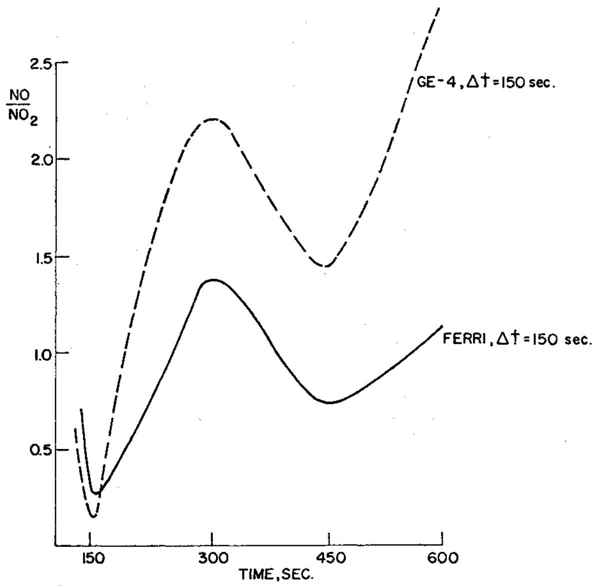

Fig. 1 Ratio of NO/NO_2 plotted as a function of time.

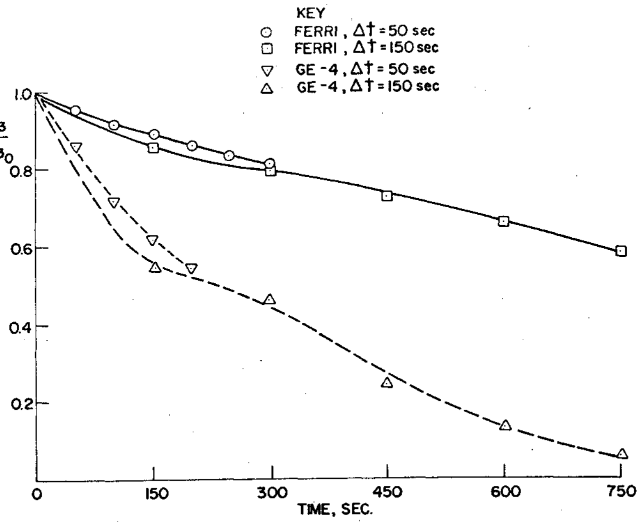

Fig. 2 Ratio O_3/O_{3_0}, plotted as a function of time.

The ratio NO/NO_2 was initially 100 for both engines. We observed this ratio to rapidly fall during the first 150-sec iteration and then rise to oscillate around 1 for the SST improvement and 2 for the GE-4. This result, which is shown in Fig. 1, is significant because, as Gupta and Grose have indicated,[6] ozone depletion is a direct function of NO/NO_2.

Figure 2 presents $0_3/0_{3_0}$ for both engines, iterated for 50 and 150 sec. During the first 150 sec, when ozone depletion is greatest, the ozone depletion effects of the GE-4 are 4 to 5 times greater than those of the improved SST engine. Our confidence in the applicability of the computational method of Rubel and Baronti[3,4] to this problem is enhanced by the slight variation in the depletion results caused by a large variation in the time interval. In the comparison of these results to results obtained using other methods, it is important to remember that we used a truncated chemical reaction series, unrealistically ignored sources of ozone, and, like Gupta and Grose,[6] we did not include the effects of atmospheric diffusion. Although our results for ozone depletion by the GE-4 are somewhat higher than the projections of Gupta and Grose,[6] it should be remembered that we utilized a higher value for k_I. Because of the relative arithmetical simplicity, it may be easier to treat diffusion rate chemistry calculations using the Rubel and Baronti approximation than would be possible through the use of other approaches.

Table 1 Relevant reactions, species production rate equations, reaction rates, and photodissociation coefficients (in cgs units)

$NO + O_3 \xrightarrow{K_I} NO_2 + O_2$	$K_I = 3.8 \times 10^{-15}$
$NO_2 + O(^3P) \xrightarrow{K_2} NO + O_2$	$K_2 = 9.1 \times 10^{-12}$
$O(^3P) + O_2 + M \xrightarrow{K_3} O_3 + M$	$K_3 = 1.08 \times 10^{-33}$
$O_3 + h\nu \xrightarrow{J_2} O(^3P) + O_2$	$J_2 = 3 \times 10^{-4}$
$NO_2 + h\nu \xrightarrow{J_3} NO + O(^3P)$	$J_3 = 8 \times 10^{-3}$

$$\partial[O_3]/\partial t = -K_I[NO][O_3] + K_3[O(^3P)]\ [O_2]\ [M] - J_2[O_3]$$

$$\partial[O(^3P)]/\partial t = -K_2[NO_2]\ [O(^3P)] + J_2[O_3] + J_3[NO_2] - K_3[O(^3P)]\ [O_2][M]$$

$$\partial[NO]/\partial t = -K_I[NO][O_3] + K_2[NO_2][O(^3P)] + J_3[NO_2]$$

$$\partial[NO_2]/\partial t = K_I[NO][O_3] - K_2[NO_2][O(^3P)] - J_3[NO_2]$$

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Pressure Dependence of Hybrid Fuel Burning Rate

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Nomenclature

a, a_I = constants
(A) = acid
b = constant
(B) = base
B' = $K_I \exp(E/RT)/Z_m\nu$
C_{Ads} = concentration of the acid adsorbed
C_B^s = concentration of the base at the fuel surface

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C_m = monolayer capacity
E = energy of desorption
G = total mass flux
k = chemical reaction rate constant
k' = constant, $kC_B^sC_m$
k'' = constant
K = equilibrium constant
K_1 = $N/(2\pi MRT)^{1/2}$
M = molecular weight of the adsorbate
n = pressure exponent
N = total number of molecules
P = pressure
r = reaction rate, gm/cm^2/sec
$\dot{r}$ = regression rate or burning rate
$\dot{r}_{\text{hetero}}$ = contribution of $\dot{r}$ due to pressure dependent heterogeneous chemical reactions at the fuel surface
$\dot{r}_{\text{homo}}$ = contribution of $\dot{r}$ due to diffusion controlled gas phase reaction in the boundary layer
R = gas constant
T = absolute temperature
Z_m = number of molecules adsorbed per unit area in a complete monolayer
θ = fraction of the surface covered
ν = oscillation frequency of adsorbed molecules
φ = fuel density

I. Introduction

THE burning rate of liquid, solid, and hybrid propellant systems has been observed to be pressure dependent by various investigators.[1-5] In spite of several attempts, no satisfactory theoretical explanation has been put forth. The treatment of Bernard et al.[4] appears to be promising, although the details are questionable. Summerfield et al.[5] have given a theory of solid-propellant combustion which predicts pressure dependence of burning rate. However, this dependence has been suggested to be caused by physical factors alone, such as flame gas density.[6,7] In liquid propellant combustion, pressure dependence of burning rate has been observed, but, again, it has been suggested to be caused by physical factors such as pressure dependence of latent heat of vaporization of the liquid.[8,9] It is important to note that this theory breaks down well before the vicinity of the critical pressure and also is not applicable far above the critical point.

It seems that the chemical factors largely have been ignored. The purpose of this paper is to examine to what extent these are responsible for the pressure dependence of burning rate.

II. Possible Chemical Factors Influencing Pressure Dependences

The pressure dependence of burning rate can arise on account of any of the following factors: pressure dependence of 1) rate constant k, 2) equilibrium constant K, and 3) adsorption-desorption equilibria. Both the chemical reaction rate k and the equilibrium constant K depend on pressure. However, these would be important only when the chemical reaction is the rate-determining factor during combustion.

Combustion of propellants can be expected to involve heterogeneous reactions at the interface, which, in turn, would be associated with the adsorption-desorption equilibria. Pressure dependence of the rate of combustion would appear automatically through Langmuir adsorption, which governs the latter equilibria.

III. Regression Rate of Hybrid Propellants

Smoot and Price[1-3] observed the pressure dependence of regression rate at high flow rates. At lower flow rates, the regression rate is independent of pressure and is governed entirely by the turbulent heat transfer in the boundary layer. Similar experimental results have been obtained by Bernard et al.[4] The following semiempirical equation[3] has been applied to correlate the pressure-flow dependent hybrid regression rate data.

$$\dot{r}=abG^{0.8}P^n/(aG^{0.8}+bP^n) \tag{1}$$

The analysis by Smoot and Price[3] shows that in such cases, there is a greater possibility that heterogeneous attack is the rate controlling factor.

In general, we can write

$$\dot{r}=\dot{r}_{\text{homo}}+\dot{r}_{\text{hetero}} \tag{2}$$

In Eq. (2), $\dot{r}_{\text{homo}}$ is the contribution to the regression rate due to diffusion controlled gas phase reactions in the boundary layer, whereas $\dot{r}_{\text{hetero}}$ is the contribution to regression rate due to pressure dependent heterogeneous chemical reactions at the fuel surface. At higher Reynolds numbers, the diffusion rate becomes high, and the process is governed by the kinetics of heterogeneous chemical reactions at the interface.

In a liquid-solid hybrid system, the basic reaction is expected to be between solid fuel and oxidizer vapor which first should be adsorbed on the fuel surface. At least near the fuel surface and away from the injector, the oxidizer would be in the gaseous form. We can write the sequence of chemical reactions in the following manner:

$$\begin{tikzcd}(A)+(B) \arrow[r] & \text{adsorption of }(A)\text{ on }(B) \arrow[r] & \text{Intermediate} \arrow[d] \\ & & \text{Decomposition}\end{tikzcd}$$

This is a distinct possibility in amine-based fuel and red fuming nitric acid systems since the earlier work of Rastogi and Munjal[10] has shown that aniline and nitric acid undergo a sequence of ractions preceded by the formation of amine nitrate,

$$C_6H_5NH_2+HNO_3 \longrightarrow C_6H_5NH_3^+NO_3^-$$

$$C_6H_5NH_3^+NO_3^-+HNO_3\ \text{(red fuming)} \longrightarrow C_6H_5NHNO$$

$$C_6H_5NHNO \longrightarrow C_6H_5N_2 \longrightarrow \text{ring rupture}$$

In the present case, we initially have a heterogeneous reaction followed by consecutive reactions. We make the following assumptions, which normally are valid: 1) adsorption-desorption equilibrium is established quickly, 2) observed rate is determined by the amount of surface covered by reacting molecules and by the specific velocity of the surface reactions, and 3) the slowest step is the rate-determining step.

The adsorption process would be the rate determining slowest step. Hence, the rate of the reaction would be given by

$$r=kC_{\text{Ads}}C_B^s \tag{3}$$

C_{Ads} can be estimated easily on the basis of Langmuir adsorption isotherm, according to which θ, the fraction of the surface covered, is given by

$$\theta=C_{\text{Ads}}/C_m=K_1P/[K_1P+z_m\nu\exp(-E/RT)] \tag{4}$$

In deriving Eq. (4), the value of average velocity as obtained from Maxwell's law of distribution of velocity has been used and further

$$K_1=N/(2\pi MRT)^{1/2} \tag{5}$$

Thus, from Eq. (4), we have

$$C_{\text{Ads}}=C_mB'P/(1+B'P) \tag{6}$$

where $B'=K_1\exp(E/RT)/Z_m\nu$

It should be noted that B' would be constant at constant temperature.

The number of molecules striking per unit area per unit time is related to pressure P when the Maxwell-Boltzmann distribution law is used. In the actual rocket conditions, where the situation is far removed from equilibrium, this would be related to P^n, where n is any index $(1<n>0)$, so that for such a case

$$C_{\text{Ads}} = C_m B'P^n/(1+B'P^n) \tag{7}$$

Since C_B^s has a fixed value, we have, from Eq. (3)

$$r = k'B'P^n/(1+B'P^n) \tag{8}$$

where k' is a constant and is given by

$$k' = kC_B^s C_m \tag{9}$$

Hence,

$$\dot r = r/\varphi = \frac{K'}{\varphi}\left[\frac{B'P^n}{1+B'P^n}\right] = \frac{k''B'P^n}{1+B'P^n} \tag{10}$$

Equation (10) predicts that, at very high pressure, when a complete monolayer has been formed,

$$\dot r = k'', \text{ since } B'P^n >> 1 \tag{11}$$

In other words, the burning rate would tend towards a limit, as has been observed experimetally by Bernard et al.[4] Further, when $B'P^n<1$, one would have

$$\dot r = k''B'P^n \tag{12}$$

It is important to note that Eq. (10) agrees with the experimental results. The experimental, results of Bernard et al.[4] in the pressure range of 1-15 bars for nitric acid-urea systems are fitted by the following equation:

$$\dot r = 0.25P^{0.88}/(1+0.37P^{0.80}) \tag{13}$$

The preceding ideas can be applied to the case of polymeric fuels also. The combustion process can be visualized as follows:

$$\text{Polymeric Fuel} + \text{Oxidizer} \rightarrow \begin{matrix}\text{Intermediate}\\ \text{Oxidative}\\ \text{Product}\end{matrix} \xrightarrow[\text{and Diffusion}]{\text{Decomposition}}$$

IV. Regression Rate of Solid Propellants

The foregoing arguments can be extended to the case of combustion of composite solid propellants also. The regression rate may be supposed to be made up of homogeneous reactions in the gas phase and heterogeneous, chemical reactions. We may therefore write,

$$\dot r = \dot r_{\text{homo}} + \dot r_{\text{hetero}} = \text{Constant} + \frac{k''B'P^n}{1+B'P^n} \tag{14}$$

where $\dot r_{\text{homo}}$ is independent of pressure.

When $1>B'P^n$, we have,

$$\dot r = \text{constant} + a_1P^n \tag{15}$$

and further, when $a_1P^n>$ constant,

$$\dot r = a_1P^n \tag{16}$$

Equation (16) is preferred for actual application[11,12] when the chamber pressure does not exceed 2000 psia. In the intermediate situations, $\dot r$ would have complex dependence on pressure.

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Unsteady Local Linearization Solution for Pulsating Bodies at $M_\infty = 1$

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Introduction

WITH the continuing development of successful techniques for solving steady transonic flows, considerable interest has been focused recently on the development of methods to solve unsteady transonic problems.[1] In this note we describe the local linearization solution for transonic flow past slender bodies of revolution undergoing oscillatory pulsatile motion of the body surface. This result provides the fundamental unsteady source solution from which higher-order multipole solutions (dipole, etc.) necessary to describe more complex unsteady motions (e.g., translation, rotation) can be obtained. The theory is based on the concept of dividing the flow into steady and unsteady

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