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SUMMARY

Calculations are made concerning the quantity of nitric oxide (NO) produced through afterburning in the plume of the solid propellant motors of the Space Shuttle. This study focuses on establishing the sensitivity of predictions of NO production to uncertainties in altitude, reaction rate coefficients, turbulent mixing rates, and Mach disc size and location. The results show that relatively large variations in parameters related to these phenomena had surprisingly little effect on predicted NO production.

INTRODUCTION

The Space Shuttle's solid propellant boosters will release large quantities of exhaust effluents into the stratosphere. Some of these effluents such as hydrogen chloride (HCl), chlorine (Cl_2), and nitric oxide (NO) are believed to adversely affect the ozone layer which protects the biosphere from solar ultraviolet radiation (ref. 1). The chlorine-containing species are emitted because they are major constituents in the present generation of solid propellants. The NO, on the other hand, is produced mainly through the turbulent mixing of the atmosphere into the hot plume with subsequent afterburning.

The first set of calculations of NO production in the stratosphere due to solid rocket motor afterburning was made by H. S. Pergament and his associates (refs. 2 to 4). In these studies the amounts of NO were predicted to be about 1/500 times the levels of HCl produced in the exhaust. These calculations were among the first applications of the computer code atmospheric interaction plume program (AIPP) developed by Pergament. There are a number of seemingly crucial initial and boundary conditions used in these studies that should be considered more closely. In particular, the Mach disc location is determined from the correlation of Lewis and Carlson (ref. 5) for jets exhausting into still air, modified by the correlation of D'Attorre and Harshbarger (ref. 6) which accounts for the effect of a supersonic free stream.

The largest nozzle exit plane of the motors used in the Lewis and Carlson measurements had an area of 1.26×10^{-4} m^2. The area of the shuttle booster exit plane, on the other hand, exceeds 10.32 m^2. Although the principles of similarity are well established in the field of fluid flow, any small differences between the laboratory situation and the launch situation will be magnified by the large differences in scale. It is advisable, therefore, to study the sensitivity of NO production to possible changes in size and position of the Mach disc as these parameters cannot be considered well established.

Pergament's calculations were carried out only for a 30-km altitude. Since the boundary conditions and position and size of the Mach disc are all affected by changes in altitude, it was considered important to determine how these changes affect NO production. In addition, the effects of uncertainties in the chemical kinetic rate coefficients and turbulent mixing parameters on NO levels were also investigated.

SYMBOLS

a	speed of sound, km/sec
A	pre-exponential factor for reaction rate coefficient
AIPP	atmospheric interaction plume program (computer program)
B	activation energy, cal/mole
EDDYK	turbulent mixing parameter
EGSF1,EGSF2	parameters related to shock-wave geometry
k	scaling factor for turbulent mixing, equal to 1/EDDYK
K_f	forward reaction rate coefficient (in terms of molecules, cm^2, sec)
LAPP	low altitude plume program (computer program)
M	Mach number
N	power law for temperature dependence in reaction rate coefficient
NOQ,NOL, etc.	arbitrary letters used to label different chemical reaction schemes used in study (table III)
r_{ex}	radius of nozzle exit, m
R	universal gas constant, cal/K-mole
T	temperature, K
u	velocity, km/sec
X	distance downstream of nozzle exit plane, m
Y	radial distance from centerline, m
ρ	density, g/cm^3
μ	eddy viscosity coefficient, $kg\text{-}sec/m^2$

SALIENT FEATURES OF AIPP CODE

The present generation of low-altitude mixing codes, such as the low altitude plume program (LAPP) (ref. 7) cannot predict many of the important features of stratospheric afterburning because they do not include shock structure. The relatively new atmospheric interaction plume program (AIPP) (ref. 8), on the other hand, is designed to consider some of the important phenomena in a high-altitude plume. Thus, it includes, as shown in figure 1, the exhaust gas shock, the air shock, and a single trailing Mach disc. The region where NO is most likely to be produced is in the high-temperature region immediately behind the Mach disc.

The AIPP code was developed by Pergament and others to calculate gas and particle properties behind the nozzle of a motor which is traveling at supersonic speeds. Because an exact solution of the hydrodynamic equations is beyond the present state of the art, a somewhat simplified set of equations is solved with appropriate empirical physical information. Thus, the code locates the Mach disc with the empirical formula of Lewis and Carlson (ref. 5) and then, using a numerical procedure incorporating a finite-difference streamtube technique, predicts the locations of the other shock waves. Using a mixed explicit/implicit form of differencing to obtain the most favorable step size and a purely implicit differencing technique for the solution of the chemical rate equations, the code "marches" downstream of the nozzle exit plane solving the boundary-layer equations of gas flow fully coupled through the energy terms to a finite-rate chemistry scheme. Turbulent mixing is included using a phenomenological eddy viscosity model. Gas and particle temperatures are allowed to differ.

Some of the more important assumptions incorporated into the code are:

(1) The vehicle velocity must be supersonic.

(2) The missile base recirculation region is negligibly small.

(3) The Mach disc location can be determined from existing experimental data.

(4) Internal plume shocks are not considered downstream of the Mach disc.

The gases (and particles) are emitted from the nozzle and quickly expand into the low pressure of the stratosphere. A fraction of these exhaust products travel downstream, passing through the Mach disc where they are greatly decelerated and their temperatures are substantially increased. This high-temperature region immediately behind the Mach disc is known as the throat region. In this throat region the hot gases are "squeezed" down and thereby reaccelerated to supersonic speeds.

Upon passing through the throat region, the gases enter a supersonic region where the code uses a coupled turbulent-mixing and finite-rate chemistry model. The turbulent mixing is simulated using the Donaldson-Gray approximation (ref. 9). Prior studies (refs. 10 and 11) have shown that without the Mach disc there would be negligible production of NO in the stratosphere. It is the Mach disc which creates the necessary high temperatures where NO production may be possible.

At the time that the original studies (refs. 2 and 3) were carried out, the AIPP code was not fully operational. The calculations were done through the Mach disc and throat region using this code, but from immediately behind the throat, proceeding far downstream of the exit plane, the LAPP code was used. The LAPP code is a standard axisymmetric afterburning plume code which considers finite rate chemistry and turbulent entrainment in a manner similar to this final region in the AIPP code. In the present study the AIPP code was used for the entire calculation.

As inputs to the AIPP code, the temperature of the gases and particles at the nozzle exit plane, their velocities and their chemical composition, the temperature and pressure of the atmosphere into which the exhaust products flow, as well as the atmospheric free-stream velocity (in the frame of reference of the motor) must be specified. In addition, it is necessary to specify the chemical reaction scheme to be used with the appropriate rate constants, thermochemical data, and turbulent mixing parameters. If particles are present, the particle size distributions and thermodynamic properties of the particles are also necessary inputs.

During the course of this research, it became necessary to make certain modifications to the existing program. Numerical instabilities occurred in the throat region (fig. 1) immediately behind the Mach disc. These instabilities were related to the geometry of the throat region, being particularly sensitive to the curvature of the dividing streamline. To alleviate the difficulty in the numerical scheme, two parameters EGSF1 and EGSF2 were added to the program. Varying EGSF1 allowed the throat to be made wider or narrower at its maximum width. Varying EGSF2 made the region longer or shorter and, in addition, the size of the disc where the flow "choked" (became supersonic) was allowed to vary. These widths and lengths were all kept within physically reasonable bounds; there was no known unique dividing line curvature.

Appropriate small changes in EGSF1 or EGSF2 which cause negligible changes in the throat geometry can keep the solution in the throat region from diverging. It was found that, up to the point where the code breaks down, all temperatures, pressures, velocities, and chemical compositions were nearly identical using values of EGSF1 and EGSF2 that cause instability or complete the solution successfully so long as the values of these parameters were close. Although the nature of the instabilities is not well understood at this time, several trial runs have shown that the use of reasonable values of EGSF1 and EGSF2 that allow completion of the solution does not appear to alter any physical or chemical properties significantly in the region from nonsuccessful values. The NO levels as well as other physical variables given by using these parameters appeared to be physically significant and fully compatible with the solutions using nonsuccessful values until the point of numerical breakdown (which tended to be sudden).

Other minor modifications were made as well, for example, altering pressure gradients along a fictitious wall boundary condition. In addition, although no new programing was involved, it was found that occasionally the effects of particles downstream of the Mach disc were causing numerical instabilities. In those cases when this happened, all particle densities downstream of the Mach disc were set equal to zero since, for calculations of NO production, particle effects (particularly this far downstream) were not important.

PHYSICAL AND CHEMICAL INPUT DATA

The four major phenomena considered in this study were (1) the effects of altitude variation on nitric oxide production, (2) the effects of kinetic reaction rate coefficients, (3) turbulent mixing rate coefficient uncertainties and (4) the size and position of the Mach disc. All of these phenomena are reflected in the physical and chemical inputs that were used.

As initial conditions for the program, it was necessary to know conditions along the solid-rocket-motor nozzle exit plane. A detailed list of the nozzle exit plane conditions including both composition and thermodynamic information is given in table I. The Space Shuttle will have two distinct solid rocket boosters. From observations of other solid propellant vehicles such as the Titan, it is expected that in the stratosphere the plumes from these two motors will quickly merge and become a single larger plume; however, the effects of plume interactions have been studied by Pergament and Hwang (ref. 4) and have been shown to be small. In the present study a single motor is used to examine the sensitivity of changes in NO production to uncertainties in input parameters.

Altitude Variations

The altitudes considered in this study were 20, 30, and 40 km. The pressure and temperature of the unperturbed atmosphere vary with altitude (ref. 12) and are included as boundary conditions. The changes in atmospheric pressure and temperature cause the Lewis and Carlson formula (ref. 5) to predict a different downstream distance from the nozzle exit plane for the Mach disc location at each altitude. In addition, the speed of the vehicle varies with altitude. A summary of these boundary conditions is given in the following table:

ALTITUDE VARIATION STUDY

Inputs		
Altitude, km	Free-stream speed of vehicle, m/sec	Mach disc location downstream of exit plane, m
20	730	23.5
30	1139	40.5
40	1444	90.0

For purposes of comparison the same mass-flow rate of 3.6×10^6 g/sec was used for all three altitudes. This rate is within the variation of mass flow from mission to mission for 20- and 30-km altitudes. It will be too high by a factor of 8 for the 40-km case.

Kinetic Reaction Rate Coefficient Uncertainties

A total of 13 chemically reacting gaseous species are considered in the model. A chemical scheme which includes 18 reactions is used. (See table II.) The reaction rate coefficients used in this study and their experimental uncertainties are taken from reference 2. To test the sensitivity of the NO levels to the effects of reaction rate uncertainties, the case of a shuttle motor at 30-km altitude with the Mach disc at 40.5 m downstream of the nozzle exit plane was run using six different chemical schemes. These schemes are shown in detail in table III. The geometry of these runs is identical to that used in reference 2 for purposes of direct comparison. In addition, this same case was run using the original chemical scheme (referred to as the nominal case).

In selecting the reactions and species that were studied in all of these schemes, a far greater number of possible species and reactions were studied. These reactions were selected because all others were found to add no variations in the production of NO.

Turbulent Mixing Study

The mixing of ambient air into the hot plume is fundamental to the production of NO in stratospheric afterburning. Behind the Mach disc, temperatures are reached at which the O_2 molecule, and even to a degree the N_2 molecule, decomposes. It is important, therefore, to have a good understanding of the mixing rates occurring in the flow field.

The Donaldson-Gray model of turbulent mixing (ref. 9) has been used in this study because of its prior success in other applications (refs. 10 and 11). The eddy viscosity coefficient μ is not well established in the situation of free supersonic flow so that all studies have to rely on the best available information. In the Donaldson-Gray model, μ is a function of many properties of the flow field as they affect the maximum velocity gradient and can be written as

$$\mu = k\ f(M,a,\rho,u)$$

where M is the local Mach number, a is the speed of sound, ρ is local density, and u is velocity. The term k is a constant which scales the value of μ. This function is called 1/EDDYK in the AIPP code. By raising values of 1/EDDYK, turbulent entrainment will occur more rapidly and in turn will affect the temperature distribution in the plume and the speed with which all chemical reactions take place.

A shuttle motor at 30-km altitude with Mach disc 40.5 m downstream of the exit plane was considered. Values of 1/EDDYK equal to twice and four times the value used in reference 2 were used as well as values equal to one-half and one-tenth of the reference 2 value. (Due to numerical instabilities in the 40.5-m location, the case of 4/EDDYK was run for the Mach disc at 35.5 m behind the nozzle exit plane. The discrepancy in Mach disc location is expected to have only a small effect on the variation of NO levels.) All attempts to run the 30-km case for the scaling factor greater than four times the original value were unsuccessful, but even four times the original value is probably too high to be physically realistic. The case of one-tenth the original scaling factor k is an extremely slow mixing situation.

Mach Disc Size and Downstream Location

Because the set of hydrodynamic equations solved by the computer model is not exact, certain information concerning the flow field must come from empirical data. Such is the case with the Mach disc size and location. For those inputs a range of values is possible with the present state of knowledge. The Mach disc size and downstream location affect NO production primarily by determining the amount of mass flowing through the Mach disc and the temperatures in the throat.

The effect of the size of the Mach disc alone was studied by using the case of a shuttle motor at 30-km altitude with a Mach disc 40.5 m downstream of the exit plane. By varying the throat-region geometry the Mach disc size at any given location can be varied within certain limits. Since the size of the Mach disc cannot be accurately predicted, variations in NO production within the limits of uncertainties are of some interest. In the cases studied a number of runs were made with different throat geometries. Of those runs which were numerically stable, the radius of the Mach disc ranged from 583 to 692 cm (table IV), which represents a variation of about 16 percent. The mass flow through the Mach disc went from 1.34×10^5 to 1.87×10^5 g/sec considering a single motor.

A study was made to determine the variation in production of NO due to changes in location of the Mach disc at an altitude of 30 km. Numerically stable runs were obtained for downstream locations of 30, 35, 40, 45, 50, and 55 m (table V). For each distinct location of the Mach disc, the size of the Mach disc changed as well as the peak afterburning temperature of the plume gases.

RESULTS AND DISCUSSION

One of the basic quantities used in the prediction of NO production in the stratosphere was the amount of NO in grams per downstream meter of plume. After the plume gases had passed through the high-temperature throat region, with increasing X (downstream distance) the temperatures in the plume decreased, the chemical reactions began to slow down, and the velocities decreased. As X approached the value at which the centerline temperature dropped below 400 K, the chemical reactions affecting NO became so slow that they were shut off in the model. Although the plume continued to diffuse and, therefore, the absolute concentration of each nonatmospheric species decreased with increasing X, the total mass flow of each of the species crossing a plane perpendicular to X was constant in this region (within small numerical deviations).

Since this study was concerned primarily with the high-temperature regions in the plume (greater than 400 K), the chlorine chemistry became simpler than in the ambient-temperature case. The only reacting species that were found to affect NO production significantly were HCl, Cl_2, and Cl. Such species as ClO were considered in prior studies (ref. 11) and were found to have negligible effect on the high-temperature afterburning processes studied here.

As the molecules passed out of the high-temperature regions, the average velocity of these molecules approached the ambient value. (All calculations were carried out in the frame of reference of the motor.) Thus, not only was the mass flow constant, but also

$$\frac{\rho u A}{u} = \rho A \rightarrow \text{Constant}$$

where ρA is that quantity of mass in a slab the dimensions of which are equal to the area of the plume determined in a plane perpendicular to X and whose width is 1 m in the X-direction. The value of ρA for a given species for large values of X is a reasonable indication of how much of a given species is deposited into the cool part of the plume. The units of this quantity are g/m.

Another quantity of interest is the ratio of NO to the quantity of gases which contain chlorine (HCl, Cl_2, and Cl). At this time chlorine is considered to be the most important effluent from the shuttle motor which affects the stratosphere. Thus, the ratio of NO to chlorine-containing species gives a rapid indication of NO's relative importance to the stratosphere.

Altitude Variation

The results of the study of NO production with changes in altitude are summarized in table VI. As can be seen, the amount of NO in g/m for each motor decreases with increasing altitude, being about 4 g/m per motor at 20 km, 2.3 g/m per motor at 30 km, and about 1.2 g/m per motor at 40-km altitude. In all three cases the ratio of NO to chlorine-containing species was about 1/630. This invariance of the NO to chlorine-containing species ratio appeared to be due to a fortuitous combination of circumstances. The mass flow of gases through the Mach disc decreased with increasing altitude (1.58×10^5 g/sec for a single motor at 20 km, 1.35×10^5 g/sec per motor at 30 km, and 0.80×10^5 g/sec per motor at 40 km), which tended to lower possible NO production with altitude. However, along with this decreasing mass flow is a phenomenon which has the opposite effect of NO production, that of increasing peak centerline temperature with increasing altitude. These two effects appear to cancel out, leaving NO-to-chlorine ratios nearly constant. The larger values of NO far downstream of the exit plane appear to be more a result of differences in the final value of free-stream velocity than of pressure and free-stream temperature variations.

In figure 2 some of the chemistry of afterburning is shown by plotting the mole fraction of certain species along the plume centerline as a function of the downstream distance from the nozzle exit plane. The case shown is that of a shuttle motor at an altitude of 20 km. As can be seen, as afterburning proceeds, CO is converted to CO_2 and H_2 is converted to H_2O. There is really no NO production until the Mach disc is reached (at 23 m) where there is a dramatic increase in both the concentrations of NO and O. The slow decrease in NO concentration along the centerline that occurs downstream of the throat region is due to the fact that NO is no longer being produced and the plume gases are being diluted with entrained air.

NO chemistry at 40-km altitude is examined in figure 3. In this graph the centerline mole fraction is plotted as a function of distance from the nozzle exit plane. At this higher altitude where the density of air is less than at 20 km, the afterburning processes occur over larger downstream distances than in the 20-km case. One unusual feature of this NO-chemistry figure is the discernible drop in the N_2 concentration immediately behind the Mach disc. The N_2 molecule is particularly stable, and in most previous studies (for example, refs. 1 and 2) the N_2 concentration drop during any point in afterburning is not nearly as large. This drop in concentration is due to the extremely high temperature of 4389 K reached in the 40-km afterburning situation.

Notice that the NO production increases rapidly immediately behind the Mach disc. The increase in N_2 and O_2 concentration downstream of the Mach disc is due to the entrainment of air into the plume.

In figure 4 is shown the NO production in g/m for each motor for the first half kilometer downstream of the nozzle exit plane in the cases of 20-, 30-, and 40-km altitude. Although the asymptotic values of NO have not been reached yet, the trend of increasing NO with decreasing altitude is seen. However, much of the difference is due to the fact that the asymptotic value of the free-stream velocity is lower for the lower-altitude cases.

Reaction Rate Coefficient Variations

As can be seen from table VII the variation of rate coefficients within experimental uncertainties for the 18 reaction schemes of table III results in very little variation in NO production. The centerline temperature, which is a key physical variable, is close to 3800 K in all cases, except the nominal case. The Mach disc size and mass flow through the Mach disc are close in all cases except for the case NOQ in which all forward reaction rates were put at their lowest values. The reasons for these slight variations are uncertain at this time and were not pursued in detail because, as can be seen in the last column in table VII, the NO production at a distance of 700 m downstream of the nozzle exit plane, which is far enough downstream so that any large differences will manifest themselves, falls within the range of 0.75 to 0.80 g/m per motor in all cases. By the time the gases have reached 700 m downstream of the exit plane, the temperatures in the plume have dropped well below 2000 K. As a result, the production of NO has dropped off to a negligible rate and the only phenomenon which increases the density of NO from this point is the slowing down of the plume gases. Since the plume gas speeds are roughly the same in all kinetic variations at this distance downstream, these strong similarities in NO production from various rate coefficients will be maintained indefinitely far downstream.

The conclusion of this sensitivity study is that NO production is not sensitive to reaction rate uncertainties; NO levels tested for cases in which reaction rates varied within the experimental uncertainties specified in table II were found to result in NO levels close to those predicted for the nominal case.

Turbulent Mixing Variation

As the turbulent mixing scale parameter 1/EDDYK varies from its nominal value of 1/40, the entrainment of air into the plume varies from rather violent mixing to almost no mixing at all. This fact is illustrated in figure 5 where the mole fraction of N_2 along the centerline of the plume is plotted as a function of distance downstream of the exit plane up to 500 m. As can be seen, by the time 500 m has been reached in the case of EDDYK = 10, the mole fraction of N_2 has attained a substantial fraction of its final value of 0.79, while in the case of EDDYK = 400 very little entrainment has taken place.

This variation in the downstream distance scale over which phenomena occur for various mixing rates is also evident from studying the decay of centerline temperature as a function of distance downstream of the nozzle exit plane. This fact is studied in table VIII under the column entitled "Downstream distance at which centerline temperature first drops below 1500 K." As can be seen, for the case used in reference 1 (EDDYK = 40), this distance is 750 m; for the most violent mixing the distance is 230 m, whereas for the slowly mixing case the centerline temperature first drops below 1500 K well beyond a kilometer.

As can be seen from figure 6, the more rapidly mixing occurs the more quickly NO (in g/m per motor) is produced. Thus, at 500 m downstream of the exit plane, the NO level in the case of EDDYK = 10 is 1.15 g/m per motor while in the case of EDDYK = 400 it is 0.64 g/m per motor. This increase is a result of two effects. The first is that oxygen, necessary for the production of NO, is entrained into the high-temperature region more quickly in the rapidly mixing cases than in the slowly mixing cases. The other reason for the greater NO density is that the speed of the gases decreases more quickly in the rapidly mixing case than in the slowly mixing case, which fact causes all densities in the plume to increase more rapidly in the EDDYK = 10 case.

In spite of the fact that NO production occurs at shorter distances downstream of the nozzle exit in the rapidly mixing cases than in the slowly mixing cases, the final asymptotic values do not vary substantially as a result of turbulent entrainment. In table VIII the last column shows the ratio of NO to HCl for various entrainment coefficients. As can be seen, there is little variation throughout the range of EDDYK; the value used in reference 1 (EDDYK = 40) seems to give NO levels slightly higher than either faster or slower entrainment, although the calculations are not really accurate enough to distinguish small effects such as this with any great certainty.

Mach Disc Size and Location Variation

A study was made of the effect of the Mach disc size variation at 30-km altitude with the Mach disc 40.5 m downstream of the exit plane. Although cases were successfully run that varied in Mach disc radius from 583 to 692 cm and with mass flows that varied between 1.34×10^5 g/sec per motor and 1.87×10^5 g/sec per motor, as can be seen from table IV there were only small effects on NO production. The most reliable indicator for the importance of the NO production rate is the ratio of NO to the relatively inert chlorine-containing gas species. As can be seen from the last column in table IV, the ratio varies between 1.5×10^{-3} and 1.6×10^{-3} without any clear trend becoming established as the numerically stable cases of varying mass flow are examined.

Mach Disc Location Variation (30-km Altitude)

In the present study, as shown in table V, a clear trend is established in which the ratio of NO to HCl (and other chlorine-containing gases) increases as the Mach disc approaches the nozzle exit plane. The much larger mass flows through the Mach disc overcome the lower temperatures that are reached for the closer Mach disc. This temperature effect is shown in figure 7. As can be seen, although the closer Mach discs do reach a lower peak temperature, the difference between the 30- and 55-m cases is only on the order of a 10-percent drop. From table V, on the other hand, the mass-flow differences are much greater, and it is surprising that larger NO production differences are not observed.

In figure 8 it is seen that a larger centerline mole fraction occurs for the Mach disc farther from the exit plane. This fact is due to the higher temperature which is reached by the farther Mach disc. The drop in NO mole fraction which occurs in both cases is due to dilution.

In figure 9, it is seen that at the downstream distance of 800 m, in spite of the large differences in mass flow through the Mach disc, the 55.5-m case has produced more NO than the closer Mach disc cases. This production is not maintained, however. Again, the most reliable indicator of the asymptotic values of NO production is the ratio of NO to the chlorine-containing species. It is apparent from the last column in table V that, far downstream of the exit plane, once all of the differences in gas and particle velocities and total densities have become small, NO production increases slowly as the Mach disc approaches the nozzle exit plane. However, it can also be seen that, if the trends exhibited by Mach discs 30 to 60 m downstream of the exit hold for Mach discs much closer to the exit plane, large increases in NO production would come only from a Mach disc within a few meters of the exit plane. The existence of the Mach disc so close to the nozzle is physically improbable.

CONCLUDING REMARKS

In this study the anticipated effects of altitude, kinetic rate coefficients, turbulent mixing, and Mach disc size and location on the production of nitric oxide (NO) in the solid rocket motor plumes of the Space Shuttle have been examined. The results show that there is surprisingly little sensitivity of NO levels to uncertainties in these parameters. Changes in the preceding parameters can increase the mass flow through the Mach disc which tends to increase NO production at constant peak temperature after the Mach disc. However, an increased mass flow is almost always accompanied by a drop in peak temperature reached by the gases flowing through the Mach disc, which tends to lower NO production. NO production rises slowly as the Mach disc nears the nozzle exit plane, at least in the range of 30 to 60 m behind the nozzle exit plane at 30-km altitude.

As a result of this study, the values predicted by Pergament and his associates can be viewed with somewhat more confidence than before and it seems clear that HCl will be by far the most abundant exhaust effluent in the Space Shuttle's solid rocket motor plumes which may have a direct effect on the ozone layer.

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TABLE I.- NOZZLE EXIT PLANE CONDITIONS

[Values shown, obtained from ref. 2, represent the average and vary slightly over the cross section of the exit plane]

Temperature, K	2100
Velocity, m/sec	2390
Mole fraction of solid particles	0.30

Composition of gases at exit plane	Mole fraction of gases
CO	2.50×10^{-1}
CO_2	2.40×10^{-2}
HCl	1.60×10^{-1}
H	2.00×10^{-3}
H_2	2.97×10^{-1}
H_2O	1.61×10^{-1}
N_2	1.02×10^{-1}
Cl	1.00×10^{-3}
N	4.00×10^{-8}
NO	3.00×10^{-3}
OH	1.00×10^{-4}
O_2	2.00×10^{-7}
O	1.00×10^{-6}

TABLE II.- REACTION MECHANISM FOR AIPP CALCULATIONS

[$K_f = AT^{-N} \exp(B/RT)$; source, ref. 2]

Reaction	Nominal A	N	B, cal/mole	Upper error bound for A (a)	Lower error bound for A (b)
1. $O + O + M = O_2 + M$	1.0(-30)	1	0	30	30
2. $O + H + M = OH + M$	1.0(-29)	1	0	30	30
3. $H + H + M = H_2 + M$	5.0(-29)	1	0	30	30
4. $H + OH + M = H_2O + M$	2.0(-28)	1	0	10	10
5. $CO + O + M = CO_2 + M$	1.0(-29)	1	-2 500	3	3
6. $OH + OH = H_2O + O$	1.0(-11)	0	-780	5	5
7. $OH + H_2 = H_2O + H$	3.6(-11)	0	-5 200	3	3
8. $O + H_2 = OH + H$	2.9(-11)	0	-9 460	3	3
9. $H + O_2 = OH + O$	1.9(-10)	0	-16 800	3	3
10. $CO + OH = CO_2 + H$	9.0(-13)	0	-1 080	3	3
11. $H + Cl + M = HCl + M$	5.5(-31)	1	0	30	30
12. $HCl + OH = H_2O + Cl$	7.2(-12)	0	-3 250	30	30
13. $H + HCl = Cl + H_2$	8.8(-11)	0	-4 620	10	10
14. $OH + Cl = HCl + O$	3.0(-11)	0	-5 000	30	30
15. $O + N_2 = NO + N$	1.3(-10)	0	-76 000	3	3
16. $N + O_2 = O + NO$	2.2(-11)	0	-6 250	3	3
17. $NO + H = N + OH$	1.5(-10)	0	-47 000	5	5
18. $N + N + M = N_2 + M$	5.6(-30)	1	0	10	10

[a]Multiply A by upper error bound for A to get maximum rate coefficient.
[b]Divide A by lower error bound for A to get minimum rate coefficient.

TABLE III.- PRE-EXPONENTIAL REACTION RATE VARIATIONS

Reaction	Chemical reaction scheme					
	NOQ	NOI	NOZ	NOK	NOL	NOE
1. $O + O + M = O_2 + M$	3.3×10^{-31}	1.0×10^{-30}	1.0×10^{-30}	1.0×10^{-30}	3.0×10^{-28}	3.0×10^{-28}
2. $O + H + M = OH + M$	3.3×10^{-31}	1.0×10^{-29}	3.3×10^{-29}	3.0×10^{-31}	3.3×10^{-28}	3.0×10^{-28}
3. $H + H + M = H_2 + M$	1.0×10^{-31}	5.0×10^{-29}	5.0×10^{-29}	5.0×10^{-29}	5.0×10^{-29}	8.4×10^{-29}
4. $H + OH + M = H_2O + M$	2.0×10^{-29}	2.0×10^{-28}	2.0×10^{-28}	2.0×10^{-28}	2.0×10^{-28}	2.0×10^{-27}
5. $CO + O + M = CO_2 + M$	3.3×10^{-31}	1.0×10^{-29}	1.0×10^{-29}	3.3×10^{-31}	3.0×10^{-29}	3.0×10^{-29}
6. $OH + OH = H_2O + O$	2.0×10^{-12}	1.0×10^{-11}	1.0×10^{-11}	5.0×10^{-11}	2.0×10^{-12}	5.0×10^{-11}
7. $OH + H_2 = H_2O + H$	1.6×10^{-11}	3.6×10^{-11}	3.6×10^{-11}	3.6×10^{-11}	3.6×10^{-11}	3.6×10^{-10}
8. $O + H_2 = OH + H$	1.6×10^{-11}	2.9×10^{-11}	2.9×10^{-11}	1.6×10^{-11}	1.5×10^{-10}	1.5×10^{-10}
9. $H + O_2 = OH + O$	1.0×10^{-10}	1.9×10^{-10}	1.9×10^{-10}	9.0×10^{-10}	1.0×10^{-10}	9.0×10^{-10}
10. $CO + OH = CO_2 + H$	1.6×10^{-13}	9.0×10^{-13}	9.0×10^{-13}	9.0×10^{-13}	9.0×10^{-29}	1.6×10^{-12}
11. $H + Cl + M = HCl + M$	1.8×10^{-32}	5.5×10^{-31}	5.5×10^{-31}	5.5×10^{-31}	5.5×10^{-31}	1.8×10^{-29}
12. $HCl + OH = H_2O + Cl$	2.4×10^{-13}	7.2×10^{-12}	7.2×10^{-12}	7.2×10^{-12}	7.2×10^{-12}	2.1×10^{-10}
13. $H + HCl = Cl + H_2$	8.8×10^{-12}	8.8×10^{-11}	8.8×10^{-11}	8.8×10^{-11}	8.8×10^{-11}	8.8×10^{-10}
14. $OH + Cl = HCl + O$	1.0×10^{-12}	3.0×10^{-11}	3.0×10^{-11}	9.0×10^{-10}	1.0×10^{-11}	9.0×10^{-10}
15. $O + N_2 = NO + N$	4.0×10^{-11}	4.0×10^{-10}	4.0×10^{-11}	4.0×10^{-10}	4.0×10^{-11}	4.0×10^{-10}
16. $N + O_2 = O + NO$	7.0×10^{-12}	6.6×10^{-11}	7.0×10^{-12}	6.6×10^{-11}	7.0×10^{-12}	6.6×10^{-11}
17. $NO + H = N + OH$	2.0×10^{-11}	2.0×10^{-11}	7.5×10^{-10}	3.0×10^{-11}	7.5×10^{-10}	7.5×10^{-10}
18. $N + N + M = N_2 + M$	5.6×10^{-31}	5.6×10^{-30}	5.6×10^{-30}	5.6×10^{-31}	5.6×10^{-29}	5.6×10^{-29}

TABLE IV.- MACH DISC SIZE STUDY

[Study run at 30-km altitude with Mach disc located 40.5 m downstream of nozzle exit plane. EDDYK = 40. A single motor is considered]

Mach disc radius, cm	Mass flow through Mach disc per motor, g/sec	Peak centerline temperature, K	NO per motor at X = 500 m, g/m	Mass ratio of NO to chlorine-containing species at X = 500 m
583	1.34×10^5	3749	0.720	1.5×10^{-3}
585	1.36	3760	.728	1.5
655	1.67	3621	.696	1.5
677	1.79	3764	.717	1.6
687	1.81	3711	.712	1.5
692	1.87	3781	.738	1.6

TABLE V.- MACH DISC LOCATION

[30-km altitude. A single motor is considered]

Mach disc location downstream of exit, m	Mass flow through Mach disc per motor, g/sec	Peak centerline temperature, K	Mach disc radius, cm	NO per motor at X = 500 m, g/m	Mass ratio of NO to chlorine-containing species at X = 500 m
30	4.27×10^5	3639	795	0.75	1.7×10^{-3}
35	2.55	3697	708	.72	1.6
40	1.35	3749	583	.72	1.6
45	.92	3812	549	.74	1.6
50	.36	3882	382	.77	1.5
55	.05	3967	160	.82	1.5

TABLE VI.- ALTITUDE VARIATION STUDY[a]

Altitude, km	Mach disc radius, cm	Mass flow through Mach disc per motor, g/sec	Peak temperature, K	NO asymptotic value per motor, g/m	Mass ratio of NO to chlorine-containing species at X = 500 m
20	339	1.58×10^5	3591	4	1/635
30	583	1.35	3749	2.3	1/637
40	969	.80	4389	1.2	1/631

[a]These values are based on a mass flow of 3.6×10^6 g/sec for each motor at all altitudes. The NO at 40 km based on the actual shuttle mass flow will be less than 0.2 g/m for each motor. The ratio of NO to chlorine-containing species is unaffected. A single motor is considered.

TABLE VII.- KINETIC RATE COEFFICIENT VARIATIONS

Scheme	Mach disc size, cm	Mass flow through Mach disc per motor, g/sec	Peak centerline temperature, K	NO per motor at X = 700 m, g/m
NOQ	712	2.00×10^5	3806	0.75
NOI	587	1.35	3810	.78
NOZ	587	1.35	3809	.76
NOK	585	1.35	3804	.80
NOL	569	1.29	3806	.78
NOE	581	1.35	3813	.77
Nominal	583	1.35	3749	.77

TABLE VIII.- TURBULENT MIXING PARAMETER VARIATIONS

EDDYK	Mach disc size, cm	Mach disc mass flow per motor, g/sec	Peak temperature, K	Downstream distance at which centerline temperature first drops below 1500 K	NO for each motor at 500 m downstream of exit plane, g/m	Mass ratio of NO to chlorine-containing species
10	573	1.746×10^5	3689	230 m	1.15	0.0016
20	398	1.259	3806	370 m	1.02	.0016
40	412	1.350	3749	750 m	.78	.0017
80	702	1.903	3812	Greater than 1 km	.66	.0016
400	521	2.130	3745	Greater than 1 km	.64	.0016

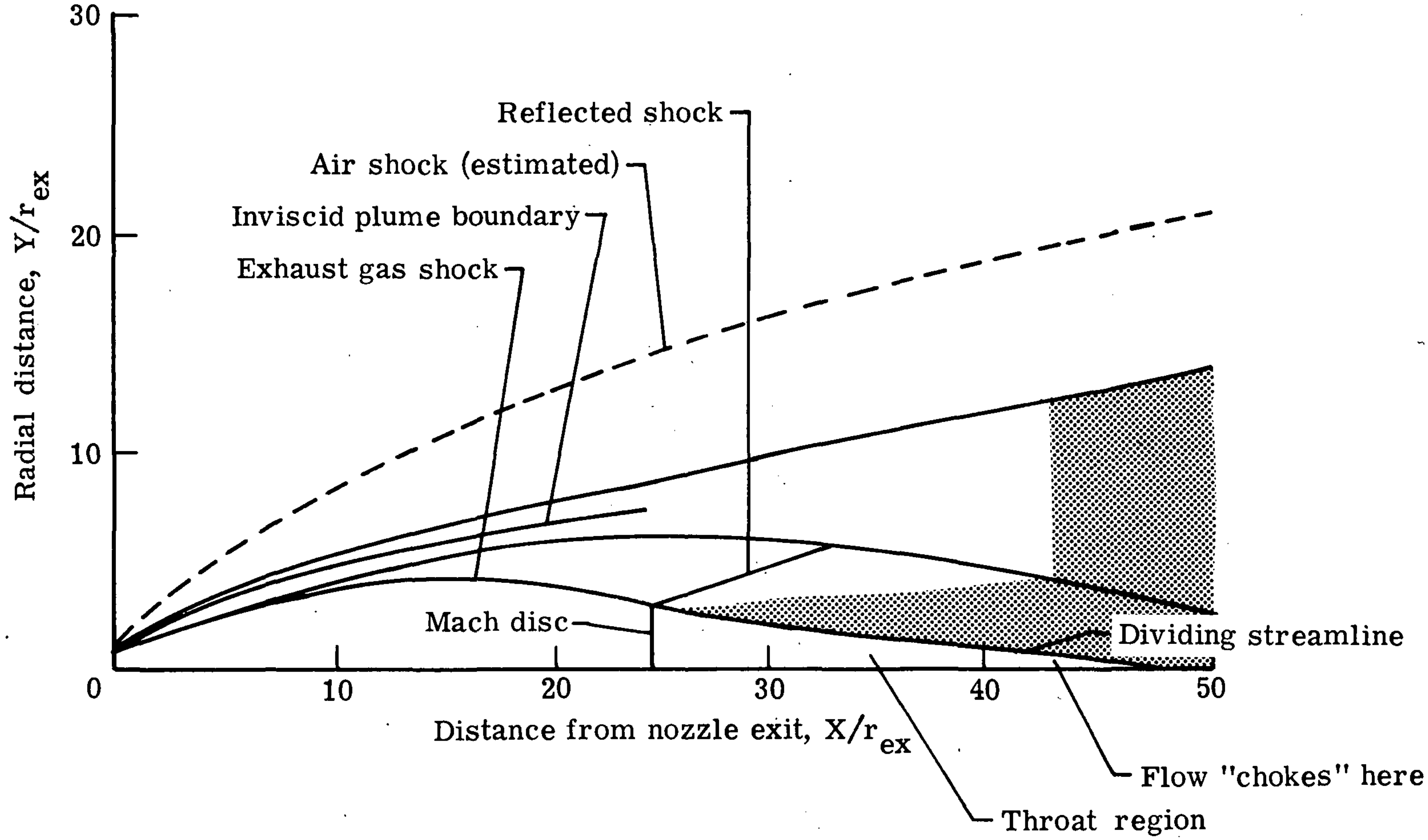

Figure 1.- Space shuttle shock structure and mixing regions.

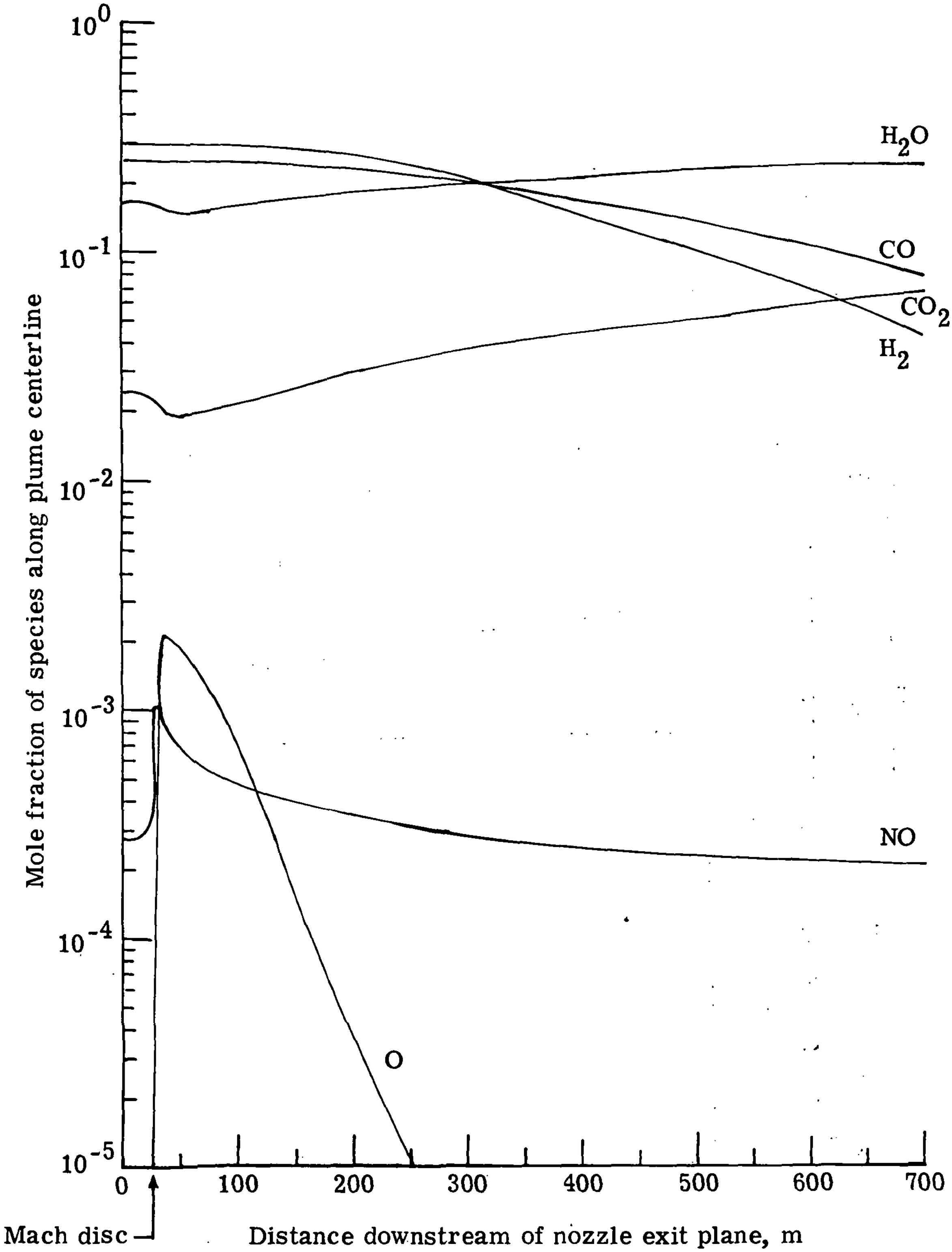

Figure 2.- Afterburning chemistry at 20-km altitude.

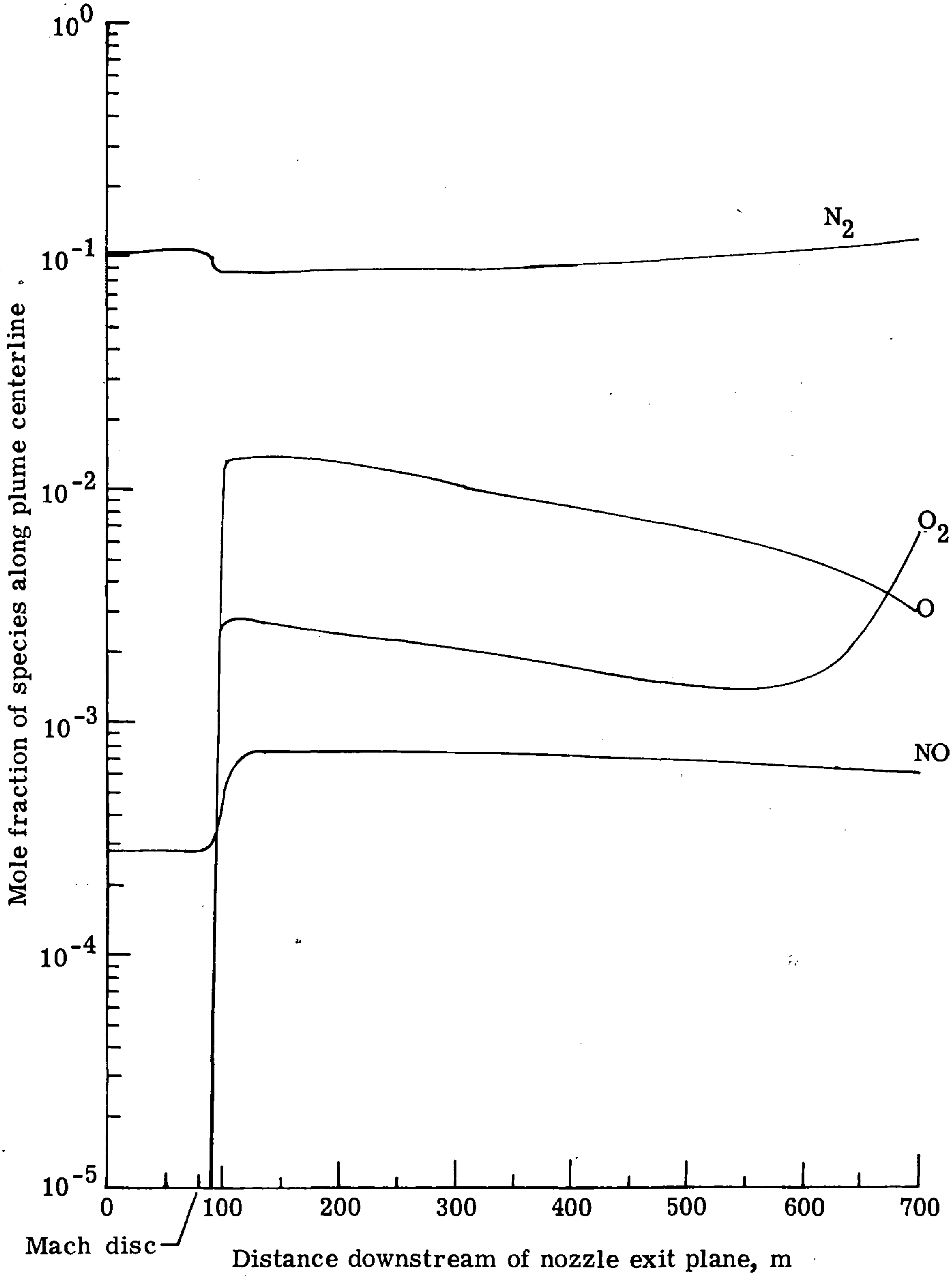

Figure 3.- NO chemistry at 40-km altitude.

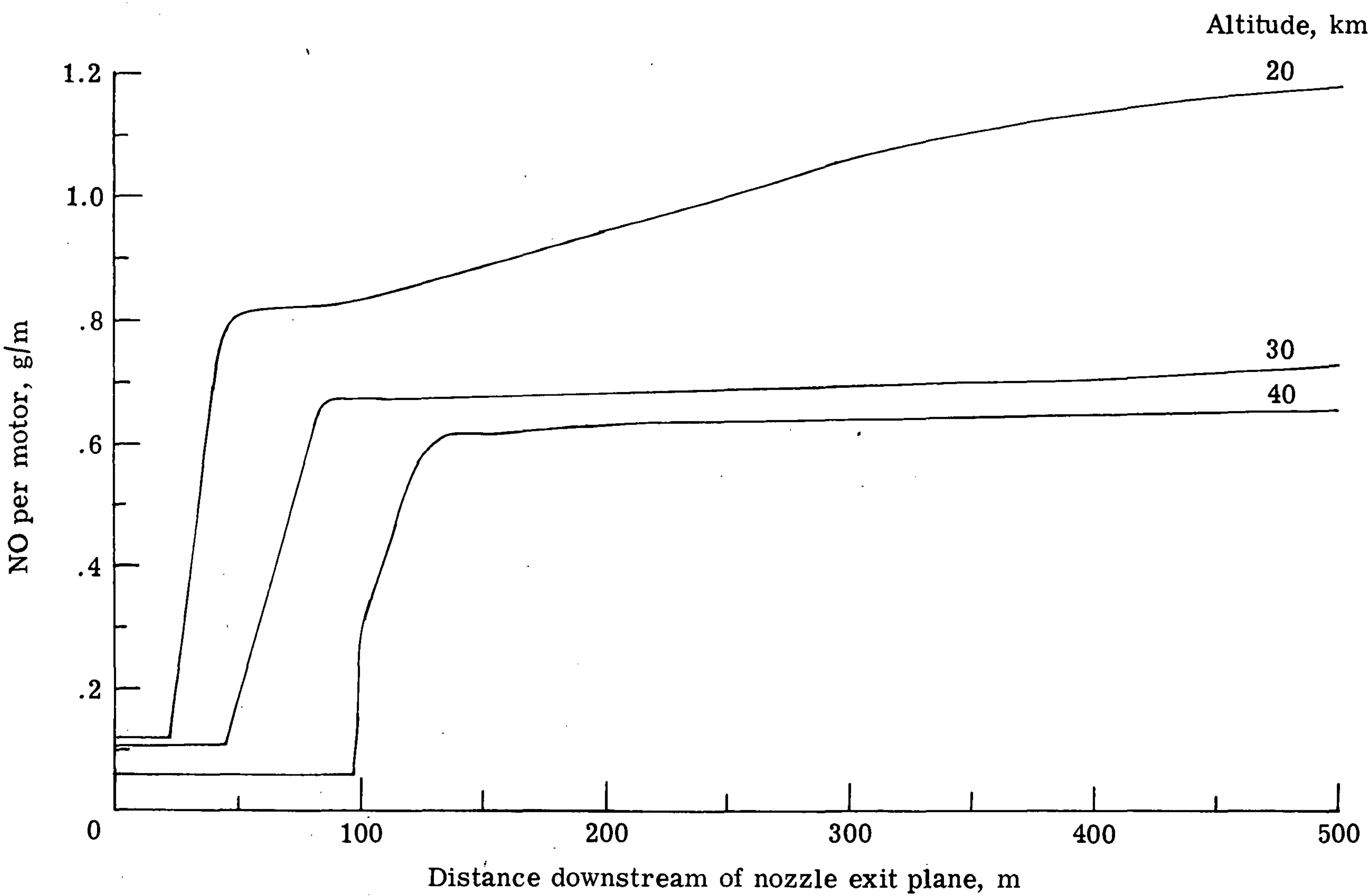

Figure 4.- NO production at three different altitudes. EDDYK = 40.

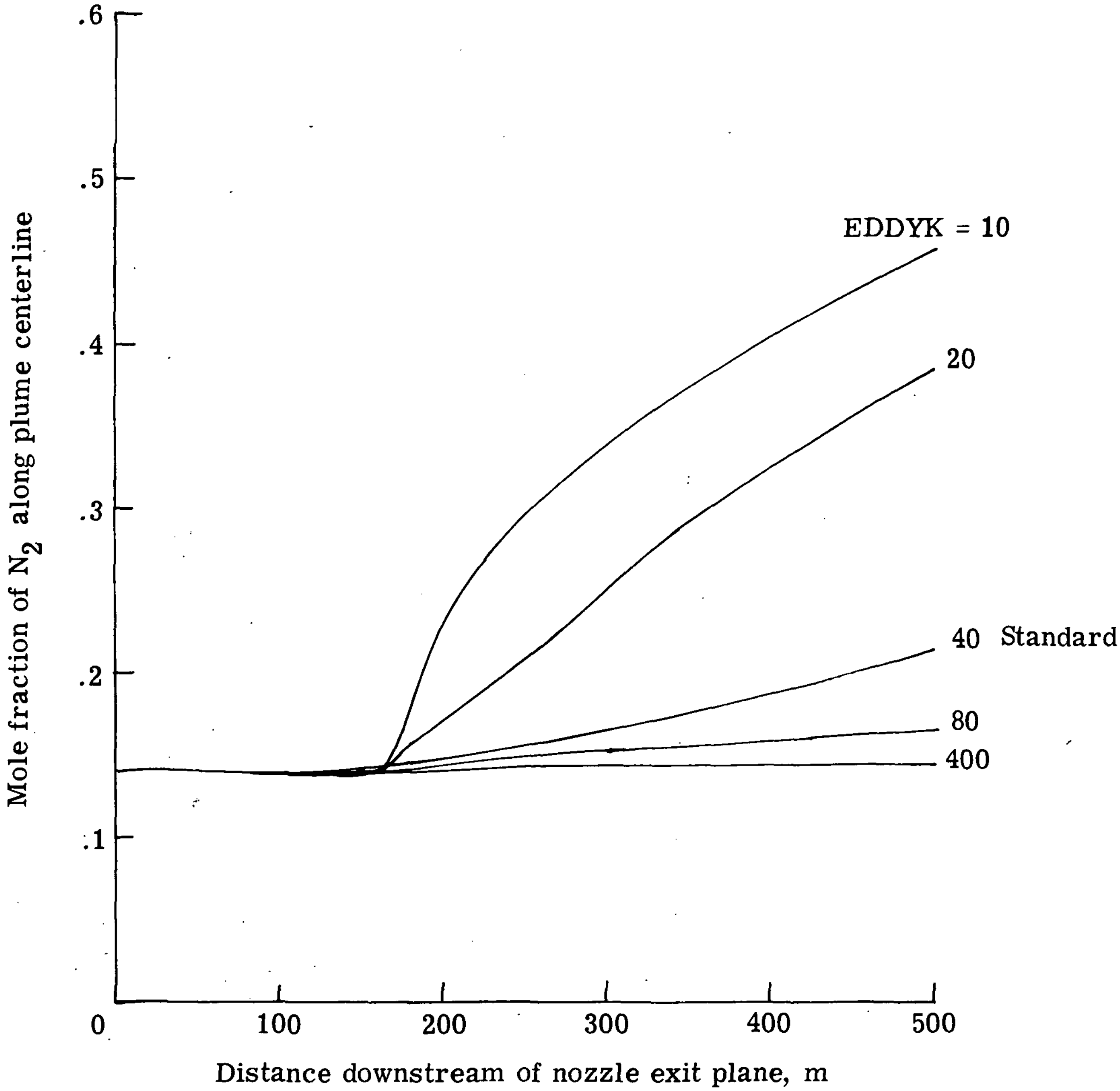

Figure 5.- Mole fraction of N_2 along centerline as a function of downstream distance for several values of turbulence parameter EDDYK, 30-km altitude.

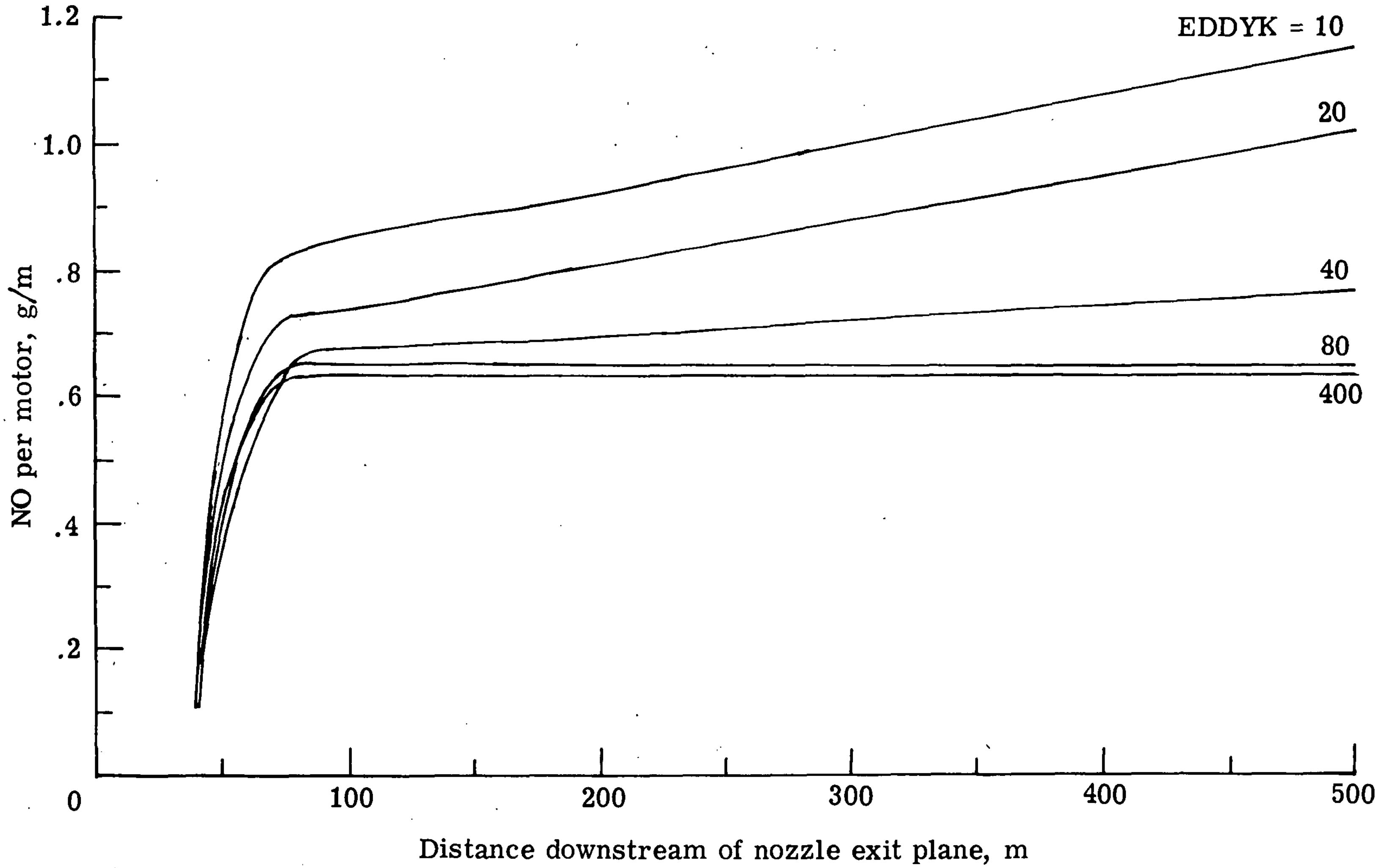

Figure 6.- NO production for several turbulent mixing parameters, 30-km altitude.

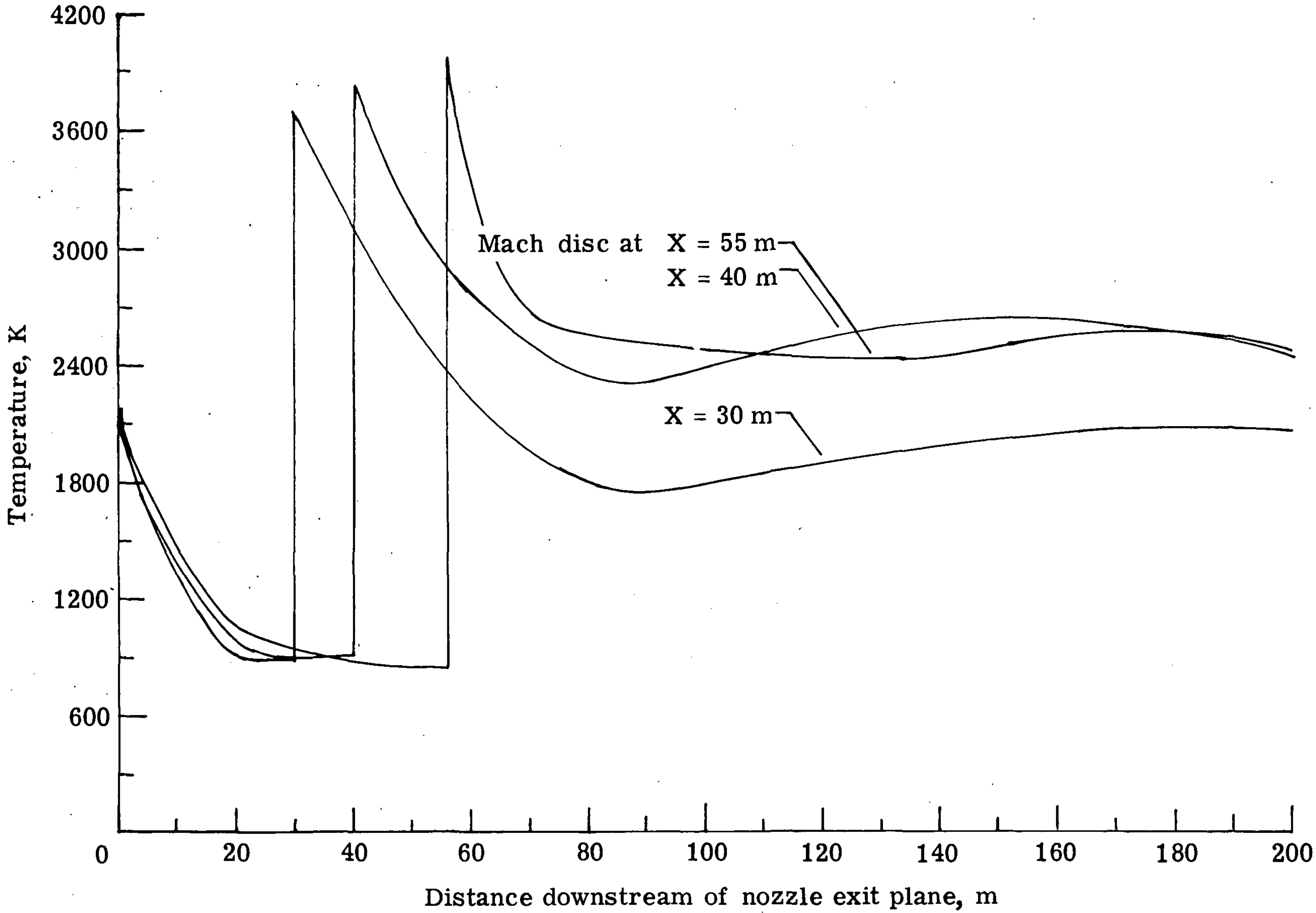

Figure 7.- Centerline temperature as a function of downstream distance at 30-km altitude for three different Mach discs at various downstream distances.

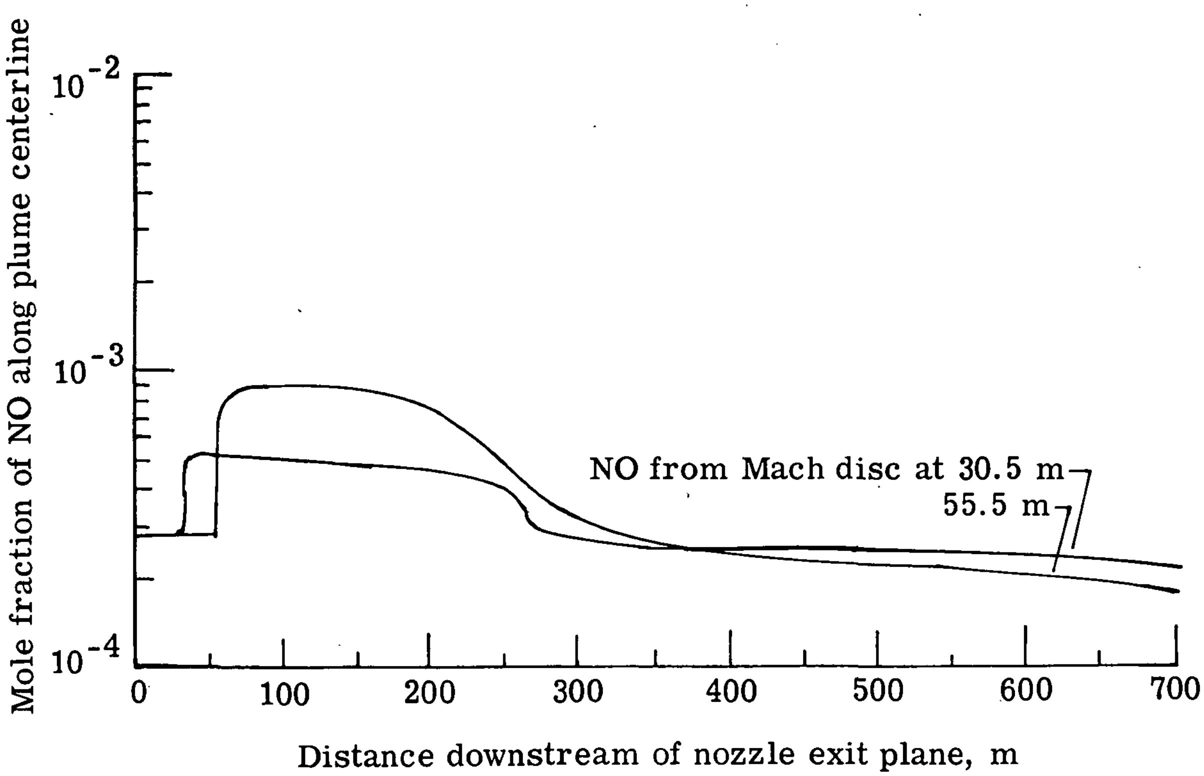

Figure 8.- NO for two different Mach disc positions, 30-km altitude.

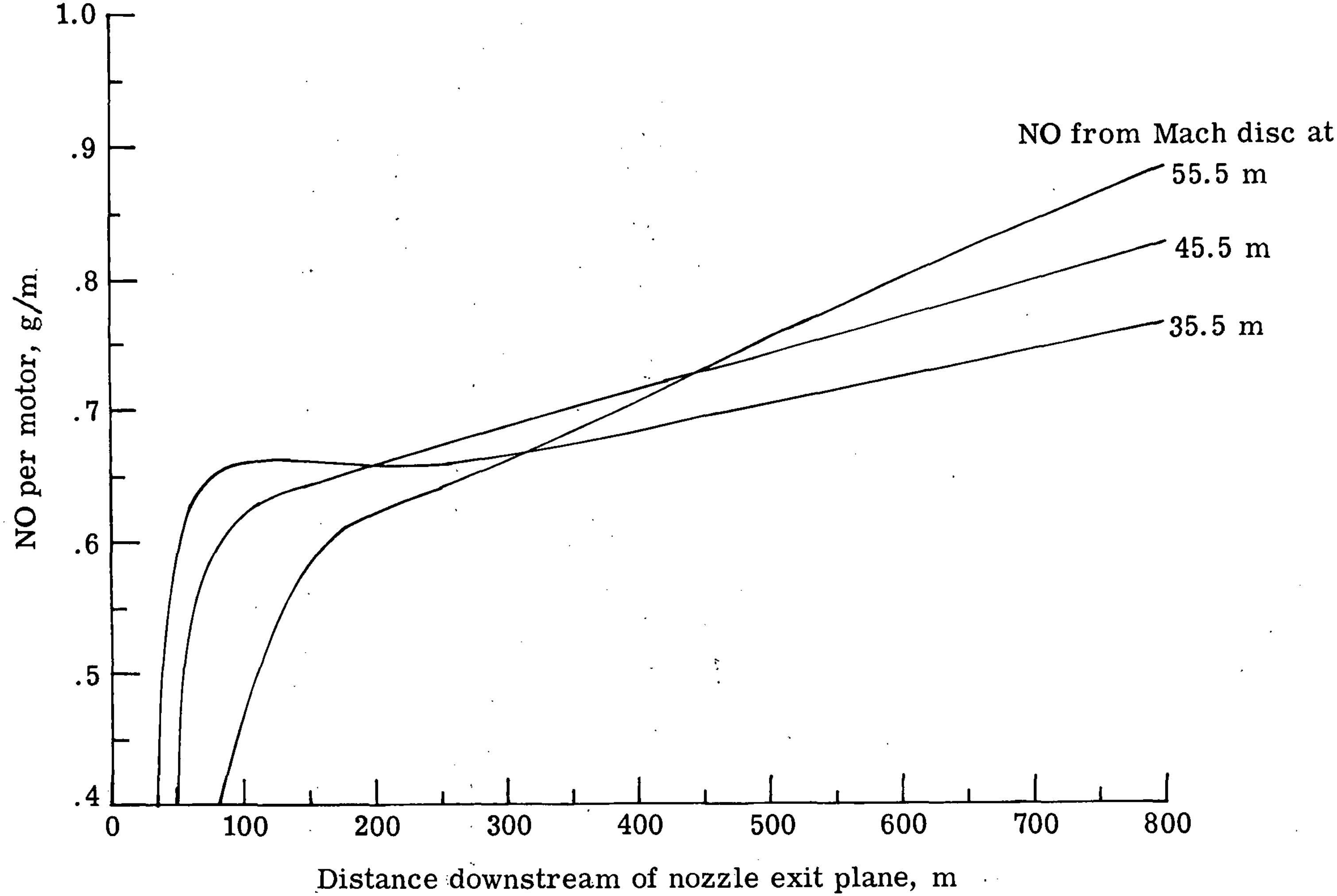

Figure 9.- NO for several Mach disc locations, 30-km altitude.

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16. Abstract

Calculations are made concerning the quantity of nitric oxide (NO) produced through afterburning in the plume of the solid propellant motors of the Space Shuttle. This study focuses on establishing the sensitivity of predictions of NO production to uncertainties in altitude, reaction rate coefficients, turbulent mixing rates, and Mach disc size and location. The results show that relatively large variations in parameters related to these phenomena had surprisingly little effect on predicted NO production.

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