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

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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

\[ \frac{C_p}{R} = \frac{a_1}{z^2} + \frac{a_2}{z} + a_3 + a_4 z + a_5 z^2 + a_6 z^3 + a_7 z^4 \quad \text{where} \quad z = T/(1000^\circ K) \]

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

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</table>
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

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

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

• 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 (\( \Delta H_{298}^0 \) and \( S_{298}^0 \)) 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
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
Comparison of Aerotherm and CEA Fits

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

\[ \text{Species: H}_2 \]

- \[ \text{Species: CO}_2 \]
• For others, the comparison is (visually) not as good
• 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
• 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.
• 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
• 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)


Stagnation Arcjet Conditions (Orion tests)

- We consider a set of stagnation conditions with heat flux and pressure above 200 W/cm² 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).

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Cold Wall Heat Flux (W/cm²)</th>
<th>Pressure (kPa)</th>
<th>Centerline Enthalpy from DPLR (MJ/kg)</th>
<th>Argon Mass Fraction†</th>
<th>Exposure Time (s)</th>
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* 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/cm², \( B'c < 0.2 \) (oxidation), and predictions differ by ~1%
- Above 750 W/cm², 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/cm² 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 C₃H and C₄H from the Aerotherm database

• I also recommend to find/calculate updated thermodynamics for C₃H and (if necessary) C₄H 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

\[ R_c = \frac{D}{16} \]

\[ R_n = D \]