

cone heating for convenience. The cylindrical front portion of the movable section experiences quite severe heating at the 15° cant position due to reattachment of the flow off the forward section of the fin. Values up to seven times cone heating were measured. The heating along the windward side of the canted aft section increases along its length to a maximum of three and a half to four times the uncanted value. This value exhibits only a very weak dependence on flow conditions.

### References

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## Modeling Sublimation of a Charring Ablator

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### Nomenclature

- $A$  = area  
 $C_i$  = mass fraction of species  $i$   
 $J_i$  = diffusive mass flux  
 $\bar{M}$  = average molecular weight  
 $M_i$  = molecular weight of species  $i$   
 $m_i$  = mass flux of species  $i$   
 $P$  = pressure  
 $P_{\text{vap}}$  = vapor pressure  
 $R$  = gas constant  
 $T$  = absolute temperature  
 $v$  = velocity  
 $\alpha_i$  = accommodation coefficient of species  $i$   
 $\omega_i$  = reaction rate of species  $i$   
 $\rho$  = density  
 $\epsilon$  = porosity

### Introduction

THE determination of the sublimation rate of carbon for a char forming ablative heat shield is necessary to fully describe the material response to aerodynamic heating. This sublimation rate is required in the surface mass and energy balances which give the interaction of the flowfield and the ablator.

The sublimation model that is used in this analysis and compared to other investigators is based on the Hertz-

Knudsen equation. The basic equation originally given by Hertz in 1882<sup>1</sup> relates in the mass of molecules striking a unit area per unit time to the pressure and temperature of the gas. The theoretical model is shown to compare quite favorably with arcjet experimental data and demonstrates its usefulness by its accuracy and simplicity.

### Model Description

For nonequilibrium such as the case where the subliming material is continually removed, the net rate of evaporation is given by the well-known Hertz-Knudsen equation<sup>2</sup>

$$\dot{m} = \alpha(A_r/A)(M/2\pi RT)^{1/2}(P_{\text{vap}} - P) \quad (1)$$

The preceding equation can be extended for vaporization of a solid into a mixture of gases by replacing the total pressure,  $P$ , with partial pressure of the vaporizing component,  $P_i$

$$\dot{m}_i = \alpha_i(1 - \epsilon)(M_i/2\pi RT)^{1/2}(P_{i, \text{vap}} - P_i) \quad (2)$$

For subliming carbon  $i$  refers to  $C_1$ ,  $C_2$ , and  $C_3$  vapor. The effective area ratio  $A_r/A$  is approximated by  $(1 - \epsilon)$  where  $\epsilon$  is the char porosity.

### Carbon Species

Studies<sup>3</sup> have shown that the three primary constituents of subliming carbon are  $C_1$ ,  $C_2$ , and  $C_3$ . These species have Arrhenius dependence of vapor pressure on temperature of the form  $\log P_i = a_i + b_i/T$ . The accommodation coefficients,  $\alpha_i$ , along with the Arrhenius vapor coefficients<sup>4</sup> are given in Table 1.

### Surface mass balance

The general species mass balance at the surface of the ablator includes convective flux to and away from the surface ( $\rho v C_i$ ), diffusive flux to and away from the surface ( $J_i$ ), and surface generation by chemical reaction ( $\omega_i$ ). The species mass balance is stated as follows:

$$\rho v C_i^- + \omega_i + J_i^- = \rho v C_i^+ + J_i^+ \quad (3)$$

In the region where the rate of sublimation is significant, surface chemical reactions and diffusion will not be important, and this is the case for the high heating rates encountered during manned return from planetary missions. The result is a porous char vaporizing into the gaseous species  $C_1$ ,  $C_2$ , and  $C_3$ . Also flowing through this porous matrix is the pyrolysis gas from the decomposition zone of the ablator. In Ref. 5 there was an error in the nitrogen composition of the pyrolysis gas from a phenolic-nylon ablator, and correct values are reported in Table 2. Also reported in Table 2 is a typical composition of the pyrolysis gases at the ablator surface computed from a nonequilibrium char zone analysis described in Ref. 6, an extension of the work of Ref. 7. The analysis considers the pyrolysis gas from the decomposition zone flowing through the char zone and reacting at a finite rate.

Combining the Hertz-Knudsen equation, Eq. (2), with the surface mass balance for these previously described conditions for  $i$  being  $C_1$ ,  $C_2$ , or  $C_3$ , the mass flux of these gaseous carbon species injected into the shock layer is given by

$$\rho v C_i^+ = \alpha_i(1 - \epsilon)(M_i/2\pi RT)^{1/2}(P_{i, \text{vap}} - P_i^+) \quad (4)$$

Table 1 Accommodation coefficients and Arrhenius coefficients for vapor pressure of  $C_1$ ,  $C_2$ , and  $C_3$  (Ref. 4)

Species	Accommodation coefficient, $\alpha_i$	$\log P_{i, \text{vap}} = a_i - b_i \times 10^4/T$	
		$a_i$	$b_i$
$C_1$	0.37	8.14	3.72
$C_2$	0.34	9.69	4.23
$C_3$	0.08	9.81	4.03

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**Table 2 Representative pyrolysis product composition of 40% (by weight) nylon—60% (by weight) phenolic resin ablative composite**

Component	Composition of pyrolysis gases (mass percent)	
	Decomposition zone	Ablator surface
H <sub>2</sub>	3.03	3.81
CH <sub>4</sub>	3.87	0.08
C <sub>2</sub> H <sub>2</sub>	3.89	5.96
C <sub>2</sub> H <sub>4</sub>	3.90	"
C <sub>2</sub> H <sub>6</sub>	0.65	"
C <sub>6</sub> H <sub>6</sub>	2.59	"
C <sub>6</sub> H <sub>5</sub> OH	23.18	"
CO	4.18	25.70
CO <sub>2</sub>	4.62	"
H <sub>2</sub> O	5.65	"
N <sub>2</sub>	4.96	4.96
CH <sub>3</sub>	"	0.32
CH <sub>2</sub>	"	3.10
C <sub>2</sub> H	"	11.80
H	"	2.88
Carbon (solid)	39.48	42.11
Total	100.00%	100.00%

Element	Elemental composition (mass percent)
C	73.03
H	7.29
N	4.96
O	14.72
Total	100.00%

"Concentration is less than 0.01%.

The aforementioned equation can be put in terms of the total pressure at the surface using  $P_i^+ = C_i^+ PM_i / M_t$  and solving for  $C_i^+$ , mass fraction of the gaseous carbon species leaving the surface, gives

$$C_i^+ = BP_{t, \text{vap}} / (\rho v + B \overline{M} P / M_i) \quad (5)$$

where

$$B = \alpha_i (1 - \epsilon) (M_i / 2\pi RT)^{1/2} \quad (6)$$

Finally, a total mass balance on carbon char says that all carbon coming to the surface as a solid leaves as a vapor

$$C(s) = \sum_{i=1}^3 C_i^+ \quad (7)$$

This does not include the possibility of erosion as a surface removal mechanism, but erosion could be readily included if important.

Using Eqs. (5-7) and the data in Tables 1 and 2, the mass flux at the surface can be computed as a function of surface temperature. Also the composition of  $C_1$ ,  $C_2$ , and  $C_3$  in the gases injected into the shock layer are determined.

#### Results of Analysis

In Fig. 1 a comparison is shown between our calculations using the Hertz-Knudsen equation and the results from Bishop and DiCristina<sup>8</sup> for a phenolic-carbon ablator. The porosity used in the Hertz-Knudsen equation was 0.2, a value given by Clayton et al.<sup>9</sup> for carbon-phenolic. The results reported by Bishop and DiCristina<sup>8</sup> were obtained from arcjet experimental data for phenolic-carbon in the sublimation regime. The theoretical predictions of the Hertz-Knudsen sublimation model correspond quite well with the experimental curve except for some divergence at higher surface temperatures. Bishop and DiCristina stated in their paper that their curve would break less sharply if their surface temperature data had been corrected for the pyrometer error due to "significant

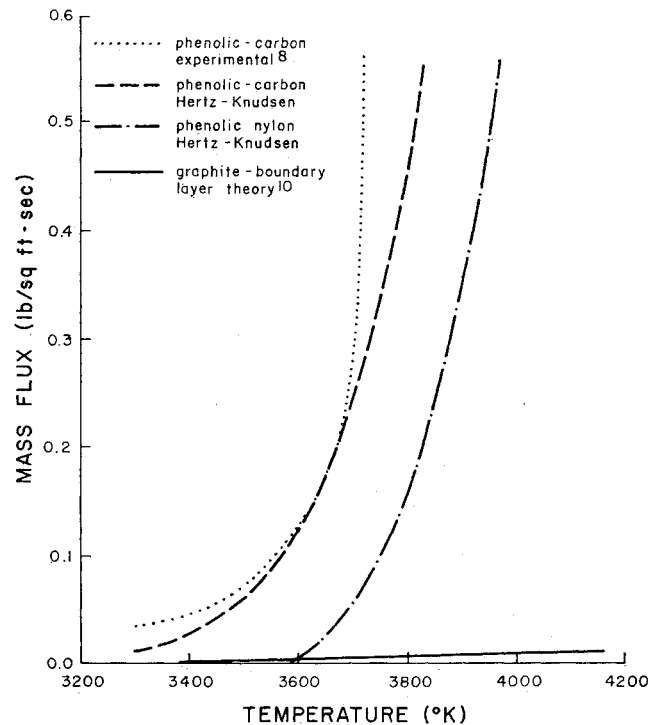


Fig. 1 Comparison of the Hertz-Knudsen analysis with other investigators.

nose curvature over the specimen area." Taking this fact into account, excellent agreement between the Hertz-Knudsen theoretical approach and the results from arcjet experimental work would be obtained.

Also shown in Fig. 1 are the results reported by Scala and Gilbert.<sup>10</sup> These results were obtained using an equilibrium chemistry boundary-layer analysis to predict the sublimation rate of graphite. These results differ greatly from both the Hertz-Knudsen predictions and the data of Bishop and DiCristina. The difference could be due to the fact that Scala and Gilbert's analysis assumed equilibrium between the

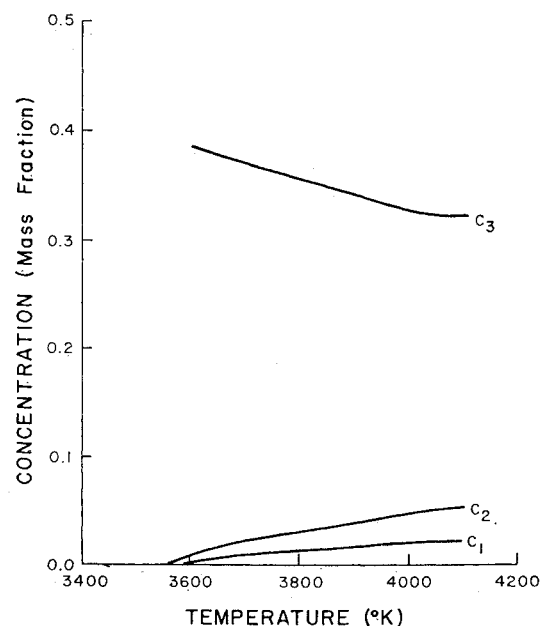


Fig. 2 Predominant carbon vapor species from the sublimation of a phenolic-nylon ablator.

graphite and the carbon vapor phase. Applying the Hertz-Knudsen analysis for graphite ablation gave essentially the same results as for the phenolic carbon. For graphite, the porosity is zero and there is no flow of pyrolysis products. These two effects shift the curve in opposite directions, and thus the curve for graphite predicted by the Hertz-Knudsen equation is essentially the same as that for carbon-phenolic which is used to compare with Scala and Gilbert's results.

To demonstrate the difference that porosity can make on the mass flux, the Hertz-Knudsen analysis was applied to a phenolic-nylon ablator with a porosity of 0.8. Referring to Fig. 1, increasing porosity has the effect of raising the surface temperature for a given mass flux.

In Fig. 2, the carbon species compositions for the phenolic-nylon ablator are given, and this shows that  $C_3$  is the predominant component that is obtained from the subliming char. This result agrees with Palmer and Shelef<sup>3</sup> who report that  $C_3$  becomes the primary constituent at these temperatures.

### Conclusions

The Hertz-Knudsen analysis has been shown to accurately predict the sublimation rate from a charring ablator. Porosity was shown to have a significant effect on the surface temperature—an increase in porosity results in an increase in surface temperature. The predominant carbon species in the vapor was  $C_3$  which agreed with previous investigations.

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