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Ignitability of Nonhypergolic Propellants in Presence of Potassium Permanganate

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MANY nonhypergolic fuels can be made hypergolic by introducing suitable additives.[1] In some cases, introduction of a hot surface brings about ignition, which presumably makes use of the fact that the temperature is increased in the zone of reaction. Since ignition is preceded by oxidative degradation processes, it seems that these would be accelerated by the use of stronger oxidizing agents. In this manner, many nonhypergolic fuels can be made hypergolic. The purpose of this note is to report the result of investigations undertaken from this angle.

An increasing amount of potassium permanganate was added to red fuming nitric acid, and the ignitability of various alcohols was tested with it. It was found that methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, secondary butyl alcohol and tertiary butyl alcohol all become hypergolic when 20% potassium permanganate is used. The ignition delay is below 0.3 sec in all cases. Studies were undertaken to elucidate the mechanism. The essential steps involved are the following:

$$\text{alcohol} \rightarrow \text{aldehyde or ketone} \rightarrow \text{acid} \rightarrow \text{degradation}$$

The intermediates in this reaction could be identified. As further confirmation of the mechanism, the ignitability of aldehydes and corresponding ketones was investigated. It was found that these ignite with red fuming nitric acid, which contains 10% potassium permanganate.

The role of potassium permanganate was investigated. It may be noted that only freshly dissolved potassium permanganate in red fuming nitric acid is effective. This gave us a strong suspicion that atomic oxygen is produced which acts as a much stronger oxidizing agent. This conclusion is supported by the fact that benzene also ignites with red fuming nitric acid containing potassium permanganate. Carbon disulfide also burns with a steel blue flame. However, the intriguing fact is that no reaction occurs with white fuming nitric acid. The role of NO_2 in the ignition reaction is not clear. Further studies are in progress.

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Normal Shock-Wave Properties in Imperfect Air and Nitrogen

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BECAUSE of the current interest in shock tube applications in the study of so-called real gas effects in gas dynamics, and since previous results did not include important imperfect gas‡ effects at high densities, recalculation and extension of previously published perfect gas calculations was necessary. The purpose of this note is to draw attention to the imperfect gas effects on the normal shock-wave properties especially at high shock strengths and quiescent gas pressures $p_1 \gtrsim 1$ atm.

Normal shock-wave properties have been computed for air[1] and nitrogen[2] in the range $M_S = 6(1)30$ into an ideal gas at a temperature of 300°K and pressures in the range from 10^{-4} to 10^3 cm Hg. The calculations were based on the recent thermodynamic data for imperfect air[3–5] and nitrogen.[3, 6, 7] Charts were presented[1, 2] for incident and reflected shock-wave conditions, stagnation conditions upstream and down-

Table 1 Imperfect and perfect gas normal shock-wave conditions in air

	Lewis and Burgess[1]	Feldman[8]
Air model	Imperfect	Perfect
M_S range	6–30	6–25
p_1 range (cm Hg)	10^{-4}–10^3	10^{-3}–76
Regions (see Fig. 2)	2, 2*s*, 20′, 20, 5	2, 2*s*, 20′, 5
Gasdynamic quantities	p, ρ, T, h, u, a, Z, S	p, ρ, T, h, u, Z^*

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‡ An ideal gas obeys $p = \rho RT$, $h = C_pT$, and $\gamma = C_p/C_v =$ const. A perfect gas will denote one obeying $p = Z^*\rho RT$ which includes dissociation and ionization neglecting intermolecular effects. An imperfect gas obeys $p = Z\rho RT$ which includes dissociation, ionization, and intermolecular forces. Local thermodynamic [i.e., thermal, mechanical (pressure), and chemical] equilibrium is assumed to exist for all conditions.

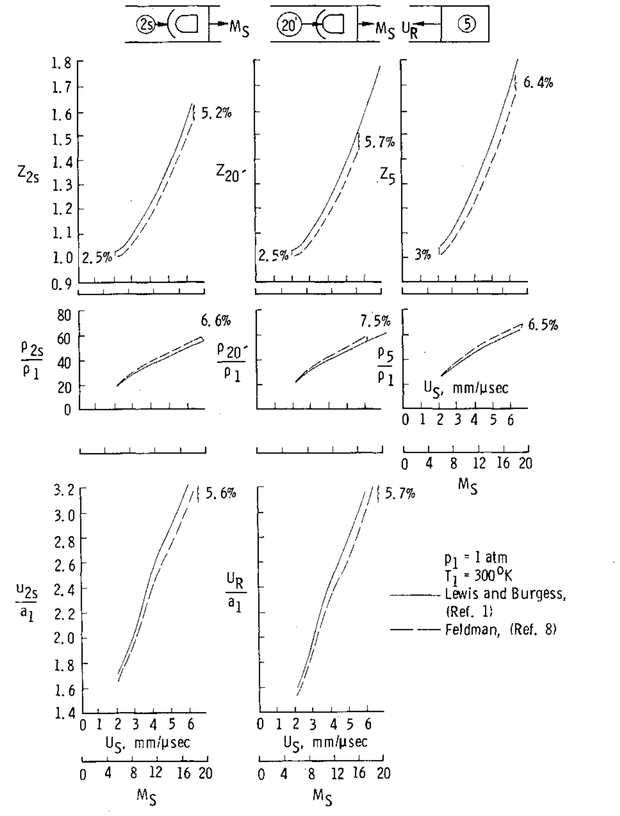

Fig. 1 Comparison between imperfect and perfect gas normal shock-wave properties in air.

stream, and conditions immediately downstream of a standing shock wave. The temperature and density in any region did not exceed, respectively, 15,000°K and 158 amagats where one amagat is the ideal gas density at one atmosphere and 273.15°K.

In the case of air, a comparison was made between the results of Lewis and Burgess[1] and the perfect gas results of Feldman[8] for a quiescent gas pressure of one atmosphere, and the results are shown in Fig. 1. The effects were found to be largest in the compressibility factor Z, the density ρ, and the velocity u or U_R in the regions shown in Fig. 1. However, Feldman did not include stagnation conditions upstream of the standing shock and a comparison was thus not possible. The effects would be largest on the same thermodynamic quantities, i.e., Z and ρ, in the upstream stagnation region as those shown in Fig. 1.

The ranges of conditions considered by Lewis and Burgess[1] and Feldman[8] are shown in Table 1. The regions are shown in Fig. 2, and the gas dynamic variables pressure p, density ρ, temperature T, enthalpy h, velocity u, speed of sound a, compressibility factor Z, and entropy S were calculated as noted in Table 1.

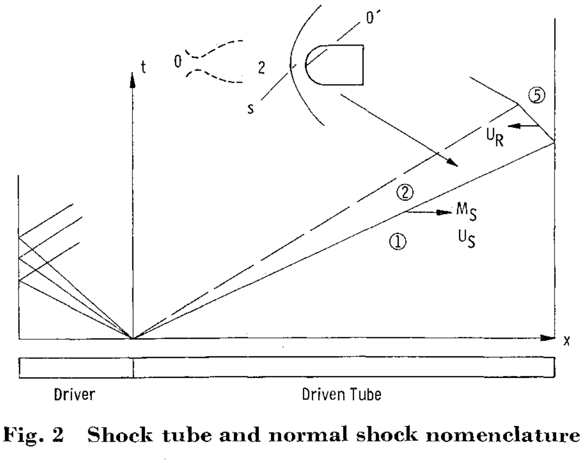

Fig. 2 Shock tube and normal shock nomenclature.

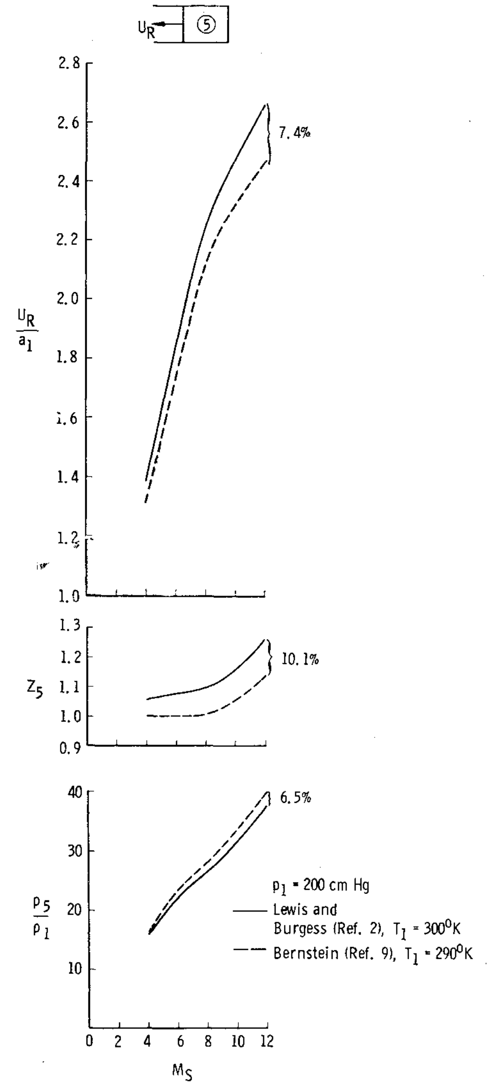

Fig. 3 Comparison between imperfect and perfect gas normal shock-wave properties in nitrogen.

The imperfect nitrogen results[2] were compared with the perfect gas results of Bernstein[9] at a quiescent gas pressure of 200 cm Hg, and the results are shown in Fig. 3. The range of Bernstein's calculations was more limited than those of Lewis and Burgess[2] (see Table 2), and he presented results only for the incident and reflected shock-wave properties. For the range of pressures available for comparison, the imperfect gas effects on the incident shock-wave properties were negligible; however, because of the higher quiescent gas pressures considered by Bernstein (p_1 = 200 cm Hg), the imperfect gas effects on the reflected shock-wave properties were larger than those for air by comparison with Feldman's results at p_1 = 76 cm Hg.

Table 2 Imperfect and perfect gas normal shock-wave conditions in nitrogen

	Lewis and Burgess[2]	Bernstein[9]
Nitrogen model	Imperfect	Perfect
M_S range	4–30	1.2–12
p_1 range (cm Hg)	10^{-4}–10^3	0.1–200
Regions (see Fig. 2)	2, 2s, 20′, 20, 5	2, 5
Gasdynamic quantities	$p, \rho, T, h, u, a, Z, S$	$p, \rho, T, h, u, a, Z^*, S$
T_1, °K	300	290

The comparisons show that the imperfect gas effects are about 5% for very strong shock waves ($M_S \sim 20$) into air at one atmosphere pressure, whereas, for strong shock waves ($M_S \sim 10$) into 2.63 atm, the effects are about 7%. These effects are, of course, maximum at highest density and therefore behind the reflected shock wave and at other stagnation conditions. For high pressure or high density shock tube studies, the results of Lewis and Burgess[1, 2] are to be preferred over the previously published perfect gas results.

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Effects of Diffusion in Laminar Hypersonic Wakes

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Introduction

DIFFUSION in laminar boundary layers has been shown[1] to reduce peak electron concentration levels by two orders of magnitude. It is the purpose of this note to describe such effects for laminar wakes since the electron densities that are generated there may, when carried into the turbulent wake, determine the observable signature of a re-entry vehicle.

Basic Equations and Solutions

The ionization due to sodium as a trace contaminant is considered. It is assumed that the presence of the sodium has no significant effect on local velocity and enthalpy, which are then described in the same manner as for the clean wake.[2] It is also assumed that the ionization reaction is far from equilibrium so that only the forward reaction is considered. To determine the sodium ion distribution, therefore, only the species equation need be considered.

For binary diffusion with constant Schmidt number in axisymmetric flow, the conservation of species for small r is[3]

$$U \frac{\partial C}{\partial x} = 2D \frac{\partial^2 C}{\partial r^2} + \frac{\dot{w}}{\rho} \tag{1}$$

For a near wake analysis, it has been shown[2] that the wake centerline velocity can be adequately described by

$$\frac{U_0}{U_e} = \left\{\frac{4\pi\mu_0 U_e x}{3D_f}\right\}^{1/2} \tag{2}$$

where D_f = frictional drag. Equation (2) is valid only up to values of U_0/U_e of roughly 0.5. The results of this note are carried only this far.

Letting the velocity for small r be represented by the centerline velocity, the conservation of species becomes

$$Ax^{1/2}(\partial C/\partial x) = 2D(\partial^2 C/\partial r^2) + (\dot{w}/\rho) \tag{3}$$

where

$$A = U_e\{4\pi\mu_0 U_e/3D_f\}^{1/2} \tag{4}$$

The boundary conditions are

$$x = 0 : C = C_0(r) \tag{5}$$

$$r = 0 : \partial C/\partial r = 0 \tag{6}$$

$$r = \infty : C = 0 \tag{7}$$

Introducing the variable t, where

$$t = x^{1/2} \tag{8}$$

Eq. (3) becomes

$$\frac{A}{2}\frac{\partial C}{\partial t} = 2D \frac{\partial^2 C}{\partial r^2} + \frac{\dot{w}}{\rho} \tag{9}$$

The source term for the reactions considered is proportional to concentrations of species which scale with some power of x.

It is therefore reasonable to represent the source term as

$$\dot{w}/\rho = W_0 t^{2n} g(r) \tag{10}$$

where W_0 and n are constants. The function $g(r)$ includes in the radial variation of ion production, the radial variation of species profiles, and temperature. In this study, $g(r)$ was taken to be the same type of function as $C_0(r)$. The constant W_0 depends on the temperature, which is approximately constant along the near wake centerline.[2] Solutions were obtained to Eq. (9) for three types of initial profile, $C_0(r)$.

Exponential Profiles

If the initial ion profile and $g(r)$ are represented by

$$C_0(r) = C_0 e^{-r/B} \tag{11}$$

$$g(r) = e^{-r/V} \tag{12}$$

where C_0 is a constant, then the solution to Eq. (9) is

$$\begin{aligned} C(r,t) = \frac{C_0}{2} e^{4Dt/B^2A} \Bigl\{ e^{-r/B} \Bigl[2 - \operatorname{erfc}\Bigl(\frac{r}{2}\left[\frac{A}{4Dt}\right]^{1/2} - \\ \left[\frac{4Dt}{B^2A}\right]^{1/2} \Bigr) \Bigr] + e^{r/B} \operatorname{erfc}\Bigl(\left[\frac{4Dt}{B^2A}\right]^{1/2} + \\ \frac{r}{2}\left[\frac{A}{4Dt}\right]^{1/2} \Bigr) \Bigr\} + \frac{e^{-r/V} 2W_0(2n)!}{A} \int_0^t \ldots 2n + \\ 1 \ldots \int_0^t e^{4Dt/V^2A} \; dt^{2n+1} - \frac{W_0}{A}(2n)! \int_0^t \ldots 2n + \\ 1 \ldots \int_0^t e^{-r/V} e^{4Dt/V^2A} \operatorname{erfc}\Bigl\{ - \left[\frac{4Dt}{V^2A}\right]^{1/2} + \\ \frac{r}{2}\left[\frac{A}{4Dt}\right]^{1/2} \Bigr\} dt^{2n+1} + \frac{W_0(2n)!}{A} \int_0^t \ldots 2n + \\ 1 \ldots \int_0^t e^{r/V} e^{4Dt/V^2A} \operatorname{erfc}\Bigl\{ \left[\frac{4Dt}{V^2A}\right]^{1/2} + \\ \frac{r}{2}\left[\frac{A}{4Dt}\right]^{1/2} \Bigr\} dt^{2n+1} \end{aligned} \tag{13}$$

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