in c_p produces the same absolute change in c_v (for perfect gases), variations in γ tend to be suppressed.

In turbopropulsion systems, the use of excess air in the combustor together with preponderance of relatively inert N_2 makes γ' at least an order of magnitude lower than $T'/\bar{T}$ when caused by local mixture of ratio fluctuations. Furthermore $W'/\bar{W}$ also is negligible compared with $T'/\bar{T}$.In such cases, the complication of γ' noise does not need to be considered. In rocket engines, however, there may be some merit in investigating γ' noise as a source of chamber pressure roughness. As examples, consider some thermochemical computations of Ref. 8. For ethyl alcohol/liquid oxygen operating at a pressure ratio of 13.6 and a chamber pressure of 200 psia, the maximum specific impulse occurs at an oxidizer to fuel mass flow ratio of 1.4. Considering a variability of mixture ratio from 1.3 to 1.5, the temperature varies by about 6.5%, the molecular weight varies by 5.4%, and γ varies by 0.59%. However, both Γ and W are positive with an increase in mixture ratio, so that they tend to cancel one another in Eq. (4). Consequently, although it would take detailed numerical computations to confirm it, the γ' contributions can be of the same order as Γ and W contributions to noise generation. On the other hand, there are some propellant combinations, for example, liquid oxygen and gasoline, which have only weak γ variations in the vicinity of the I_{sp} maximum. Finally, γ' noise also may arise in some industrial processes involving turbulent flow and mixing of dissimilar gases.

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Technique for Atmospheric Rate Chemistry Calculations

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Introduction

THE possibility that predictions of atmospheric photochemistry/transport models are sensitive to uncertainties in reaction rates and other inputs underscores the need for rapid numerical integration schemes in rate photochemistry problems.[1,2] Reducing the computational burden has an obvious advantage in facilitating sensitivity studies to assess the influence of such uncertainties on, say, predicted ozone dimunitions from nitrogen oxides ($NO_x = NO + NO_2$) in the exhaust plume of SST engines.

Analysis and Results

An algorithmic approach to integration of rate chemistry problems in combustion has been developed by Rubel and Baronti and described by Ferri.[3,4] In this approach, the production rate for the "*i*th" chemical species is written:

$$dX_i/dt = -A_iX_i + B_i \tag{1}$$

where X_i, A_i, and B_i are, respectively, the concentration, loss coefficient, and gain coefficient. Integration of Eq. (1) yields

$$X_{i_t} = \exp\left(-\int_0^t A_i dt\right)\left[X_{i_0} + \int_0^t B_i \exp\left(\int_0^t A_i dt\right) dt\right] \tag{2}$$

where X_{i_0} and X_{i_t} are the concentrations at the beginning and end of the time step, respectively. According to Rubel and Baronti,[5] if the time step is small enough and the temperature is fixed during the time step, Eq. (2) can be approximated

$$X_{i_t} \approx X_{i_0}\exp(-A_{i_0}\Delta t) + \frac{B_{i_0}}{A_{i_0}}[1 - \exp(-A_{i_0}\Delta t)] \tag{3}$$

where Δt is the duration of the time step, and A_{i_0} and B_{i_0} are loss and gain coefficients at the start of the time step. The validity of the approximation can be determined by observing the effect of shortened Δt upon results obtained using Eq. (3).

In a recent consideration of the plume chemistry for a current SST engine, the GE-4 engine, Gupta and Grose utilized a 20-reaction chemical model.[6] They did note however, that a simplified five-reaction model is accurate to 10%. These five reactions are listed in Table 1, along with species production-rate equations, reaction rates, and photodissociation coefficients. The photodissociation coefficients are those of Gupta and Grose.[6] Reaction rates have been calculated from the tabulation of Wuebbles and Chang[7] and Stewart and Hoffert,[8] for a temperature of 220 K and a height of 20 km. Reaction rate k_1, when corrected for the number density at 20 km ($M = 2\times10^{18}$ cm^{-3}) and converted to units of ppm^{-1} sec.$^{-1}$, is 12% higher than the rate utilized by Gupta and Grose.[6]

The set of reactions listed in Table 1 have been solved using a pocket electronic calculator for the following initial conditions. Volumetric molecular oxygen concentration is constant at 0.21 and total particle number density M is constant an 2×10^{18} cm^{-3}. The initial ozone concentration is 1.5×10^{-6}.

We have considered two projected SST engines. One of these is the GE-4 considered by Gupta and Grose.[6] The other is based on experiments discussed by Ferri[9] regarding NO_x effluent reductions that are within the reach of current technology. For the GE-4 engine,[6] initial concentrations of NO and NO_2 are, respectively, 5×10^{-7} and 5×10^{-9}. For the SST improvement projected by Ferri, initial NO and NO_2 concentrations are, respectively, 10^{-7} and 10^{-9}.

Because the ambient atmospheric concentration of $O(^3P)$ is so low,[10] we have set it at zero. We also have assumed that the function $R = 1$, where R is defined as[6]

$$R = \frac{\partial O/\partial t \text{ Depletion}}{\partial O/\partial t \text{ Photoproduction}} \tag{4}$$

If R were greater than 1, the small amount of atomic oxygen in the plume soon would be depleted completely. On the other hand, if $R<1$, ozone depletion rates will be lower than calculated. By maintaining $R = 1$, we are overestimating ozone depletion.

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Index categories: Thermochemistry and Chemical Kinetics; Combustion in Gases; Airbreathing Propulsion, Subsonic and Supersonic.

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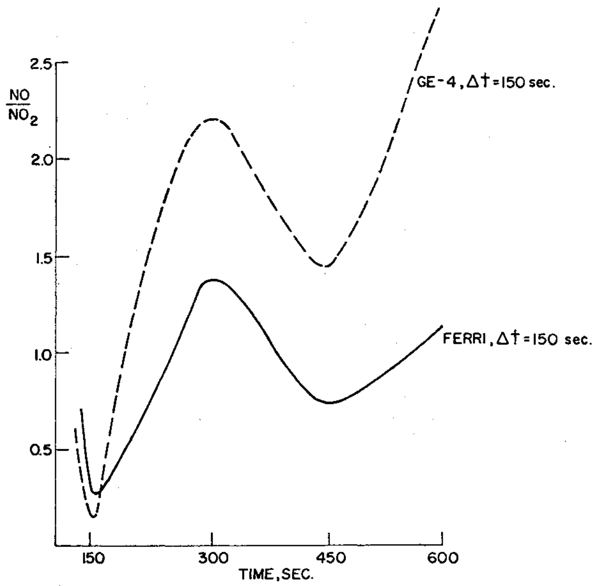

Fig. 1 Ratio of NO/NO_2 plotted as a function of time.

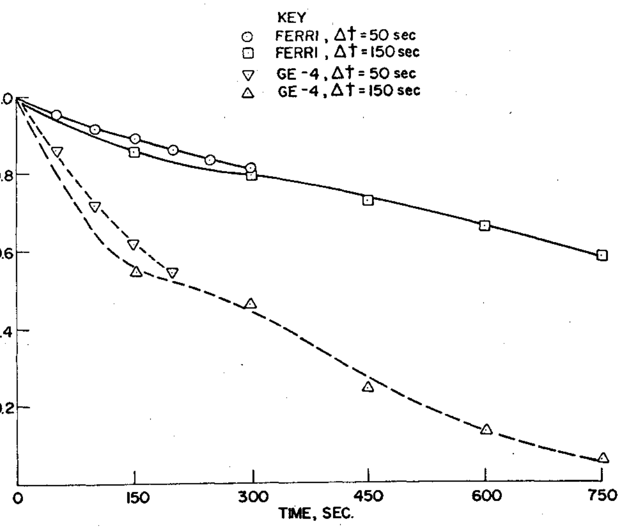

Fig. 2 Ratio O_3/O_{3_0}, plotted as a function of time.

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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