predominate ablation species in the outer regions of the viscous layer.

A correlation of a number of boundary-layer solutions for a wide range of boundary conditions (i.e., $3500 < T_w < 7000°\text{R}$, $10.0 < P_e < 100$ atm, and $100.0 < H_e < 6000.0$ btu/lb) led to the results shown in Fig. 3. In this figure, the stagnation point mass transfer parameter $\dot{m}_w (R_B/P_e)^{1/2}$ is plotted as a function of the enthalpy difference $(H_e - h_w)$ across the boundary layer. These results indicate that when $H_e < h_w$ the diffusion controlled oxidation rate is reduced by as much as 20% from the rate which would be predicted for hypersonic re-entry conditions (i.e., where $H_e \gg h_w$). This reduction in oxidation rate for $H_e < h_w$ has been observed experimentally.[8-10] It should be noted, however, that theoretical calculations for graphite vaporization with "hot-wall—cold gas" boundary conditions yielded no significant deviation in the magnitude of the mass transfer rate from that which would be predicted for hypersonic re-entry.[2-3]

Discussion

The numbers on Fig. 3 indicate the computer run number for the boundary-layer solutions obtained during this study. The differences obtained in the mass transfer parameter due to differences in the transport properties utilized are clearly indicated by the results of Run #1 and #2. The properties for the air species used in Run #2 are based on the Scala-Baulknight model.[11] The higher oxidation rate calculated in Run #1 is due to the higher binary diffusion coefficients for the atomic species which are predicted by the Yun and Mason[12] atomic cross sections. Compare this, however, with the oxidation rates calculated from Runs #11 (Ref. 11 properties) and #12 (Ref. 12 properties). Now for these later boundary conditions (i.e., Runs #11 and 12), the air at the edge of the boundary layer is not dissociated as it was for Runs #1 and #2. When the edge temperature is low, atomic oxygen is not present to enter into the combustion reaction, and for this situation the properties of Refs. 11 and 12 for air lead to the same prediction for the oxidation rate.

The explanation for the reduction in the oxidation rate for the "hot wall—cold gas" boundary conditions is related to the magnitude of the species CO_2 which can be produced within the boundary layer away from the oxidizing surface. Recall that the expression for the oxidation $(\dot{m}_w)$ rate is defined[1,3] in terms of diffusion fluxes (j_i) and mass fractions (c_i)

$$\dot{m}_w = (j_{CO} + j_{CO_2})_w / (1 - C_{CO} - C_{CO_2})_w \tag{1}$$

and for the purposes of clarifying this point, let us consider the Fick's Law approximation for the diffusion flux vector.

$$j_{i_w} \cong -\left(\frac{\mu Le}{Pr} \nabla C_i \right)_w \tag{2}$$

where μ, Le and Pr are the viscosity and Lewis and Prandtt numbers of the gas mixture, and ∇C_i is the concentration gradient. Now it has been demonstrated[1,3] that for the equilibrium diffusion-controlled oxidation of graphite, it is the species CO_2 which diffuses back to the surface and provides the oxygen for the heterogeneous reaction $CO_2 + 2\,C(s) \rightarrow 2\,CO$. The carbon monoxide which is formed then diffuses away from the surface. Note that the composition profiles (Fig. 2) show that the gradient of the species CO_2 is positive, and the gradient of CO is negative at the surface. This means that the diffusion flux [Eq. (2)] of CO_2 is negative while the diffusion flux [Eq. (2)] of CO_2 is negative while the diffusion flux of CO at the surface is positive. Examination of Eq. (1) shows that increasing the diffusion flux of CO_2 tends to reduce the overall oxidation rate. One can conclude, therefore, that for these boundary conditions where the magnitude of the species CO_2 can be maximized in the boundary layer, its gradient and diffusion flux at the surface is also increased, leading to a reduction in the overall oxidation rate.

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Exponent Breaks in Composite Solid Propellants

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IT has been noted by Miller, Hartman, and Myers[1] that the Summerfield granular diffusion flame (GDF) rate-pressure relationship[2] implies

$$\lim_{d_{ox} \rightarrow \infty} r = 0 \tag{1}$$

where r is burning rate and d_{ox} is oxidizer particle size. Since this limit is physically unattractive, they modified the GDF relation to

$$r = ap^s + (b/p + cd_{ox}/p^{1/3})^{-1} \tag{2}$$

where p is pressure and a,b,c, and s are constants; s and a were identified with the binder. However, for composite

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propellants with endothermic binders and ammonium perchlorate (AP) oxidizer, the aforementioned limit suggests that a and s should be identified with the AP. On the other hand, if the "binder" were active and able to sustain rapid deflagration, a and s might then be identified with the binder. The objective of this note is to show that Eq. (2) possesses "qualitative" exponent break information.

In the high pressure regime $(b/p) \ll (c\, d_{ox}/p^{1/3})$, so Eq. (2) becomes

$$r = a\, p^s + g\, p^{1/3} \tag{3}$$

Differentiating Eq. (3) with respect to p [assuming $s = s\,(p)$], multiplying by p, dividing by r, and employing Eq. (3) to eliminate g yields

$$\partial \ln r/\partial \ln p = \{1 + a\, p^s[3(s + s'p \ln p) - 1]/r\}/3 \tag{4}$$

where $s' = ds/dp$. The function $s(p)$ is not readily obtainable from AP burning rate data while $n = d \ln r_{AP}/d \ln p$ is (r_{AP} is AP burning rate). Integration of this expression from a reference pressure p_o to p gives

$$\ln r_{AP} = \int_{p_o}^{p} n\, d \ln p + \ln r_{AP}(p_o) \tag{5}$$

Since $a\, p^s$ is identified with the AP, $r_{AP} \propto a\, p^s$. Taking the logarithm of this expression and comparing that result with Eq. (5) shows

$$s = \int_{p_o}^{p} n\, d \ln p/\ln p \tag{6a}$$

$$a = r_{AP}(p_o)/m \tag{6b}$$

where $0 < m < 1$ is a proportionality constant between r_{AP} and $a\, p^s$.[†] Differentiating Eq. (6a) with respect to p yields

$$s' = (n/p - s/p)/\ln p \tag{7}$$

Substituting Eq. (7) into Eq. (4) yields

$$d \ln r/d \ln p = [1 + (3n - 1)a\, p^s/r]/3 \tag{8}$$

Associating propellant exponent break with $d \ln r/d \ln p = 1$ and denoting exponent break conditions with an asterisk, Eq. (8) shows that

$$r^* = [3\, n(p^*) - 1] r_{AP}(p^*)/(2m) \tag{9}$$

Equation (9) defines the r,p exponent break locus in terms of AP properties and m and shows the following: a) $r^* > r_{AP}(p^*)$ for $n > 1$; b) $r^* \gtrless r_{AP}(p^*)$ for $1/3 < n < 1$; and c) $r^* \leq 0$ when $n \leq 1/3$. These results show that in r,p coordinates the exponent break locus should lie above the r_{AP},p curve when $n > 1$. However, when $1/3 < n < 1$ the exponent break locus may be either above or below the AP deflagration curve. Moreover, since $r > 0$, c) suggests that exponent breaks are impossible when $n \leq 1/3$.

The rate-pressure characteristics of AP are not unique because polycrystaline and single crystal data may differ significantly.[3] Indeed, polycrystalline data itself is not self-consistent[3]; a principal variable appears to be compaction pressure. There are two reasons for employing "loosely compacted" polycrystalline data herein. First, composite propellant r,p characteristics suggestive of single crystal r_{AP}, p characteristics are uncommon. Second, single crystal data reflects true steady-state conditions while "steady-state" composite propellant (and polycrystalline AP) combustion is an ensemble of transients that is "steady" only in the mean.[1] Polycrystalline AP data reported by Martin and Henderson[4] will be employed here. This data has been previously employed with exponent break hypotheses.[4]

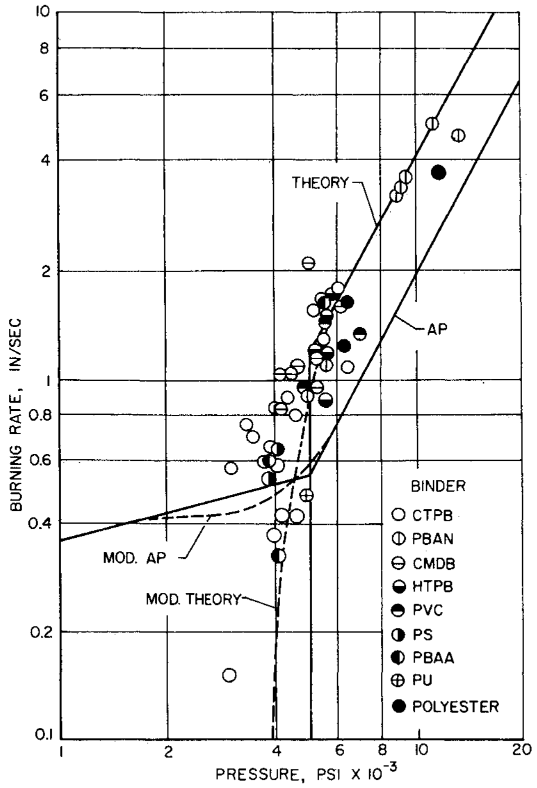

Fig. 1 Comparison of data and theory.

Figure 1 presents Martin and Henderson's exponent break data, an AP deflagration curve, and the theoretical exponent break relation derived from that curve when $m = 1$. The shape of the theoretical exponent break locus is suggestive of the general trend shown by the data. For $p > 5000$ psi where exponents from mono- and polycrystalline data agree theory and data are in rough agreement. However, for 3000 psi $< p < 5000$ psi where mono- and polycrystalline data may not agree exponent breaks occur where forbidden by theory. A reason for this disagreement is the discontinuous slope of the AP deflagration curve.[‡] If transition from $n < 1$ to $n > 1$ were smooth and spread over the 3000 to 6000 psi range, better agreement between theory and data would occur. The dashed lines show a modified AP deflagration curve that is an improved fit to the AP data reported by Martin and Henderson. The resulting modification to the exponent break locus demonstrates the importance of the 3000 $< p < 6000$ psi portion of the AP deflagration curve.

In summary, it has been demonstrated that embedding r_{AP},p characteristics in a combustion model imparts exponent break characteristics suggestive of reality. For $p > 5000$ psi where the slope of the AP decomposition curve is reasonably unambiguous theoretical results are in rough agreement with data. For $3000 < p < 5000$ psi where n is ambiguous, agreement depends strongly on the r_{AP},p characteristic selected. Therefore, since there are no rules to select a valid r_{AP},p characteristic and Eq. (2) has no valid physiochemical basis, this work must be viewed as an interesting exercise.

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[†] Since the propellent is heterogeneous,

$$\lim_{d_{ox} \to \infty} r < r_{AP}$$

Therefore, m should be largely dependent upon the physical structure of the propellant.

[‡] Since the oxidizer populating the deflagrating surface contains all sizes and stages of decomposition, a discontinuous slope is improbable.

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Theoretical Performance of Polyvinyl Chloride Plastisol Propellants: A Comparative Study

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Introduction

AMONG the possible plastisol composite propellant systems polyvinyl chloride (PVC) propellants are used extensively. Despite this, theoretical performance of these propellants are not fully available in open literatures. Rumbel[1] briefly gives the theoretical performance of an unmetallized propellant and a metallized propellant in this class. The aim of the present work is to make available the results of the theoretical performance of ammonium perchlorate (AP) - PVC plastisol propellants for many plasticizers of relatively wide variation in properties and to present a useful comparative study. Although the final composition of a propellant is usually decided on through various other factors like processing, physical properties, and aging requirements rather than through small changes in theoretical performance, the present work can be of help as an initial step towards propellant formulation.

II. Analysis

Rumbel[1] mentions dibutyl sebacate (DBS), dioctyl sebacate (DOS), and di-2-ethylhexyl adipate (DOA) as good plasticizers; dioctyl phthalate (DOP) is also used. Dibutyl phthalate (DBP) is rarely used as a sole plasticizer because of its poor low temperature flexibility characteristics and high volatility. Nevertheless, in addition to these four plasticizers, DBP is also considered for the analysis as a typical high-density low-molecular-weight plasticizer of relatively high oxygen and low hydrogen content. The method of group contribution technique by Handrick[2] was used for the estimation of heats of formation of the plasticizers. Properties of the plasticizers are summarized in Table 1. For the PVC resin, a mean value of 1.25 g/cm^3 is assumed for the density, and -22.6 kcal/mole is taken as the heat of formation per monomer.[3] The analysis is carried out for the propellants, having equal parts by weight of PVC and plasticizer along with aluminum, as the only metallic component. Chamber pressure of 70 atm with optimum expansion to one atmospheric pressure is assumed throughout. The computer program and the other thermochemical data given in Ref. 4 were used for the performance calculations.

III. Results and Discussions

A. Unmetallized Propellants

For the simple two component system of PVC binder and AP oxidizer, variation of specific impulse and density specific impulse for the cases of equilibrium flow and frozen flow are shown in Fig. 1. The vertical arrows in the figure indicate the stochiometric conditions. In the useful binder content range (around 20%), the high-density plasticizers along with the property of "low fuel rich" proportion give higher values of density specific impulse. But this advantage can be offset by the low-density plasticizers because of their capacity to accommodate higher solid loading with lower binder content without much loss in the mechanical properties of the propellant. However, one disadvantage of the low density plasticizers, should be noted. For any particular type of plasticizers, say the esters of sebacic acid, as the molecular weight increases the density decreases while the viscosity shows an upward trend (Table 1). Therefore considering the limitations imposed on the fluidity of mixed propellant controlled by the plasticizer viscosity, the improved solid loading capacity of the low-density plasticizers may not be fully realized.

B. Aluminized Propellants

Triangular composition diagrams of all five propellant systems were obtained for equilibrium flow, and these show the same pattern of constant specific impulse curves. The values of the overall maximum specific impulse and the corresponding percentage composition for the propellant systems are given in Table 1. The DBS-system is shown in Fig. 2 as a representative composition diagram.

With a close variation in the aluminum loading, maximum specific impulse and the corresponding aluminium loading were determined for different values of the binder content.

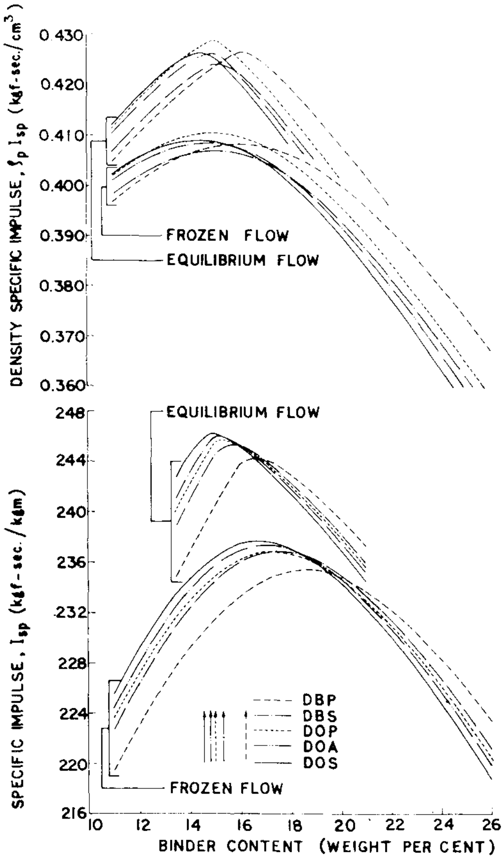

Fig. 1 Specific impulse and density specific impulse for AP-PVC propellants.

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