Outline

- Why this tutorial?
- Ablative TPS - early studies
- Organic resin composites
- **Surface recession mechanisms/modeling**
- High fidelity model development
- Testing approaches/requirements
- Future needs

Empirical Approach

- Potentially, very accurate (if data is well-behaved), but what parameter(s) does one correlate recession rate with?
  - Surface temperature
  - Pressure
  - Heat transfer-coefficient
- Empirical correlations do not provide any insight to ablation *mechanisms*
- Validity of correlations typically limited to range of ground test data
  - Extrapolation beyond data range carries significant *risk*
  - Capability to *simultaneously* simulate flight environment parameters (e.g., heat flux, pressure, enthalpy) in ground test is the exception rather than the rule

Empirical correlations

- Heat of ablation (Q*)
  - This approach has been/is being (erroneously) used to estimate surface recession
  - Typically, recession rate estimated from $\rho\dot{s} = \dot{q}_{cw} / Q^*_{cw}$
  - For environments other than very severe heating, this approach will overestimate recession
- Curvefits
  - Typical form: $\dot{s} = f(T_w)$ or $\dot{s} = f(p, T_w)$
  - Has been used with some success for materials that vaporize (e.g., glass) or sublime (e.g., teflon)
  - Not demonstrated to be a viable approach for reinforced organic resin composites
- Limited applicability
  - How to apply empirical correlations developed in ground test facilities operating on air (existing arc jet facilities) to performance in planetary atmospheres (e.g., N_2/CH_4, CO_2, H_2/He)

Ablation Mechanisms

- Melting (metals, glass, ceramics, etc.)
  - Heat of fusion (not very significant)
  - $M(s)^* \Leftrightarrow M(l)^*$
- Vaporization (liquid layer from melted metals, glass, ceramics)
  - Heat of vaporization
  - $M(l)^* \Rightarrow M(g)^*$
- Oxidation (graphite, carbon chars, etc.)
  - Exothermic
  - $M(s)^* + O_2(g) \Rightarrow MO_2(g)$
- Sublimation
  - Heat of sublimation (can be significant)
  - $M(s)^* \Rightarrow M(g)$
- Spallation
  - Mass loss with minimal energy accommodation

Melting

- Melting is a common ablation mechanism, but doesn't absorb much energy
- Rapid melt runoff due to aerodynamic shear results in significant (inefficient) ablation
- In contrast, a stable liquid layer on the surface can be attractive (due to the potential for vaporization)

Specie	Tmelt (K)	Heat of Fusion (J/g)
K*	336	60
Li*	454	432
Al*	933	397
Cu*	1358	206
Be*	1556	1297
Fe*	1809	247
Li_2O*	1843	1960
Ti*	1933	388
SiO_2*	1996	150
TiO*	2023	654
Zr*	2125	229
TiO_2*	2130	838
Al_2O_3*	2315	1159
Mo*	2896	375
ZrO_2*	2950	706
TiB_2*	3193	1443
W*	3680	192

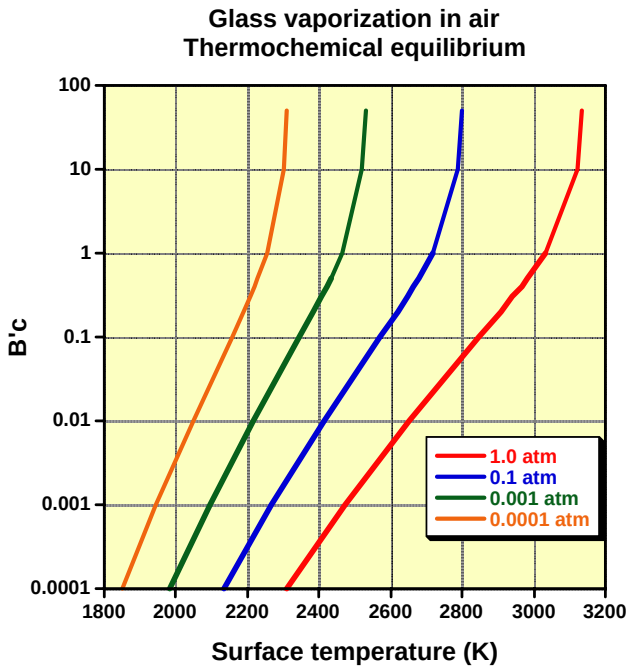
Vaporization

- Vaporization absorbs significant amount of energy
- Example:

$$SiO_2(l) \rightarrow SiO(g) + \frac{1}{2}O_2(g)$$

$$\Delta H_v \approx 12.5\ kJ/g_{SiO_2}$$

- However, typically, liquid layers have low-moderate hemispherical emissivity (reduces re-radiation)



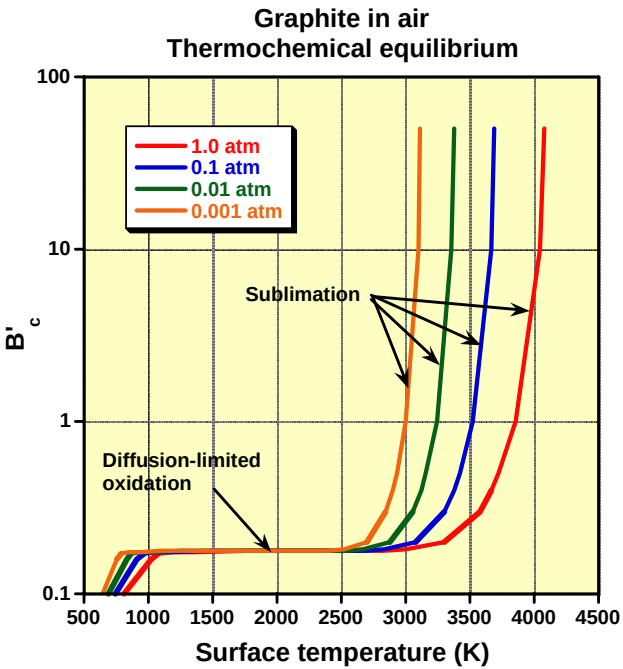
Oxidation - 1

- Oxidation is an *exothermic* process
- Example:

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

$$\Delta H_{comb} \approx -4170 \ kJ/g_{carbon}$$

- Note: the B' curve for carbon in air was generated with assumptions of thermochemical equilibrium, equal diffusion coefficients, etc.
- The "equilibrium" assumption allows the diffusion-limited plateau to extend to *unrealistically low* surface temperatures



Oxidation - 2

- The diffusion-limited value of B' can be calculated from the mass ratios of the reactants and products, i.e.,

$$2C(s)+O_2(g)+3.718N_2(g)\leftrightarrow 2CO(g)+3.718N_2(g)$$

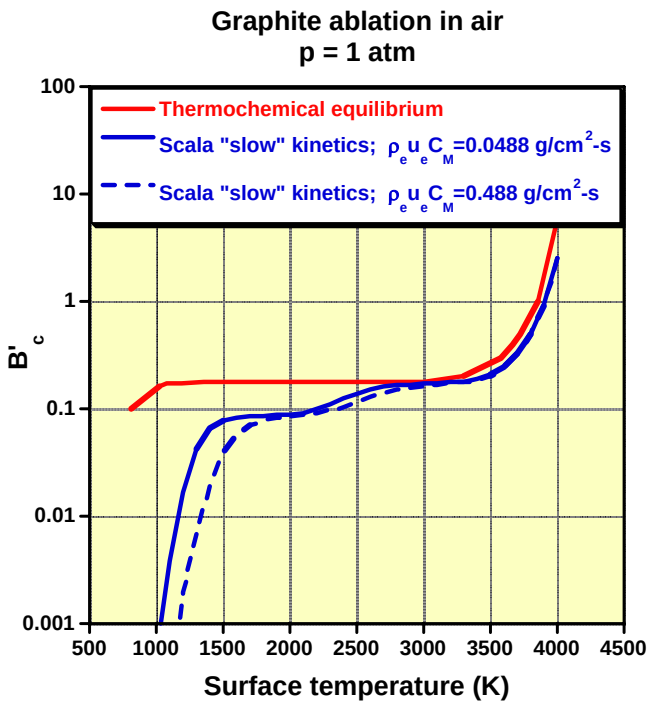
where there are 3.718 moles of N_2 for each mole of O_2 in air. The approximate value of B' for this reaction can be defined as the ratio of the mass of the solid reactants to the mass of the gaseous reactants, i.e.,

$$B'=\frac{mass\ of\ carbon}{mass\ of\ air}=\frac{2(12.011)}{[32.0+(3.718)28.014]}=0.176$$

- Realistic estimates of carbon ablation at low surface temperatures requires consideration of reaction-rate limited oxidation processes
  - Complex problem where rates are dependent upon oxygen partial pressure, mass transfer coefficient, temperature, surface morphology, etc.

Oxidation - 3

- Comparison of equilibrium solution vs. rate-limited solutions for carbon oxidation demonstrates that equilibrium solutions will overestimate surface recession over much of the oxidation regime
- Developing kinetic rate constants requires careful experimentation
- Results will be material-specific since absorption/ desorption is dependent on surface morphology



Sublimation

- Carbon sublimation is a highly *endothermic* process

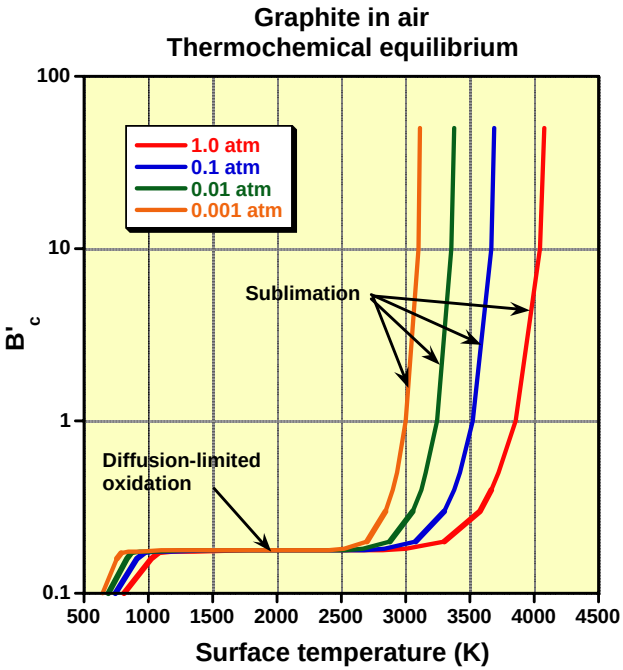
$$C(s) \rightarrow aC_1(g) + bC_2(g) + cC_3(g) + \ldots nC_n(g)$$

- Example (for simplicity):

$$3C(s) \rightarrow C_3(g)$$

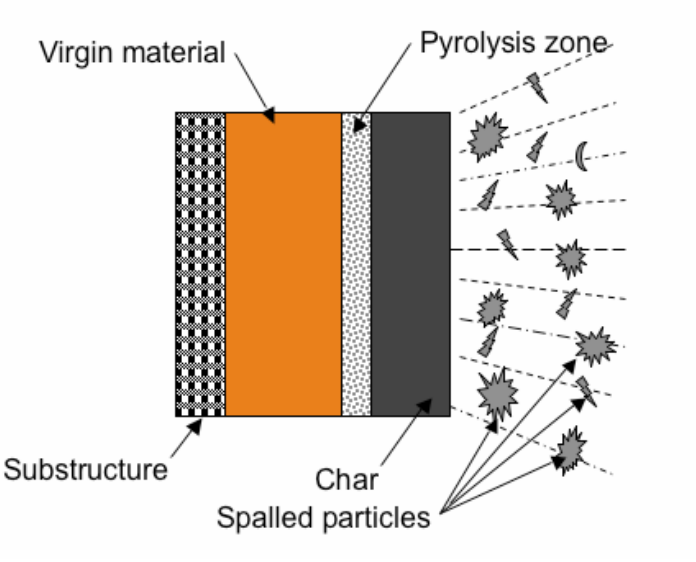
$$\Delta H_{sub} \approx 22.7\ kJ/g_{carbon}$$

- Carbon sublimation predictions exhibit some sensitivity to species thermochemical data (e.g., JANAF, Livermore, etc.)



Spallation

- Spallation refers to thermo-structural failure of the material and ejection of solid char and particulates[10,11,17,18,22]
  - More common in organic resin composites than homogeneous materials
- All organic resin composites have a spallation threshold $= f(\dot{q}, p)$
- Spallation threshold, in general, increases with increasing density

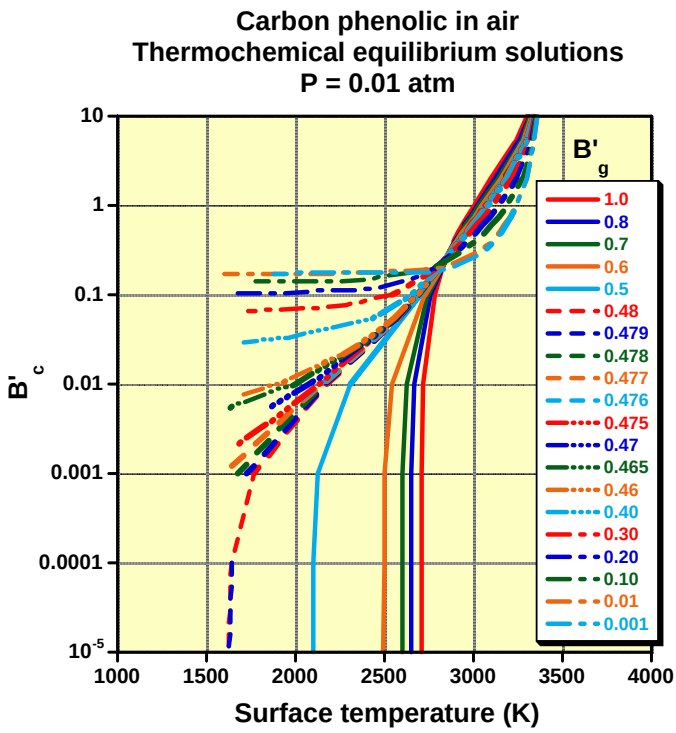


Organic Resin Composites

- Generating surface thermochemistry tables for organic resin composites requires thought and care

$$B'_c = f\left(p, T_w, B'_g\right)$$

- Useful to plot the solutions to ensure that the thermal response code is capable of interpolating between adjacent solutions with credible results
- Thermochemical equilibrium solutions are reasonably complex; incorporating rate-limited reactions is very complex



Summary

- Modeling surface ablation is best accomplished if the focus is on understanding ablation *mechanisms*
  - Requires careful experimentation
    - Film or video
    - Surface temperature (key discriminator)
    - Post-test inspection/autopsy
- Use theoretical models (e.g., thermochemical equilibrium) for pre-test/post-test predictions
  - Compare data with predictions (mass loss rate, surface temperature, surface species, etc.)
  - Identify other parameters that could influence performance (e.g., surface catalycity)
- Ability to model material performance mechanisms using thermochemical models allows extrapolation to conditions beyond ground test data base (within limits)

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