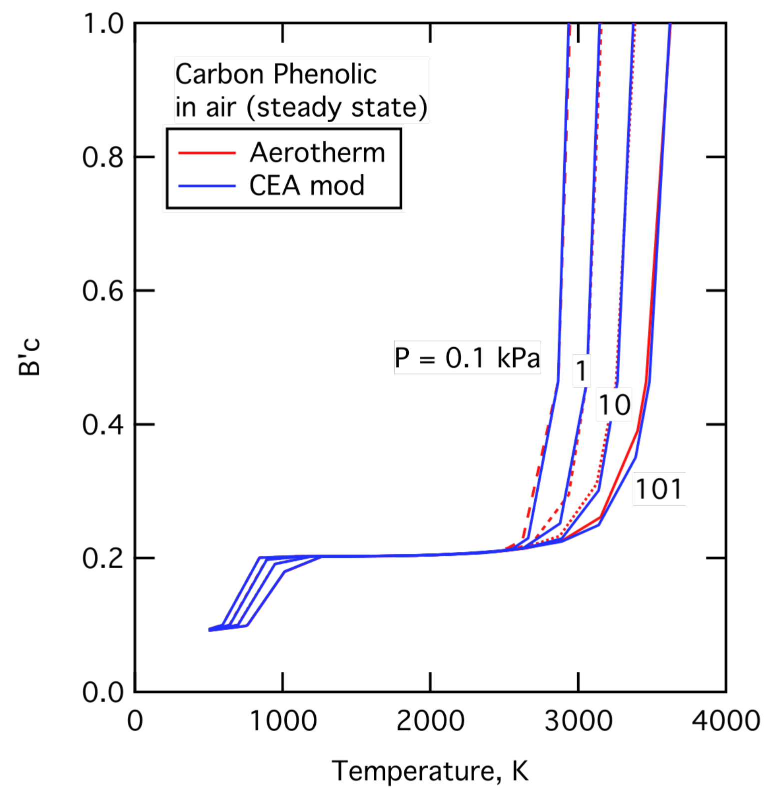
- For ablation of both carbon and carbon phenolic in hydrogen gas, the two models differ significantly for temperatures above 2500 K
- This difference could be important for missions to the giant planets





Nondimensional Ablation Rate - slide 4

- The Aerotherm database contains a full set of hydrocarbon radicals and molecules (C_nH_m) up to n,m = 6
- If I modify the CEA database by adding the “missing” species, then the difference between the predictions is greatly reduced !!
- Most of the difference is attributed to species C_3H and C_4H
  - How reliable are the source data for these species? Computations are from the 1960’s.
- Note: for this system, hydrogen is in the pyrolysis gas



Do C_3H and C_4H Really Exist?

- Neither species is included in Gurvich or CEA
- C_3H is observed in interstellar gas and is produced in a lab by reaction of carbon ablation products with hydrocarbon gas
- C_4H also is produced in the same lab experiment
- Some references (there are many)

Kaiser, R.I., et al., "A Combined Experimental and Computational Study on the Ionization Energies of the Cyclic and Linear C_3H Isomers," ChemPhysChem, Vol. 8, 2007, pp. 1236-1239.

Ding, H., et al., "Gas phase electronic spectrum of C_3H in the visible," Journal of Chemical Physics, Vol. 115, 2001, pp. 6913-6919.

Yamagishi, H., et al., "The structures of the cyclic-C_3H radical – an interstellar molecule," Chemical Physics Letters, Vol. 250, 1996, pp. 165-170.

Stanton, J.F., "Strong pseudo Jahn-Teller effect in the cyclic C_3H radical," Chemical Physics Letters, Vol. 237, 1994, pp. 20-26.

Stagnation Arcjet Conditions (Orion tests)

- We consider a set of stagnation conditions with heat flux and pressure above 200 W/cm^2 and 8 kPa, respectively
- Equilibrium ablation should be a good assumption for conditions 2-8
- Test gas is air + argon (composition varies from run to run)

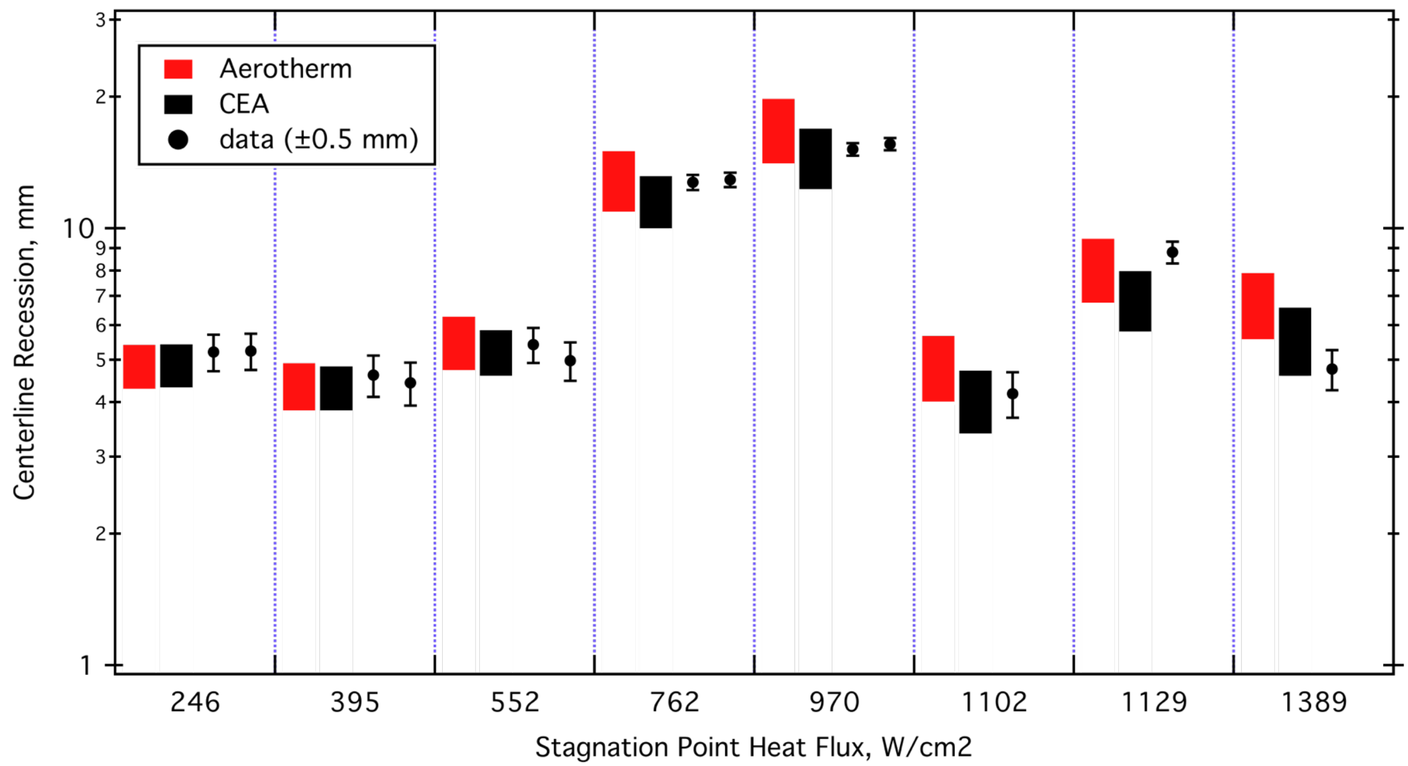
Test Condition	Cold Wall Heat Flux (W/cm^2)	Pressure (kPa)	Centerline Enthalpy from DPLR (MJ/kg)	Argon Mass Fraction†	Exposure Time (s)	Number of Models
1	246	8.5	19.3	0.108	60	2
2	395	17.2	21.4	0.080	34	2
3	552	27.3	23.3	0.076	30	2
4	762	46.6	23.7	0.084	45	2
5*	970	63.4	23.6	0.085	40	2
6	1102	84.4	25.6	0.078	10	1
7	1129	111.2	23.0	0.075	15	1
8	1389	107.3	28.1	0.077	10	1

* This test used 7.62-cm diameter models. All other tests used 10.16-cm diameter models.

† We assume complete mixing of the main air, add air, and argon streams in the arcjet.

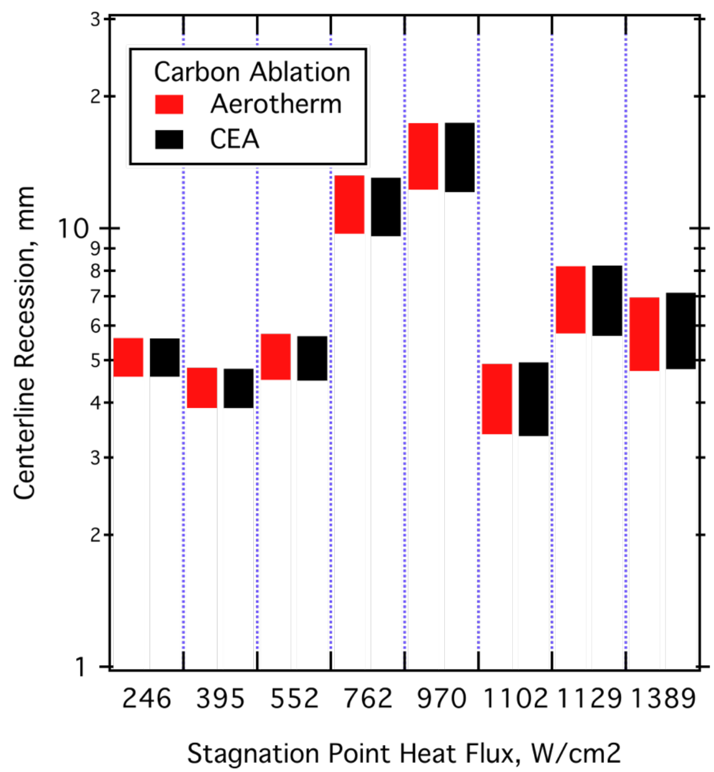
Ablation of PICA

- Procedure: vary heating ±10%, plot the range of predicted recession (calculated by FIAT), and compare with the measured centerline recession
- Below 552 W/cm^2, B'c < 0.2 (oxidation), and predictions differ by ~1%
- Above 750 W/cm^2, the difference between predictions is greater, but comparison with data is inconclusive



Ablation of Carbon

- Same test conditions, but no data
- Maximum B'c < 0.4
  - Little difference between predictions (as expected)

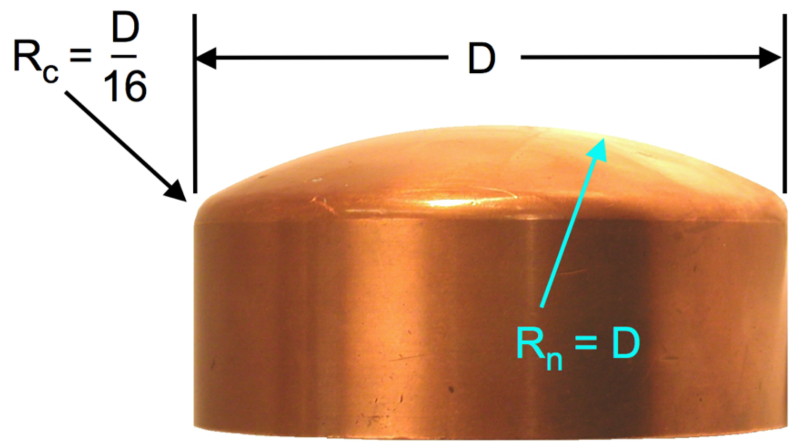


Summary

- Although there are significant differences in Aerotherm and CEA thermodynamics for important gaseous species, ablation predictions for carbon and carbon-phenolic are comparable for test conditions in the NASA arcjets (below 120 kPa and 1400 W/cm^2 in air)
- To really distinguish between these models, we need to test at more extreme conditions or in a different atmosphere, such as hydrogen
- For prediction of ablation of carbonaceous materials, the CEA thermodynamics database may be used, but I recommend inclusion of C_3H and C_4H from the Aerotherm database
- I also recommend to find/calculate updated thermodynamics for C_3H and (if necessary) C_4H to determine whether or not these species really are significant

Iso-q Shape

- Nose radius equals cylindrical body diameter
- In ARC arcjets, the heat flux is relatively constant along the front face, for model diameters up to 15 cm



"Iso-q" Calorimeter