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ESTIMATES OF NITRIC OXIDE PRODUCTION FOR LIFTING SPACECRAFT REENTRY

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ABSTRACT

The amount of nitric oxide which may be produced by heating of air during an atmospheric reentry of a lifting spacecraft is estimated by three different methods. Two assume nitrogen fixation by the process of sudden freezing, and the the third is a computer calculation using chemical rate equations.

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ESTIMATES OF NITRIC OXIDE PRODUCTION FOR LIFTING SPACECRAFT REENTRY

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SUMMARY

An approximate analysis is carried out to estimate the quantity of nitric oxide that could be formed in the wake of a reentering, lifting spacecraft. Three different approaches are undertaken, i.e. two simplified analytical models utilizing the sudden-freezing concept named "trailing edge-freezing" and "wake-freezing" approximations and a computer calculation involving numerical integration of chemical rate equations. The wake-freezing calculations indicate that the maximum mass of nitric oxide formed for each reentry is about 9.5 percent of the spacecraft mass, while the trailing-edge freezing model predicts only one-third as much. The numerical integration yields 8 percent of vehicle mass as the amount of nitric oxide produced. Based upon existing knowledge of NO production in the upper atmosphere by natural causes, these amounts are exceedingly small, even for 100 missions of a vehicle with a mass of 100 tons.

INTRODUCTION

The presence of nitric oxide in the wake of a non-lifting hypersonic vehicle has been shown experimentally at ambient pressures roughly one-tenth that of standard atmosphere (Ref. 1). A theory (Ref. 2) has been developed that explains the observed data. These early studies predict that the molar concentration of nitric oxide in a wake would rise within the near-wake region to a peak typically of several percent and decay to an unknown small concentration far downstream of the vehicle. These past studies are inapplicable directly to the reentry of a lifting vehicle such as the space shuttle because a lifting reentry occurs typically at density regimes four orders of magnitude smaller than those examined above, while the vehicle size is four orders of magnitude greater.

Nitric oxide is considered to be a harmful pollutant gas at the earth's surface. It is known, however, that the natural atmosphere contains a large concentration of nitric oxide at high altitudes. To investigate whether or not repeated flights of spacecraft might cause a significant perturbation of the natural nitric oxide distribution, a simplified estimate is made here through three different approaches. In the first two methods, the chemical process is assumed to quench suddenly at a certain point in the flow field. The "trailing edge-freezing" approximation assumes that the quenching occurs as the air flow passes the wing trailing edge while the "wake-freezing" approximation is based on the assumption that the freezing occurs within the wake. In the third method, the conservation equations are integrated numerically along the particle path allowing the chemical reactions to proceed with finite rates. The numerical calculation is carried out for the altitude of 230,000 ft and an angle of attack of 25 degrees. The reentering lifting spacecraft is approximated by a triangular flat plate for the present calculations, and only the flow that passes beneath the plate is treated. The rate of nitric oxide fixation predicted by the present estimate is finally compared with the rate of natural nitric oxide production believed to occur in the upper atmosphere.

NOTATION

A	frontal area of the spacecraft
C_D	drag coefficient based on frontal area
F	wake-volume factor defined as the ratio of wake volume (at the instant of freezing) to the volume of air swept by spacecraft
ΔH	enthalpy increase in wake due to the passage of spacecraft
M	mass of spacecraft
Q	mass of nitric oxide produced
r	radial distance
S	span
s	distance along the flight path of spacecraft
x	chordwise length of wing of spacecraft
y	distance normal to the surface of spacecraft wing
z	spanwise distance measured from the centerline dividing streamline
U	flight velocity
u	local velocity within boundary layer
α	angle of attack
δ_p	thickness of nitric oxide-boundary layer, Fig. 3
ρ	density

<u>Subscripts</u>

b	boundary of wake
e	edge of boundary layer
o	origin of wake

1 initial condition of reentry where U_1 = 26,000 fps

2 final condition of reentry where U_2 = 17,000 fps

MECHANISM OF NITRIC OXIDE GENERATION

When air is heated, nitric oxide, NO, is generated mainly through the following two processes

$$N_2 + O_2 + 79 \text{ kcal/mole} \rightarrow O + N_2O \rightarrow 2NO + 36 \text{ kcal/mole}$$

$$N_2 + O + 75 \text{ kcal/mole} \rightarrow N + NO$$

Since the activation energies involved are lower than those for dissociation of oxygen (117 kcal/mole) or nitrogen (214 kcal/mole), nitric oxide is formed before the dissociation of oxygen or nitrogen occurs, i.e. at lower temperatures and in earlier stages in time. In the density range of interest, the NO concentration under equilibrium is the highest at temperatures between 2500°K and 3000°K. The equilibrium concentration tends to increase slightly as pressure increases. In the flow around a reentering spacecraft, the heating of air takes place mainly in two different modes, namely shock-heating and boundary-layer recovery phenomena, which are described in detail in the following paragraph.

Figure 1 shows the formation of NO behind a normal shock wave at a speed of 5 km/sec (16,000 fps) in an ambient pressure (at room temperature) of 0.02 torr, which corresponds to the conditions behind an oblique shock wave formed over a flat plate inclined at 31° flying at 26,000 fps at an altitude of approximately 200,000 ft. As is also shown in Figure 1, which is reproduced from Ref. 3, the nitric oxide concentration overshoots the equilibrium value and reaches a peak of more than 10 percent at a condition typical of spacecraft reentry, attaining equilibrium after around 1000 freestream mean-free-paths. Since the freestream mean-free-path in the space shuttle flight environment is of the order of one-hundredth to one-tenth of an inch, this means that the equilibrium concentration will be reached within approximately one to ten feet behind a shock wave. It seems fair - although not absolutely correct, to assume, therefore, that the nitric oxide concentration reaches equilibrium within the inviscid regime of the shock layer over the lower surface of the space shuttle when the vehicle is flying at a substantial angle of attack, e.g. over 25°.

When a lifting spacecraft is flying at a very low angle of attack, nitric oxide will be formed mainly in the second mode, i.e., as a result of the boundary layer recovery phenomenon. At a low angle of attack, the flow at the boundary layer edge is hypersonic and the temperature recovery phenomenon within the boundary layer becomes prominent. When the wall temperature is fixed at a relatively low value, e.g. 1000°K, the peak temperature would occur within the boundary layer. As the inviscid flow is slowly drawn into the boundary layer, air is gradually heated by shear work, leading to the generation of NO. The chemical process by which NO is generated here is no different from the case of the normal shock; the rate, however, is considerably slower. The calculation in Ref. 4 and an unpublished result of a calculation carried out by the High-Enthalpy Research Branch of Ames Research Center following the method of Ref. 4 indicate that chemical equilibrium is nearly, but not quite, reached at the peak temperature point within the boundary layer at the trailing edge of a typical orbiter on the plane of symmetry under this condition. This means that the chemistry has nearly, but not quite, passed the NO-overshoot period shown in Fig. 1 at the trailing edge on the centerline streamline. In this case, therefore, the NO concentration at the peak temperature at this point should be taken equal to or greater than the equilibrium value corresponding to the peak temperature. At wing points, i.e., trailing edge points away from the plane of symmetry, the flow will be mostly in the NO-overshoot region, and could generate widely varying quantities up to four times the equilibrium value. It must be added here, for future reference, that such a calculation indicates also that the boundary layer flow is chemically frozen between the peak temperature point and the wall surface.

QUANTITY OF NITRIC OXIDE FIXED

The quantity of nitric oxide produced, or "fixed", during each reentry can be estimated either (1) by utilizing the concept of sudden freezing of chemistry which has proved useful in the calculation of nonequilibrium reacting nozzle flows, or (2) through a numerical integration of rate equations along the particle path. For the sudden-freezing approximation, two different approaches can be taken in estimating the freezing point. In the first approach, to be referred to here as the "trailing edge-freezing" method, chemistry is assumed to freeze at the trailing edge of the vehicle wing due to the rapid expansion thereafter. In the second method, referred to here as the "wake-freezing" model, chemistry is assumed to reach equilibrium in the hot near-wake behind the vehicle and freeze there because of the rapid turbulent mixing and cooling. In both models, the exact amount of residual NO left in the cold wake will depend on both reentry trajectory and flight attitude. However, for the purpose of rough estimation, a simplified two-step calculation method is developed which does not depend on the individual mission profile. By this method, one first estimates the average molar fraction of NO to be found at the freezing point. Then, as the second step, the total mass of air in which the reaction is taking place is calculated. The total quantity of NO produced is obtained simply by multiplying the air mass involved by the NO fraction.

For this simplified analysis, the spacecraft will be represented by a flat plate of zero thickness, as this reproduces all limiting cases of chemical phenomena correctly. The reentry phase is assumed to commence at a velocity of 26,000 fps and to end at 17,000 fps, and these initial and final conditions are denoted by suffixes 1 and 2, respectively. Three different angles of attack will be considered, namely 0°, 25° and 45°, for both trailing-edge freezing and wake-freezing calculations. In both models, the cases of 25° and 45° incidence can be treated by the same technique since the inviscid shock layer will reach equilibrium in both cases and since the boundary layer recovery phenomenon would contribute relatively little to the total NO production. Zero degree incidence alone requires special treatment as will become apparent.

In the third method, i.e. the numerical method, the equations of conservation of mass, momentum and energy are integrated numerically together with the species conservation equations containing the chemical reaction rate expressions. The integration is carried out from behind the oblique shock wave over the inclined flat plate to far downstream in the wake, under the assumption that the characteristics of the wake of a lifting spacecraft is the same as that of a sphere. This approach is not only time consuming but involves several uncertainties. Therefore, its use is limited in the present work to justifying the first two approximations. For this reason, the numerical integration is carried out for only one particular case, namely that of a flat plate inclined at 25° flying at 230,000 ft altitude.

A. Trailing-Edge Freezing Model

Figure 2 shows the equilibrium molar fractions of NO to be found in the shock layer at two finite angles of attack. The figure was constructed from the U. S. Standard Atmosphere table of 1962 (Ref. 5), the AVCO charts (Ref. 6) and the Hilsenrath thermodynamic tables of 1965 (Ref. 7). If the tables of Moekel and Weston of 1958 (Ref. 8) were used instead of the Hilsenrath tables, the NO concentrations would be only 1/3 of those shown. Conversely, if the NAVORD data (Ref. 9) were used for atmospheric conditions instead of the U. S. Standard Atmosphere, the NO concentration would be roughly 50 percent higher. The selected combination of references were chosen because they represent the most recent data available. As seen in figure 2, on the average, around 2.5 percent of the air in the shock layer would be in the form of nitric oxide at 25° and roughly 0.4 percent at 45° incidence.

The total air mass swept by the vehicle can be estimated as follows. First one writes the drag of the vehicle in the form of $(1/2)C_D\rho U^2A$ where A is the frontal area of the vehicle, C_D the drag coefficient based on the frontal area and ρ and U are the ambient air density and flight speed, respectively. Then denote the mass of the vehicle by M. Since the work done on the vehicle in the form of drag must equal the kinetic energy drop of the vehicle, one can write the energy conservation equation as

$$\frac{1}{2} C_D \rho U^2 A\, ds = \frac{1}{2} M\, d(U^2) \tag{1}$$

or

$$\rho A ds = \frac{M}{C_D} \frac{d(U^2)}{U^2} \tag{1a}$$

in which s is the distance along the flight path. For a fixed finite angle of attack Eq. (1a) can be integrated along the flight path to yield

$$\int_{s_1}^{s_2} \rho A ds = 2\frac{M}{C_D} \ln \frac{U_1}{U_2}$$

One notices then that $\int \rho A ds$ is nothing but the total air mass swept by the vehicle and so

$$\text{Air mass processed} = 2\frac{M}{C_D} \ln \frac{U_1}{U_2} \tag{2}$$

Substituting U_1 = 26,000 fps, U_2 = 17,000 fps and using the Newtonian hypersonic approximation for C_D (for a flat plate $C_D = 2 \sin^2 \alpha$ where α = angle of attack), there follows:

$$\text{Air mass processed} \simeq 2.4M \text{ for } \alpha = 25° \quad (3a)$$

$$\simeq .85M \text{ for } \alpha = 45° \quad (3b)$$

On multiplying the average NO fractions of 0.025 and 0.004 found from Figure 2, the total masses of nitric oxide produced, Q, for the two cases are

$$\text{Mass of NO} = Q \simeq .06M \quad \text{for } \alpha = 25° \quad (4a)$$

$$\simeq .0034M \quad \text{for } \alpha = 45° \quad (4b)$$

For the hypothetical case of zero angle of attack, a similar simple result can be obtained if one neglects the formation of a shock wave due to boundary layer displacement and assumes a laminar Blasius velocity profile over the entire flat plate. Fig. 3 is a schematic showing the variation of temperature and NO concentration across the boundary layer over such a flat plate. The location and the value of the peak temperature within the boundary layer varies according to the freestream temperature, wall temperature and Prandtl number. According to Ref. 4 and the unpublished calculation mentioned earlier, for a typical flight condition of interest, the peak temperature occurs at such a point and to such a magnitude that the static enthalpy at that point would be roughly 30 percent of the total enthalpy at the boundary layer edge when the Prandtl number is 0.7. As explained above in the section entitled Mechanism of Nitric Oxide Generation, the NO concentration is at least as large as the equilibrium value at this peak temperature, and the NO concentration at that peak temperature is the maximum value within the entire boundary layer. The equilibrium concentrations at this point are found again from the local static enthalpy and the known ambient pressure and are shown in Figure 4 as the lower bounds. The true NO concentrations could be lower or higher than these values up to a factor of four due to the overshoot effect described earlier, and the maximum values constitute the upper bounds in the figure. In the absence of further data, the average value will be taken as the logarithmic mean between the two limits, i.e., 2.5 percent, with an uncertainty allowance factor of 2.5 in both directions.

Since, as mentioned above, the chemistry would be frozen between this peak point and the wall surface, the NO concentration would remain constant between this peak point and the wall if the wall were noncatalytic to NO decomposition, or would decay to zero at the wall if it were fully catalytic, as shown in Figure 3. Outside of the peak temperature point the NO concentration would be negligibly small.

Therefore, the region between the peak temperature point and the wall will be referred to as the "NO layer" in later descriptions and thickness will be designated by δ_p.

The quantity of air processed by the reacting boundary layer can be approximated in a way similar to the case of high angles of attack. For the laminar compressible flat plate flow under consideration, the skin friction integrated over the chord length for unit span is

$$\text{Integrated skin friction} = \sqrt{2}\, f_w'' \rho_e U^2 x \sqrt{\frac{\mu_e}{\rho_e U x}}$$

where f_w'' is the wall curvature of the dimensionless stream function of Blasius and μ is viscosity. A careful comparison of this quantity with the calculation presented in Ref. 4 reveals that the integrated skin friction is approximately equal to $(1/2)U^2 \int_0^{\delta_p} \rho \, dy$ where y is the distance normal to the wall. Since, assuming no wave drag, the friction work done on the flat plate must equal the change in the kinetic energy of the vehicle, the energy conservation equation is

$$2\left(\frac{U^2}{2}\right)\left(\int_{-S/2}^{S/2}\int_0^{\delta_p} \rho \, dy\right) dz\, ds = \frac{M}{2} d(U^2) \tag{5}$$

where z is the span-wise length measured from the dividing streamline and S is the span. The multiplicative factor 2 on the left-hand-side accounts for the fact that there are two identical friction surfaces, i.e., top and bottom. Equation (5) can be integrated in a manner similar to Eq. (1), and since the quantity $2\iiint \rho\, dy\, dz\, ds$ is the mass of air that passes through the NO layer, one obtains

$$\text{Air mass processed} = 2\int_{s_1}^{s_2}\int_{-S/2}^{S/2}\int_0^{\delta_p} \rho \, dy\, dz\, ds$$

$$= 2M \ln \frac{U_1}{U_2} \simeq 0.85M \tag{6}$$

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Thus, the air mass processed by a flat plate boundary layer corresponds to the case of $C_D = 1$ in Eq. (2). If the wall is noncatalytic, the total amount of NO produced per reentry is simply the quantity expressed by Eq. (6) multiplied by the average NO concentration of 0.025 found from Figure 4, i.e.

$$Q = 0.02M \text{ for } \alpha = 0°, \text{ noncatalytic wall} \tag{7a}$$

For a fully catalytic wall, the total quantity of NO produced will be roughly 1/2 of the noncatalytic case if one makes the assumption that the peak temperature within the boundary layer is three times the wall temperature and properties vary linearly within the NO layer. Thus, for a fully catalytic wall, there results

$$Q = 0.01M \text{ for } \alpha = 0°, \text{ fully-catalytic wall} \tag{7b}$$

Eqs. (4a), (4b), (7a) and (7b) express the quantity of nitric oxide produced per reentry as obtained through the trailing-edge freezing model. These results are plotted in Fig. 5 along with the estimated error limits. The error bands are caused mainly from the possible deviation of the true NO concentration from the assumed mean value over various flight altitudes, i.e. the possible error in representing the varying concentration, shown by the solid curves in Figs. 2 and 4, by simple average values shown by dotted lines. As shown in the figure, among the three different angles of attack considered, 25° reentry results in the largest amount of NO according to this model, the absolute quantity being approximately 6 percent of the vehicle mass. This is because equilibrium NO concentration is the highest at around 2600°K which is the typical temperature of the inviscid shock layer at 25° incidence. At an angle of attack higher than 25°, the equilibrium temperature is so high that NO molecules would decompose into N and O, and this explains the low degree of NO formation at 45° angle of attack. The case of zero degree incidence is somewhat uncertain, but judging from the values arrived at, it seems that the amount of NO generated at this incidence is not very different from the case of 25°. It is worth noting that a factor of two reduction in NO quantity can be attained by coating the surface of the vehicle by a fully-catalytic material for the zero degree incidence case.

B. Wake-Freezing Model

In the wake-freezing approximation, chemical relaxation is assumed to proceed behind the wing trailing edge. Since the abrupt expansion behind the trailing edge is in reality followed by a series of compressions and turbulent shear motion that tend to generate heat, as well as expansion, the chemical process could proceed toward equilibrium inside the hot near-wake behind the vehicle until turbulent diffusion cools the wake and quenches the reaction. For simplicity it is assumed here that the air volume in the wake is uniformly heated and that the rise in temperature is the same everywhere within the wake. The heating of air in the wake results naturally from the conversion of the kinetic energy of the spacecraft since the static pressure in the far wake is roughly the same as the ambient pressure, the overall energy balance dictates that the initial kinetic energy should ultimately be converted to raising the enthalpy of the wake and heating of the vehicle. A portion of the heat absorbed will be radiated away and permanently lost from the control volume under consideration. Except for the case of zero incidence angle which shall be treated separately, however, the heat transmitted to the vehicle is a small fraction of the total energy and therefore, can be neglected.

In equating the enthalpy rise in the wake with the kinetic energy drop of the vehicle, one must account for the fact that the volume of the wake is generally larger than the volume swept by the vehicle because of the turbulent mixing occurring behind the vehicle (see Fig. 6). In general, therefore, the cross-sectional area of the wake will be expressed by F x A where A is the frontal area as before and F is the multiplicative factor accounting for the growth of the cross section, or the volume per unit length of the wake (see Fig. 6). Since the diameter of the wake grows approximately as 1/3 power of the distance behind the vehicle (Ref. 2), the factor F will eventually become greater than 1. The enthalpy rise in the wake is to be denoted by ΔH. The assumption described above was used also in Ref. 2 for the calculation of species variation along the wake, and was referred to there as a "one-dimensional wake" model.

Let us first concentrate on the high incidence angle cases (25° and 45°). The energy conservation equation is

$$F \int_{s_1}^{s_2} \Delta H \rho A ds = 1/2\, M\, (U_1^2 - U_2^2)$$

Assuming ΔH to be constant along the flight path and introducing the expression for the air mass processed as in Eq. (2), there results

$$\Delta H = \frac{C_D}{4F} \frac{U_1^2 - U_2^2}{\ln U_1/U_2} \qquad (8)$$

Eq. (8) and the known ambient pressure at the given altitude specify the equilibrium concentration of NO for any given value of F. According to the present wake-freezing model, the chemistry is assumed to proceed in equilibrium until a certain time limit after the passage of the vehicle. Then, at the particular value of F, chemistry will be frozen suddenly. The value of F needed for the NO concentration calculation in the residual air is then the value at the instant of freezing.

The wake flow is afforded with a practically unlimited residence time for the gas to reach equilibrium, and so the assumption of sudden freezing may seem unrealistic at first. However, considering that the nitric oxide concentration freezes in a terrestrial power plant furnace and remains so for several hours at sea level until it is removed by combining with water vapor (Refs. 10, 11), freezing in the wake of an entering spacecraft should be considered quite likely. The occurrence of freezing is manifested also in the computer calculation which will be described later. The sudden-freezing approximation does not reveal any information on the freezing point or the F-value at the freezing point. Therefore, the F value will be left arbitrary.

Figure 7 shows the equilibrium NO concentration at the freezing point within the wake as a function of the freezing point volume factor F as found from Eq. (8) and the given ambient pressure. As seen here, the concentration is the highest at an F value of around 5 for the 45° angle of attack. That is, for this case if equilibrium is maintained until the time when the turbulent wake has grown in diameter to contain approximately 5 times the volume of air swept by the vehicle, and if chemistry freezes there, NO concentration in the wake will be the highest. At this value, the mean temperature in the wake has reached approximately 2600°K which gives the maximum NO concentration, and this explains the peak; at either side of the peak, the equilibrium temperature is either too high or too low for NO formation. It is worth noting that the peak concentration is the same for both 25° and 45° incidence since it depends solely on the temperature attaining a value of 2600°K. The figure also shows a higher peak NO concentration at 200,000 ft altitude than at 250,000 ft, indicating the pressure dependence on equilibrium NO concentration.

For a flat plate at zero angle of attack, the heat transfer to the body cannot be neglected. Since the wall temperature is much smaller than the total temperature of the freestream in the cases of interest, the wall will be considered to be highly cooled. In a compressible laminar boundary layer over a flat plate with zero pressure gradient, one can easily show that the heat transmitted to a highly cooled wall equals approximately half the total kinetic energy dissipated, if one assumes Prandtl number to be unity. Thus, an approximation is made here that the energy remaining in the wake is half the drop in the kinetic energy of the vehicle, i.e.

$$2F\Delta H \int_{s_1}^{s_2} \int_{-S/2}^{S/2} \int_{0}^{\delta_p} \rho \, dy \, dz \, ds = \frac{M}{4}(U_1^2 - U_2^2) \tag{9}$$

With equation (6), the enthalpy rise in the wake is found as

$$\Delta H = \frac{1}{8F} \frac{U_1^2 - U_2^2}{\ln(U_1/U_2)} \tag{10}$$

The enthalpy given by Eq. (10) and the known ambient pressure specify the equilibrium NO concentration at the freezing point for any freezing point volume factor F. Fig. 7 shows the NO concentration determined thusly in comparison with those for high incidence angle cases. As seen here, the maximum NO concentration is attained at a value of F of about 2.5 but the maximum magnitude is the same as for the large incidence cases.

By multiplying the freezing point NO concentration shown in Fig. 7 by the total air mass swept by the vehicle (given by Eqs. (3a), (3b), and (6)), and by the volume factor F, one obtains the total of NO produced per flight. Fig. 8 shows the results of the total mass calculations. As shown in the figure, the total mass of NO can be up to 9.5 percent of the mass of the vehicle if the vehicle flies at incidence angles of 25° or 45°. No difference is seen in the maximum NO between the 25° and 45° cases. This is an expected result since the maximum total quantity of NO depends only on the energy delivered into the wake. In comparison, the case of zero angle of attack shows half as much NO as the high incidence angle cases simply because only half as much energy is liberated into the wake (the rest of the half being assumed radiated away). There is no difference between the catalytic and noncatalytic wall in the NO quantity produced for the same reason. According to this wake-freezing model, therefore, incidence angle least productive of NO is 0°, which contradicts the result of trailing-edge freezing calculation shown in Fig. 5. On the other hand, if the freezing point F value is over 20, the amount of NO produced will be very small regardless of angle of attack. If one can maintain equilibrium for an indefinite length of time, the freezing point F value will be infinitely large and there will be no nitric oxide left in the wake according to this wake-freezing model. In reality, however, the chemical reactions effectively cease at large F-values, and hence the complete removal of nitric oxide is not expected to occur, as will become apparent from the outcome of the computer calculation described below.

An interesting finding of the wake-freezing calculation is that the maximum quantity of NO produced per flight can be as large as 9.5 percent of the vehicle mass instead of 6 percent found by the trailing-edge freezing technique. The main reason for the larger NO production is that the air mass heated in the wake is larger than that passing through the inviscid shock layer over the vehicle. As shown in Fig. 6, the cold air which is drawn into the wake mixes with the hot core. The mixing causes the average temperature to drop from the total temperature of around 6000°K to around 2500°K at which point the NO concentration is the maximum. The combination of the larger air volume and the lowered temperature account for the increase in the total amount of nitric oxide. The maximum value of 9.5 percent found here agrees roughly with the results of Refs. 1 and 2 although the agreement should be regarded fortuitous. Ref. 2 predicts the maximum amount of NO to be produced roughly 10 diameters behind a sphere projectile flying at 5 km/sec at 100 torr ambient pressure, at which point the quantity of NO would reach 8 percent of the air mass swept. One experimental data point in Ref. 1, when interpreted through Ref. 2 and equation (2), shows the amount of nitric oxide to be 6.7 percent of the volume swept by the vehicle.

C. Numerical Integration of Finite Rate Equations

The foregoing estimates of nitric oxide fixation are made under the assumption that the flow maintains chemical equilibrium until it reaches a sudden freezing point. In reality, the chemical reactions proceed with a finite rate in most of the flow regime. In addition to the sudden-freezing approximation, which is only marginally realistic, the trailing-edge freezing model assumes that the heating of air occurs only in the volume swept directly by the spacecraft. This last assumption tends to underestimate the total nitric oxide fixed because it ignores the heating by the extended shock wave, i.e. the shock wave that extends beyond the trailing edge of the lifting body (see Fig. 9).

In order to test the validity of the two analytic freezing models, a computer calculation of the nonequilibrium flow has been carried out for a typical flight path of a reentering lifting spacecraft. The calculation consists of two parts; the first part computes the inviscid one-dimensional flow along a streamtube that starts from the oblique shock wave and ends 200 ft behind the trailing edge (see Fig. 9);

the second part deals with the chemical reactions in the wake thereafter. The first part was carried out by AVCO-Everett Research Laboratory; the second part was performed by the author.

In unpublished data supplied to the author, nitric oxide concentration in the first part of the flow was calculated by AVCO under the following assumptions; (1) altitude is 230,000 ft, (2) shock wave over the lifting body is inclined at 30°, which corresponds to the angle of attack of approximately 25°, (3) the shock-heated air moves a distance of 100 ft at constant pressure, (4) at the end of 100 ft, the flow expands according to the simple formula $p = A+B/s$ where s is the distance along the streamtube and the constants A and B are chosen such that at 200 ft behind the onset of expansion the static pressure falls to 5 times the ambient pressure. The chemical model is an improved version of that described in Ref. 2 and incorporates changes in the chemical reaction rates due to vibrational nonequilibrium. The calculation is performed for flight velocities of 19,000 fps, 20,000 fps, 22,000 fps, 24,000 fps and 26,000 fps. The results are summarized in Fig. 10 in which the computed data are indicated by the circles.

In the second part of the computation, the changes in chemical composition are calculated for the wake using the homogeneous mixing model derived for the wake of a sphere (Ref. 12). Assuming that the wake of the lifting body is the same as that of a sphere, the governing equations for cylindrically symmetric wake flow, Eqs. (4) through (7) of Ref. 12, are integrated numerically. In this formulation, in which the conservation of mass, momentum and energy along the wake is properly taken into account, the properties are considered to be uniform across the wake; the wake entrains surrounding air that is instantly mixed homogeneously within the wake; the concentrations of species O, N and NO are controlled by both the chemical reactions and the dilution resulting from the entrainment. Six reactions with rate constants listed on pages 230 and 231 of Ref. 13 involving O, N, NO, O_2 and N_2 are considered in the calculation. Vibrational nonequilibrium effects are neglected. This chemical model is essentially the same as that used in Ref. 2. The wake is assumed to have an initial diameter of 50 ft and its boundary is taken to vary according to the formula (Ref. 2).

$$\frac{r_b}{r_o} = 0.7\left(\frac{s'}{r_o}\right)^{1/3} \qquad (11)$$

where s' is the distance measured from a fictious source (see Fig. 9). In the present case, the fictitious source is 73 ft upstream of the initiation of the wake. In order to use this model, two parameters must be specified (Ref. 12), i.e. (1) the pressure variation along the wake, and (2) the radial variation of state properties outside of the wake as caused by the extended shock wave. These are fixed as follows; (1) the pressure varies as $p = C+D/s'$ in such a way that it matches the first calculation at $s = 300$ ft and becomes 3 times the ambient at $s = 373$ ft; and (2) the molar fractions of species O, N and NO in the flow outside of the wake vary inversely as the fourth power of radial distance r. The first assumption is completely arbitrary, but is believed to be inconsequential. The second assumption is equivalent to assuming that the extended shock wave fixes roughly the same amount of nitric oxide as the shock layer, and is discussed in more detail later.

Fig. 10 shows the results of the computation. In the figure the ordinate is the ratio of local nitric oxide number density integrated across the wake to the same quantity integrated at the reference point ($r = r_0$, πr_0^2 = frontal area of vehicle)

$$\frac{\int_0^{r_b} (\text{nitric oxide number density}) \times 2\pi r dr}{\int_0^{r_0} (\text{sum of number densities of all species}) \times 2\pi r dr}$$

The result shows that, for instance, if an observation is made 10^7 ft behind the vehicle flying at 26,000 fps at 230,000 ft altitude, an amount equivalent to 4% of the air processed by the vehicle would remain as nitric oxide. The abscissa, which is the distance s, extends to 10^9 ft. Such a long trail is of course inconceivable. But if one converts the coordinate from the Eulerian system (fixed vehicle, moving flow) adopted here into the Lagrangian system (moving vehicle, following the air particles), one realizes that 10^9 ft merely means roughly 1 week of residence time after the passage of the spacecraft.

As seen in the figure, the total nitric oxide population integrated across the wake increases initially and reaches a peak at around 30 body lengths. From then on, there is a slow removal of NO, and the NO quantity reaches an asymptotic value at approximately $s=10^8$ ft or one day. The results are now shown beyond 10^9 ft since the computer outputs tended to oscillate around the value at $s=10^9$ ft due to numerical difficulties; the species O and N reach the machine zero at these distances and this is believed to cause the oscillation. The asymptotic values of the quantity of NO are nearly the same as the initial values, i.e. the values at s=300 ft, which is interesting but may be only incidental. It should be noted here that, although the ordinate is the local nitric oxide quantity within the wake, the local molar concentration is very low at large distances because of dilution. For instance, at s = 10^9ft, the molar concentration of NO within the wake is less than one part per million.

The total amount of nitric oxide that remains in the atmosphere after a single reentry of a lifting spacecraft can be approximated by integrating quantities shown in Fig. 10 with respect to velocity and ignoring the effects of altitude. After a simple manipulation of Newton's equation of motion for the spacecraft, one can show that the desired quantity is:

$$\frac{Q}{M} = \frac{\text{total mass of NO produced}}{\text{mass of vehicle}} = \frac{2}{C_D} \int_{U_1}^{U_2} (\text{quantities in Fig. 10 at } s \to \infty) \frac{dU}{U}$$

A graphical integration of the area under the curve fitted through the points corresponding to the five velocities on Fig. 10 reveals that, for C_D = 0.356 corresponding to a 25° angle of attack, the above ratio is approximately 0.08. That is, a 100 ton spacecraft would produce 8 tons of nitric oxide if it decelerates entirely at the altitude of 230,000 ft, which is roughly midway between the 6 ton minimum and 9.5 ton maximum predicted by the two sudden-freezing methods. This agreement lends support to the belief that the sudden freezing approximations yield roughly correct answers.

The computer calculation involves several assumptions for which no verification exists at present. However, reasons to surmise that the calculation is basically sound are enumerated below.

(1) The present calculation is carried out for a streamline that travels 100 ft inside the shock layer along the lower surface (see Fig. 9). Streamlines that travel less than 100 ft, such as the alternate streamlines 1 and 2 shown in Fig. 9, would have different NO concentrations as they emerge from the shock layer. The shorter pathlengths inside the shock layer, however, do not necessarily imply less NO-formation. Because of the overshoot phenomenon seen in Fig. 1, shorter paths may or may not decrease the NO concentration. An equivalent behavior has been studied for the wake of a sphere; it is known that the peak NO concentration occurs not on the stagnation streamline but on an off-center streamline (sometimes on the streamline that passes through the extended shock wave).

(2) The stream tube immediately outside of the wake is assumed to be predissociated as a result of heating by the extended shock wave such that the concentrations of O, N and NO vary as negative-fourth power of radial distance. This implies that the extended shock wave contributes an equal amount in the fixation of nitric oxide as the shock layer. This assumption is consistent with the known characteristics of the sphere wake flow. Depending on the flight velocity, the extended shock wave of a sphere can produce up to 3 times more nitric oxide than can the shock layer. Since the drag coefficient of a lifting body is only half that of a sphere, however, the contribution of the extended shock wave is probably only half that of the sphere. This justifies the negative-fourth power assumption used here.

(3) The wake growth law, Eq. (11), assumes that the ambient air is perfectly still and that turbulent diffusion is caused solely by the passage of the spacecraft. In reality, there is a finite natural atmospheric turbulence and hence the diffusion and dilution of species would occur faster than Eq. (11) implies. For example, using the momentum balance equation and the wake growth law, Eq. (11), it can be shown that at $s=10^5$ ft, the mean particle velocity in the wake would decrease to 30 fps which is the same order as the velocity of natural turbulence. From this point on, therefore, the dispersion of NO molecules would proceed as the 1/2-power of time (according to the Einstein's random walk theory) instead of 1/3-power represented by (11). This in turn would slow down the chemical reactions since the concentration of NO would be lower. But this consideration leads to an increase of NO at most of only 20%.

(4) The magnitudes of the rate constants, which are uncertain within a factor of 3, do not affect the net amount of NO production appreciably. This was verified by repeating the calculation with all the rate constants increased by a factor of 10. The result of the calculation, which was carried out for a velocity of 26,000 fps, is shown in Fig. 10 as the dotted curve.

WHAT HAPPENS TO THE NITRIC OXIDE PRODUCED

The foregoing calculations indicate that nitric oxide in amounts equivalent to as much as 9.5 percent of the mass of the lifting spacecraft could be produced at each reentry from the air that passes beneath the vehicle. A space shuttle orbiter as presently projected would weigh approximately 80 tons on reentry, comprising 60 tons of empty weight and 20 tons of downward payload. In addition, there is an extra mass consisting of a separable fuel tank weighing 20 to 40 tons that must reenter the atmosphere eventually. Thus, the effective weight of an orbiter at reentry is taken as 100 tons. Space activities by NASA, by countries other than the United States and possibly by the military could conceivably result in up to 100 missions per year. Thus up to 950 tons of nitric oxide could be produced each year over the globe by continued traffic into space.

Assuming that 950 tons of nitric oxide is produced every year by space flights, the next question is how large a perturbation of nature this represents. Nine hundred and fifty tons is certainly a negligibly small quantity compared with the 15 million tons produced in the continental United States by automobiles and stationary power plants every year at present (Refs. 10 and 11), or compared even with an expected 2 million tons after 1976. However, the perturbation of NO at high altitudes may have an ecological effect totally different from that at sea level.

As is apparent from the present analysis, any object that enters the earth's atmosphere with sufficiently high speed would produce nitric oxide. Meteors, which have over 10 times the kinetic energy per unit mass of a typical spacecraft, on the average could possibly produce nitric oxide in an amount equal to their own masses.

According to recent meteoroid influx rates to earth (Ref. 14) one can estimate that between 10^4 and 10^5 tons per year of meteoroids penetrate the atmosphere to altitudes below 250,000 ft. The amount of volume production of NO by these meteoroids is unknown. But if they were as efficient in converting their kinetic energy to the production of NO as a space vehicle they would produce as much as 100 times the NO produced by 100 missions of a 100 ton shuttle.

Airborn spectroscopic measurements of the upper atmosphere by Meira (Ref. 15) reveal the presence of a large concentration of NO at altitudes centered around 100 km. Its origin is not quite understood although several explanations are offered. Most importantly, it is not known exactly how large a rate of NO production by natural processes this observed NO concentration implies. The downward flux of nitric oxide at 90 Km, which is a measure of the net rate of natural production of NO above this altitude, has been estimated by Strobel (Ref. 16) at around 2 million tons a year. If this estimate (which is subject to uncertainty because the value of downward diffusivity is unknown) is correct, the contribution of forseeable space flight traffic would be only 0.04 percent of the natural production rate of NO. If meteoroids were more efficient producers of NO than a spacecraft they could appreciably affect Strobel's downward flux rate for NO since meteors were not included as a source of NO in his analysis.

The question of what effect on the ecology of the earth repeated space flights would bring could be answered relatively easily once the natural atmosphere is understood. It would merely involve repeating the numerical calculation with an extra 950 tons per year of NO included. If Strobel's value of 2 million tons of NO is believed, there would be little impact, if any, of repeated space flight.

In summary, therefore, it is difficult to accurately assess the degree of perturbation of natural distribution of NO without knowing the following; (1) the exact magnitudes of diffusion coefficients in the upper atmosphere, (2) the magnitude of mass flux of meteors that decelerate in the upper atmosphere, (3) the rate at which a meteor produces nitric oxide, and perhaps (4) a more refined knowledge of the nonequilibrium chemical kinetics and radiative properties of various species of air found in the upper atmosphere. Work is currently being undertaken at Ames Research Center to obtain the answers to these questions.

CONCLUSIONS

Three analytical models are developed to estimate the amount of nitric oxide produced during a reentry of a lifting spacecraft. The trailing edge freezing model predicts a maximum NO production of 6 percent of the vehicle mass and a finite minimum, the minimum amount being predicted for a high angle of attack reentry. The wake-freezing model predicts nitric oxide production of up to 9.5 percent of the spacecraft mass at high angle of attack, and 4.8% at zero angle of attack. A numerical calculation of finite rate processes indicates the nitric oxide production rate to be around 8% of the mass of the vehicle at 25° angle of attack. Based on our current knowledge of the subject, the degree of perturbation of the upper atmosphere's natural burden of NO by the space shuttle program is very small. More precise estimates require (1) knowledge of the rate at which meteors produce nitric oxide, and (2) study of the chemistry and dynamics of NO generation and depletion in the upper atmosphere.

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FIGURES

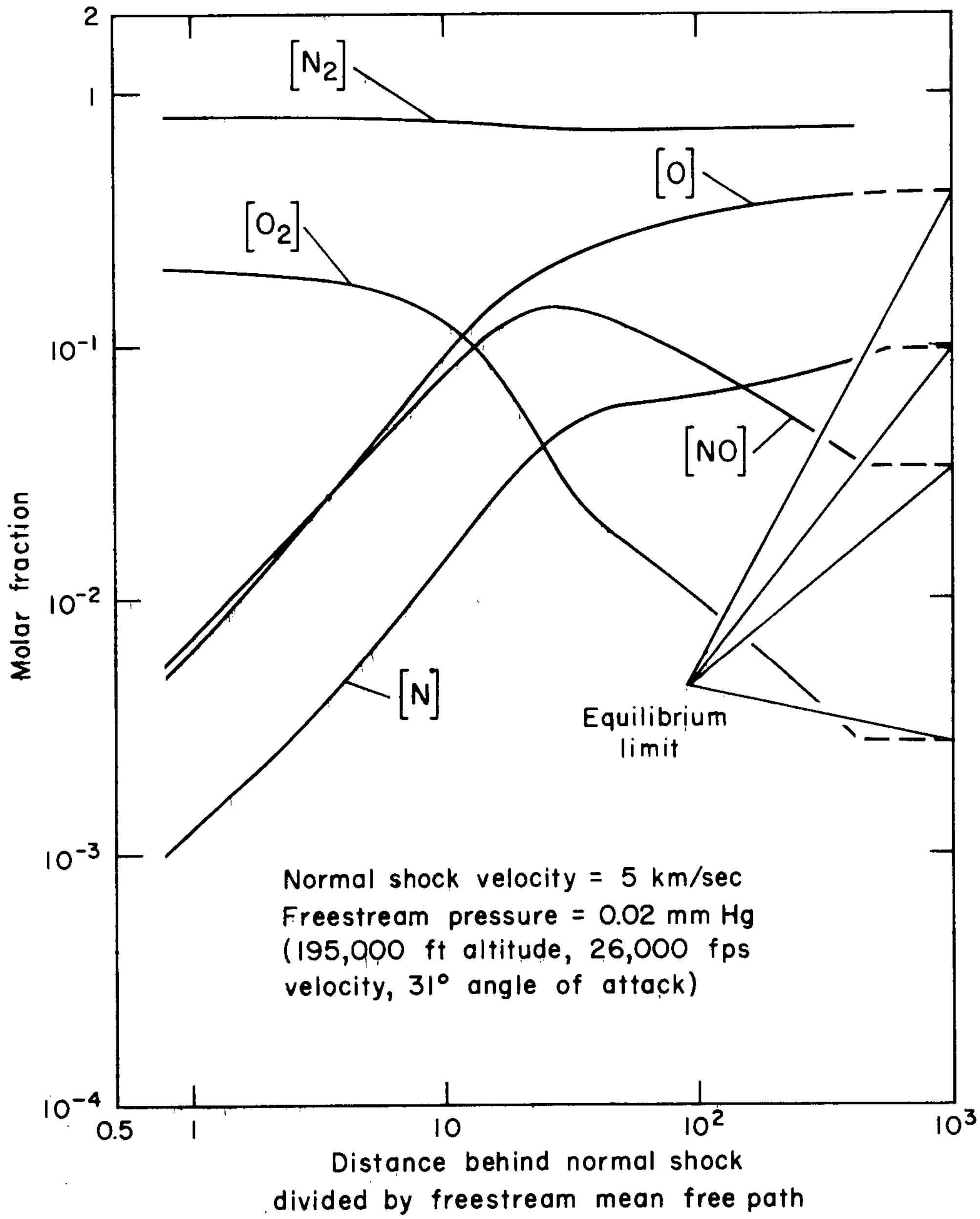

Figure 1.- Production of nitric oxide behind a shock wave (Reproduced from Ref. 3).

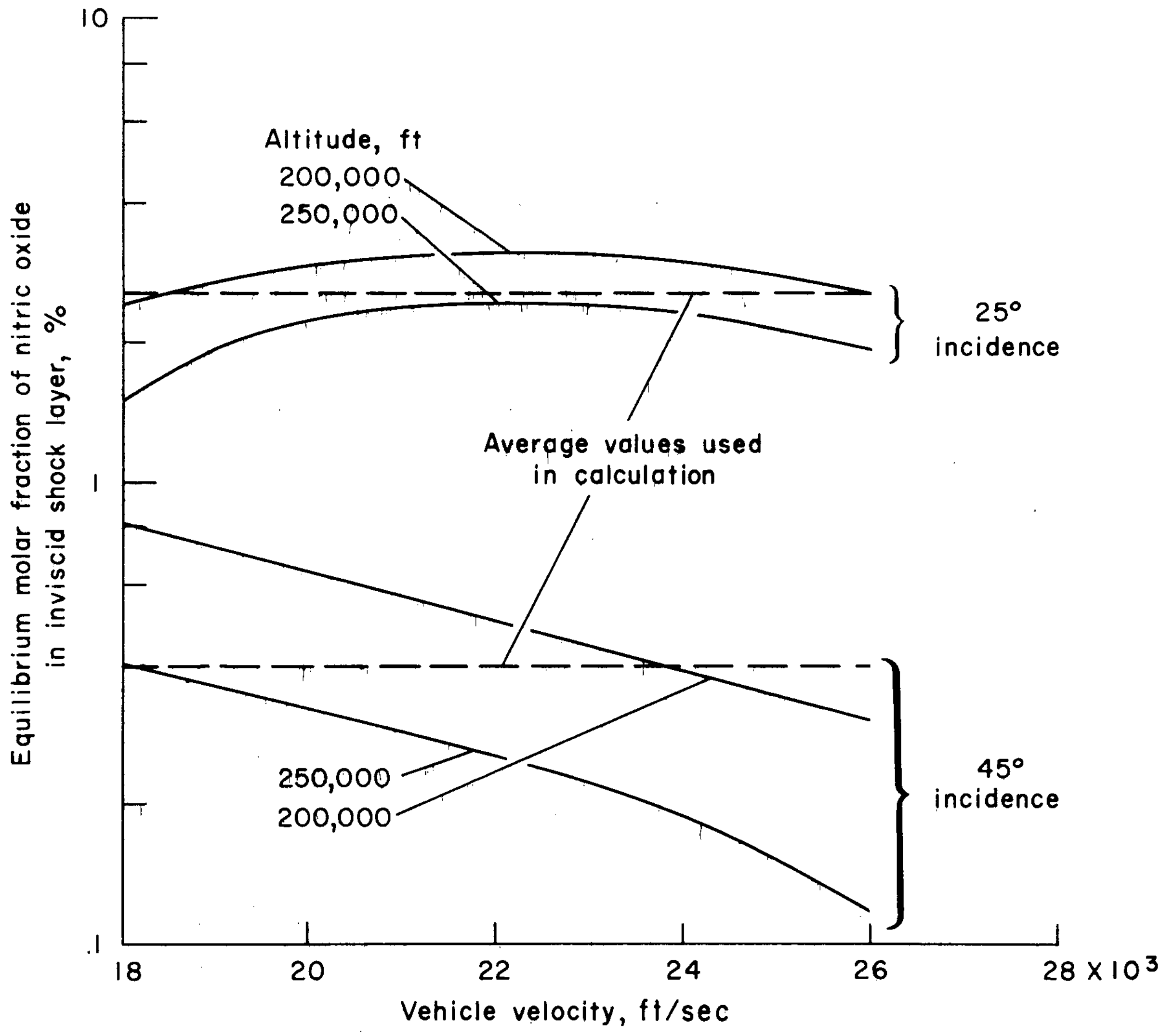

Figure 2.- Equilibrium molar fraction of nitric oxide behind oblique shock wave of a flat plate inclined at 25° and 45°, based on Refs. 7, 8, and 9.

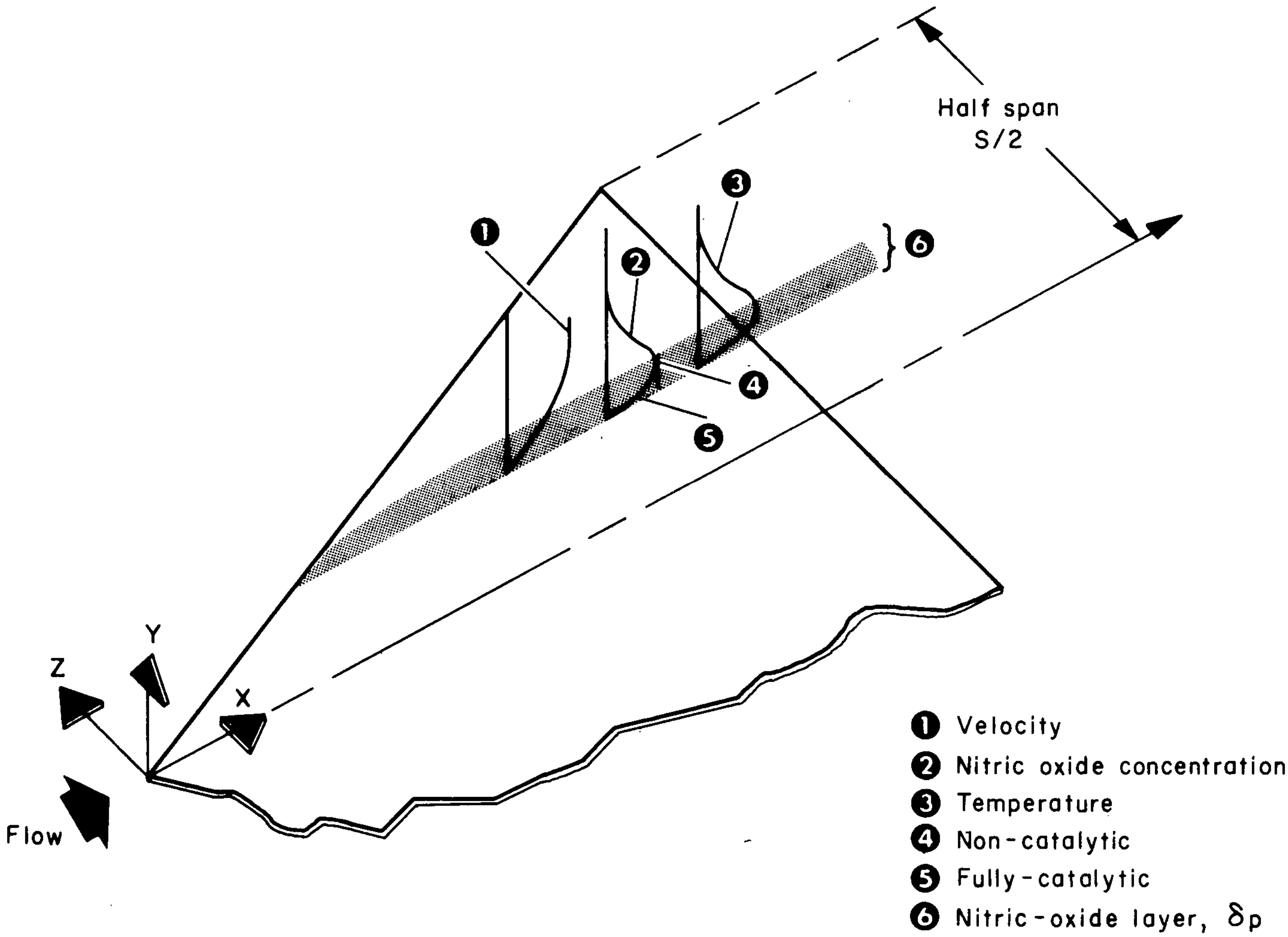

Figure 3.- Schematic of boundary layer flow past a spacecraft wing, approximated by a swept flat plate, flying at zero angle of attack.

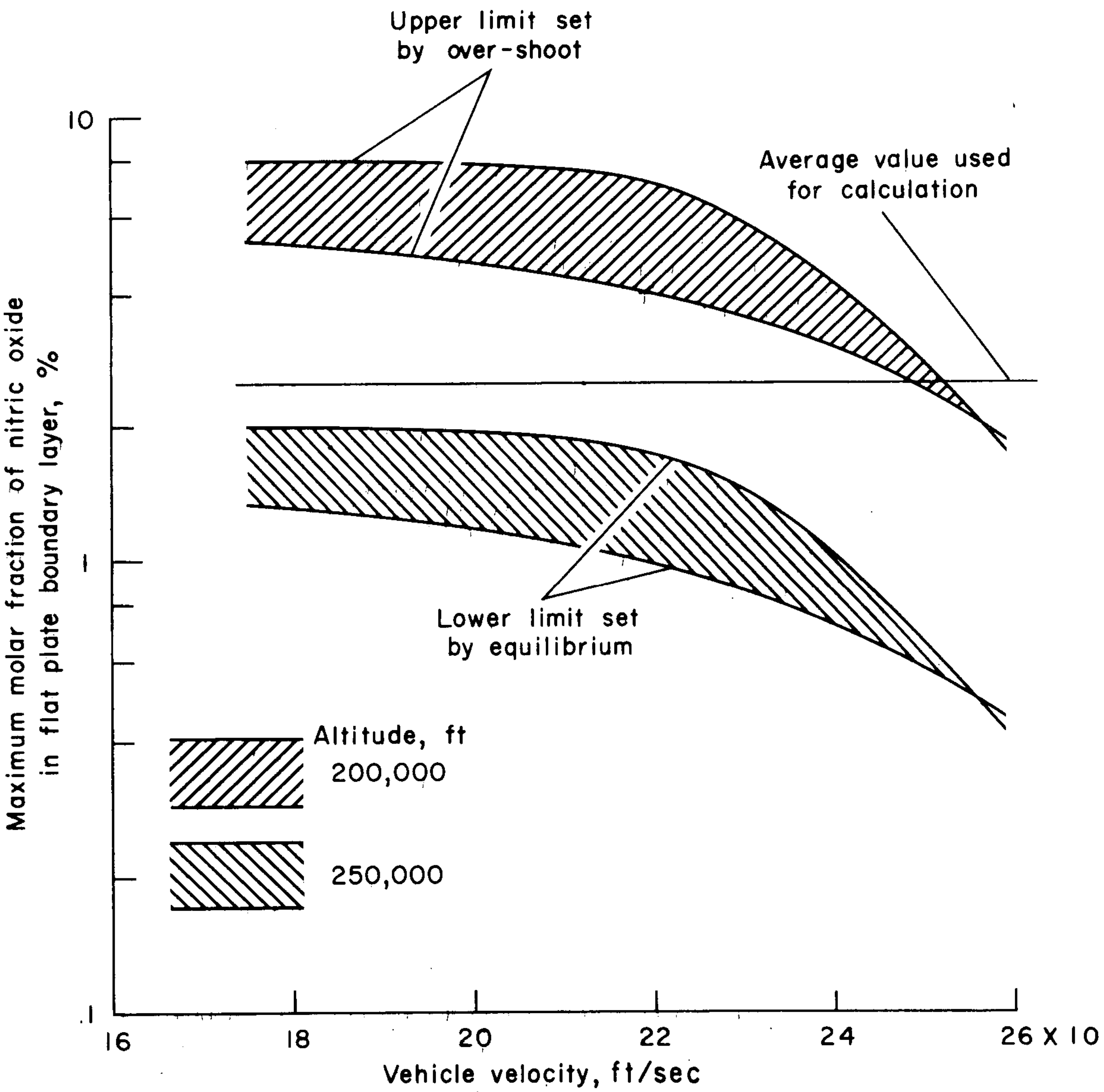

Figure 4.- Maximum molar fraction of nitric oxide at peak-temperature point in the boundary layer over a flat plate at zero incidence.

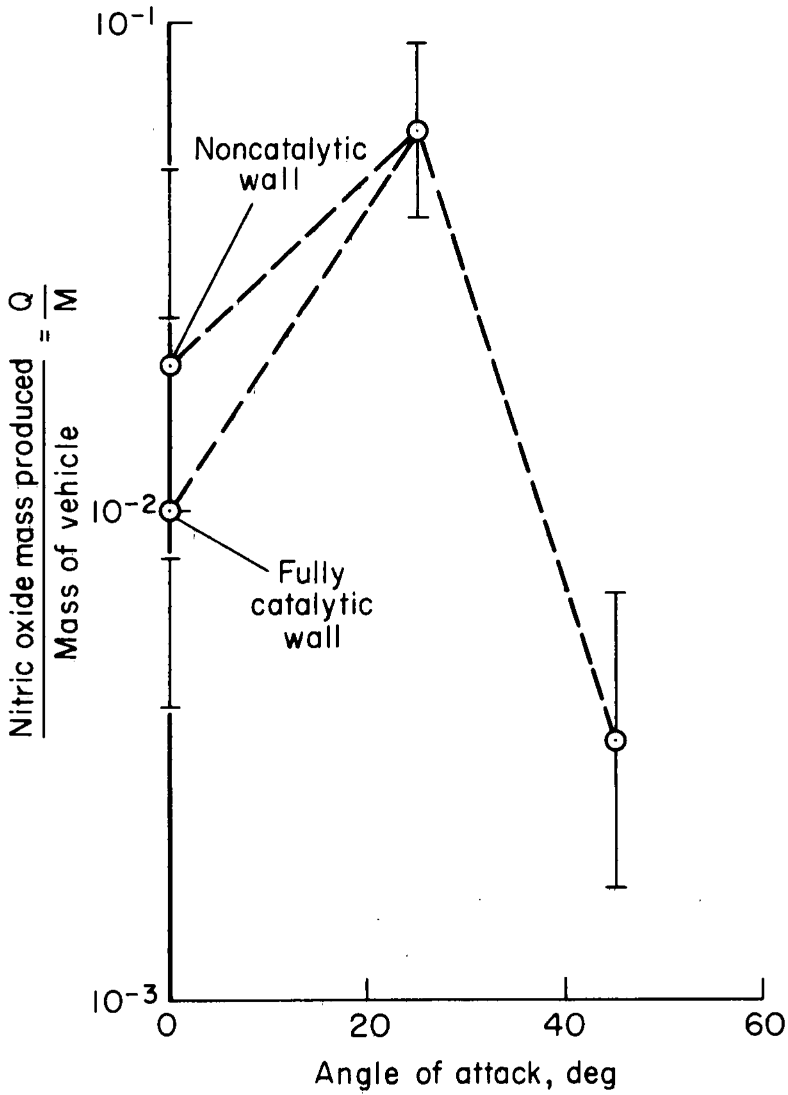

Figure 5.- Ratio of nitric oxide mass produced per flight to mass of vehicle as function of angle of attack, obtained by "trailing-edge freezing" approximation.

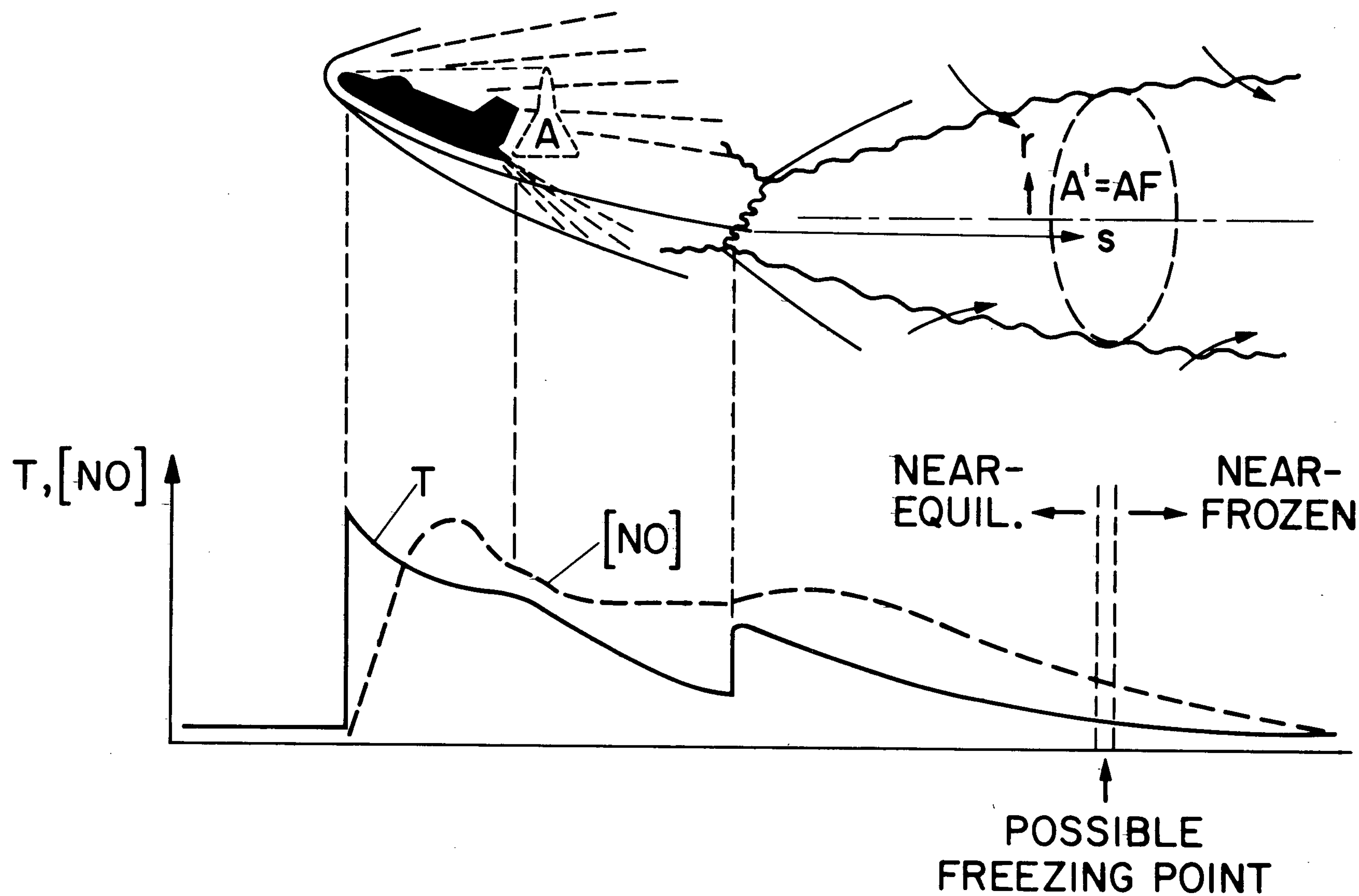

Figure 6.- Schematic of reacting turbulent wake behind a lifting spacecraft explaining the origin of the wake volume factor F.

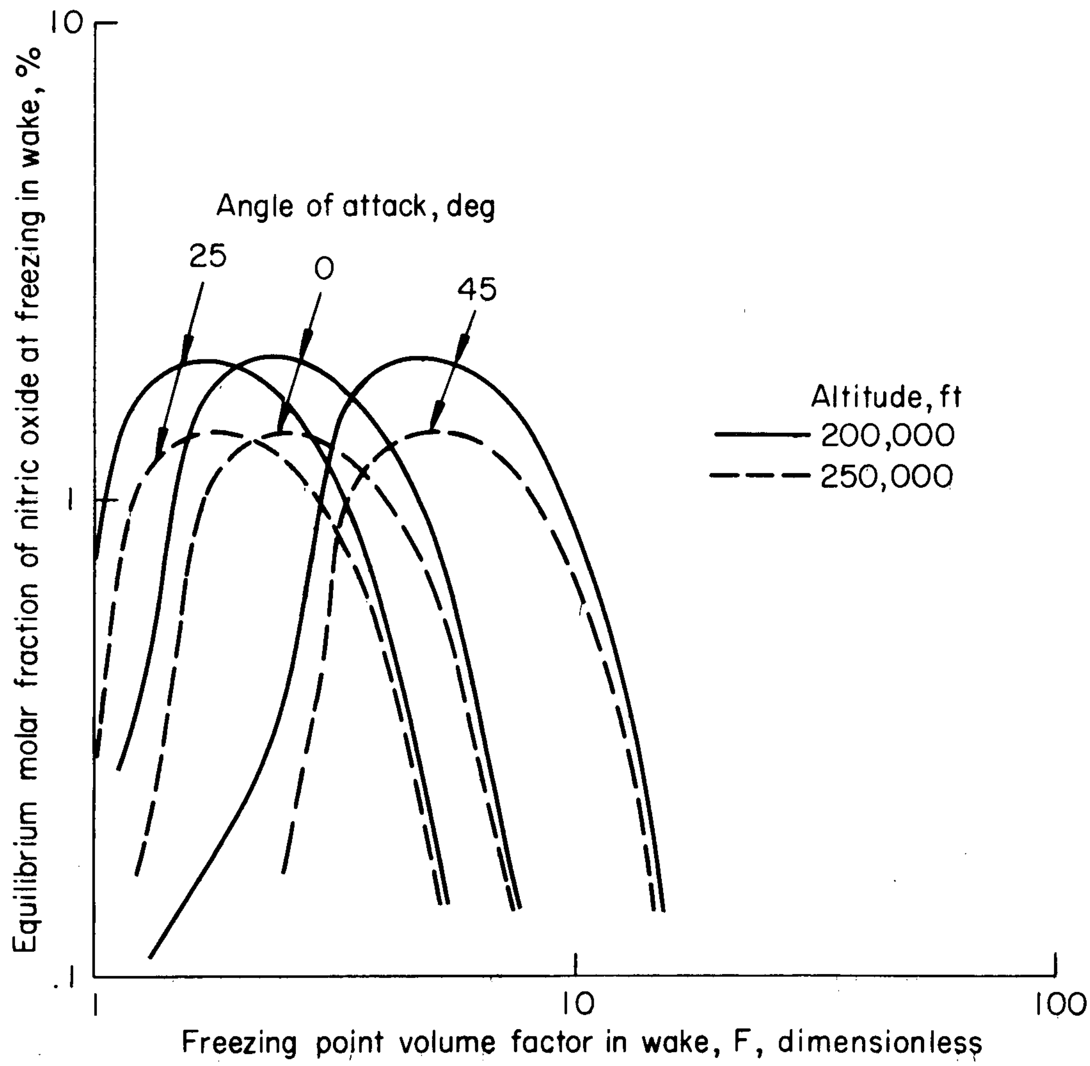

Figure 7.- Equilibrium molar fraction of NO at freezing point volume factor F. The volume factor F is the ratio of air mass in wake to the air mass swept by reentry vehicle (wake-freezing approximation).

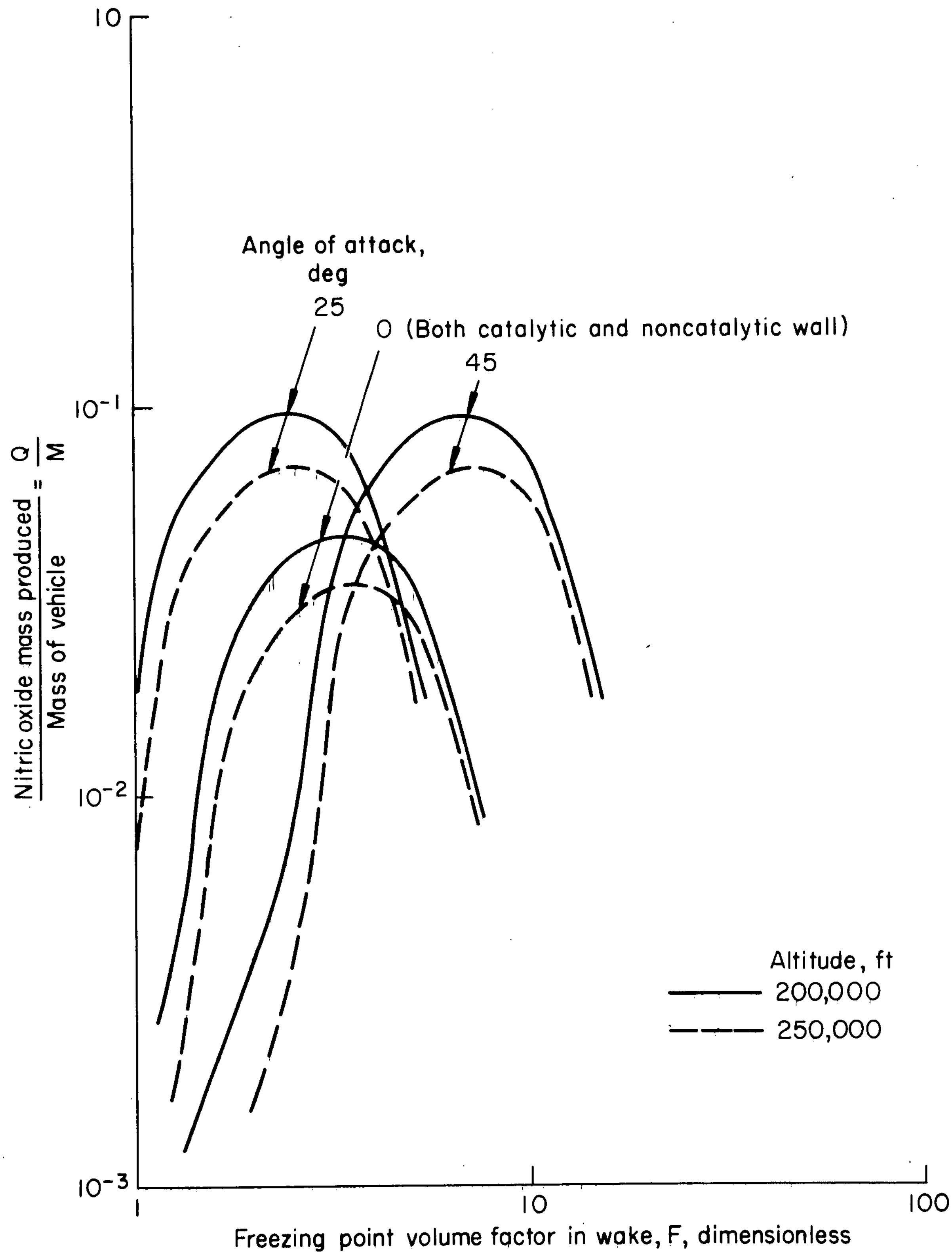

Figure 8.- Ratio of nitric oxide mass produced per flight to mass of spacecraft as function of freezing point volume factor F, according to "wake-freezing" approximation.

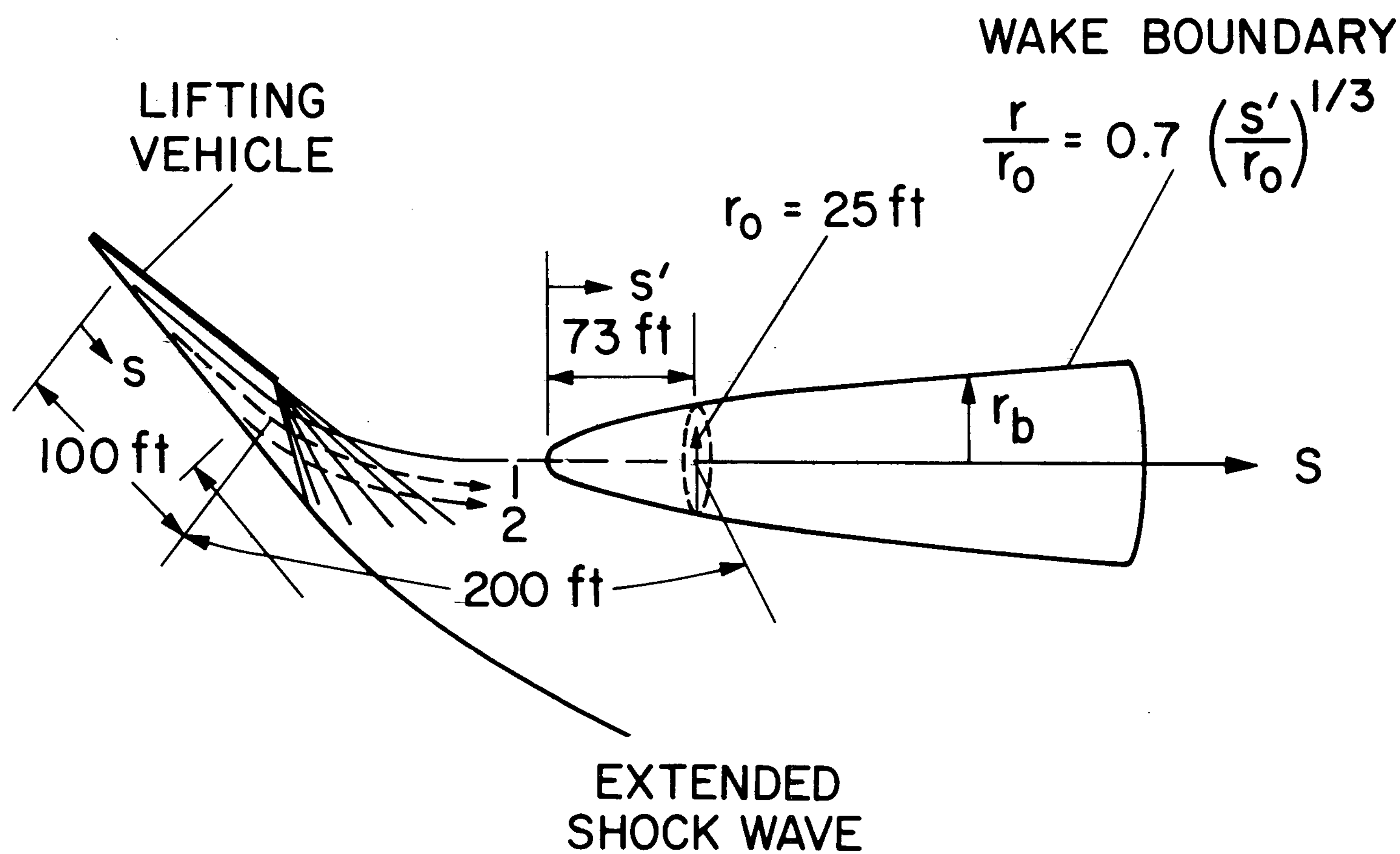

Figure 9.- Schematic of two-step flow field model used in computer calculation.

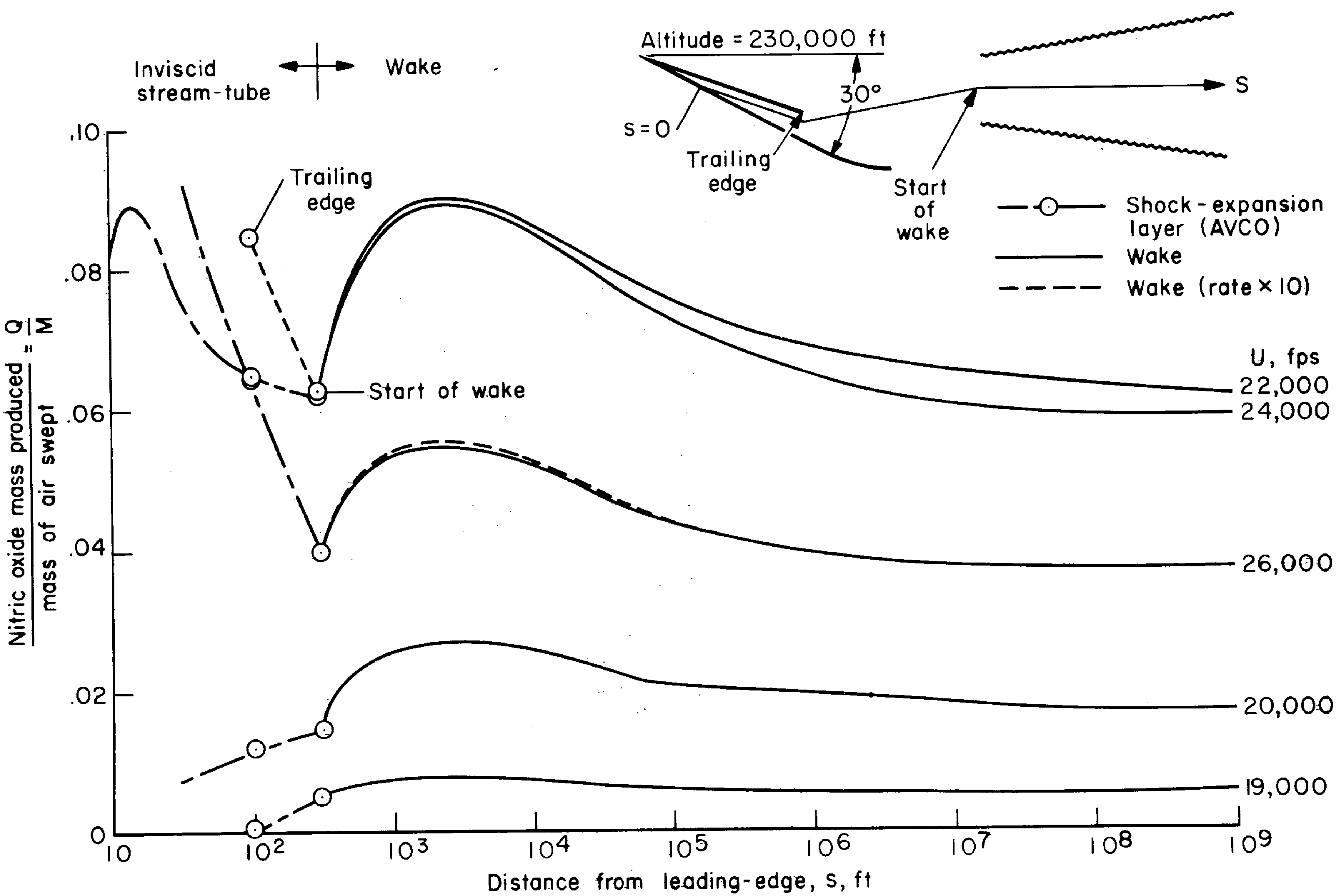

Figure 10.- Result of computer calculation of finite reaction rate chemistry. Altitude = 230,000 ft, angle of attack = 27°.