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CATALYTIC REDUCTION OF STRATOSPHERIC OZONE BY NITROGEN OXIDES

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ABSTRACT

A 1970 study (reference 3) of the possible environmental impact of a fleet of supersonic transport (SST) planes estimated that the exhaust gases from the SST would increase the oxides of nitrogen (NO and NO_2) in the stratosphere between 7 and 70 parts per billion; the report simultaneously stated that such small quantities of NO_x "may be neglected". Even though these quantities are small, NO and NO_2 act as a catalyst for the destruction of ozone, and one molecule of NO_x in time can destroy a large number of ozone molecules in the stratosphere. This report presents quantitative calculations of two kinds: (1) the rate of destruction of ozone by NO_x relative to the ozone destruction rate by the couple, O, O_3, and by free radicals derived from water; (2) steady-state calculations of the profile of ozone in the stratosphere for a wide range of uniform and non-uniform distributions of NO_x. Although four cases with NO_x at 3, 7, 30, and 70 ppb are given especial attention, most calculations cover the complete range from zero to 100 ppb. Over the entire range of stratospheric variables, the oxides of nitrogen, NO and NO_2, have a powerful effect in reducing ozone, and a quantity (30 ppb) previously accepted as negligible would reduce the ozone column by about a factor of two, according to two different methods of computation. However, it is possible that NO and NO_2 will not reach the previously expected levels: NO and NO_2 may be converted

to HNO_3 (or other relatively inert forms) at a rate faster than indicated by current knowledge, or the SST engines may be (or may be made to be) cleaner with respect to NO_x than anticipated. The stratosphere has large scale transport of air masses, subsidence, and molecular and turbulent diffusion, which complicate the quantitative calculation of, but do not eliminate, the effect of NO and NO_2 on stratospheric ozone. This catalytic effect is a very large one, and it may not "be neglected".

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INTRODUCTION

What would happen to the ozone layer of the stratosphere if 500 supersonic transport (SST) planes emitted the expected amount of nitric oxide (NO) and nitrogen dioxide (NO_2) at 20 kilometers for a two year period? A report in Science[1] presented a new look at this question, and this report contains supplementary material to that report.

The chemistry and photochemistry of the oxides of nitrogen, ozone, and oxygen are, in general, very well understood. Over the past 50 years these reactions have been repeatedly studied and the constants have been refined and checked. Reliable calculations can be made over a wide range of temperature, concentration, wave length of radiation, and intensities of radiation. A qualification here is that the rate constants are usually known only to two significant figures, rarely more and sometimes less.

As reported in Science,[2] the Massachusetts Institute of Technology sponsored a "Study of Critical Environmental Problems" (SCEP)[3] in the summer of 1970, which looked for possible dangers to the global environment. According to Science,[2] "...the group raised a possibility apparently never considered heretofore in the SST debate--that the SST fleet, by discharging combustion products such as soot, hydrocarbons, nitrogen oxides, and sulfate particles would cause stratospheric smog...." The authors of the SCEP report are to be complimented in raising this question, but they were too hasty in reaching the following conclusion:

"Both carbon monoxide and nitrogen in its various forms can also play a role in stratospheric photochemistry, but despite greater uncertainties in the reaction rates of CO and NO_x than for water vapor, these contaminants would be much less significant than the added water vapor and may be neglected." Subsequent calculations by Harrison[4] showed that "with added water from the exhausts of projected fleets of stratospheric aircraft, the ozone column may diminish by 3.8 percent...." Park and London[5] have presented results from a computer study that indicate water to have an effect even less than that found by Harrison. The argument seems to be that water is worse than oxides of nitrogen (SCEP), water is not very serious (refs. 4 and 5), and therefore the SST poses no serious threat to stratospheric ozone. The original postulate that the oxides of nitrogen may be neglected is re-examined in this report and in the shorter report in Science.[1]

This report is aimed at a fairly broad scientific group. Part IA is a detailed, elementary discussion of chemical reactions and catalytic cycles. The only stratospheric data used are taken from a handbook, and the presentation is exclusively from a chemist's point of view. Part IA is designed as a classroom lecture to undergraduate students. Part IB, on the other hand, is a research article on the relative effect of ozone, oxides of nitrogen, and free radicals based on water with respect to destruction of "odd oxygen". Part IIA presents a simplified method of calculating the steady-state ozone profile as a function of added oxides of nitrogen. Equations are derived and quantities are tabulated so that anyone, including students as a homework problem, can carry out these calculations and verify the arguments presented. Part IIB presents a very detailed method of recalculating the distribution of ultraviolet radiation throughout the stratosphere for every change of any variable.

Such a detailed computation is required if large changes of ozone are to be considered. This method averages the solar intensity over 24 hours (or 12 hours for some purposes) instead of considering a single solar angle. With this method, steady state profiles of ozone are calculated for a large range of uniform and non-uniform distributions of oxides of nitrogen in the stratosphere. Part III compares some observed quantities with those calculated by the photochemical theory, on a world-wide basis. Some complexities of the real stratosphere are considered in Part III, and the report ends with a list of conclusions.

PART IA. STRICTLY CHEMICAL CONSIDERATIONS

In this section, I start with the SCEP distribution of NO_x in the stratosphere, and I reduce it to correspond more nearly to contemporary jet airplanes. I take from the literature a model of the stratosphere with respect to temperature, composition, ozone concentration, and oxygen atom concentration between 15 and 45 kilometers. No detailed use of this model is made except to identify the minimum and maximum values of these variables in the daytime stratosphere. Calculations are presented for the daytime photochemistry, covering the entire range of stratospheric variables. A special effort is made in Part I to present all arguments in a form that can be followed and checked by every scientist who has studied calculus and freshman chemistry. Up to a certain point, the content of this section should not be "controversial"; it should be self-evident to all careful readers.

Stratospheric Model

A convenient recent monograph gives the temperature, total gas concentration [M], ozone concentration $[O_3]$, and oxygen atom concentration [O] as a function of elevation.[6] These quantities are listed in Table I for the stratosphere between 15 and 45 kilometers. The pressure of the stratosphere decreases approximately a factor of two for every five kilometers. For input of nitric oxide into the stratosphere, the SCEP report used engine data as supplied by General Electric engineers, Table 2; and it used flight statistics from the Federal Aviation Administration: 500 SST aircraft by 1985 (334 with 4 engines and 116 with 2 engines), and each SST cruising in the stratosphere an average of seven hours per day. According to these estimates available during the summer of 1970, the SST would emit nitric oxide, NO, at 1000 parts per million (ppm) of exhaust. However, current commercial jet planes in

Table 1. Distribution of ozone and oxygen atoms in the natural stratosphere and distribution of additional oxides of nitrogen from SST according to SCEP and as revised here.

Elevation	km	15	20	25	30	35	40	45	ref.
Temperature	°K	220	217	222	227	235	250	260	6
$\log[M]/cm^{3*}$		18.60	18.27	17.93	17.58	17.26	16.92	16.60	6
$\log[O_3]/cm^3$		11	12	12.6	12.3	12	11.6	11	6
$\log[O]/cm$		6	8	9	10	10.2	10.4	10.6	6
Approximate Particle Residence Time		6 mo	2 yr	2 yr	2 yr	2 yr	2 yr	2 yr	8
$\log[NO_x]/cm^3$	I	11.43	11.10	10.76	10.41	10.09	9.75	9.43	2
	II	10.98	10.65	10.31	9.96	9.64	9.30	8.98	
	III	10.43	10.10	9.76	9.41	9.09	8.75	8.43	2
	IV	9.98	9.65	9.31	8.96	8.64	8.30	7.98	

Models for NO_x. $\alpha = [NO_x]/[M]$

III. SCEP expected world-wide stratospheric average, $\alpha = 6.8 \times 10^{-9}$.

IV. The above reduced by a factor of 2.8, $\alpha = 2.4 \times 10^{-9}$.

I. SCEP expected local maximum over an area the size of continental U. S. or the North Atlantic, $\alpha = 6.8 \times 10^{-8}$.

II. The above reduced by a factor of 2.8, $\alpha = 2.4 \times 10^{-8}$.

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[*] Concentrations represented by square brackets are in particles per cubic centimeter.

Table 2. A. Statistics of emission from one GE-4 engines in cruise mode (ref. 3) in pounds per hour.

Constitient	Input	Exhaust	Exhaust (as revised here)
Air	1,380,000		
Fuel	33,000		
N_2		1,039,000	
O_2		208,000	
Ar		19,300	
CO_2		103,500	
H_2O		41,400	
CO		1,400	
NO		1,400	490*
SO_2		33	
Soot		5	
Hydrocarbons		16.5	

B. Anticipated flight statistics 500 SST (334 with 4 engines, 166 with 2 engines) 7 hours stratosphere cruise time per day per SST.

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[*] See Appendix.

their cruise mode emit very much less NO in the exhaust.[7] Thus I reduce the SCEP estimates of nitric oxide by the factor 0.35. Table 1 lists four models for the mole fraction of nitric oxide in the stratosphere: I. SCEP estimate for the maximum amount to be expected over a high traffic locality such as the North Atlantic; II. The above reduced by the factor 0.35; III. SCEP estimate of the world-wide steady state distribution of nitrogen oxides in the stratosphere after several years of SST operation, considering the input by SST and losses due to mixing and diffusion both upward and downward; IV. Case III reduced by the factor 0.35.

The stratosphere (by virtue of photochemical heating) represents a profound temperature inversion with great stability against vertical mixing. The lowest part of the stratosphere is stirred by the underlying troposphere, and contaminant residence half life is about 6 months. At 20 km, the cruise height of the SST, and above 20 km, the residence half-time is variously quoted[8] as from one to five years. The SECP report used two years throughout, and this estimate is listed in Table 1.

From Table 1 we see that the entire range of daytime stratospheric variables (including nitric oxide from operation of the SST) can be embraced by the following range (where concentrations are rounded off to one significant figure.

Height 15 to 45 km
Temperature 220 to 260°K
$[O_3]$ 6×10^{10} to 6×10^{12}
$[NO_2]$ 10^8 to 10^{11}
$[M]$ 4×10^{16} to 4×10^{18} particles/cm^3 (1)
$[O]$ 10^6 to 10^{10} particles/cm^3
$[NO]$ 10^8 to 10^{11} particles/cm^3

If a negligible effect of NO_x on O_3 is found throughout this range of conditions, it could be argued that NO_x may indeed be neglected. If a large effect is found throughout this range of conditions, then a large effect is to be expected in the stratosphere regardless of diffusion rates, because diffusion would merely carry material from one region of large effect to another region of large effect. If the effect of NO_x on O_3 is large for some regions and negligible for others, then a detailed consideration of diffusion and photochemistry would be required to assess the magnitude of the problem in the stratosphere.

Oxygen-Ozone Photochemistry[9,10]

Mostly between 30 and 120 km, the oxygen molecule is dissociated by radiation below 242 nm

(a) $O_2 + h\nu \text{ (below 242 nm)} \rightarrow 2O$

Ozone is formed by addition of an oxygen atom to an oxygen molecule as catalyzed by any molecule M

(b) $O + O_2 + M \rightarrow O_3 + M$

Ozone is photolyzed in two regions of the spectrum. There is a strong absorption between 200 and 300 nm, and a very weak absorption of visible light between 450-650 nm. Ozone in the stratosphere shields the surface of the earth from the blinding and lethal radiation between 300 nm and the oxygen cut-off below 242 nm. In each absorption region the chemical reaction is

(c) $O_3 + h\nu \rightarrow O_2 + O$

Oxygen atoms are removed by recombination

(d) $O + O + M \rightarrow O_2 + M$

and both ozone and oxygen atoms are removed by the reaction

(e) $O + O_3 \rightarrow O_2 + O_2$

The heat released following the photolysis of O_2 sets up the steep temperature inversion above 80 km. The heat released following photolysis of O_3 sets up the steep temperature inversion 15 and 50 km, which stabilizes the stratosphere.

In the oxygen-ozone photochemical system there are two separate kinds of reactions. The molecule O_2 has an even number of atoms, but O and O_3 have an odd number of atoms. The two kinds of reactions are: (1) those that increase or decrease the number of odd molecules

Increase (a)

Decrease (d) and (e)

and (2) those in which the number of odd molecules remains constant

Constant: (b) and (c)

These two sets are distinct by symmetry, and they have different relaxation times. The set of reactions (b) and (c)

$$\begin{array}{l} O_3 + h\nu \rightarrow O_2 + O \\ \underline{O_2 + O + M \rightarrow O_3 + M} \\ \text{net: no chemical change} \end{array} \qquad (2)$$

establishes a certain degree of equivalence between O and O_3; the steady state for this set is attained within a few seconds in the stratosphere; and it involves no net destruction of ozone. The net destruction of ozone is governed by the relaxation of odd molecules, $k_d[M][O]^2$ plus $k_e[O][O_3]$; the steady state for this set is slowly attained with a half-time between a year or so at 20 km to a day or so in the upper stratosphere. The five reactions and the associated rate expressions are given in Table 3. The values of the rate constants are given in Table 4.

The differential equations for formation and removal of oxygen atoms and ozone are readily set up, and this analysis is based on an examination of terms in the differential equations. In the pure oxygen

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Table 3. Twelve elementary reactions involved in ozone photochemistry including the lower oxides of nitrogen.

	Reaction	Rate expression
(a)	$O_2 + h\nu$ (below 242 nm) $\rightarrow 2O$	$k_a I_a[O_2] = j_a[O_2]$
(b)	$O + O_2 + M \rightarrow O_3 + M$	$k_b[O][O_2][M]$
(c)	$O_3 + h\nu$(200-300, 450-650 nm)$\rightarrow O_2 + O$	$k_c I_c[O_3] = j_c[O_3]$
(d)	$O + O + M \rightarrow O_2 + M$	$k_d[M][O]^2$
(e)	$O + O_3 \rightarrow O_2 + O_2$	$k_e[O][O_3]$
(f)	$NO + O_3 \rightarrow NO_2 + O_2$	$k_f[NO][O_3]$
(g)	$O + NO_2 \rightarrow NO + O_2$	$k_g[O][NO_2]$
(h)	$NO_2 + h\nu$(300-400 nm) $\rightarrow NO + O$	$k_h I_h[NO_2] = j_h[NO_2]$
(i)	$NO + NO + O_2 \rightarrow NO_2 + NO_2$	$k_i[NO]^2[O_2]$
(j)	$O + NO + M \rightarrow NO_2 + M$	$k_j[M][NO][O]$
(k)	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$k_k[NO_2][O_3]$
(l)	$NO_3 + h\nu$(500-700 nm) $\rightarrow NO + O_2$	$j_l[NO_3]$

Table 4. Values of rate constants.

Rate Constant	k(T)	k(220°K)	k(240°K)	k(260°K)	Ref.
k_b	$2.04\times10^{-35}\exp(2100/RT)$ $(\text{cc/particle})^2\text{sec}^{-1}$ where M is O_2	2.48×10^{-33}	1.67×10^{-33}	1.19×10^{-33}	10
k_d	$3.80\times10^{-30}T^{-1}\exp(-340/RT)$ $(\text{cc/particle})^2\text{sec}^{-1}$ where M is O_2	8.0×10^{-33}	7.8×10^{-33}	7.6×10^{-33}	10
k_e	$1.33\times10^{-11}\exp(-4200/RT)$ cc/particle-sec	8.93×10^{-16}	1.99×10^{-15}	3.91×10^{-15}	10,11
k_f	$1.33\times10^{-12}\exp(-2500/RT)$ cc/particle-sec	4.36×10^{-15}	7.03×10^{-15}	1.05×10^{-14}	12
k_g	$1.67\times10^{-11}\exp(-600/RT)$ cc/particle-sec	4.12×10^{-12}	4.62×10^{-12}	5.10×10^{-12}	13
k_i	$3.33\times10^{-39}\exp(1046/RT)$				13
k_j	$2.9\times10^{-33}\exp(1870/RT)$				13
k_k	$9.8\times10^{-12}\exp(-7000/RT)$				10
j_1	$> 10^{-2}$				*
j_h	7×10^{-3}				14

* Estimate from absorption coefficient (compare reference 30).

system the rate of change of oxygen atom concentration at a particular region of space is

$$\frac{d[O]}{dt} = 2j_a[O_2] - k_b[M][O_2][O] + j_c[O_3] - 2\,k_d[M][O]^2 - k_e[O_3][O] \tag{3}$$

(See Table 3 for definitions of the rate constants.) The rate of change of ozone concentration is

$$\frac{d[O_3]}{dt} = k_b[M][O_2][O] - j_c[O_3] - k_e[O_3][O] \tag{4}$$

The rate of change of odd oxygen species is given by the sum of the rates for O and for O_3

$$\frac{d([O_3]+[O])}{dt} = 2j_a[O_2] - 2\{k_d[M][O]^2 + k_e[O_3][O]\} \tag{5}$$

From the rate constants in Table 4 and the stratospheric model of Table 1, one can see that $k_d[M][O]^2$ is very much less than $k_e[O_3][O]$ at all levels of the stratosphere (barely so at 45 km). Also ozone is in great excess over oxygen atoms at and below 40 km. Thus as an excellent approximation between 15 and 40 km, one may write

$$\frac{d([O_3]+[O])}{dt} = 2j_a[O_2] - 2\,k_e[O_3][O] \tag{6}$$

The rate of destruction of odd oxygen (essentially ozone in the stratosphere) is $2\,k_e[O_3][O]$.

In this paragraph, I derive the expression for the "half-time" of ozone. It is a formal definition, and close attention must be given to just what it means. Equation (6) is integrated subject to the (unrealistic) assumption of constant oxygen atom concentration

$$\int \frac{d(-2k_e[O][O_3])}{2j_a[O_2]-2k_e[O][O_3]} = -2k_e[O]\int dt \tag{7}$$

The integral is

$$\ln \frac{(j_a[O_2]-k_e[O][O_3])_o}{(j_a[O_2]-k_e[O][O_3])} = 2\ k_e[O]t \qquad (8)$$

where $[O_3]_o$ is the concentration of ozone at zero time. At the photochemical steady state odd molecules are created and destroyed at an equal rate, and then

$$j_a[O_2] = k_e[O][O_3]_s \qquad (9)$$

where $[O_3]_s$ is the steady-state concentration of ozone. In this way it is seen that

$$\Delta = j_a[O_2] - k_e[O][O_3] \qquad (10)$$

is a measure of the departure from the photochemical steady state, and Eq. (8) may be written

$$\ln \frac{\Delta_o}{\Delta} = 2\ k_e[O]t \qquad (11)$$

The time for an initial perturbation Δ_o to be reduced in one half, $\Delta = 1/2\ \Delta_o$, is called the "half-time", $\tau_{1/2}$. The half time in this system is thus

$$\tau_{1/2} = \ln 2/2\ k_e[O] \qquad (12)$$

It should be recognized that the oxygen atom concentration will not remain constant while ozone decreases by one half. Even so, use of the concept of half time as defined by Eq. (12) provides us with an easily grasped measure of reaction rate for an instantaneous value of oxygen atom concentration.

Nitric Oxide Catalyzed Destruction of Ozone

In a pure atmosphere the photochemistry of ozone is given by the five chemical reactions, (a) through (e) in Table 3, and upon addition of NO or NO_2 or both there are many additional reactions, three of which,[11-1 (f) - (h) are considered here. In a subsequent section the large number of further reactions of the oxides of nitrogen are considered. The analysis given in this section is similar to that given by Nicolet[15] in 1965, and in the discussion of catalytic cycles it follows an analysis[10] made in 1968. The eight reactions and the associated rate expressions are given in Table 3, and rate constants are given in Table 4. The eight reactions are classified below in terms of change of odd oxygen and change of odd nitrogen

Reaction	Change of odd oxygen	Change of odd nitrogen
a	+2	
b	0	
c	0	
d	-2	
e	-2	
f	-1	0
g	-1	0
h	+1	0

(13)

These reactions of nitric oxide and nitrogen dioxide participate in the increase and decrease of odd nitrogen.

Consider the pair of reactions

$$\begin{array}{ll} (f) & NO + O_3 \rightarrow NO_2 + O_2 \\ (g) & \underline{NO_2 + O \rightarrow NO + O_2} \\ \text{net:} & O_3 + O \rightarrow O_2 + O_2 \end{array} \qquad (14)$$

The cycle (f) and (g) has the same chemical effect as reaction (e), decreasing odd oxygen by two with no net change in either NO or NO_2. This couple is one of the simplest cases of chemical catalysis: NO and NO_2 change the rate of ozone destruction with no change in NO or NO_2 concentration. Not every nitrogen dioxide produced by reaction (f) is followed by reaction (g), but some goes by way of reaction h. The triplet of reactions

$$\begin{array}{ll} \text{(f)} & NO + O_3 \rightarrow NO_2 + O_2 \\ \text{(h)} & NO_2 + h\nu \rightarrow NO + O \\ \underline{\text{(b)}} & \underline{O + O_2 + M \rightarrow O_3 + M} \\ \text{net:} & \text{no chemical change} \end{array} \qquad (15)$$

is a "do nothing" cycle, and it acts to reduce the catalytic rate of Eq. 14. The catalytic rate is not that of reaction (f), but rather

$$\left\{ - \frac{d([O_3]+[O])}{dt} \right\}_{\text{catalytic}} = k_f[NO][O_3] \frac{k_g[O]}{k_g[O]+h} \qquad (16)$$

The intuitive discussion of catalysis given above can be made more definite by forming the differential equation for all 8 reactions in a manner parallel to the development of Eq. 5. The relation between nitric oxide and nitrogen dioxide is determined by the fast reactions

$$\begin{array}{ll} \text{(f)} & NO + O_3 \rightarrow NO_2 + O_2 \\ \text{(g)} & NO_2 + O \rightarrow NO + O_2 \\ \text{(h)} & NO_2 + h\nu \rightarrow NO + O \end{array}$$

The rate of change of nitrogen dioxide is

$$\frac{d[NO_2]}{dt} = k_f[NO][O_3] - k_g[O][NO_2] - j_h[NO_2] \qquad (17)$$

Since there is no net change in the catalysts NO or NO_2, the derivative $d[NO_2]/dt$ is zero, and the relation between NO and NO_2 is

$$\frac{[NO_2]}{[NO]} = \frac{k_f[O_3]}{k_g[O] + j_h} \qquad (18)$$

The partition of total oxides of nitrogen (NO_x) between NO and NO_2 is thus

$$[NO_2] = \frac{k_f[O_3]}{k_f[O_3] + k_g[O] + j_h} \; [NO_x] \qquad (19)$$

$$[NO_2] + [NO] = [NO_x] \qquad (20)$$

The steady state assumption for odd oxygen is

$$\begin{aligned} \frac{d([O_3]+[O])}{dt} = 2j_a[O_2] + j_h[NO_2] - k_d[M][O]^2 - k_e[O_3][O] \\ - k_f[NO][O_3] - k_g[NO_2][O] \approx 0 \end{aligned} \qquad (21)$$

Addition of Eq. 17 to Eq. 21, with the steady state assumption for NO_2, gives

$$\frac{d\ [O_3]+[O]}{dt} = 2\ j_a[O_2] - 2\{\ k_d[M][O]^2 + k_e[O_3][O]\ \} - 2\ k_g[O][NO_2] \qquad (22)$$

This differential equation is to be compared with Eq. 5. The positive term, 2 $j_a[O_2]$, which forms ozone, is the same in both the catalyzed Eq. 22 and in the uncatalyzed Eq. 5; the terms in Eq. 5 that represent destruction of odd oxygen also appear in Eq. 22; but in addition, a new destruction term, $-2\ k_g[O][NO_2]$, appears. If we make the same approximation that was made to obtain Eq. 6

$$k_e[O_3][O] >> k_d[M][O]^2 \qquad (23)$$

then Eq. 22 reduces to the form

$$\frac{d\,[O_3]+[O]}{dt} = 2\,j_a[O_2] - 2\,k_e[O_3][O]\left\{1 + \frac{k_g[NO_2]}{k_e[O_3]}\right\} \qquad (24)$$

It is convenient to give a special name and symbol to the expression in braces in Eq. 24

$$\begin{aligned}\rho &= \text{catalytic ratio}\\ &= \frac{\text{rate of ozone destruction with catalysts}}{\text{rate of ozone destruction without catalysts}} \qquad (25)\\ &= \frac{k_e[O_3][O] + k_g[O][NO_2]}{k_e[O_3][O]}\\ &= 1 + \frac{k_g[NO_2]}{k_e[O_3]}\end{aligned}$$

By use of Eq. 18, the catalytic ratio may be expressed in an alternative form

$$\rho = 1 + \frac{[NO](k_f k_g/k_e j_h)}{1 + k_g[O]/j_h} \qquad (26)$$

The expression for catalytic ratio, Eq. 26, is closely related to the intuitively derived catalytic rate, Eq. 16.

The catalytic ratio ρ may be expressed either in the set of variables [O] and [NO], Eq. 26 or in terms of the variables $[O_3]$ and $[NO_2]$. By virtue of the relations between $[O_3]$ and [O] and between $[NO_2]$ and [NO], the expressions are equivalent. However, it is somewhat simpler to regard [NO] and [O] as the independent variables and to examine the magnitude of ρ for the entire range of [NO] and [O] in the stratosphere. The oxygen atom concentration is determined by the rate of photolysis of O_2, O_3, and NO_2 and by the rate of combination of O with O_2, reaction (b). The catalytic ratio depends on these variables only through their effect on [O]. However, if $k_g[O]$ is small compared to the photolysis constant j_h

$$k_g[O] \ll j_h \qquad (27)$$

then the catalytic ratio assumes the particularly simple form

$$\rho = 1 + \frac{k_f k_g[NO]}{k_e j_h} \qquad (28)$$

In this case, the catalytic ratio is independent of [O], $[O_2]$, $[O_3]$, [M] and $[NO_2]$. From Table 4 it can be seen that at 220°K k_g is 4.12×10^{-12} cm^3/particle-sec, h is 7×10^{-3} sec^{-1}, and thus $k_g[O]$ is equal to h when the oxygen atom concentration is 1.7×10^9 per cm^3. The catalytic ratio has the simple form of Eq. 28 when oxygen atoms are much less than 10^9 molecules/cm^3. Then the catalytic ratio depends only on four rate constants and the nitric oxide concentration. This calculation will be illustrated here for 10^{10} molecules of nitric oxide per cc, the median value for case II in Table 1; and by use of the rate constants at 220°K in Table 4:

$$\begin{aligned}\rho &= 1 + \frac{(4.36\times 10^{-15})(4.12\times10^{-12})10^{10}}{(8.93\times10^{-16})(7\times10^{-3})}\\ &= 1 + 29 = 30\end{aligned} \qquad (29)$$

This simple calculation shows that under these conditions, nitric oxide destroys ozone 29 times faster than the pure oxygen background; and with $\sqrt{30}$ fold reduction of ozone. The half-time to destroy ozone under these conditions is

$$\tau_{1/2} = \ln 2/2\,k_e[O]\rho \qquad (30)$$

To carry out this calculation a value of oxygen atom concentration must be assigned; the value 10^7 satisfies the condition of Eq. 27 and it is a typical value in the stratosphere. The half time is then

$$\tau_{1/2} = 0.693/2(8.9\times10^{-16})(10^7)(30)$$

$$= 1.29\times10^{6} \text{ sec} = 350 \text{ hours}$$

These very direct calculations imply a fast (350 hour half time), almost total (up to $\sqrt{30}$ fold) destruction of ozone by nitric oxide catalysis for this special case of $[NO] = 10^{10}$ per cc and $[O] = 10^{7}$ per cc.

Calculations based on Eq. 26 were made for all conditions of the stratosphere as given by Eq. 1, and the results are presented in Table 5. Table 5A has 60 entries for the catalytic rate ratios based on three temperatures, a thousand-fold range of concentrations of nitric oxide, and a ten-thousand-fold range of concentrations of oxygen atoms. An effect greater than 10 percent is shown for 57 cases out of 60; an effect greater than a factor of two is shown in 42 out of 60 cases; an effect greater than a factor of 10 is shown in 27 out of 60 cases; and an effect greater than a factor of 100 is shown in 12 out of 60 cases. The half-times are given in Table 6, and in only 6 out of 60 cases is the half time for catalytic destruction of ozone greater than the two-year persistence half-time of contaminants in the stratosphere. In 43 out of 60 cases the half time is less than one month.

These calculations embrace the full range expected in the photochemically active stratosphere, and large effects of ozone destruction by nitric oxide are found under virtually all conditions. Any uncertainty created by unknown diffusion and mixing rates is negligible compared to the large catalytic effects at all levels.

As can be seen from Eq. 25, an alternative set of independent variables is $[NO_2]$ and $[O_3]$. In the normal stratosphere, ozone varies from about 6×10^{10} to 6×10^{12} molecules/cm^3, and nitrogen dioxide may be considered between 10^{8} and 10^{11} molecules/cm^3. For these ranges of variables, the catalytic rate ratio is calculated from Eq. 25, and the results are presented in Table 5B. Again we see such large chemical

Table 5. A. Ratio of catalytic rate to natural rate of ozone destruction as a function of temperature and oxygen atom and nitric oxide concentration.

		ρ, catalytic rate ratio (Eq. 26)				
	[O]	10^{6}	10^{7}	10^{8}	10^{9}	10^{10}
T°K	[NO]					
220	10^{11}	288	286	272	182	42.6
	10^{10}	29.7	29.5	28.1	19.1	5.16
	10^{9}	3.87	3.85	3.71	2.81	1.42
	10^{8}	1.29	1.29	1.27	1.18	1.04
240	10^{11}	234	232	220	141	31.7
	10^{10}	24.3	24.1	22.9	15.0	4.07
	10^{9}	3.33	3.31	3.19	2.40	1.31
	10^{8}	1.23	1.23	1.22	1.14	1.03
260	10^{11}	196	195	183	114	24.5
	10^{10}	20.5	20.4	19.2	12.3	3.35
	10^{9}	2.95	2.94	2.82	2.23	1.24
	10^{8}	1.20	1.19	1.18	1.11	1.02

Table 5. B. Ratio of catalytic rate to natural rate of ozone destruction as a function of temperature, nitrogen dioxide concentration, and ozone concentration.

		ρ, catalytic rate ratio (Eq.25)						
T°K	$[NO_2]$ \ $[O_3]$	6×10^{10}	10^{11}	3×10^{11}	6×10^{11}	10^{12}	3×10^{12}	6×10^{12}
220	10^{11}	7690	4615	1539	770	462	155	78
	10^{10}	770	462	155	78	47.1	16.4	8.7
	10^{9}	78	47.1	16.4	8.7	5.6	2.5	1.77
	10^{8}	8.7	5.6	2.5	1.77	1.46	1.15	1.08
240	10^{11}	2870	2323	775	388	233	78.4	39.7
	10^{10}	388	223	78.4	39.7	24.2	8.7	4.9
	10^{9}	39.7	24.2	8.7	4.9	3.3	1.77	1.39
	10^{8}	4.9	3.3	1.77	1.39	1.23	1.08	1.04
260	10^{11}	2170	1305	436	218	131	44.5	22.7
	10^{10}	218	131	44.5	22.7	14.0	5.4	3.2
	10^{9}	22.7	14.0	5.4	3.2	2.3	1.44	1.22
	10^{8}	3.2	2.3	1.44	1.22	1.13	1.04	1.02

Table 6. Half-times for catalyzed and uncatalyzed decomposition of ozone.

		$\tau_{1/2}$, seconds				
T°K	[NO] \ [O]	10^6	10^7	10^8	10^9	10^{10}
220	10^{11}	1.35×10^6	1.36×10^5	1.43×10^4	2.1×10^3	9.1×10^2
	10^{10}	1.31×10^7	1.32×10^6	1.38×10^5	2.0×10^4	7.5×10^2
	10^{9}	1.0×10^8	1.01×10^7	1.05×10^6	1.38×10^5	2.6×10^4
	10^{8}	3.0×10^8	3.0×10^7	3.1×10^6	3.3×10^5	3.7×10^4
	0	3.9×10^8	3.9×10^7	3.9×10^6	3.9×10^5	3.9×10^4
240	10^{11}	7.4×10^5	7.5×10^4	7.9×10^3	1.23×10^3	5.5×10^2
	10^{10}	7.2×10^6	7.2×10^5	7.6×10^4	1.15×10^4	4.3×10^3
	10^{9}	5.2×10^7	5.2×10^6	5.4×10^5	7.2×10^4	1.32×10^4
	10^{8}	1.41×10^8	1.41×10^7	1.42×10^6	1.52×10^5	1.68×10^4
260	10^{11}	4.5×10^5	4.5×10^4	4.8×10^3	7.8×10^2	3.6×10^2
	10^{10}	4.3×10^6	4.3×10^5	4.6×10^4	7.2×10^3	2.6×10^3
	10^{9}	3.0×10^7	3.0×10^6	3.1×10^5	4.0×10^4	7.1×10^3
	10^{8}	7.4×10^7	7.4×10^6	7.5×10^5	8.0×10^4	8.7×10^3
	0	8.8×10^7	8.8×10^6	8.8×10^5	8.8×10^4	8.8×10^3

1 hour = 3.6×10^3 sec

1 day = 8.6×10^4 sec

1 month = 2.6×10^6 sec

1 year = 3.2×10^7 sec

effects that they dwarf considerations of diffusion and mixing. Table 5B emphasizes that nitrogen dioxide (NO_2) is just as much a catalyst for ozone destruction as nitric oxide (NO), for the catalytic cycle, Eq. 14, involves each of them.

Equation 24 may be rewritten as

$$\frac{d([O_3]+[O])}{dt} = 2j_a[O_2] - 2k_e[O_3][O]\rho \qquad (31)$$

If the steady state oxygen-atom concentration is determined primarily by photolysis of O_2 and NO_2, then it will be essentially constant as ozone is depleted, and the reduction of ozone below its natural value is inversely proportional to the catalytic ratio ρ. If, however, the main source of oxygen atoms is the photolysis of ozone, then the oxygen-atom concentration is proportional to ozone, and the reduction of ozone will vary as the square root of ρ. From the values of the rate constants j_a and j_c, (see Part II of this report) it can be seen that the latter is more nearly the actual situation in the stratosphere. Thus the reduction of ozone by oxides of nitrogen is expected to be very nearly given by the factor $1/\sqrt{\rho}$.

In the stratosphere a reduction of ozone by a factor of 2 would lead to great changes in temperature, structure, and dynamics. For this reason it cannot be said that a four-fold increase in loss rate would equal precisely a two fold reduction in ozone, but it can be said that a major reduction in ozone would occur under any of the four models of Table 1.

An Ultra-Simple Model

A typical vertical column of ozone contains an amount equal to a thickness of 3 mm of gas at standard temperature and pressure, or 6.4×10^{-4} g/cm^2. Over the surface of the earth (5×10^{18} cm^2) the total mass of ozone is 3.2×10^{15} grams. One SST (Table 2) produces 8.9×10^5 grams of NO or 1.36×10^6 grams of NO_2 per hour. As can be seen from Eq. 26 the catalytic rate ratio is simply one plus $k_g[O][NO_2]/k_e[O][O_3]$, and in this expression the difficulty evaluated concentration of oxygen atoms always cancels out. The catalytic ratio is two (factor of $\sqrt{2}$ reduction in ozone) when (at 220°K)

$$\frac{[NO_2]}{[O_3]} = \frac{k_e}{k_g} = \frac{1}{4600} \qquad (32)$$

When NO_2 in the stratosphere builds up to 7×10^{11} grams, the ratio of its mass to the mass of ozone becomes equal to the concentration ratio of Eq. 32. If 500 (four engine) SST flew 7 hours per day, this mass of NO_2 would be emitted in about 5 months. The problem, of course, is more complicated than this, but this ultra-simple model shows that the effect of oxides of nitrogen on ozone could be very large.

Applications to SST Flight Patterns

In considering the increase in nitric oxide in the real stratosphere, two approaches must be made: (1) the initial distribution from fleets of planes and (2) the long term distribution throughout the stratosphere. A single SST will leave thin, spreading ribbon (thin because vertical mixing is so much less than horizontal mixing in the stratosphere) of highly concentrated NO. Overlapping ribbons from fleets of planes could be expected (Tables 5 and 6) quickly to reduce almost to zero the ozone at the cruising altitude of 20 km. Since much ozone now below 20 km arrived there by transport and subsidence, a film of NO_x at about 20 km would intercept further downward diffusion, and ozone in the lowest portion of the stratosphere would fade out upon mixing with the lower atmosphere. The time and manner of the diffusion of the NO_x film into the upper stratosphere is an exceedingly complicated problem, and presumably this would be very slow (years). There is, therefore, the possibility of a long continued worsening of the NO catalytic destruction of ozone even after SST flights were stopped, as the concentrated film around 20 km slowly worked its way upward.

A single four-engine SST would burn 132,000 pounds of fuel per hour[2] and emit 1960 pounds (350 ppm of exhaust gases[7]) of NO per hour of flight. Thus 1.8×10^{28} molecules of NO per hour would be left in the wake of the plane. I assume, for order of magnitude calculations, that the initial plume behind the plane would be 100 meters high and 200 meters wide. In the stratosphere, horizontal mixing is very much greater than vertical mixing, and the wake of the plane would be a steadily widening ribbon 100 meters high and x cm wide with a nitric oxide concentration of $6 \times 10^{15}/x$ (assuming the plane flies at 1800 miles per hour). In the initial wake 200 meters wide, the concentration of NO would be 3×10^{11} molecules per cm^3. The concentration would be 3×10^{10} at a width of 2 km, 3×10^{9} at 20 km, and 3×10^{8} at 200 km. As can be seen by Tables 1 and 6, a single pass by the SST could lay down a ribbon 100 meters high and 200 km wide with enough nitric oxide to catalyze the destruction of ozone at twice the background rate.

With multiple flights, these ribbons would overlap to produce an irregular film of nitric oxide covering large fractions of the earth. The surface of the earth is 5×10^{18} cm^2, and the volume of a global shell 100 meters thick is 5×10^{22} cm^3. The world wide average concentration of the initial film at the cruise height of 20 km would be 3.5×10^5 y, where y is the number of hours of SST flight. Each SST is expected to cruise in the stratosphere for 7 hours per day[2], and 500 SST would total 3500 hours per day. In ten days of flights the global average in a film 100 meters thick would be 1.2×10^{10} molecules per cm^3. This concentration of NO (Tables 1, 5 and 6) would destroy ozone at $\sqrt{30}$ times the normal rate and the half time for ozone destruction would be 40 hours.

Other Reactions of the Oxides of Nitrogen

There are several other mechanisms whereby oxides of nitrogen catalyze the formation and the decomposition of ozone (removal of odd oxygen) in a photochemical situation.[10]

(i) $2NO + O_2 \rightarrow 2NO_2$ (33)

(h) $2\{NO_2 + h\nu(260\text{-}400\ nm) \rightarrow NO + O\}$

net: $O_2 + h\nu(260\text{-}400\ nm) \rightarrow O + O$ (compare a)

(j) $O + NO + M \rightarrow NO_2 + M$ (34)

(g) $O + NO_2 \rightarrow O_2 + M$

net: $O + O + M \rightarrow O_2 + M$ (compare d)

(k) $NO_2 + O_3 \rightarrow NO_3 + O_2$ (35)

(l) $NO_3 + h\nu(600\text{-}700\ nm) \rightarrow NO + O_2$ (day)

(f) $NO + O_3 \rightarrow NO_2 + O_3$

net: $2O_3 \rightarrow 3O_2$

At night reaction k is followed by

(m) $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$

The di-nitrogen pentoxide is also a catalyst of ozone destruction

(n) $N_2O_5 + M \rightarrow NO_2 + NO_3$ (36)

(k) $2(NO_2 + O_3 \rightarrow NO_3 + O_2)$

(o) $2NO_3 \rightarrow 2NO_2 + O_2$

(m) $M + NO_2 + NO_3 \rightarrow N_2O_5 + M$

---

net: $2\ O_3 \rightarrow 3O_2$

(q) $N_2O_5 + O \rightarrow 2NO_2 + O_2$ (?) (37)

(k) $NO_2 + O_3 \rightarrow NO_3 + O_2$

(m) $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$

---

net: $O_3 + O \rightarrow O_2 + O_2$ (compare e)

Under daylight conditions at the earth's surface, N_2O_5 is photolyzed[16]

(p) $N_2O_5 + h\nu(300\text{-}380) \rightarrow 2NO_2 + O$

and the absorption cross section increases strongly below 300 nm. There are a number of other reactions of the oxides of nitrogen, which are relatively unimportant under stratospheric conditions

$NO_3 + NO \rightarrow NO_2 + NO_2$ (38)

$NO_2 + NO_2 \rightleftharpoons N_2O_4$

$NO + NO_2 \rightleftharpoons N_2O_3$

$NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$

In the mesosphere and ionosphere, there is a well-known set of important reactions involving nitric oxide[15]

(w) $N_2 + h\nu(\text{below 120 nm}) \rightarrow N + N$ (39)

(x) $N + O_2 \rightarrow NO + O$

(y) $N + NO \rightarrow N_2 + O$

(z) $N + O + M \rightarrow NO + M$

Nitric oxide is formed in both, x and z, and destroyed, y, by nitrogen atoms. Above 80 km photo-ionization reactions occur, and ion-molecule reactions are important.

The oxides of nitrogen are a minor natural ingredient of the upper atmosphere, and a great deal of attention has been given to the role of NO in the ionosphere. Nitric oxide has been observed in the mesosphere. By means of a sounding rocket, Pearce[17] found a constant mole fraction of NO of 7.9×10^{-7} above 74 km decreasing to about 3×10^{-7} at 60 km; Meira[18] observed a constant mole fraction of NO of 5×10^{-8} between 70 and 80 km (his lowest range of measurements) and an increasing mole fraction above 80 km. An infrared spectrum taken from a balloon flight detected nitric acid HNO_3, (and perhaps NO_2) in the stratosphere between 22 and 30 km.[19] The role of oxides of nitrogen in the upper atmosphere has been repeatedly considered by Nicolet,[15] and Crutzen[20] has called attention to the possible role of oxides of nitrogen in limiting stratospheric ozone.

PART IB. THE ROLE OF WATER VAPOR IN OZONE PHOTOCHEMISTRY

Above 310 nm the photolysis of ozone produces ground-state triplet oxygen atoms

(c') $O_3 + h\nu(\text{above 310 nm}) \rightarrow O_2 + O(^3P)$

Below 310 nm the photolysis of ozone can form singlet oxygen atoms

(c") $O_3 + h\nu(\text{below 310 nm}) \rightarrow O_2 + O(^1D)$

Although $O(^3P)$ does not react with water, $O(^1D)$ rapidly reacts with water to produce two hydroxyl radicals

(1) $O(^1D) + H_2O \rightarrow 2HO$

However, both N_2 and O_2 very rapidly deactivate singlet oxygen

(2) $O(^1D) + M \rightarrow O(^3P) + M$

The photolysis of moist ozone at room temperature leads to quantum yields of more than 100. The chain reaction

$$\begin{array}{ll} (3) & HO + O_3 \rightarrow HOO + O_2 \\ (4) & HOO + O_3 \rightarrow HO + 2O_2 \\ \hline & \text{net: } 2O_3 \rightarrow 3O_2 \end{array} \qquad (40)$$

is sometimes postulated to explain this high quantum yield, but there is no direct evidence for reaction (4) and some evidence that it does not occur.[21,22] More important catalytic cycles that reduce odd oxygen include:[10]

$$\begin{array}{ll} (3) & HO + O_3 \rightarrow HOO + O_2 \\ (5) & O + HOO \rightarrow HO + O_2 \\ \hline & \text{net: } O + O_3 \rightarrow O_2 + O_2 \end{array} \qquad (41)$$

$$\begin{array}{ll} (6) & O + HO \rightarrow O_2 + H \\ (7) & H + O_3 \rightarrow O_2 + HO \\ \hline & \text{net: } O + O_3 \rightarrow O_2 + O_2 \end{array} \qquad (42)$$

$$\begin{array}{ll} (6) & O + HO \rightarrow O_2 + H \\ (8) & H + O_2 + M \rightarrow HO + O_2 \\ (5) & O + HOO \rightarrow HO + O_2 \\ \hline & \text{net: } O + O + M \rightarrow O_2 + M \end{array} \qquad (43)$$

The free radicals derived from water may be written in general as HO_x, which is the sum of HO and HOO. These radicals are generated in the stratosphere by singlet oxygen, reaction 1, and also by photolysis of water.

$H_2O + h\nu(\text{below 200 nm}) \rightarrow H + HO$

However, this process is of importance only in the uppermost stratosphere and above.[23] The reactions (3, 5, 6, 7, and 8) giving the catalytic cycles for destruction of odd oxygen do not change the number of free radicals, but they are primarily responsible for setting the relative concentrations of H, HO, and HOO. The reactions terminating these free radicals are primarily the fast disproportionation reactions:

(9) $HO + HO \rightarrow H_2O + O$

(10) $HO + HOO \rightarrow H_2O + O_2$

(11) $HOO + HOO \rightarrow H_2O_2 + O_2$

The rate constants for these reactions are given in Table 7 with references.[25-28]

For the set of reactions (1, 3, 5, 6, 7, 8, 9, 10, and 11) the differential equation may be written for [H], [HO], and [HOO]. The steady-state assumption, $d[H]/dt \approx 0$, may be made for hydrogen atoms. The differential equation for HO_x has the simple form:

$$\frac{d([HO] + [HOO])}{dt} = 2\,k_1[O(^1D)][H_2O] - 2\,k_9[HO]^2 - 2\,k_{10}[HO][HOO] - 2\,k_{11}[HOO]^2 \qquad (44)$$

The rate constant k_1 is very large, though not known precisely. As a good approximation it may be taken to be equal to k_2. In this case the rate of formation of hydroxyl radicals is (see Figs. 1 and 2)

$$d[HO]/dt = 2j''_c[O_3]\ \alpha_{H_2O} \tag{45}$$

where α_{H_2O} is the mole fraction of water. Nicolet[23] used an ingenious method to simplify Eq. (44). The three rate constants, k_9, k_{10}, and k_{11}, are all very large. Nicolet assumed that

$$k_9 = k_{11} = k_{10}/2. \tag{46}$$

At 300°K (Table 7) one sees that these constants are respectively: 5.4×10^{-12}, 3.6×10^{-12}, 10×10^{-12}. Thus for the rough comparisons at hand, Nicolet's approximation is quite satisfactory. With these assumptions the differential equation for HO_x becomes

$$\frac{d([HO] + [HOO])}{dt} = 2j''_c[O_3]\alpha_{H_2O} - 2\ k_9([HO] + [HOO])^2$$

which may be written

$$\frac{d[HO_x]}{dt} = 2\ j''_c\ [O_3]\alpha_{H_2O} - 2\ k_9[HO_x]^2 \tag{47}$$

The steady-state concentration of HO_x is then

$$[HO_x] = (j''_c[O_3]\alpha_{H_2O}/k_9)^{1/2} \tag{48}$$

Nicolet evaluated this steady-state concentration of HO_x for an overhead sun. I evaluated $[HO_x]$ as averaged over a 12 hour day at 45° latitude and at the solar equinox (by the method presented in Part II). The model atmosphere, thermal rate constants, photolysis rate constants c'', the rate of formation of hydroxyl radicals, and the steady-state concentration of HO_x in a stratosphere with $\alpha_{H_2O} = 5 \times 10^{-6}$ (and no oxides of nitrogen) are given in Table 8. The concentrations of HO_x

Table 7. Rate constants for reactions involving water.

	Ref.
$10^{-16} < k_3 < 5\times10^{-13}$ at 300°K	10,24
$k_4 \approx 0$	21,22
$k_5 \geq 1\times10^{-11}$	24
$k_6 = 3.3\times10^{-11}$ at all T	25
$k_7 = 1.5\times10^{-12}T^{\frac{1}{2}}$	26
$k_8 = 4.4\times10^{-33}\exp(1000/RT)$	27
$k_9 = 9.5\times10^{-12}\exp(-780/RT)$	28
$= 5.4\times10^{-12}$ at 300°K	
$k_{10} = 10\times10^{-12}$ at 300°K	24
$k_{11} = 3.6\times10^{-12}$ at 300°K	22

Table 8A. Model stratosphere for water reactions and the rate of formation of hydroxyl radicals (mole fraction of water is 5×10^{-6}).

Elevation km		15	20	25	30	35	40	45	α
T °K		220	217	222	227	237	250	260	
$[M]\times10^{-17}$		39.7	18.5	8.35	3.83	1.78	0.831	0.423	
$k_5\times10^{11}$		2	2	2	2	2	2	2	
$k_6\times10^{11}$		3.3	3.3	3.3	3.3	3.3	3.3	3.3	
$k_9\times10^{12}$		4.4	4.3	4.4	4.5	4.6	5.8	4.9	
$k_{10}\times10^{12}$	*	4.4	4.3	4.4	4.5	4.6	4.8	4.9	
$k_{11}\times10^{12}$	*	8.8	8.6	8.7	9.0	9.2	9.6	9.8	
j_c'' $\sec^{-1}\times10^4$	†	(0.02)	0.026	0.090	0.264	0.813	2.85	13.9	0
		0.047	0.055	0.108	0.280	0.837	2.91	14.0	10^{-9}
		0.140	0.147	0.197	0.387	1.05	3.52	15.0	10^{-8}
		0.427	0.457	0.597	1.11	2.64	8.27	23	10^{-7}
$[O_3]\times10^{-12}$	†	0.63	3.62	5.90	6.69	4.60	1.81	0.47	0
		0.077	1.38	4.71	6.32	4.47	1.76	0.46	10^{-9}
		0.061	0.79	2.73	4.62	3.58	1.42	0.40	10^{-8}
		0.086	0.52	1.60	2.33	1.39	0.46	0.16	10^{-7}
$\frac{d[HO]}{dt}$ $\frac{\text{molecules}}{\text{cc-sec}}$ Eq. 45	*	(10)	94	530	1770	3740	5160	6550	0
		3.6	76	508	1770	3740	5110	6450	10^{-9}
		8.6	116	537	1790	3760	5000	5950	10^{-8}
		37	238	955	2590	3670	3800	3770	10^{-7}
$\frac{d[HO]}{[M]dt}$ $\frac{\text{mole fraction}}{\text{year}}$ $\times10^7$	*	(10^{-3})	0.016	0.203	1.48	6.72	19.9	49.5	0
		0.003	0.041	0.366	2.16	6.59	14.6	28.5	10^{-7}

* k_{10} and k_{11} related to k_9 by Nicolet's approximation.

† 24 hour average, 45° latitude, solar equinox, as calculated in Part II.

Table 8B. Partition of HO_x between HOO and HO, for assumed values of k_3.

Elevation	km	15	20	25	30	35	40	45
$[HO_x]$	*	2.1×10^6	6.6×10^6	1.6×10^7	2.8×10^7	4.0×10^7	4.6×10^7	5.2×10^7
[O]	†	1.4×10^4	3.5×10^5	3.2×10^6	2.2×10^7	1.0×10^8	4.2×10^8	1.7×10^9
$[O_3]\times10^{-12}$	†	0.63	3.62	5.90	6.69	4.60	1.81	0.47
$k_9[HO_x]$		9.2×10^{-6}	2.8×10^{-5}	6.9×10^{-5}	1.3×10^{-4}	1.9×10^{-4}	2.2×10^{-4}	2.5×10^{-4}
$k_5[O]$		2.8×10^{-7}	7.0×10^{-6}	6.5×10^{-5}	4.3×10^{-4}	2.1×10^{-3}	8.4×10^{-3}	3.3×10^{-2}
$k_5[O]+k_9[HO_x]$		9.5×10^{-6}	3.5×10^{-5}	1.3×10^{-4}	5.6×10^{-4}	2.3×10^{-3}	8.6×10^{-3}	3.3×10^{-2}
$k_3[O_3]$	$k_3=10^{-14}$	6.3×10^{-3}	3.6×10^{-2}	5.9×10^{-2}	6.7×10^{-2}	4.6×10^{-2}	1.8×10^{-2}	4.7×10^{-3}
	10^{-15}	6.3×10^{-4}	3.6×10^{-3}	5.9×10^{-3}	6.7×10^{-3}	4.6×10^{-3}	1.8×10^{-3}	4.7×10^{-4}
	10^{-16}	6.3×10^{-5}	3.6×10^{-4}	5.9×10^{-4}	6.7×10^{-4}	4.6×10^{-4}	1.8×10^{-4}	4.7×10^{-5}
[HO]	$k_3=10^{-14}$	3.2×10^3	6.4×10^3	3.5×10^4	2.3×10^5	1.9×10^6	1.5×10^7	4.5×10^7
	10^{-15}	3.2×10^4	6.4×10^4	3.5×10^5	2.1×10^6	1.3×10^7	3.8×10^7	5.2×10^7
	10^{-16}	2.7×10^5	5.8×10^5	2.9×10^6	1.3×10^7	3.3×10^7	4.6×10^7	5.2×10^7
[HOO]	$k_3=10^{-14}$	2.1×10^6	6.6×10^6	1.6×10^7	2.8×10^7	3.8×10^7	3.1×10^7	7.0×10^6
	10^{-15}	2.1×10^6	6.6×10^6	1.6×10^7	2.6×10^7	2.7×10^7	8.0×10^6	7.3×10^5
	10^{-16}	1.8×10^6	6.0×10^6	1.3×10^7	1.5×10^7	7.0×10^6	9.5×10^5	7.4×10^4

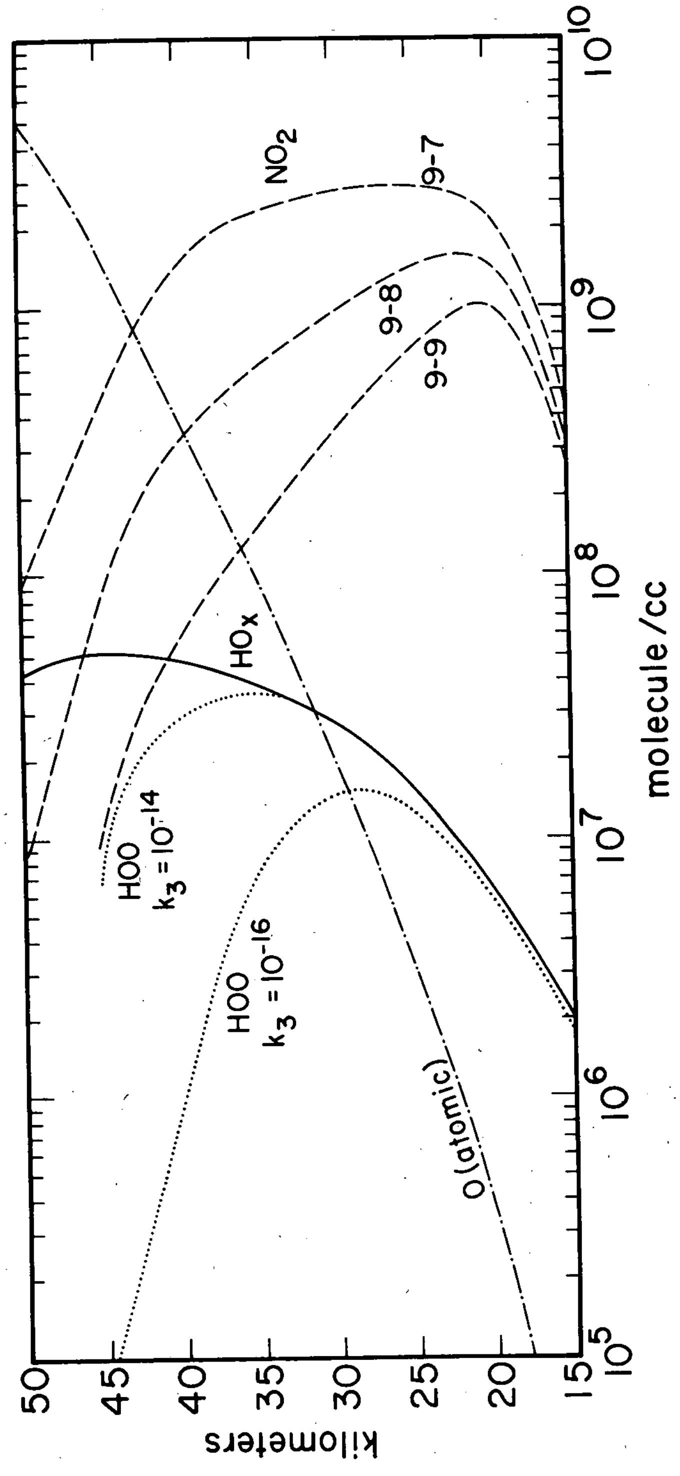
* Based on 12 hour daytime average, 45° latitude, solar equinox.

† Calculated in Part II of this report.

Fig. 1. Concentrations of oxygen atoms, NO_2, HO_x, and HOO subject to various assumed values of the rate constant k_3 as a function of elevation in the stratosphere for the standard temperature profile (Table 1), and standard conditions of 45° latitude at the solar equinox.

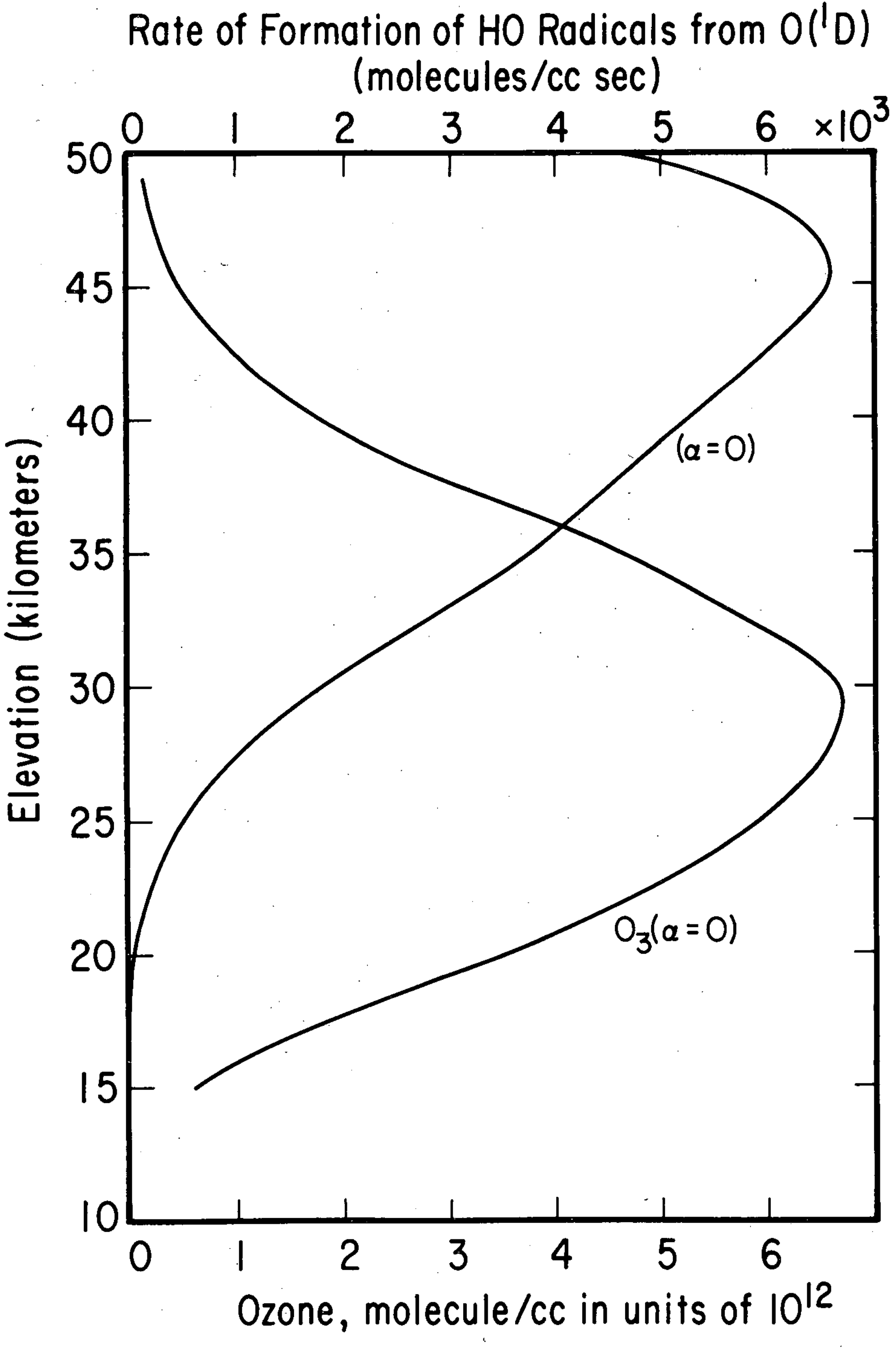
Fig. 2. Calculated ozone profile (see Part IIB) and calculated rate of hydroxyl radicals for O('D), as a function of elevation, no oxides of nitrogen (Eq. 45).

Fig. 3. Lower-limit half times to convert NO_2 to HNO_3 by way of N_2O_5 for various mole fractions of NO_x.

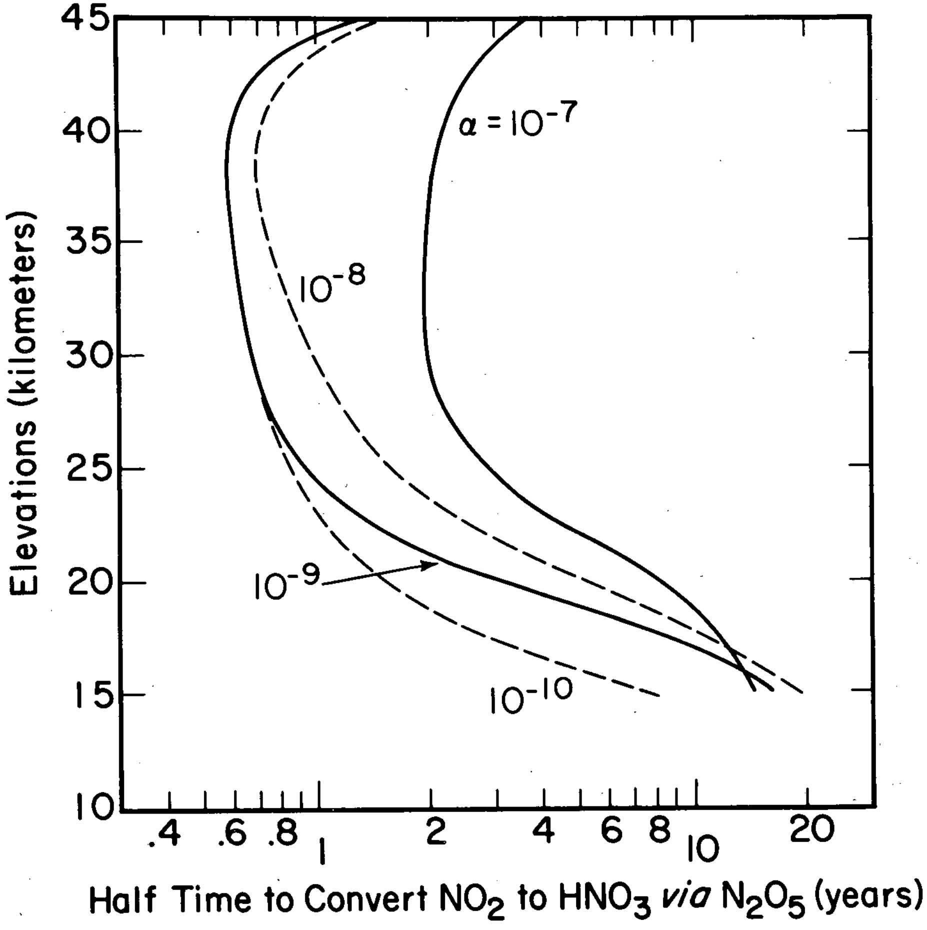


XBL 716-6839

Fig. 1



XBL 716-6841



XBL 716-6840

Fig. 3

are in agreement with Nicolet if allowance is made for the difference between an overhead sun and a 12 hour average; also I used a somewhat different value of k_9 (in another report,[1] I used Nicolet's value of k_9).

The usual way to find the ratio of HOO to HO is to write the steady-state expression for HOO. The rate of change of the hydroperoxyl free radical is

$$\frac{d[HOO]}{dt} = k_3[HO][O_3] + k_8[H][O_2][M]$$

$$-k_5[O][HOO] - k_{10}[HO][HOO] - 2\,k_{11}[HOO]^2 \quad ,$$

In the stratosphere the rate of reaction 8 is usually greater than reaction 7, and the steady state assumption for hydrogen atoms replaces $k_8[H][O_2][M]$ above by $k_6[O][HO]$. The steady-state assumption for HOO then gives

$$[HO](k_3[O_3] + k_6[O]) = [HOO](k_5[O] + k_{10}[HO] + 2k_{11}[HOO] \qquad (49)$$

The unfortunate situation here is that the rate constant k_3 is not known except between wide limits. Kaufman[24] found it to be less than 5 × 10^{-13} and I[10] estimated it to be greater than 10^{-16} cc/molecule sec.

$$10^{-16} < k_3 < 5 \times 10^{-13} \text{ at } 300°K \qquad (50)$$

For the problem in the next section (the rate of the reaction $HO + NO_2 + M \rightarrow HNO_3 + M$) it is necessary to know the concentration of hydroxyl radicals between 20 and 30 km, which could be obtained from Eqs. (49) and (47) if $k_6[O]$ is large compared to $k_3[O_3]$. The relative importance of reactions 3 and 6 can be found by considering the ratio

$$\frac{\text{Rate 3}}{\text{Rate 6}} = \frac{k_3[O_3]}{k_6[O]} \qquad (51)$$

The value of k_6 is 3.3 × 10^{-11}, a value of [O] is about 3 × 10^6 at 25 km, and a typical value of ozone is about 5 ×10^{12} at 25 km. Thus

the numerical value of the ratio in Eq. (51) is 5 k_3 × 10^{16}, and within the limits of Eq. (50) it is between 5 and 5000. It appears that reaction 3 is faster than reaction 6, and thus it is impossible to get separate values of HO and HOO until a definite value is found for k_3. (A similar analysis shows that reaction 3 is much faster than reaction 9, between 20 and 30 km).

With the result indicated above, that $k_3[O_3]$ is much larger than $k_6[O]$, some further simplification of Eq. (49) is possible. Nicolet[23] assumed $k_9 = k_{11} = k_{10/2}$ [Eq. (46)]. Using k_9, to be consistent with Eqs. (46)-(48), we can write Eq. (49) as

$$[HO]\,k_3[O_3] \approx [HOO]\,(k_5[O] + k_9[HO_x]) \qquad (52)$$

The ratio of HOO to HO is then

$$\frac{[HOO]}{[HO]} \approx \frac{k_3[O_3]}{k_5[O] + k_9[HO_x]} \qquad (53)$$

The ratio of hydroperoxyl radical to total radicals of hydrogen is

$$\frac{[HOO]}{[HO_x]} = \frac{k_3[O_3]}{k_3[O_3] + k_5[O] + k_9[HO_x]} \qquad (54)$$

In Table 8B the relative magnitude of the terms in the denominator of Eq. (54) are compared; these terms determine the partitioning of HO_x between HOO and HO. In the absence of a definite value for k_3, no calculations can be carried through. However, if we assume various values of k_3 within the range of Eq. (50), we can explore the range of possible effects. The concentrations of ozone and oxygen atoms in an NO_x-free atmosphere at 45° latitude and solar equinox (as calculated in Part II) are listed in Table 8B. The terms $k_5[O]$ and $k_9[HO_x]$ are evaluated and given in Table 8B, and the term $k_3[O_3]$ is evaluated for each assumed value of k_3: 10^{-14}, 10^{-15}, and 10^{-16}. For each assumed value of k_3, the concentration of HO and of HOO are calculated and listed in Table 8B. Below 25 km HOO is by far the predominant species. Low values of k_3 and high elevation favor HO relative to HOO. For this case (45° latitude, solar equinox, mole fraction of water is 5×10^{-6}) the concentrations of oxygen atoms, HO_x, and HOO subject to different assumed values of k_3 are plotted in Fig. 1.

The Three Way System: O_x, NO_x, HO_x

The first thing considered here is the relative effect of $O_x(O, O_2, O_3)$, NO_x(NO and NO_2), and HO_x(HO and HOO) on the rate of destruction of odd oxygen in a photochemical, stratospheric situation. The reactions considered are: a, b, c, e; f, g, h; 3, 5, 6, and 8. The rate equation for odd oxygen is then:

$$\frac{d([O] + [O_3])}{dt} = 2j_a[O_3] - 2\,k_e[O][O_3] \qquad (55)$$

$$-2k_g[O][NO_2] - 2\,k_5[O][HOO]$$

Equation (55) is particularly valuable in assessing the relative importance of the pure oxygen species, the oxides of nitrogen, and the free radicals derived from water in destroying odd oxygen and thereby setting the steady-state concentration of ozone. The convenient aspect of Eq. (55) is that the difficulty determined, highly variable concentration os oxygen atoms occurs as a common factor in the three destruction terms. In assessing the relative effect of any pair, the concentration of oxygen atoms cancels out. The relative effect (on ozone) of the oxides of nitrogen and water is thus

$$\frac{\text{ozone destruction by } NO_x}{\text{ozone destruction by } HO_x} = \frac{k_g[NO_2]}{k_5[HOO]} \qquad (56)$$

The relation of NO_2 to NO_x is given by Eq. (19), and the relation of HOO to HO_x is given by Eq. (54). Ozone tends to convert NO to NO_2, HO to HOO; oxygen atoms and radiation tend to convert NO_2 to NO, HOO to HO. For gross comparisons (no fine points should be based on this argument) the ratio NO_2/HOO is taken to be about the same as the ratio NO_x/HO_x

$$\frac{[NO_2]}{[NO_x]} \approx \frac{[HOO]}{[HO_x]} \qquad (57)$$

With this approximation, Eq. (56) becomes

$$\frac{\text{ozone destruction by } NO_x}{\text{ozone destruction by } HO_x} \approx \frac{k_g\,[NO_x]}{k_5\,[HO_x]} \qquad (58)$$

The concentration of NO_x and three cases of NO_x (two from Table 1 and one from Part II) are given in Table 9. The ratio $k_g[NO_x]/k_5[HO_x]$ is evaluated at each elevation from 15 to 45 km in Table 9. (The value of k_5 used here is slightly different from that used by Nicolet[23] and in another study I made of this comparison[1]). At 20 km, the ratio is 1400 for Case II and 140 for Case IV of projected SST performance. On this basis alone it can be seen that oxides of nitrogen are a much more serious threat to stratospheric ozone than is water.

For various assumed values of the constant k_3 within its estimated range, Eq. (50), the actual concentration of HOO was calculated and entered in Table 8B. The concentrations of HO_x and HOO for $k_3 = 10^{-14}$ and $k_3 = 10^{-16}$ cc/molecule-sec are plotted in Fig. 1 as a function of elevation. Photolysis of N_2 in the mesosphere and ionosphere produces nitric oxide, Eq. (39), which is incident at the top of the stratosphere presumably with a mole fraction between 10^{-8} and 10^{-7}. In the stratosphere (next section) it is slowly converted to nitric acid. Three

Table 9. Interactions between O_3, NO_x, and HO_x.

Elevation	km	15	20	25	30	35	40	45
log $[HO_x]$	*	6.32	6.82	7.19	7.45	7.61	7.67	7.71
log $[NO_x]$	case II	10.98	10.65	10.31	9.96	9.64	9.30	8.98
	case IV	9.98	9.65	9.31	8.96	8.64	8.30	7.98
	case V	8.60	8.27	9.43	10.08	9.88	9.67	9.48
log k_g		-11.38	-11.38	-11.37	-11.36	-11.34	-11.30	-11.30
$\frac{k_g[NO_x]}{k_5[HO_x]}$	case II	9500	1400	280	71	25	10.7	4.7
	case IV	950	140	28	7.1	2.5	1.1	0.47
	case V	40	5.9	37	93	43	25	15
log $k_s[M]$	†	-12.80	-13.12	-13.46	-13.82	-14.14	-14.48	-14.80
Minimum $\tau_{\frac{1}{2}}$ years Eq. 61	$k_3=10^{-14}$	84	90	36	12	3.2	0.84	0.60
	10^{-15}	8.4	9.0	3.6	1.3	0.46	0.34	0.50
	10^{-16}	1.0	1.0	0.44	0.22	0.18	0.28	0.50

* Based on 12 hour daytime average. Eq. 48.

† $k_s = 4\times10^{-32}$ based on long extrapolation from high temperature.

profiles of NO_2 in the stratosphere are given in Fig. 1 where the mole fraction, $\alpha = [NO_x]/[M]$, varies. The profile 9-7 has $\alpha = 10^{-9}$ at 15 km and 10^{-7} at 50 km, and the mole fractions are interpolated logarithmically between. The profile 9-8 similarly varies between 10^{-9} and 10^{-8} over the stratosphere. The profile 9-9 has a uniform NO_x mole fraction of 10^{-9} throughout the stratosphere. For each of these profiles, the concentration of NO_2 was calculated (by the procedures of Part II), and it is plotted in Fig. 1. With these curves of NO_2 concentrations and HOO concentrations (subject to assumed values of k_3) the exact comparison [Eq. (56)] of the effect of NO_x and of HO_x on the destruction of ozone can be made. The ratio k_g/k_5 is 0.2; for the (perhaps realistic) curves 9-7 or 9-8, the concentration of NO_2 is greater than 5[HOO] at all elevations. Again we see that NO_x is much more important than water in the problem of SST exhaust and ozone.

Conversion of Nitrogen Dioxide to Nitric Acid Vapor in the Stratosphere

There are two mechanisms for converting the oxides of nitrogen to nitric acid vapor in the stratosphere; one is a thermal process effective only at night and the other is a photochemical process.

Thermal process

During the day, reaction k produces the radical[29] NO_3 which is very rapidly photolyzed[30] by process l. At night, however, the radical NO_3 is capable of entering into a series of reactions.[31]

$$NO_3 + NO \rightarrow 2NO_2$$

$$NO_3 + NO_2 \rightarrow NO_2 + O_2 + NO$$

$$(m)\quad NO_3 + NO_2 + M \rightarrow N_2O_5 + M$$

$$NO_3 + NO_3 \rightarrow 2NO_2 + O_2$$

Although the first reaction above has a very large rate constant, photolysis of NO_3 (reaction l) during the day and conversion of NO to

NO_2 by O_3 (reaction f) are much faster. The second and fourth reactions have activation energies respectively 4.4 and 7.7 kcal, and they are slow compared to reaction m in the stratosphere. Thus at night reaction k is mostly followed by reaction m, and the overall reaction is the formation of N_2O_5 from NO_2 and ozone.[29]

$$\begin{array}{ll} (k) & NO_2 + O_3 \rightarrow NO_3 + O_2 \\ (m) & NO_3 + NO_2 + M \rightarrow N_2O_5 + M \text{ (night)} \\ \hline \text{net:} & 2NO_2 + O_3 \rightarrow N_2O_5 + O_2 \text{ (night)} \end{array}$$

The half-time for conversion of NO_2 to N_2O_5 by way of reaction k is

$$\tau_k = \ell n\ 2/2\underline{k}[O_3] \qquad (59)$$

These half times are calculated for each level of the stratosphere and are listed in Table 10. The half time is between 0.5 and 120 nights for NO_x mole fractions between 10^{-10} and 10^{-7}.

The dinitrogen pentoxide so formed undergoes both thermal and photochemical reactions

$$\begin{array}{lll} (n) & N_2O_5 + M \rightarrow NO_2 + NO_3 + M & \\ (p) & N_2O_5 + h\nu \rightarrow 2NO_2 + O & \\ (q) & N_2O_5 + O \rightarrow 2NO_2 + O_2 & (?) \\ (r) & N_2O_5 + H_2O \rightarrow 2HNO_3 & \end{array}$$

At 300°K, the rate constant r has been tentatively reported[32] to have the value of 1.7×10^{-18} cm^3/molecule-sec, and our experience in the laboratory would place this as an upper limit. For a bimolecular reaction to have so low a rate constant, it must have an activation energy, and thus the rate would be substantially lower at stratospheric temperatures. An estimate of the activation energy can be made from the single rate constant by assigning a "normal" pre-exponential factor to reaction r of 10^{-12} cm^3/molecule-sec. In this case, the activation energy is

8.0 kcal/mole, and the rate constant as a function of temperature is $\underline{k_s} = 10^{-12}$ exp-(8.0/RT)cc/molecules sec. The effect of M on the rate of reactions n is more complicated than that indicated by the simple second order relation,[31] especially in the lower stratosphere, but this extra complexity is not important in this context. The rate constant for reaction n at low pressures (where M is nitrogen) is[31]

$$u = 5.10 \times 10^{-6} \exp -(19.27/RT)\ cm^3/\text{molecules -sec.}$$

At night the following reactions are the important ones in this set

$$\begin{array}{ll} (k) & NO_2 + O_3 \rightarrow NO_3 + O_2 \\ (m) & NO_2 + NO_3 + M \rightarrow N_2O_5 + M \\ (n) & N_2O_5 + M \rightarrow NO_2 + NO_3 + M \\ (r) & N_2O_5 + H_2O \rightarrow 2HNO_3 \end{array}$$

Differential equations are written for NO_2, NO_3, N_2O_5, and HNO_3. The steady-state assumption is made only for NO_3. The resulting simultaneous equations for NO_2, N_2O_5, and HNO_3 are

$$\frac{d[NO_2]}{dt} = -2k_k[O_3][NO_2]$$

$$\frac{d[N_2O_5]}{dt} = k_h[O_3][NO_2] - k_r[H_2O][N_2O_5]$$

$$\frac{d[HNO_3]}{dt} = 2k_r[H_2O][N_2O_5]$$

Because ozone and water vapor are always in large excess over the oxides of nitrogen, they may be regarded as constant, and the set of equations is readily integrated:

$$[HNO_3] = [NO_2]_o \left\{(1-e^{-\beta t}) - \frac{\beta}{\gamma}(1-e^{-\gamma t})\right\} \qquad (60)$$

where $\beta = 2k_r [H_2O]$ and $\gamma = 2k_r [H_2O] + 2k_k [O_3]$. The mole fraction of water was assumed to be 5×10^{-6} throughout the stratosphere. N_2O_5 is formed during the night by reactions k and m and decomposed to NO_x during the day by reactions n, q, and by photolysis p. (Reaction n alone is much faster than s.) Thus Eq. (60) was solved for the 12 hr of night to give a fractional yield of nitric acid, $[HNO_3]/[NO_2]_o$. The half-time in number of nights is 0.50 divided by the fractional yield of HNO_3 in one night. These half-times in years are given in Table 10 and Fig. 3. The maximum rate of conversion of NO_2 to HNO_3 via N_2O_5 occurs between 35 and 40 km, and the minimum half-time is over half a year based on the upper limit rate constant.[32] Below 25 km the half-time ranges from one to twenty years. (The rate constant for the reaction of N_2O_5 and water vapor should be re-investigated in a large inert reaction chamber.)

The absorption spectrum of N_2O_5 was obtained by Jones and Wulf.[16] There is a weak continuous absorption decreasing from 300 to 380 nm, and there is a stronger continuous absorption increasing from 300 to 240 nm with no signs of a maximum. Based on the 12 hour average light intensity at 20 km for 45° latitude and at solar equinox, the photolysis rate constant for

(p) $N_2O_5 + h\nu(300\text{-}380) \rightarrow 2NO_2 + O$

is $j_p = 2.2 \times 10^{-5} sec^{-1}$. This rate constant implies a 9 hour half-life for photolysis of N_2O_5 at 20 km. This rate constant would increase sharply at higher elevations.

Photochemical process

Photochemically produced hydroxyl radicals add to nitrogen dioxide to form nitric acid

(s) $HO + NO_2 + M \rightarrow HNO_3 + M$

Table 10. Conversion of NO_2 to HNO_3 (mole fraction H_2O taken as 5×10^{-6}) by way of N_2O_5.

Elevation, km	15	20	25	30	35	40	45	log α
$\tau_{1/2}$ ($NO_2 \rightarrow N_2O_5$)	44	3.2	1.1	0.65	0.50	0.58	1.32	-10
nights	94	6.7	1.4	0.68	0.52	0.60	1.35	-9
	119	12	2.3	0.93	0.65	0.74	1.57	-8
	85	18	4.0	1.84	1.66	2.39	3.78	-7
$\tau_{1/2}$ ($NO_2 \rightarrow N_2O_5$	7.6	1.5	0.75	0.68	0.61	0.54	1.4	-10
$\rightarrow HNO_3$)*	16	3.1	0.92	0.68	0.60	0.56	1.4	-9
years	20	5.5	1.6	0.99	0.76	0.69	1.6	-8
	14	8.2	2.7	2.0	2.0	2.1	4.0	-7

* This is not a firm calculation but rather it is a lower limit on the half time, that is, this reaction is this fast or slower.

This reaction has been studied in detail at high temperatures,[33] but its rate constant under stratospheric conditions is not satisfactorily known. By means of a very long extrapolation, I estimate k_s to be 4×10^{-32} cm^6/molecule^2-sec. Nitric acid is photolyzed[34,35] especially at short wave lengths (maximum absorption around 260 nm).

(t) $HNO_3 + h\nu \rightarrow HO + NO_2$

and it is destroyed by reaction with hydroxyl radicals

(u) $HO + HNO_3 \rightarrow H_2O + NO_3$

Nitric acid would be destroyed as well as formed in the upper stratosphere, but it would be relatively inert in the lower stratosphere.

An upper limit on the rate of formation of nitric acid from NO_2 and HO is the rate of photochemical production of hydroxyl radicals, Table 8A. In an NO_x free atmosphere the rate of production of HO in units of mole-fraction per year is 10^{-10} at 15 km, 10^{-9} at 20 km, 10^{-7} at 30 km, and 10^{-6} at about 37 km. These rates are increased by a mole fraction of NO_x of 10^{-7} only about a factor of two or three at low elevations and not at all at upper elevations.

If the rate constant k_3 was known, then the rate of formation of nitric acid by way of reaction s̲ could be calculated. Three values of k_3 were assumed, and values of the steady-state concentration of hydroxyl radicals (in an NO_x free atmosphere) are included in Table 8A. The values of $k_{\underline{s}}[M]$ as a function of elevation are entered in Table 9. The rate of converting NO_2 to HNO_3 in terms of the half life is given by

$$\tau_{1/2} = \ell n2/k_s[M][HO] \qquad (61)$$

This would be the half life for converting NO_2 to HNO_3 if other processes (reactions c", 1, 2, 3) maintained the steady-state concentration of hydroxyl radicals at a constant value. The steady-state hydroxyl radical concentrations in Table 8B are based on a 12 hour day. To change the half-life from seconds to years, another factor of 2 comes in since these reactions do not occur at night. The half times for the three assumed values of k_3 are included in Table 9. If k_3 is 10^{-14} cc/molecule-sec, the half-life is more than 10 years at and below 30 km, but the half time is less than one year above 40 km with a minimum half time of seven months at 45 km. If k_3 is as small as 10^{-16} cc/molecule-sec, the half life for forming nitric acid from NO_2 is one year at 15 km and at 20 km and faster at higher elevations, with a minimum half life of two and one-half months at 35 km. These calculations point out the importance of reaction 3 for the SST problem with ozone. Its effect in directly destroying ozone is negligible (at most a percent or so), but is has a very important role in shifting the balance from HO to HOO, thereby decreasing the rate of formation of nitric acid.

The importance of water in the stratosphere is its role in neutralizing NO_x by converting it to nitric acid. The rate constants for the conversion of NO_2 to HNO_3 are not well known; this statement applies both to the thermal process and to the photochemical process. The main body of available information indicates that the half time to convert NO_2 to HNO_3 is a matter of a year or more between 15 and 25 km and about a half-year in the upper half of the stratosphere. These half-times could be either an over-estimate or an under-estimate. Chemical analyses of NO, NO_2, N_2O_5, HNO_3, and O_3 are needed at all elevations during daytime hours, and of NO_2, N_2O_5, HNO_3, and O_3 at night. Laboratory investigations or reinvestigations are needed for reactions: k̲, ℓ̲, p̲, q̲, r̲, s̲, t, u̲; 1, 3, 4 (?).

Attention should be given to other reactions that may form nitric acid

$$HOO + NO \rightarrow HNO_3 \quad (?)$$

Investigations in our laboratory failed to find any HNO_3 from this reaction. Nitrous acid can presumably be formed from hydroxyl radicals

$$HO + NO + M \rightarrow HNO_2$$

but nitrous acid is very rapidly photolyzed by near ultraviolet (320-390 nm) radiation. If the reaction between HOO and NO is fast[36]

$$HOO + NO \rightarrow HO + NO_2$$

it would serve to redistribute HOO and HO, increasing HO and thereby enhancing reaction s. Preliminary experiments in our laboratory[37] indicate that this reaction is fairly slow, $k \leq 2 \times 10^{-15}$ at room termperature. However it is very difficult to separate this reaction from others, and its rate constant must be regarded as unknown and as very important.

PART II. STEADY-STATE OZONE PROFILES

The calculation of the steady-state concentration of ozone in the stratosphere is somewhat of an artificial exercise: there is some vertical and much horizontal diffusion; half times to obtain a photochemical steady state vary from a year or so at 20 km to a day or so at 45 km; some species (for example, NO_2, N_2O_5, HNO_3, H_2O_2) build up at night and are partially destroyed by day (the steady-state method is very inappropriate for some of these oscillations); and a large change of ozone in the stratosphere would lead to large changes of temperature, structure, and dynamics. In spite of these overwhelming obstacles to a total quantitative analysis of the problem, the calculation of steady-state ozone profiles is a valuable tool in assessing the direction of change to be expected from an added ingredient, namely NO_x.

The differential equations were set up for the full set of reactions a through l. The steady-state relation for NO_3 immediately reduces the set from 12 to 11 reactions, since k during the day is very rapidly followed by l. The steady-state assumption for the oxides of nitrogen

$$\frac{d[NO_2]}{dt} \approx 0$$

gives the relation between NO, NO_2, and NO_x as a function of O, O_2, O_3, M and the rate constants. The steady-state assumption for the following difference

$$\frac{d[O_3]}{dt} - \frac{d[O]}{dt} + \frac{d[NO_2]}{dt} \approx 0$$

gives an expression for the concentration of oxygen atoms. The steady-state assumption for the following sum

$$\frac{d[O_3]}{dt} + \frac{d[O]}{dt} + \frac{d[NO_2]}{dt} \approx 0$$

gives an expression for the steady-state concentration of ozone. The expressions are rather complicated, but they are readily factored into the dominant terms multiplied by a sum of dimensionless ratios. In this form the equations are set up for efficient and rapid solution by a process of successive approximations.

To avoid an undue accumulation of symbols, I make the following definitions: $X = [O_3]$, $Y = [O]$, $Z = [O_2]$, $V = [NO_2]$, $W = [NO]$, $M = [M]$, α = mole fraction of $NO_x = [NO_x]/[M]$; $A = j_a[O_2]$, $B = k_b[M][O_2]$, $C = j_c$ $D = k_d[M]$, $E = k_e$, $F = k_f$, $G = k_g$, $H = j_h$, $I = k_i[O_2]$, $J = k_j[M]$, $K = k_k$. The zero approximation is

$$\begin{aligned} X_o &= (AB/CE)^{1/2} \\ Y_o &= X_o C/B \\ V_o &= \alpha MFX_o/[FX_o+(G+J)Y_o+H] \qquad (62) \\ W_o &= \alpha M - V_o \end{aligned}$$

The expression for the general iteration is

$$X_{n+1} = X_o \left\{ \frac{\left(1 + \frac{IW_n^2}{A}\right)\left(1 + \frac{DY_n}{B} + \frac{IW_n^2}{BY_n} + \frac{JW_n}{B}\right)}{\left(1 + \frac{GV_n}{EX_n} + \frac{DY_n}{EX_n} + \frac{KV_n}{EY_n}\right)\left(1 + \frac{A}{CX_n} + \frac{HV_n}{CX_n} + \frac{KV_n}{C}\right)} \right\}^{1/2} \qquad (63)$$

$$Y_{n+1} = X_n \frac{C}{B} \frac{\left(1 + \frac{A}{CX_n} + \frac{HV_n}{CX_n} + \frac{KV_n}{C}\right)}{\left(1 + \frac{DY_n}{B} + \frac{IW_n^2}{BY_n} + \frac{JW_n}{B}\right)} \qquad (64)$$

$$V_{n+1} = \frac{\alpha MFX_n \left(1 + \frac{2IW_n}{FX_n} + \frac{JY_n}{FX_n}\right)}{FX_n + (G+J)Y_n + H + 2IW_n} \qquad (65)$$

$$W_{n+1} = \alpha M - V_{n+1} \qquad (66)$$

Thermal rate constants were evaluated at each kilometer of the stratosphere at its standard temperature and pressure.[6]

A. Method Suitable for Desk Calculator

The rate constant j_a for photolysis of O_2 is a summation over wave length of the quantum yield Q, the absorption cross section σ ($L = L_o \exp -\sigma N$, where N is total number of molecules in the path) and the flux of radiation L (photons/cm^2-sec) where

$$j_a(S) = \sum_{\lambda} Q(\lambda)\, \sigma(\lambda)\, L(S,\lambda)$$

where S is elevation above sea level. The radiation flux may be examined for a particular solar angle or averaged over solar angles of the day at one location and season. The constants j_c for O_3 and j_h for NO_2 are similar in nature. Ten years ago Dütsch[38] presented a graph of j_a and j_c as a function of elevation in the stratosphere, but he expressed several reservations about the function j_a, including uncertainty at that time about the intensity of incoming solar radiation below 220 nm and about the absorption cross sections. Model calculations are made here with Dütsch's function, j_a' in Table 11, and with this function reduced by about a factor of 6, j_a in Table 11. These two sets of j_a are used to explore the variation brought about by a large perturbation in this function. The constant $\underline{c}$ depends primarily on radiation between 200 and 300 nm and secondarily on the ranges 190 to 200, 300 to 350, and 450 to 650 nm. The constant j_h depends on radiation between 300 and 400 nm, which is only weakly absorbed by any other atmospheric species, and it is taken to be constant with elevation in this sub-section. If the photolysis constants j_a, j_c, and j_h are assumed to be a function only of elevation, then the set of Eqs. (62)

Table 11. Stratospheric model with rate constants as a function of elevation.

Height km	15	20	25	30	35	40	45	Ref.
Temperature °K	220	217	222	227	235	250	260	6
log [M] *	18.60	18.27	17.93	17.58	17.26	16.92	16.60	6
log $[O_2]$ *	17.92	17.59	17.25	16.90	16.58	16.24	15.92	6
log j_a sec^{-1}	-15.5	-13.7	-12.5	-11.7	-11.0	-10.6	-10.2	38
log $j_{a'}$ sec^{-1}	-14.5	-13.0	-11.8	-10.9	-10.2	-9.8	-9.4	38
log j_c sec^{-1}	-3.2	-3.2	-3.1	-3.0	-2.8	-2.4	-2.0	38
log j_h sec^{-1}	-2.15	-2.15	-2.15	-2.15	-2.15	-2.15	-2.15	14
log j_1 sec^{-1}	-2	-2	-2	-2	-2	-2	-2	30
log k_b †	-32.61	-32.58	-32.63	-32.67	-32.73	-32.85	-32.92	10,11
log k_d †	-32.10	-32.10	-32.10	-32.10	-32.11	-32.12	-32.12	10,11
log k_e **	-15.06	-15.10	-15.01	-14.92	-14.78	-14.55	-14.41	10,11
log k_f **	-14.36	-14.40	-14.34	-14.29	-14.20	-14.06	-13.98	12
log k_g **	-11.38	-11.38	-11.37	-11.36	-11.34	-11.30	-11.28	13
log k_i †	-37.44	-37.42	-37.45	-37.47	-37.50	-37.56	-37.60	13
log k_j †	-30.68	-30.66	-30.70	-30.74	-30.80	-30.91	-30.97	13
log k_k **	-17.96	-18.06	-17.90	-17.75	-17.52	-17.12	-16.89	29

* molecule/cm^3. M refers to all molecules of air

** cm^3/molecule -sec

† cm^6/$molecule^2$ -sec

to (66) can readily be solved by a desk calculator, although I used a simple computer program to permit extensive variation of parameters. For hand calculations I use as convergence criterion $(X_{n+1}-X_n)/X_{n+1}<10^{-3}$, and 3 or 4 iterations are usually sufficient. For the computer, the convergence criterion was set at 10^{-8}, and sometimes scores of iterations were required. A separate calculation was made for each elevation in Table 11 and for a wide range of mole fractions of NO_x. To this approximation, each calculation is independent of all others, and the effect of non-uniform mole fraction of NO_x can be studied by rearrangement of the calculated ozone concentrations.

For a given set of constants, the steady-state ozone concentrations are listed in Table 12 for 7 elevations between 15 and 45 km and for 14 mole fractions of NO_x including mole fraction zero. The integral of ozone concentration with elevation (actually the sum over 5 km blocks) for each set of rate constants and for each mole fraction of NO_x is compared to the value of this integral with zero NO_x in Figs. 4-6.

The rationale for the various sets of constants used is as follows. Dütsch's quoted uncertainty in the constant j_a is embraced by the range between j_a and j_a', and thus it is desirable to explore this range. The reactions *i*, *j*, and *k* are relatively slow, compared to *f*, *g*, and *h* in the stratosphere. Over a long enough period of time they would register their effect on the steady-state concentration of ozone, but in a much shorter time the reactions *f*, *g*, and *h* would have reached a different pseudo-steady state. Thus it is of interest to consider separately the full set of reactions and the set omitting *i*, *j*, and *k*. Table 12A shows an interesting reversal at 15 km with an increase in O_3 with increasing NO_x between $\alpha = 4.7 \times 10^{-8}$ and $\alpha = 10^{-7}$. To pinpoint the source of this effect, calculations were made with the rate constant *i*

Table 12. Calculated ozone concentrations in the stratosphere, without and with catalysis by oxides of nitrogen. Ozone in multiples of 10^{11} molecules/cm^3.

A. Model as given in Table 11, a through k.

log(mole fraction NO_x) Km	15	20	25	30	35	40	45
α = 0	19.72	54.32	50.70	29.17	13.64	2.82	0.73
log α = -11.00	17.66	53.73	50.54	29.13	13.63	2.82	0.73
-10.67	15.80	53.06	50.36	29.07	13.63	2.81	0.73
-10.33	12.88	51.62	49.95	28.95	13.58	2.81	0.73
-10.00	9.57	48.79	49.12	28.70	13.51	2.80	0.73
-9.67	6.64	43.55	47.42	28.18	.3.37	2.79	0.73
-9.33	4.41	34.95	43.94	27.07	13.05	2.75	0.73
-9.00	2.95	24.94	37.91	24.99	12.44	2.68	0.72
-8.67	1.98	16.32	29.17	21.41	11.30	2.54	0.71
-8.33	1.34	10.23	19.66	16.32	9.41	2.27	0.68
-8.00	1.00	6.49	12.53	11.29	7.12	1.89	0.63
-7.67	0.91	4.10	7.83	7.38	4.96	1.44	0.54
-7.33	1.04	2.51	4.76	4.66	3.27	1.01	0.42
-7.00	1.29	1.55	2.86	2.93	2.14	0.69	0.30

Table 12. B. Replace a by a', b through k.

	15	20	25	30	35	40	45
α = 0	62.4	121.6	113.5	73.3	34.3	7.1	1.8
log α = -11.00	59.2	120.9	113.3	73.2	34.3	7.1	1.8
-10.67	55.8	120.1	113.1	73.1	34.2	7.1	1.8
-10.33	49.4	118.4	112.6	73.0	34.2	7.1	1.8
-10.00	39.4	114.9	111.7	72.7	34.1	7.1	1.8
-9.67	27.7	107.8	109.6	72.0	33.9	7.0	1.8
-9.33	17.6	94.2	105.3	70.6	33.4	7.0	1.8
-9.00	11.1	73.3	96.8	67.7	32.6	6.9	1.8
-8.67	7.0	49.2	81.8	62.0	30.8	6.6	1.8
-8.33	4.5	29.5	59.6	51.5	27.3	6.1	1.8
-8.00	2.9	17.6	37.9	37.9	21.9	5.3	1.8
-7.67	2.0	10.5	22.4	24.5	15.6	4.2	1.7
-7.33	1.5	6.2	12.9	14.6	9.9	2.9	1.6
-7.00	1.4	3.5	7.3	8.7	6.2	1.9	1.4

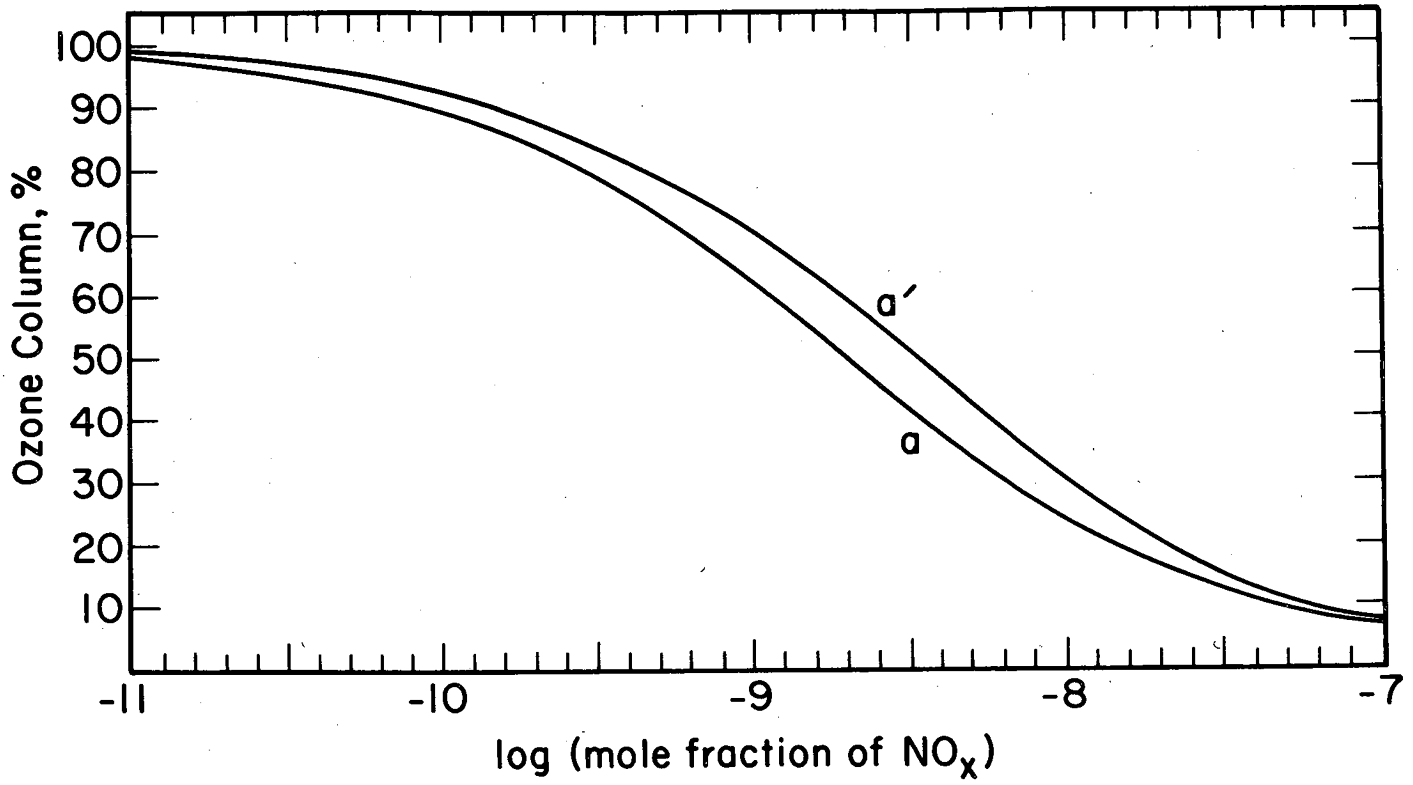
Table 12.C. Model of *a*, *c*, and *h* as calculated from Eq. 71 for 45° latitude, equinox.

	15	20	25	30	35	40	45	50
α = 0	6.34	36.2	59.0	66.9	46.0	18.1	4.70	0.95
log α = -11.00	4.00	35.3	58.8	66.9	46.0	18.1	4.70	0.95
-10.67	3.06	34.2	58.6	66.8	46.0	18.1	4.70	0.95
-10.33	2.23	32.1	58.2	66.7	45.9	18.0	4.70	0.95
-10.00	1.64	28.6	57.4	66.5	45.9	18.0	4.70	0.95
-9.67	1.23	23.5	55.7	66.0	45.7	18.0	4.68	0.95
-9.33	0.95	18.0	52.4	65.1	45.4	17.8	4.66	0.95
-9.00	0.77	13.8	47.1	63.2	44.7	17.6	4.61	0.95
-8.67	0.66	11.0	39.9	59.6	43.3	17.1	4.52	0.94
-8.33	0.61	9.06	32.7	53.6	40.5	16.0	4.32	0.93
-8.00	0.61	7.86	27.3	46.2	35.8	14.2	3.96	0.91
-7.67	0.66	6.99	23.3	38.5	29.1	11.2	3.34	0.87
-7.33	0.76	6.15	19.7	30.9	21.1	7.62	2.47	0.78
-7.00	0.86	5.25	16.0	23.3	13.9	4.59	1.64	0.65
-6.67	0.94	4.23	11.7	15.4	8.21	2.59	1.01	0.46
-6.33	0.96	3.16	7.33	8.73	4.32	1.44	0.60	0.29
-6.00	0.91	2.21	4.20	4.48	2.24	0.83	0.37	0.18

Fig. 4. Relative ozone column as a function of uniform mole fractions of NO_x by the method of Part IIA, Table 11. Dütsch's constant for photolysis of O_2 is changed by a factor of about 6 between *a* and *a'*, with all other terms held the same.

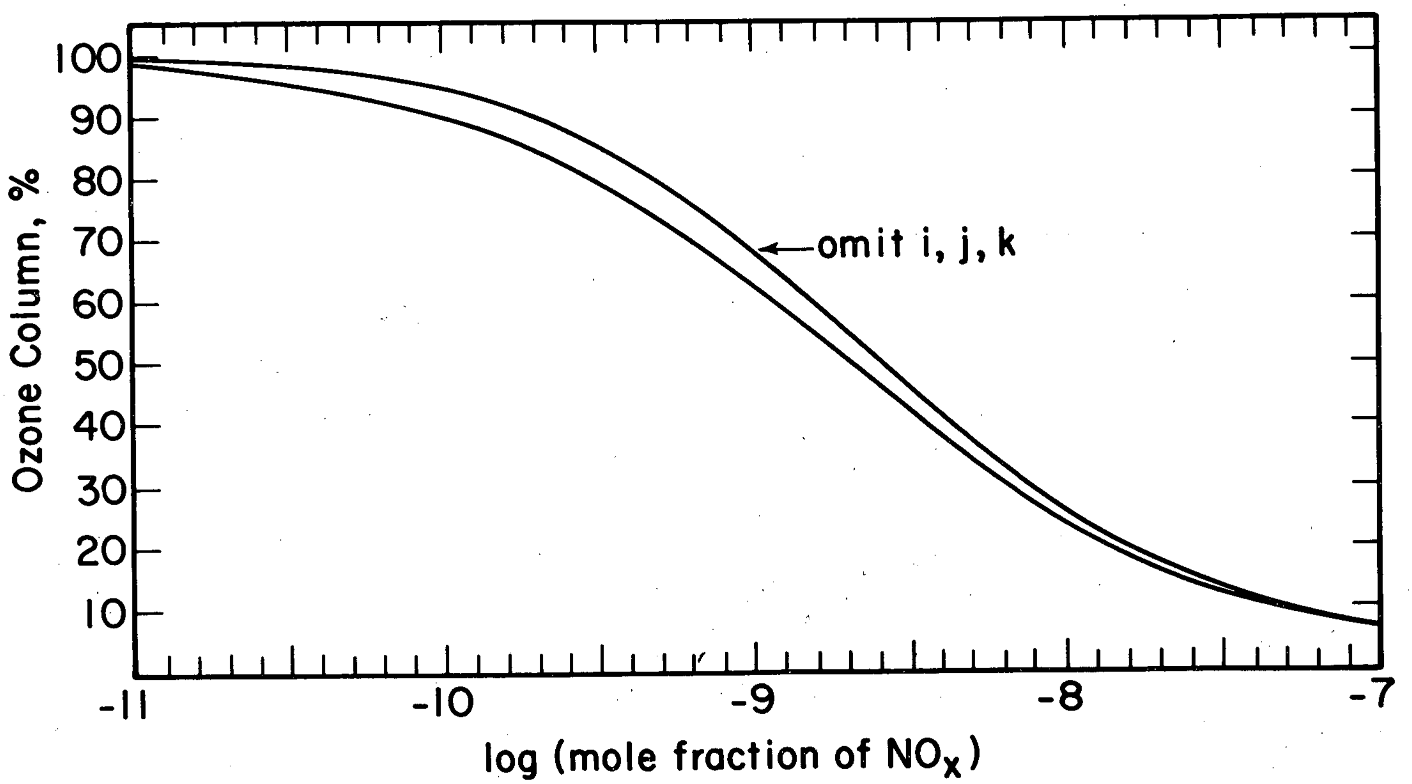
Fig. 5. Relative ozone column as in Fig. 4 with and without reactions *i*, *j*, and *k*.

Fig. 6. Relative ozone column as in Fig. 4 with the constant k_i set 10,000 times too big.



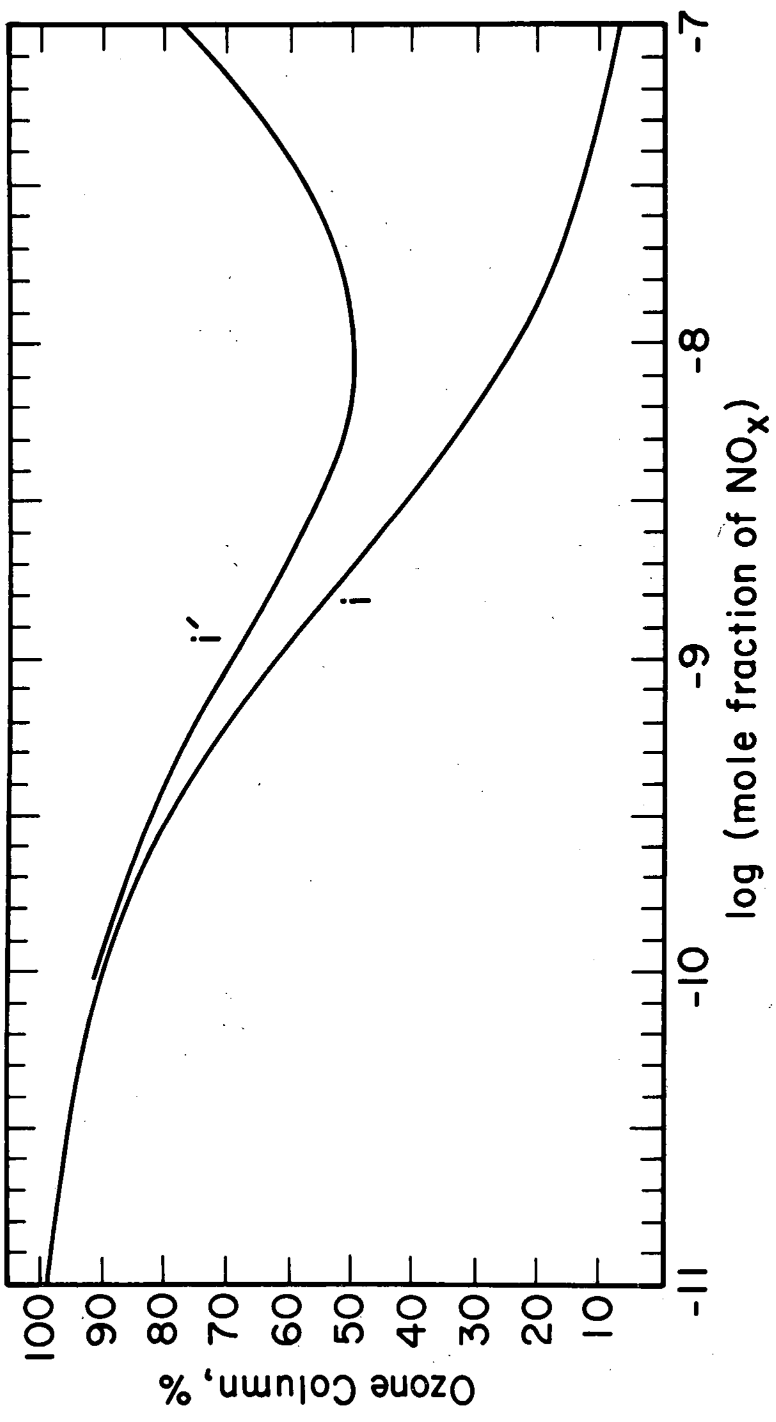
XBL 716-6842

Fig. 4



XBL 716-6843

Fig. 5



XBL 716-6844

Fig. 6

about 10,000 times too big, namely, 1.00×10^{-33} $cm^6/molecules^2$-sec at all levels. The results of those various cases are discussed below.

Figure 4 shows that the relative effect of oxides of nitrogen on the ozone column is very nearly the same for the photolysis function a and the photolysis function a', which is about 6 fold larger. The reduction of the ozone column by NO_x relative to zero NO_x is a very large effect.

The effect of omitting reactions i, j, and k from the calculation is presented in Fig. 5. Addition of NO_x to a pure air system would reduce ozone to the top curve in Fig. 5 with a relatively short half-time (compare Table 6), and over a substantially longer time it would further decrease to the lower curve. The difference between the two curves in Fig. 5 is not great.

The effect of a drastically incorrect value of the rate constant i is given by Fig. 6. If i were 1.00×10^{-33}, instead of over 10,000 times smaller, then the reduction of ozone by NO_x would go through a minimum at $\alpha = 10^{-8}$ and increase thereafter. Steady-state calculations can be very treacherous, and a single misplaced or misevaluated term can cause a large error in the result.

B. Method Requiring a Computer

The extremely large reduction of ozone indicated by Fig. 4 leads to conditions that make the photolysis no longer simply a function of elevation. The photolysis constants a, c, and h at a given elevation S depend on all radiation absorbing substances above S. If ozone at 40 km, for example, is reduced by NO_x, then the radiation flux at 35 km will be different from the unperturbed situation. To account for this perturbation and to provide a self-consistent, self-contained model for photochemistry in the stratosphere, the rate constants j_a, j_c. and j_h are calculated here directly from modern values of incoming solar radiation[39] and absorption cross sections for O_2,[40] O_3,[41] and NO_2.[42]

The solar radiation at the top of the atmosphere was obtained from a NASA report[39] based on rocket studies:

$$L_o = L_o(\lambda) \tag{67}$$

Radiation flux in photons/cm^2-sec-nm were used for each nm between 190 and 400 nm. The solar flux at wave length λ, elevation S, and solar zenith angle ϕ is

$$L(\lambda,S,\phi) = L_o \exp-(\sigma_x N_x+\sigma_z N_z+\sigma_v N_v)\text{secant}\phi \tag{68}$$

where N is the vertical column of a species above elevation S in units of molecules/cm^2 and other terms are defined in connection with Eqs.(62) to (66).At the time of the solar equinox the secant of the solar angle is

$$\text{secant}\phi = \text{secant}\Lambda \ \text{secant}\theta \tag{69}$$

where Λ is the latitude on the earth and θ is the local solar angle where $\theta = 0$ corresponds to local solar noon. The average intensity $\overline{L(\lambda,s)}$ is found for a given latitude by summing Eq. (68) over every 5 degrees of solar angle from 0 to 85 for day; there are 18 steps in this sum for half the day and dividing the sum by 36 gives the day and night average.

$$\overline{L(\lambda,s)} = \frac{1}{36} \sum_{\theta=85^\circ}^{0^\circ} L(\lambda,s,\phi) \tag{70}$$

in 18 increments of 5° each

The photolysis rate constants are

$$\begin{aligned} \underline{A} &= j_a\,[O_2] \sum_{190}^{242} \overline{L(\lambda,S)}\,\sigma_z[O_2] \\ \underline{C} &= j_c = \sum_{190}^{350} \overline{L(\lambda,S)}\ \sigma_x + \sum_{450}^{650} \overline{L(\lambda,S)}\ \sigma_x \\ \underline{H} &= j_h = \sum_{260}^{400} \overline{L(\lambda,S)}\ \sigma_v \end{aligned} \tag{71}$$

Since a and c both involve radiation between 190 and 242 nm, each of these constants at an elevation S depends on the total column of both O_2 and O_3 above S. The column of O_2 is a fixed function of elevation, for a given temperature profile, but the column of ozone at an elevation S depends strongly on the oxides of nitrogen above S. The calculations begin at 50 km with the model of no O_3 or NO_x above that elevation. (Actually there is a small amount of O_3 above 50 km; by the time one reaches 45 km with this model, the effect of the assumed absence of O_3 above 50 km is small.) The constants A, C and H at 50 km are evaluated from Eq. (71). The steady-state concentrations of O_3, O, NO_2, and NO are evaluated in the segment from 49 to 50 km by means of Eqs. (62) to (66), and the column of O_2, O_3 and NO_2, respectively, N_z, N_x, N_v are computed. With these quantities for use in Eqs. (68) to (71), values of A, C, and H are found for 49 km. The computations are made for each kilometer from 50 down to 15 and at 5 km increments to the ground. At each level the average radiation flux is evaluated at each wavelength, acknowledging all light-absorbing substances above that level.

If the only purpose of a photochemical calculation is to solve for the steady-state concentration of ozone, then the method used to evaluate light intensities is not especially critical since ozone depends on the ratio j_a/j_c. However if other photochemical quantities are desired, such as the average rate of formation of HO (Eq. 45), effect of NO_x, life-times etc., it is necessary to be as realistic as possible. Very often ozone calculations are made by means of the "Joshua model," that is, for a constant solar angle (even though it may take months or years to reach the photochemical steady state). The angular dependence appears in the exponential term, Eq. (68), and the radiation intensity averaged over solar angles is not the same as the radiation intensity associated with some single average angle. Also, I found that when I tried to make calculations with a fixed, average solar angle, I was tempted to use the solar angle as an adjustable parameter. The method used here averages the radiation intensity every 5 degrees of solar angle, in effect over the 12 hour period from midnight to noon (omitting the anomalous case precisely at sunrise). This calculation, then, involves no adjustable parameter of any sort. The entire calculation is based on observed solar fluxes, absorption cross sections, quantum yields, and a model for temperature and density of the atmosphere as a function of elevation.

There is some uncertainty about how to handle data for oxygen[40] below 200 nm, where the sharp intense Schumann-Runge bands have been almost totally removed, but the radiation between these bands is present with only slight diminution. For this calculation the radiation wavelength was divided into a grid 1 nm wide; average intensities and average cross sections were used; and radiation below 190 nm was not considered. The most penetrating, oxygen-dissociating radiation is that between 200 and 208 nm, and at 20 km (45° latitude) oxygen is dissociated almost exclusively between 197 and 211 nm. Whereas a more realistic model could be used between 180 and 200 nm by employing an exceedingly fine grid to account for the details of the Schumann-Runge bands, the difference would be noticeable only in the upper stratosphere, and there would be little effect at the main ozone levels. In the Herzberg continuum[40] the absorption cross section has an anomalous pressure dependence. Calculations were made including and also omitting this pressure dependence; the difference with respect to ozone with and without this term is negligible above 20 km and the matter of only a percent or two at 15 km.

The basic conditions used here for making the steady-state calculations are the stratospheric model in Table 11, and an average world-wide, year-long situation, 45° latitude at the solar equinox. The effect of oxides of nitrogen was examined both for models with uniform mole fraction throughout the stratosphere and for various non-uniform models (in an effort to approximate the present steady-state distribution of NO_x and to account for insertion of NO_x at 20 km by the SST). The models with uniform mole fractions of NO_x were varied with respect to temperature and adhering to the standard temperature profile varied with respect to latitude.

The values of the photolysis constants, j_a, j_c, and j_h, as obtained here are compared with those of Dütsch[38] and Leighton[14] in Table 13. Dütsch's values for $\underline{j_a}$ and $\underline{j_c}$ are based on the incoming solar flux and a model for the observed ozone distribution that was available to him. Both ozone and oxygen absorb in the region below 240 nm, and the photolysis constant for oxygen $\underline{j_a}$ at any level depends strongly on the actual vertical distribution of ozone above that level. My photolysis constant $\underline{j_a}$ for $\alpha = 10^{-7}$ agrees rather closely with Dütsch's constant j_a', and my function is larger and smaller than Dütsch's at other values of NO_x. Thus Dütsch's function falls within the range of my functions, $\underline{j_a}$. Dütsch's constant for the photolysis of ozone is based on an overhead sun, and my function $\underline{j_c}$ is a 24 hour average. When this factor is considered, the agreement between the two is satisfactory. Leighton's value for $\underline{j_h}$ is based on ground level radiation and an overhead sun. My 24 hour averaging gives a lower radiation intensity, but being in the stratosphere gives a slightly larger radiation flux in this range than at ground level. Again, my photolysis function agrees satisfactorily with that of an expert in the field.

Table 13. Comparison of photolysis rate constants from the literature with those calculated here for 45° latitude at equinox.

Elevation, km	15	20	25	30	35	40	45	50
log j_a (Dütsch)	-15.50	-13.70	-12.50	-11.70	-11.00	-10.60	-10.20	
log $j_{a'}$ (Dütsch)	-14.50	-13.00	-11.80	-10.90	-10.20	-9.80	-9.40	
log j_a $\alpha=0$	-17.02	-14.49	-12.98	-11.67	-10.65	-9.91	-9.44	
log $\alpha=-10$	-16.87	-14.45	-12.97	-11.67	-10.65	-9.91	-9.44	
-9	-16.51	-14.29	-12.87	-11.63	-10.64	-9.90	-9.43	
-8	-15.79	-13.66	-12.41	-11.37	-10.51	-9.85	-9.42	
-7	-14.63	-12.69	-11.55	-10.68	-10.05	-9.61	-9.36	
-6	-12.88	-11.48	-10.60	-9.99	-9.63	-9.42	-9.29	
log j_c (Dütsch)	-3.20	-3.20	-3.10	-3.00	-2.80	-2.40	-2.00	
log j_c								
$\alpha=0$	-3.74	-3.73	-3.72	-3.68	-3.58	-3.33	-2.80	-2.30
log $\alpha=-10$	-3.74	-3.73	-3.72	-3.68	-3.58	-3.32	-2.80	-2.30
-8	-3.71	-3.70	-3.69	-3.66	-3.54	-3.28	-2.77	-2.30
-6	-3.44	-3.40	-3.32	-3.13	-2.82	-2.56	-2.40	-2.30
log j_h (Leighton)	-2.15	-2.15	-2.15	-2.15	-2.15	-2.15	-2.15	
log j_h								
$\alpha=0$	-2.36	-2.35	-2.35	-2.34	-2.33	-2.32	-2.32	-2.32
log $\alpha=-7$	-2.40	-2.38	-2.36	-2.34	-2.33	-2.32	-2.32	-2.32
-6	-2.62	-2.52	-2.42	-2.36	-2.33	-2.32	-2.32	-2.32

Results for Uniform NO_x Mole Fractions

For four mole fractions of NO_x (0, 10^{-9}, 10^{-8}, and 10^{-7}) full details at every kilometer are given in Table 14, where X, Y, V, and W are respectively the concentrations of ozone, oxygen atoms, NO_2, and NO and NX, NV are the columns of ozone and NO_2 above the given elevation.

Ozone concentrations as a function of elevation in the stratosphere and mole fraction, α, of NO_x are entered in Table 11C for the standard conditions and for this model. Five ozone profiles as a function of elevation are given in Fig. 7. (The ozone profile for zero NO_x was also given in Fig. 2. Figure 7 also includes as its upper scale the rate of formation of hydroxyl radicals in units of mole fraction per year.) Ozone concentrations are reduced by oxides of nitrogen at all elevations, but from this figure it can be seen that the lower parts of the stratosphere are much more sensitive to reduction of ozone by NO_x than the higher levels. This especial sensitivity of the lower levels is brought out even more clearly by Fig. 8, which gives the relative (to zero NO_x) reduction in ozone at individual elevations as a function of mole fraction of oxides of nitrogen. At 20 km ozone is cut in half by a mole fraction of 5×10^{-10}, whereas at 25 km reduction to one half requires a mole fraction of 7×10^{-9}. The integrated column of ozone from 15 to 50 km relative to that for zero NO_x is given for a range of mole fractions of the oxides of nitrogen in Fig. 9. This figure should be compared with Fig. 4. The relative effect of NO_x on O_3 is less in Fig. 9 than in Fig. 4, because Fig. 9 takes into consideration the second-order effect of a large reduction of ozone on the distribution of radiation that can be absorbed by oxygen. For the four cases of NO_x from SST operation as given in Table 1, the reduced ozone column relative to zero NO_x is respectively 33%, 47%, 62%, and 73%.

Table 14. Detailed concentrations and vertical columns.

A. α = 0.

H(KM)	X	NX	Y	V	NV	W
50	9.49364E+10	0.	4.91152E+09	0.	0.	0.
49	1.31895E+11	9.49364E+15	4.12168E+09	0.	0.	0.
48	1.78954E+11	2.26882E+16	3.39324E+09	0.	0.	0.
47	2.46260E+11	4.05335E+16	2.73810E+09	0.	0.	0.
46	3.40610E+11	6.52096E+16	2.15769E+09	0.	0.	0.
45	4.69984E+11	9.92705E+16	1.66583E+09	0.	0.	0.
44	6.45919E+11	1.46269E+17	1.26130E+09	0.	0.	0.
43	8.70765E+11	2.10361E+17	9.48996E+08	0.	0.	0.
42	1.14853E+12	2.97937E+17	7.15530E+08	0.	0.	0.
41	1.46552E+12	4.12791E+17	5.45042E+08	0.	0.	0.
40	1.80614E+12	5.59343E+17	4.18461E+08	0.	0.	0.
39	2.29106E+12	7.39957E+17	3.22399E+08	0.	0.	0.
38	2.76820E+12	9.69063E+17	2.44662E+08	0.	0.	0.
37	3.41707E+12	1.24538E+18	1.86867E+08	0.	0.	0.
36	4.03104E+12	1.58759E+18	1.40385E+08	0.	0.	0.
35	4.60278E+12	1.99069E+18	1.03678E+08	0.	0.	0.
34	5.10079E+12	2.45097E+18	7.64606E+07	0.	0.	0.
33	5.55109E+12	2.96105E+18	5.59346E+07	0.	0.	0.
32	5.98920E+12	3.51516E+18	4.05489E+07	0.	0.	0.
31	6.34759E+12	4.11508E+18	2.90780E+07	0.	0.	0.
30	6.69698E+12	4.74984E+18	2.12222E+07	0.	0.	0.
29	6.71448E+12	5.41954E+18	1.48559E+07	0.	0.	0.
28	6.58791E+12	6.09098E+18	1.02239E+07	0.	0.	0.
27	6.48352E+12	6.74978E+18	7.08057E+06	0.	0.	0.
26	6.20862E+12	7.39813E+18	4.81202E+06	0.	0.	0.
25	5.90470E+12	8.01899E+18	3.24714E+06	0.	0.	0.
24	5.60209E+12	8.60946E+18	2.16794E+06	0.	0.	0.
23	5.13115E+12	9.16967E+18	1.42426E+06	0.	0.	0.
22	4.71804E+12	9.68278E+18	9.21071E+05	0.	0.	0.
21	4.16639E+12	1.01546E+19	5.76281E+05	0.	0.	0.
20	3.63520E+12	1.05712E+19	3.52491E+05	0.	0.	0.
19	2.84165E+12	1.09347E+19	2.04022E+05	0.	0.	0.
18	2.14839E+12	1.12189E+19	1.14968E+05	0.	0.	0.
17	1.55169E+12	1.14337E+19	6.26008E+04	0.	0.	0.
16	1.02976E+12	1.15889E+19	3.10937E+04	0.	0.	0.
15	6.42875E+11.	1.16919E+19	1.43083E+04	0.	0.	0.

Table 14. B. α = 10^{-9}.

H(KM)	X	NX	Y	V	NV	W
50	9.45880E+10	0.	4.89107E+09	7.88816E+05	0.	2.06112E+07
49	1.31124E+11	9.45380E+15	4.10056E+09	1.36244E+06	7.88816E+10	2.31376E+07
48	1.77530E+11	2.25712E+16	3.37185E+09	2.32677E+06	2.15126E+11	2.56732E+07
47	2.43614E+11	4.03241E+16	2.71690E+09	4.01748E+06	4.47803E+11	2.81825E+07
46	3.35772E+11	6.46856E+16	2.13768E+09	6.84114E+06	8.49551E+11	3.01589E+07
45	4.61528E+11	9.82628E+16	1.64821E+09	1.11969E+07	1.53366E+12	3.11031E+07
44	6.32018E+11	1.44416E+17	1.24673E+09	1.74932E+07	2.65335E+12	3.09068E+07
43	8.49903E+11	2.07617E+17	9.37431E+08	2.55516E+07	4.40267E+12	2.97484E+07
42	1.11967E+12	2.92608E+17	7.06393E+08	3.52595E+07	6.95784E+12	2.82405E+07
41	1.42816E+12	4.04575E+17	5.37819E+08	4.59814E+07	1.04838E+13	2.68186E+07
40	1.75978E+12	5.47391E+17	4.12741E+08	5.73545E+07	1.50819E+13	2.57455E+07
39	2.23156E+12	7.23369E+17	3.17800E+08	7.15858E+07	2.08174E+13	2.49142E+07
38	2.69583E+12	9.46524E+17	2.41026E+08	8.74317E+07	2.79760E+13	2.45683E+07
37	3.32659E+12	1.21611E+18	1.83911E+08	1.06506E+08	3.67191E+13	2.44936E+07
36	3.92004E+12	1.54877E+18	1.37908E+08	1.26773E+08	4.73698E+13	2.52273E+07
35	4.46961E+12	1.94077E+18	1.01625E+08	1.51391E+08	6.00470E+13	2.66095E+07
34	4.94113E+12	2.38773E+18	7.47130E+07	1.78216E+08	7.51861E+13	2.87845E+07
33	5.35686E+12	2.88184E+18	5.44197E+07	2.09136E+08	9.30076E+13	3.18637E+07
32	5.74835E+12	3.41753E+18	3.92241E+07	2.46070E+08	1.13921E+14	3.59298E+07
31	6.04498E+12	3.99237E+18	2.79053E+07	2.88602E+08	1.38528E+14	4.13981E+07
30	6.32091E+12	4.59686E+18	2.01856E+07	3.35274E+08	1.67388E+14	4.77264E+07
29	6.24686E+12	5.22895E+18	1.39318E+07	3.90863E+08	2.00916E+14	5.71368E+07
28	5.99729E+12	5.85364E+18	9.38625E+06	4.53738E+08	2.40002E+14	7.02618E+07
27	5.73603E+12	6.45337E+18	6.32216E+06	5.26190E+08	2.85376E+14	8.68105E+07
26	5.26253E+12	7.02597E+18	4.12099E+06	6.04153E+08	3.37995E+14	1.10847E+08
25	4.71328E+12	7.55322E+18	2.62280E+06	6.90498E+08	3.98410E+14	1.44502E+08
24	4.11116E+12	8.02455E+18	1.61328E+06	7.86930E+08	4.67460E+14	1.93070E+08
23	3.36189E+12	8.43567E+18	9.49013E+05	8.72179E+08	5.46153E+14	2.67821E+08
22	2.66329E+12	8.77186E+18	5.30850E+05	9.59161E+08	6.33371E+14	3.80839E+08
21	1.95831E+12	9.03319E+18	2.78066E+05	1.01060E+09	7.29287E+14	5.59397E+08
20	1.38769E+12	9.23402E+18	1.39126E+05	1.02706E+09	8.30347E+14	8.22943E+08
19	8.47474E+11	9.37279E+18	6.35978E+04	9.53250E+08	9.33053E+14	1.21675E+09
18	5.13832E+11	9.45753E+18	2.90875E+04	8.08639E+08	1.02838E+15	1.70136E+09
17	2.93191E+11	9.50892E+18	1.27005E+04	6.36183E+08	1.10924E+15	2.28382E+09
16	1.53420E+11	9.53824E+18	5.06059E+03	4.43920E+08	1.17286E+15	2.96608E+09
15	7.79397E+10	9.55358E+18	1.92607E+03	2.80562E+08	1.21725E+15	3.68944E+09

Table 14. C. $\alpha = 10^{-8}$.

H(KM)	X	NX	Y	V	NV	W
50	9.10995E+10	0.	4.71199E+09	7.84225E+06	0.	2.06158E+08
49	1.24470E+11	9.10995E+15	3.91757E+09	1.34363E+07	7.84225E+11	2.31564E+08
48	1.65483E+11	2.15569E+16	3.18924E+09	2.27081E+07	2.12786E+12	2.57292E+08
47	2.21784E+11	3.81052E+16	2.53920E+09	3.86689E+07	4.39867E+12	2.83331E+08
46	2.97037E+11	6.02836E+16	1.97366E+09	6.47401E+07	8.26556E+12	3.05260E+08
45	3.95833E+11	8.99873E+16	1.50680E+09	1.04176E+08	1.47396E+13	3.18824E+08
44	5.26518E+11	1.29571E+17	1.13178E+09	1.60866E+08	2.51572E+13	3.23134E+08
43	6.93402E+11	1.82222E+17	8.47282E+08	2.34475E+08	4.12438E+13	3.18525E+08
42	9.03877E+11	2.51563E+17	6.35876E+08	3.25648E+08	6.46914E+13	3.09352E+08
41	1.14976E+12	3.41950E+17	4.82526E+08	4.28776E+08	9.72562E+13	2.99224E+08
40	1.41668E+12	4.56927E+17	3.69365E+08	5.39504E+08	1.40134E+14	2.91496E+08
39	1.79486E+12	5.98594E+17	2.83371E+08	6.78851E+08	1.94084E+14	2.86149E+08
38	2.17012E+12	7.78081E+17	2.14372E+08	8.34682E+08	2.61969E+14	2.85318E+08
37	2.67926E+12	9.95093E+17	1.62852E+08	1.02279E+09	3.45438E+14	2.87209E+08
36	3.14826E+12	1.26302E+18	1.21005E+08	1.22136E+09	4.47717E+14	2.98641E+08
35	3.57744E+12	1.57784E+18	8.82896E+07	1.46216E+09	5.69852E+14	3.17844E+08
34	3.92438E+12	1.93559E+18	6.40144E+07	1.72242E+09	7.16068E+14	3.47575E+08
33	4.19742E+12	2.32803E+18	4.57685E+07	2.01957E+09	8.88311E+14	3.90433E+08
32	4.41892E+12	2.74777E+18	3.22459E+07	2.37142E+09	1.09027E+15	4.48582E+08
31	4.52763E+12	3.18956E+18	2.23038E+07	2.77080E+09	1.32741E+15	5.29202E+08
30	4.62269E+12	3.64242E+18	1.57386E+07	3.20678E+09	1.60449E+15	6.23221E+08
29	4.40489E+12	4.10469E+18	1.04842E+07	3.71110E+09	1.92517E+15	7.68897E+08
28	4.03339E+12	4.54518E+18	6.75802E+06	4.25915E+09	2.29628E+15	9.80845E+08
27	3.68082E+12	4.94352E+18	4.36478E+06	4.87555E+09	2.72219E+15	1.25445E+09
26	3.20397E+12	5.31660E+18	2.72051E+06	5.49275E+09	3.20975E+15	1.65725E+09
25	2.73286E+12	5.63700E+18	1.66704E+06	6.13323E+09	3.75902E+15	2.21677E+09
24	2.28975E+12	5.91028E+18	9.99623E+05	6.80017E+09	4.37235E+15	2.99983E+09
23	1.83146E+12	6.13926E+18	5.86744E+05	7.28732E+09	5.05236E+15	4.11268E+09
22	1.44432E+12	6.32241E+18	3.35348E+05	7.73353E+09	5.78110E+15	5.66647E+09
21	1.08080E+12	6.46684E+18	1.84959E+05	7.83820E+09	6.55445E+15	7.86180E+09
20	7.90298E+11	6.57492E+18	9.95622E+04	7.68973E+09	7.33827E+15	1.08103E+10
19	5.03486E+11	6.65395E+18	5.05105E+04	6.90057E+09	8.10724E+15	1.47994E+10
18	3.18826E+11	6.70430E+18	2.56275E+04	5.72846E+09	8.79730E+15	1.93715E+10
17	1.90030E+11	6.73618E+18	1.25646E+04	4.47912E+09	9.37014E+15	2.47209E+10
16	1.05614E+11	6.75518E+18	5.74653E+03	3.19729E+09	9.81806E+15	3.09027E+10
15	6.16879E+10	6.76574E+18	2.68820E+03	2.26377E+09	1.01378E+16	3.74362E+10

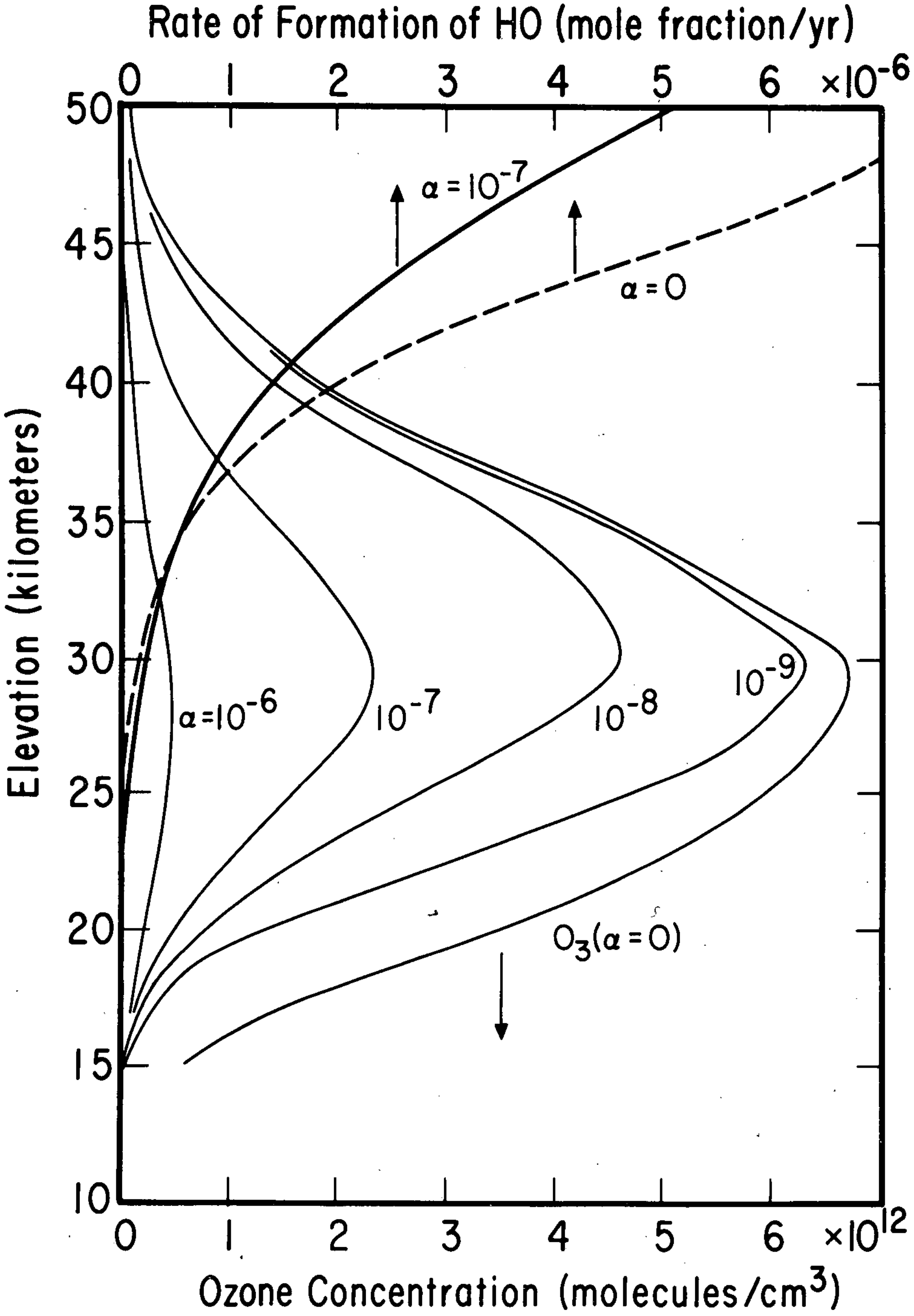
Table 14. D. $\alpha = 10^{-7}$.

H(KM)	X	NX	Y	V	NV	W
50	6.46876E+10	0.	3.35679E+09	7.36647E+07	0.	2.06634E+09
49	8.00849E+10	6.46876E+15	2.65472E+09	1.18084E+08	7.36647E+12	2.33192E+09
48	9.58635E+10	1.44772E+16	2.06220E+09	1.84670E+08	1.91749E+13	2.61533E+09
47	1.14694E+11	2.40636E+16	1.57674E+09	2.87327E+08	3.76419E+13	2.93267E+09
46	1.36977E+11	3.55330E+16	1.19745E+09	4.36644E+08	6.63746E+13	3.26336E+09
45	1.63902E+11	4.92306E+16	9.13172E+08	6.42530E+08	1.10039E+14	3.58747E+09
44	1.97765E+11	6.56208E+16	6.95162E+08	9.27966E+08	1.74292E+14	3.91203E+09
43	2.40809E+11	8.53973E+16	5.31098E+08	1.31017E+09	2.67088E+14	4.21983E+09
42	2.97583E+11	1.09478E+17	4.04834E+08	1.83144E+09	3.98106E+14	4.51856E+09
41	3.70334E+11	1.39237E+17	3.10178E+08	2.50102E+09	5.81250E+14	4.77898E+09
40	4.59158E+11	1.76270E+17	2.38791E+08	3.31310E+09	8.31352E+14	4.99690E+09
39	5.91949E+11	2.22186E+17	1.82726E+08	4.42534E+09	1.16266E+15	5.22466E+09
38	7.39837E+11	2.81381E+17	1.39119E+08	5.76048E+09	1.60520E+15	5.43952E+09
37	9.47427E+11	3.55364E+17	1.06447E+08	7.44430E+09	2.18124E+15	5.65570E+09
36	1.16425E+12	4.50107E+17	8.02612E+07	9.26075E+09	2.92567E+15	5.93925E+09
35	1.39069E+12	5.66532E+17	5.97833E+07	1.14968E+10	3.85175E+15	6.30320E+09
34	1.61019E+12	7.05601E+17	4.44097E+07	1.39309E+10	5.00143E+15	6.76906E+09
33	1.81818E+12	8.66620E+17	3.25857E+07	1.66995E+10	6.39452E+15	7.40053E+09
32	2.01737E+12	1.04844E+18	2.36081E+07	1.99638E+10	8.06447E+15	8.23615E+09
31	2.17294E+12	1.25017E+18	1.68504E+07	2.36294E+10	1.00609E+16	9.37058E+09
30	2.33236E+12	1.46747E+18	1.23234E+07	2.76843E+10	1.24238E+16	1.06157E+10
29	2.31726E+12	1.70070E+18	8.57421E+06	3.22031E+10	1.51922E+16	1.25969E+10
28	2.19422E+12	1.93243E+18	5.81310E+06	3.69292E+10	1.84125E+16	1.54708E+10
27	2.06086E+12	2.15185E+18	3.97532E+06	4.22003E+10	2.21055E+16	1.90997E+10
26	1.83792E+12	2.35794E+18	2.65873E+06	4.71946E+10	2.63255E+16	2.43054E+10
25	1.60170E+12	2.54173E+18	1.77036E+06	5.21949E+10	3.10450E+16	3.13051E+10
24	1.36993E+12	2.70190E+18	1.17062E+06	5.72524E+10	3.62644E+16	4.07476E+10
23	1.11945E+12	2.83889E+18	7.69452E+05	6.05134E+10	4.19897E+16	5.34866E+10
22	9.04426E+11	2.95084E+18	4.99847E+05	6.34941E+10	4.80410E+16	7.05059E+10
21	6.96631E+11	3.04128E+18	3.17727E+05	6.37307E+10	5.43904E+16	9.32693E+10
20	5.27717E+11	3.11094E+18	1.98696E+05	6.24515E+10	6.07635E+16	1.22548E+11
19	3.52271E+11	3.16372E+18	1.21563E+05	5.66231E+10	6.70087E+16	1.60377E+11
18	2.36874E+11	3.19894E+18	7.29699E+04	4.85209E+10	7.26710E+16	2.02479E+11
17	1.55142E+11	3.22263E+18	4.38566E+04	4.08000E+10	7.75231E+16	2.51200E+11
16	1.04154E+11	3.23814E+18	2.66531E+04	3.45284E+10	8.16031E+16	3.06472E+11
15	8.64355E+10	3.24856E+18	1.88841E+04	3.41154E+10	8.50559E+16	3.62885E+11

Fig. 7. Five calculated ozone profiles by the method of Part IIB for various uniform mole fractions of NO_x. The upper curves are the rate of formation of hydroxyl radicals in units of mole fraction for year (compare Fig. 2).

Fig. 8. Relative ozone concentration as a function of NO_x at various elevations.

Fig. 9. Relative ozone column as a function of uniform mole fraction of NO_x by the method of Part IIB.



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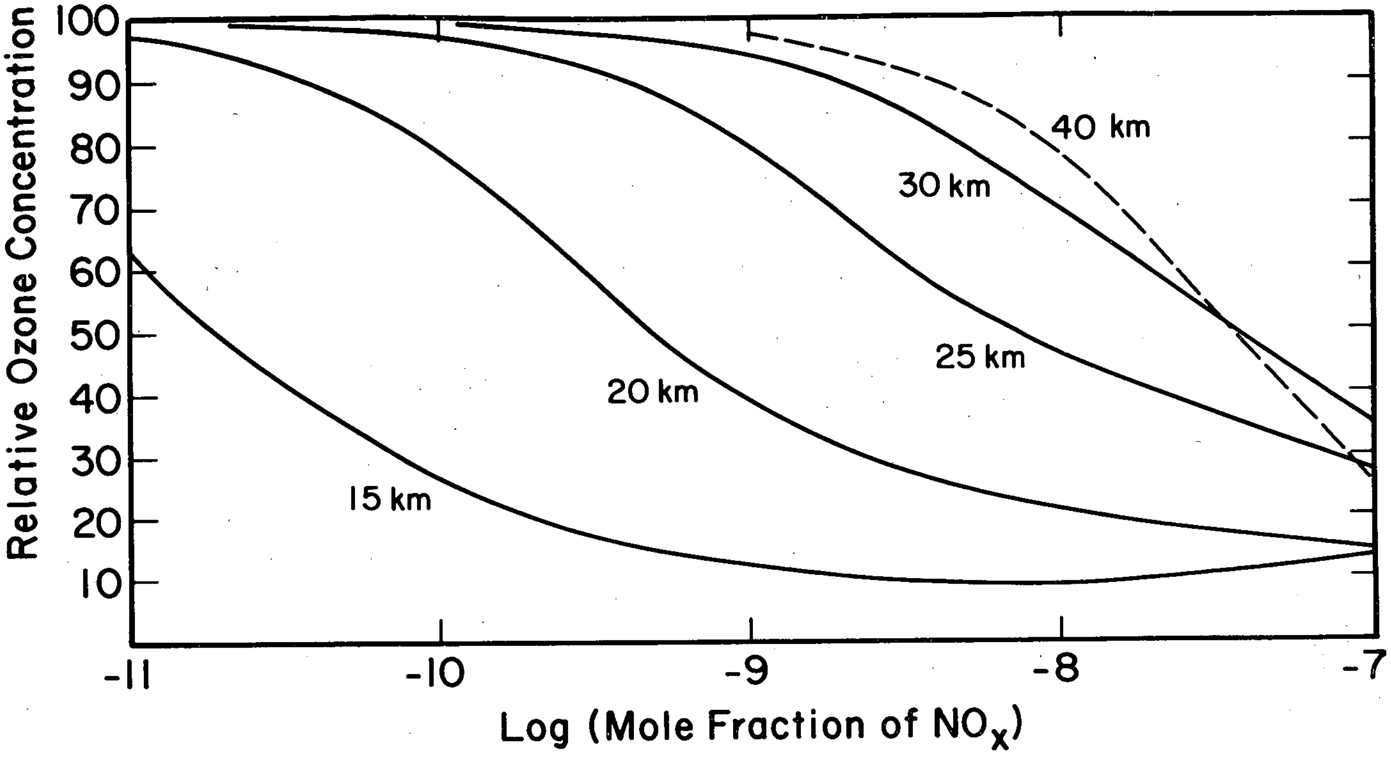

Fig. 8

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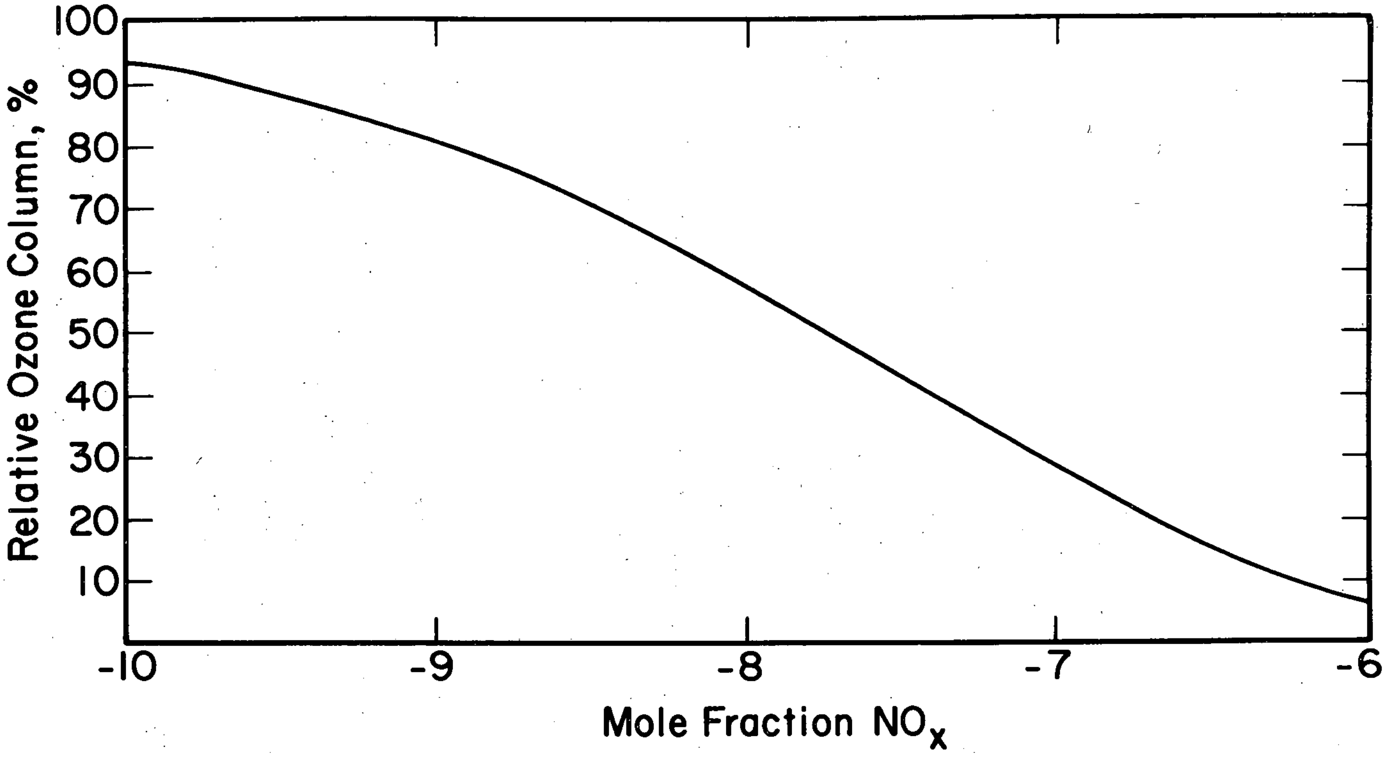

Fig. 9

XBL 716-6847

As pointed out in the introduction to Part II, a steady-state calculation for the effect of NO_x on ozone is an artificial exercise that cannot include all the details of the stratosphere. For the standard conditions (45° latitude, solar equinox, standard temperature profile), there is a large reduction of ozone by NO_x. It is necessary to see if this large sensitivity of ozone to NO_x is a peculiarity of the standard conditions or if it obtains more generally. It is desirable, therefore, to explore a wide range of conditions in terms of ozone profiles. With this wide range of conditions, it is convenient to summarize the profiles in terms of a small number of parameters, since complete tables of data or a figure for each profile takes up entirely too much space. The ozone profiles are characterized here by five quantities: N_x, the integrated vertical column of ozone in units of molecules per cm^2; X_m, the maximum concentration of ozone in units of molecules per cm^3; the elevation where ozone has its maximum concentration; the lower elevation where the ozone concentration is one-tenth the value at the maximum; and the upper elevation where ozone is one-tenth the value at the maximum. Such data are given in Table 15.

The standard conditions represent the first bloc in Table 15A, and these condensed results can be compared with the more extensive data given in previous figures and tables. The standard temperature profile was decreased by 10°C at every level of the stratosphere. The absolute value of the ozone column was increased by about 10%, but the relative decrease with added NO_x is very nearly the same as for the standard case. Likewise, the temperature profile was increased by 10°C at each level. The absolute value of the ozone column was decreased by about 10%, but the effect of NO_x on ozone is about the same as for the standard case.

Table 15. Total ozone vertical column N_x, maximum ozone concentration X_m, and elevations at X_m and $X_m/10$.

A. Effect of temperature, uniform mole fractions of NO_x.

α	Λ degrees	T	$10^{-18}N_x$ molecules/cm^2	$10^{-12}X_m$ molecules/cm^3	Elevation (km) X_m	$X_m/10$	
0	45	st.	11.87	6.71	29	15	44
10^{-11}			11.68	6.70	29	16	44
10^{-10}			11.09	6.66	29	17	44
10^{-9}			9.58	6.32	30	18	44
10^{-8}			6.81	4.62	30	19	44
10^{-7}			3.37	2.33	30	18	43
10^{-6}			0.87	0.47	28	<15	43
0		st.-10°C	13.14	7.34	30	15	45
10^{-11}			12.96	7.33	30	15	45
10^{-10}			12.34	7.28	30	17	45
10^{-9}			10.70	6.85	30	18	45
10^{-8}			7.72	4.94	30	18	45
10^{-7}			4.07	2.69	30	18	44
10^{-6}			1.17	0.62	29	<15	43
0		st.+10°C	10.74	6.16	29	15	43
10^{-11}			10.54	6.16	29	16	43
10^{-10}			9.96	6.12	29	17	43
10^{-9}			8.55	5.78	29	18	43
10^{-8}			6.00	4.27	30	19	44
10^{-7}			2.80	2.00	30	18	43
10^{-6}			0.66	0.36	27	<15	44

Table 15. B. Effect of latitude. Standard temperatures, uniform mole fraction of NO_x.

α	Λ	$10^{-18}N_x$ molecules/cm^2	$10^{-12}X_m$ molecules/cm^3	Elevation (km)		
				X_m	$X_m/10$	
0	0	17.50	9.66	27	<15	43
10^{-10}		16.53	9.57	27	15	43
10^{-9}		14.14	9.09	29	17	43
10^{-8}		10.06	6.90	30	18	43
10^{-7}		5.02	3.52	29	17	41
0	15	17.26	9.30	27	<15	43
10^{-10}		15.89	9.21	27	16	43
10^{-9}		13.60	8.77	29	17	43
10^{-8}		9.68	6.64	30	18	43
10^{-7}		4.82	3.39	29	17	41
0	30	15.15	8.30	29	<15	43
10^{-10}		14.02	8.25	29	16	43
10^{-9}		12.04	7.82	29	17	43
10^{-8}		8.57	5.88	30	18	44
10^{-7}		4.26	2.98	29	17	42
0	45	11.87	6.71	29	15	44
10^{-10}		11.09	6.66	29	17	44
10^{-9}		9.58	6.32	30	18	44
10^{-8}		6.81	4.62	30	19	44
10^{-7}		3.37	2.33	30	18	43
0	60	7.74	4.60	30	17	45
10^{-10}		7.34	4.56	30	18	45
10^{-9}		6.40	4.25	30	20	45
10^{-8}		4.56	2.96	32	20	46
10^{-7}		2.27	1.50	30	19	45
0	75	3.37	1.98	32	20	48
10^{-10}		3.24	1.96	33	21	48
10^{-9}		2.88	1.84	34	22	48
10^{-8}		2.07	1.31	35	23	49
10^{-7}		1.09	0.60	34	22	49

Table 15. C. Steady-state ozone column N_x, maximum ozone X_m, and elevations at X_m and $X_m/10$ for a model of fixed solar angle ϕ.

α	ϕ degrees	$10^{-18}N_x$ molecules/cm^2	$10^{-12}X_m$ molecules/cm^3	Elevation (km)		
				X_m	$X_m/10$	
0	0	15.12	8.88	30	15	43
10^{-10}		14.42	8.84	30	16	43
10^{-9}		12.88	8.55	30	18	43
10^{-8}		9.83	6.81	30	18	43
10^{-7}		5.53	3.89	30	18	43
0	30	12.73	7.60	30	16	44
10^{-10}		12.21	7.56	30	17	44
10^{-9}		10.95	7.27	30	18	44
10^{-8}		8.38	5.70	30	19	44
10^{-7}		4.71	3.29	30	18	43
0	40	10.98	6.62	30	17	44
10^{-10}		10.57	6.59	30	18	44
10^{-9}		9.52	6.31	30	19	44
10^{-8}		7.30	4.93	30	19	45
10^{-7}		3.11	2.82	30	19	44
0	50	8.86	5.39	30	17	45
10^{-10}		8.58	5.35	30	18	45
10^{-9}		7.79	5.09	30	19	45
10^{-8}		5.98	3.99	32	20	45
10^{-7}		3.39	2.24	30	19	45
0	60	6.49	3.93	30	19	46
10^{-10}		6.34	3.90	30	20	46
10^{-9}		5.79	3.74	32	21	46
10^{-8}		4.48	2.97	44	21	47
10^{-7}		2.57	1.58	32	20	47

Adhering to the standard temperature distribution, I calculated the steady-state ozone profiles for 0, 15, 30, 45, 60, and 75 degrees latitude, all at solar equinox. The results are summarized in Table 15B. There is a wide variation in the calculated ozone profile for no NO_x, but in all cases the fractional reduction with added NO_x is about the same as for the standard case. (The absolute values and the height of the maximum concentration as a function of latitude are discussed further in Part III).

To compare the method of averaging radiation intensities over all solar angles with the method of making the calculation with a single average angle, I give in Table 15C the results for five fixed solar angles between zero and 60 degrees. It is interesting that the steady-state ozone for a fixed solar angle (compare zero, 30, or 60 degrees between Table 15B and 15C) is less than for the daylong average at that latitude. This difference is based on the well known fact that ozone depends on the <u>ratio</u> of $\underline{j_a}$ to $\underline{j_c}$, not the absolute value. For this model, too, NO_x has a very strong effect on the ozone steady-state concentration.

<u>Non-Uniform NO_x Mole Fractions</u>

If the initial stratosphere had no NO_x and if NO_x was distributed with an equal mole fraction throughout the stratosphere, the ozone column (Fig. 9) for the four cases of NO_x from SST as given by Table 1 (relative to 100% for no NO_x) would be respectively: 33%, 47%, 62% and 73%. Of course, there must now be NO_x in the stratosphere by virtue of the observed NO in the mesosphere[17,18] and the region of the stratosphere (Figs. 2 and 3) where NO is converted to HNO_3. Also NO_x is injected at 20 km, not uniformly distributed. With NO_x injected at 20 km, slowly converted to HNO_3 in the upper stratosphere and lost by turbulence to the troposphere in the lower stratosphere (eventually washing out in rain), there would never be a uniform distribution, but rather there would be a distribution function centered in the stratospheric air layer of SST flight (20 km originally and pushed downward by subsidence toward the polar regions).

To assess the effect of non-uniform mole fraction of NO_x in the stratosphere, calculations were made for cases where log α varied linearly by one unit between 15 and 50 km, with the value at 50 km taken to be -9, -8, or -7. Similarly log α was allowed to vary linearly by two units between 15 and 50 km, again with the value at 50 km taken to be -9, -8, or -7. The results are given in Table 16A.

Observed ozone profiles[43,44,45] were compared with the calculated ones. It was concluded that so much ozone is observed at 20 km that the mole fraction of NO_x cannot be much above 10^{-9} at this elevation. In Part I a study was made of the region of the stratosphere where NO is converted to HNO_3. Nitric acid is both formed and photolyzed high in the stratosphere, and it is expected to become relatively inert to photolysis and destruction by hydroxyl radicals only toward the lower stratosphere, probably between 30 and 25 km. The NO_x incident on the top of the stratosphere would be 5×10^{-8} according to Meira or about 3×10^{-7} according to Pearce. It is not clear to me whether the difference between these two results is all a matter of improved techniques on Meira's part or whether there are large real differences in mesospheric NO from time to time and from place to place. At any rate we take models of NO_x at 50 km between 10^{-7} and 7.9×10^{-7}. With NO_x fixed at 50 km, slowly decreasing from 50 to 30 km, rapidly decreasing from 30 to 25 km, and fixed at 10^{-9} at 20 km, eleven different non-uniform models of NO_x were constructed, Table 17. These models are taken as possible natural background distributions of NO_x in the

Table 16. Ozone Vertical column N_x, maximum ozone concentration X_m for non-uniform mole fractions of NO_x.

A. Linear variation with elevation of log α between 15 to 50 km.

α 15 km	α 50 km	$10^{-18}N_x$	$10^{-12}X_m$	Elevation (km) X_m	$X_m/10$	
0	0	11.87	6.71	29	15	44
10^{-10}	10^{-9}	10.88	6.60	30	17	44
10^{-9}	10^{-8}	8.90	5.94	30	18	44
10^{-8}	10^{-7}	5.61	4.04	30	18	42
10^{-11}	10^{-9}	11.59	6.69	29	16	44
10^{-10}	10^{-8}	10.58	6.51	30	17	44
10^{-9}	10^{-7}	8.00	5.61	30	18	42

B. Non-uniform mole fractions of NO_x as given in Table 17.

Number	$10^{-18}N_x$	$10^{-12}X_m$	X_m	$X_m/10$	
(1)	9.14	7.01	27	18	41
(2)	9.13	7.13	27	18	40
(3)	9.12	7.25	27	18	40
(4)	9.11	7.36	27	18	39
(5)	8.28	6.94	26	18	40
(6)	8.28	7.05	26	18	39
(7)	8.27	7.15	26	18	38
(8)	8.26	7.29	27	18	38
(9)	7.44	6.57	25	17	38
(10)	7.43	6.64	25	17	37
(11)	7.43	6.70	25	17	36

Table 17. Eleven non-uniform distribution of oxides of nitrogen in terms of log α , where α = $[NO_x]/[M]$.

km Number	15	20	25	30	35	40	45	50
(1)	-9.0	-9.0	-9.0	-8.0	-7.75	-7.50	-7.25	-7.00
(2)	-9.0	-9.0	-9.0	-8.0	-7.68	-7.35	-7.02	-6.7
(3)	-9.0	-9.0	-9.0	-8.0	-7.60	-7.20	-6.80	-6.4
(4)	-9.0	-9.0	-9.0	-8.0	-7.52	-7.05	-6.58	-6.1
(5)	-9.0	-9.0	-8.5	-7.50	-7.38	-7.25	-7.12	-7.00
(6)	-9.0	-9.0	-8.5	-7.50	-7.30	-7.10	-6.90	-6.70
(7)	-9.0	-9.0	-8.5	-7.50	-7.22	-6.95	-6.76	-6.40
(8)	-9.0	-9.0	-8.5	-7.50	-7.15	-6.80	-6.45	-6.10
(9)	-9.0	-9.0	-8.0	-7.00	-6.92	-6.85	-6.78	-6.70
(10)	-9.0	-9.0	-8.0	-7.00	-6.85	-6.70	-6.55	-6.40
(11)	-9.0	-9.0	-8.0	-7.00	-6.78	-6.55	-6.32	-6.10

stratosphere. (When the rate constants for the conversion of NO_2 to HNO_3 are found, it would, of course, be desirable to solve for the stratospheric distribution of NO_x as a combined problem of reaction rates and vertical diffusion). The results in terms of ozone column, maximum ozone concentration and its elevation, and the elevations where ozone has one tenth the maximum value are given in Table 16B. With these models, the calculated ozone column is about the same as that observed at 45° latitude.

A computer "experiment" was carried out with the eleven non-uniform models of NO_x as specified in Table 17. The two-year accumulation of NO_x from SST operation was distributed uniformly worldwide to various depths of the stratosphere: 20 to 21, 19 to 23, 18 to 25, 17 to 27, 16 to 29, and 15 to 31 km. These uniform horizontal increments of NO_x were added to the pre-existing amounts, based on the model of Table 17, and the steady-state concentration of ozone was calculated at each elevation. For model number 5 of Table 17 (which is also case V of Table 9) the results are presented graphically in Fig. 10. Figure 10A including the dotted line is the basic, background ozone profile with NO_x according to Table 17, number 5. The solid line of Fig. 10A represents the steady-state profile with NO_x from the SST distributed uniformly, worldwide between 20 and 21 km. For this situation the ozone column is reduced to 97% of its pre-existing value. Figure 10B shows the effect of NO_x added uniformly between 19 and 23 km, and the ozone column is reduced to 88%. Figure 10C shows the spread of added NO_x from 17 to 27 km, for which the ozone column is reduced to 77%. With further spread, 15 to 31 km (Fig. 10D) the ozone column increases relative to Fig. 10C, and it is 80% of the original. Following the policy of the SCEP report of treating a situation ten times worse than the

Fig. 10. Effect of injection of NO_x at 20 km into the pre-existing NO_x profile given by number 5 in Table 17. A through D, worldwide distribution of two year accumulation of NO_x; E through H, ten times higher dose over heavily traveled region of world. Additional NO_x spread as follows: A and E, between 20 and 21 km; B and F, between 19 and 23 km; C and G, between 17 and 25 km; D and H, between 15 and 31 km. The ozone columns relative to that before the insertion of NO_x at 20 km are: A, 97%; B, 88%; C, 77%; D, 80%; E, 97%; F, 86%; G, 58%; H, 50%.

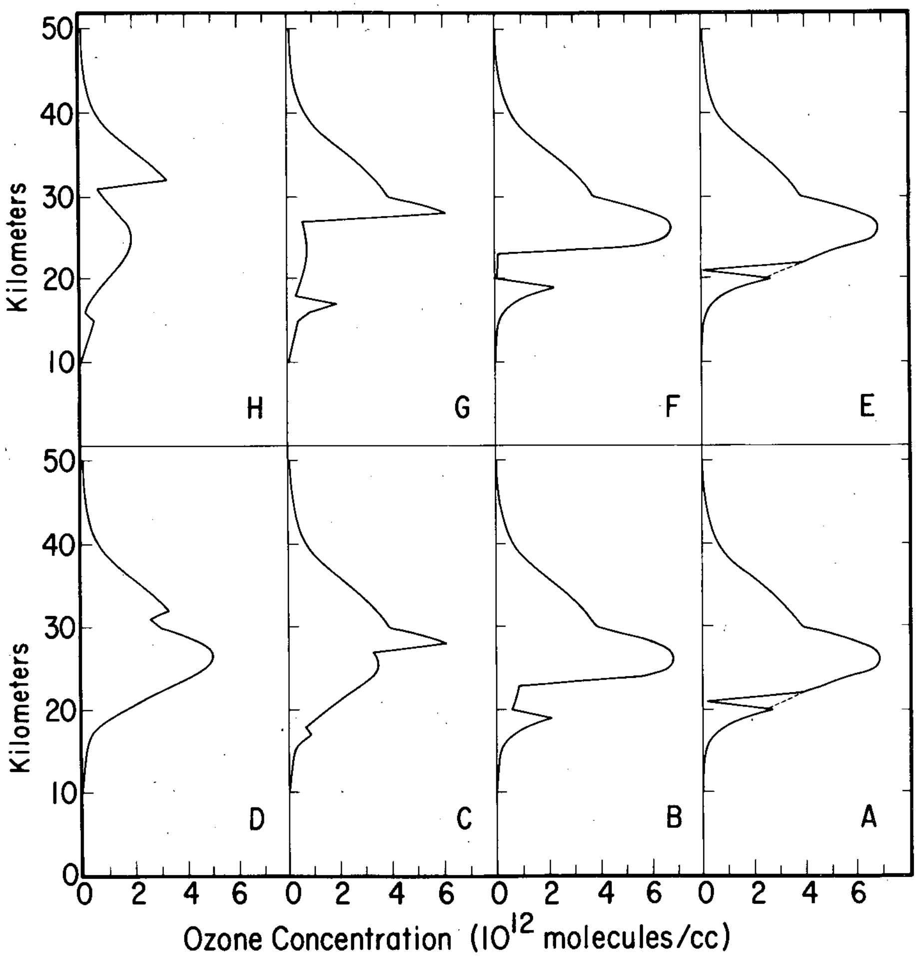

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Fig. 10

Table 18A. Two year burden of SST exhaust spread in a world-wide uniform shell to various thicknesses about the injection level at 20 km. for the eleven non-uniform distributions of NO_x as given by Table 17.

		O_3 column in units of 10^{18} molecules/cm^2						
Number		none	20-21	19-23	18-25	17-27	16-29	15-31
(1)	N_x	9.14	8.95	8.27	7.50	7.02	6.95	7.07
	%	100	98	91	82	77	76	77
(2)	N_x	9.13	8.94	8.26	7.48	7.00	6.93	7.05
	%	100	98	90	82	77	76	77
(3)	N_x	9.12	8.93	8.24	7.46	6.98	6.91	7.04
	%	100	98	90	82	77	76	77
(4)	N_x	9.11	8.92	8.23	7.44	6.96	6.90	7.02
	%	100	98	90	82	76	76	77
(5)	N_x	8.28	8.05	7.31	6.67	6.40	6.51	6.65
	%	100	97	88	81	77	79	80
(6)	N_x	8.28	8.04	7.30	6.65	6.40	6.50	6.65
	%	100	97	88	80	77	78	80
(7)	N_x	8.27	8.03	7.29	6.64	6.41	6.49	6.65
	%	100	97	88	80	78	79	80
(8)	N_x	8.26	8.03	7.28	6.63	6.39	6.48	6.64
	%	100	97	88	80	77	78	80
(9)	N_x	7.44	7.15	6.32	5.88	5.86	5.99	6.13
	%	100	96	85	79	79	81	82
(10)	N_x	7.43	7.15	6.31	5.87	5.85	5.98	6.12
	%	100	96	85	79	79	81	82
(11)	N_x	7.43	7.14	6.31	5.87	5.84	5.97	6.12
	%	100	96	85	79	79	80	82

Table 18B. Local maximum of NO_x is assumed to be ten times as high as that for A.

			O_3 column in units of 10^{18}, molecules/cm^2					
Number		none	20-21	19-23	18-25	17-27	16-29	15-31
(1)	N_x	9.14	8.94	8.12	6.97	5.79	4.91	4.49
	%	100	98	89	76	63	54	49
(2)	N_x	9.13	8.93	8.11	6.95	5.75	4.86	4.44
	%	100	98	89	76	63	53	49
(3)	N_x	9.12	8.92	8.09	6.93	5.72	4.81	4.38
	%	100	98	89	76	63	53	48
(4)	N_x	9.11	8.91	8.08	6.91	5.69	4.76	4.34
	%	100	98	89	76	63	52	48
(5)	N_x	8.28	8.03	7.10	5.95	4.89	4.31	4.16
	%	100	97	86	72	58	52	50
(6)	N_x	8.28	8.03	7.09	5.93	4.86	4.26	4.12
	%	100	97	86	72	59	52	50
(7)	N_x	8.27	8.02	7.08	5.91	4.83	4.22	4.08
	%	100	97	86	71	58	51	49
(8)	N_x	8.26	8.01	7.07	5.90	4.80	4.18	4.05
	%	100	97	86	71	58	51	49
(9)	N_x	7.44	7.13	6.03	4.95	4.15	3.84	3.86
	%	100	96	81	67	56	52	52
(10)	N_x	7.43	7.13	6.02	4.93	4.13	3.82	3.84
	%	100	96	81	66	56	51	52
(11)	N_x	7.43	7.13	6.02	4.92	4.11	3.80	3.82
	%	100	96	81	66	55	51	51

worldwide average as a probable high-traffic situation, I repeated the injection calculations for a ten-fold heavier dose of NO_x. The effect of this injection on the ozone profile is shown as Fig. 10E through H. The ozone column for these four spreads of NO_x relative to Number 5 natural background is respectively: 97%, 86%, 58%, 50%. These calculations were made for all eleven non-uniform models in Table 17. The results in terms of ozone column and ozone column relative to no added NO_x are given in Table 18. The total NO_x assumed to be in the stratosphere varies substantially for the eleven cases given in Table 17. However, the effect of various horizontal shells of added NO_x does not differ greatly for all the cases of 18A or for all the cases of 18B.

The points, $\alpha = 2.4 \times 10^{-9}$ and 2.4×10^{-8}, of Fig. 9 give the calculated reduction of the ozone column for cases II and IV of Table 1, if the NO_x from the SST spread uniformly over the stratosphere with no pre-existing NO_x. The two examples in Fig. 10 treat essentially the same two cases, II and IV, in more nearly realistic terms: a pre-existing NO_x distribution (consistent with observed NO and HNO_3) and insertion of NO_x at the cruise height of the SST. In each case, the uniform, vertical or non-uniform, horizontal insertions indicate a reduction of the ozone column to about 3/4 the present value for case IV and to about 1/2 the present value for case II.

Summary of Part II

Although the calculation of steady-state profiles of ozone on the basis of photochemical theory gives an incomplete account of all the variables of the stratosphere, such calculations have been made for a wide range of conditions, and in every case it is found that NO_x has a profound effect in reducing the steady-state ozone column. These calculations over a wide range of conditions give strong evidence for the vulnerability of the stratosphere to added, man-made NO_x.

PART III. THE REAL STRATOSPHERE

The calculations of Parts I and II are compared with some observations of the real stratosphere in this section, and certain variables not previously considered are discussed here.

A widely used measure of the ozone vertical column is the thickness in centimeters or millimeters (or other units) of a column of gas at one atmosphere pressure and 0°C containing the same number of molecules as the actual vertical column. One cubic centimeter of gas at standard temperature and pressure (STP) contains 2.687×10^{19} molecules. Typical observed columns of ozone are 0.2 to 0.4 cm or about $(5 \text{ to } 10) \times 10^{18}$ molecules/cm^2. Sometimes the concentration of ozone is expressed in units of mm STP of ozone per kilometer of height. One mm (STP)/km is 2.687×10^{13} molecules/cm^3.
Three classic distributions of ozone as obtained by rocket flights[43] are given in Figure 11, together with the calculated ozone profile for 45° latitude, solar equinox, and no NO_x. Since the observed curves were obtained and published, there have been some refinements in the cross section for ozone absorption by ultraviolet radiation, but the basic structure is still of interest: the ozone column at one location is variable from time to time, the calculated curve is too high in the upper stratosphere and it agrees with the observed curves around 20 km.

There is a worldwide network of meteorological stations that regularly measure the ozone column and shape by the "umkehr" method.[44] These results are correlated, and published by meteorological Branch of the Canadian Department of Transport in Cooperation with the World Meteorological Organization. For the volume published as 1968 (some

Fig. 11. Comparison of calculated ozone profile with no oxides of nitrogen with three observed profiles of ozone as observed by rocket soundings.

Fig. 12. Comparison of calculated ozone vertical column at different latitudes with observed values from stations all over the world. The effect of temperature at 45° latitude is shown by the bar graphs.

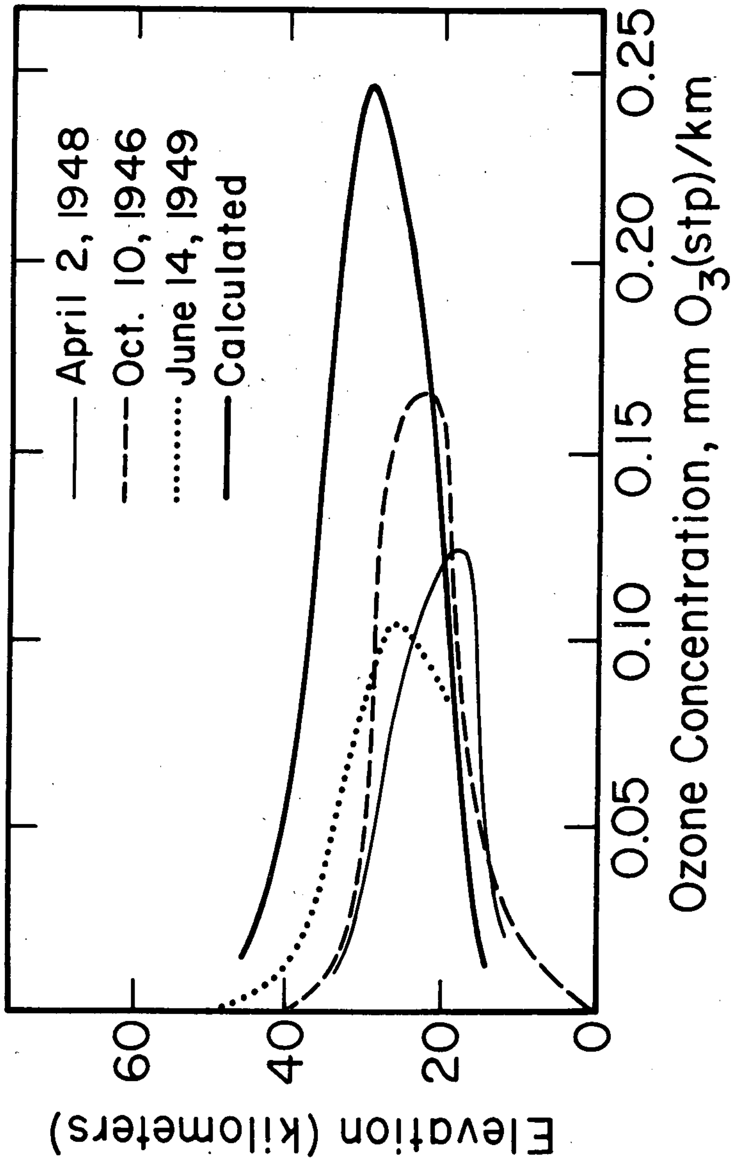

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Fig. 11

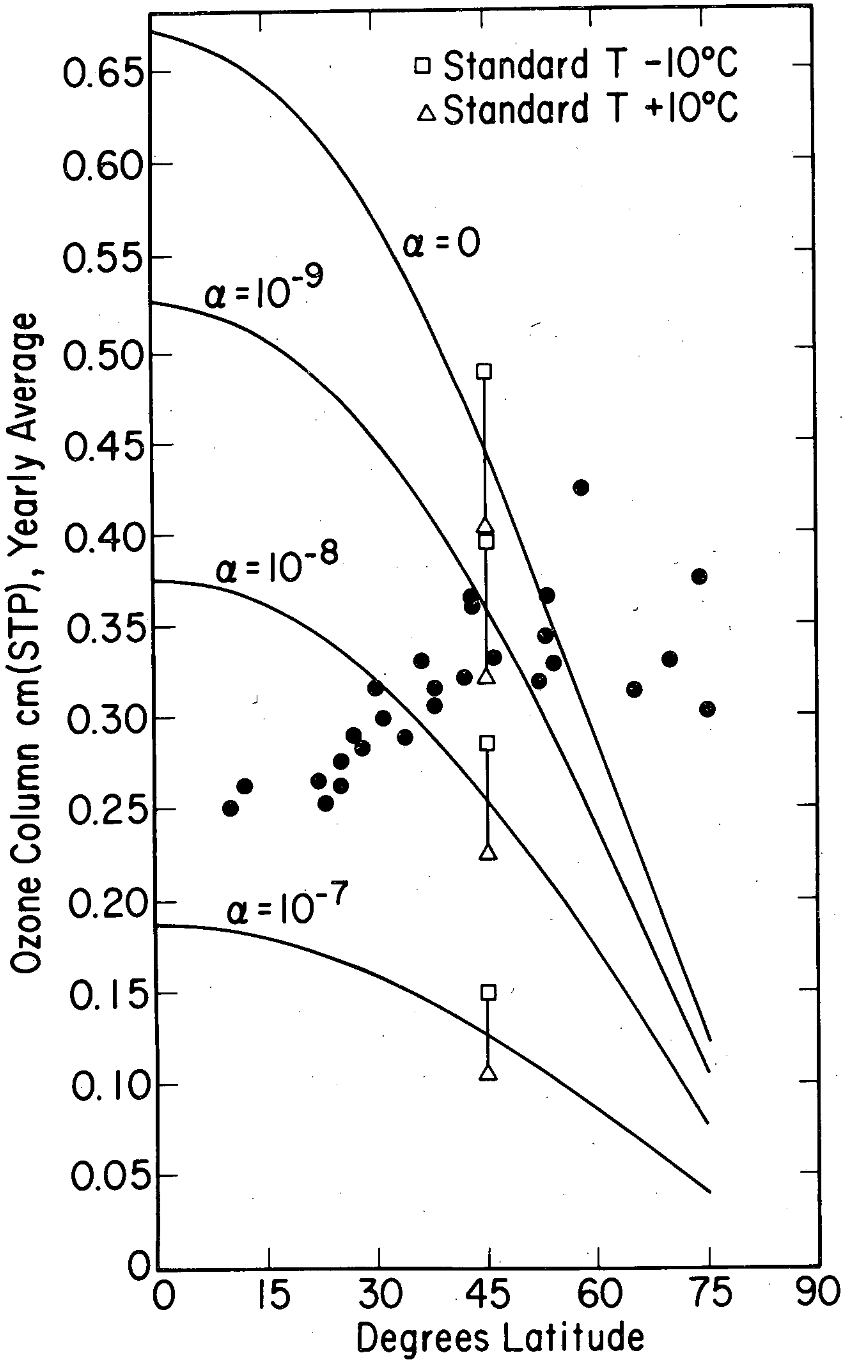

Fig. 12

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data go back to 1958 though most was for 1967 and 1968) there were 27 stations with averages for "all years" of observation and which varied in latitude from 12S to 75S and from 10N to 74N. The all year averages, ozone column in cm, are plotted in Figure 12. There is an increase in the ozone column from about 0.25 ± 0.02 cm around 15° to 0.36 ± 0.06 cm between 60° and 75°. The calculated steady-state curves (Table-15B) show a strong decrease from the equator toward the poles. This effect has long been observed and in general understood, as this quotation from Dütsch[38] shows:

> "The mean value over the earth of the total amount of ozone is fairly well reproduced by the theory - - - Complete disagreement, however, is obtained with respect to seasonal and latitudinal variations of the total ozone. The theory suggests a maximum value at the equator, where observations show a pronounced minimum. - - - This striking discrepancy does not disprove the photochemical theory, but it shows that the ozone distribution is also influenced otherwise, namely, through transport by air motions."

In his calculations Dütsch (1961) used rate constants for reactions b and e that were obtained in the 1930's and that have been greatly changed by numerous recent reinvestigations. By using modern values of the solar flux and of the rate constants[10] k_b and k_e, I disagree with Dütsch's first sentence quoted above: Figure 12, for the stratosphere with no oxides of nitrogen. The mean value over the earth of the total amount of ozone is fairly well represented by theory if the oxides of nitrogen in the stratosphere average between 10^{-8} and 10^{-9} mole fractions (when the rate constant k_3 becomes known, it may be that water vapor in the upper stratosphere will be found to have a non-negligible effect on the ozone column).

The other point raised by Dütsch in the quotation above is of great pertinence to this problem. There is large scale vertical motion above the equator, and transport toward the poles with subsidence. As Paetzold[45] has emphasized, sometimes the ozone profile at 70° latitude has not one maximum as given by photochemical theory but two or three peaks, occuring for example at 22, 18, and 10 km. These low-lying multiple peaks represent successive waves of subsidence of the stratospheric ozone band.

As can be seen from Table 15B, the elevation for the ozone peak is calculated to increase from 27 km at the equator to 32 km at 75° latitude. The observed trend is just the opposite; for example, Epstein and Adel showed a smooth graph of decreasing height of the ozone peak from 29 km at 10° latitude to 22 km at 75° latitude.[46] Again the results indicate subsidence of the ozone layer in the polar areas and transport from equatorial to polar regions.

In considering the real stratosphere it is important to be quantitative in comparing ozone relaxation times with stratospheric transport times and vertical mixing times. Where ozone is in large excess over oxygen atoms, $d([O_3] + [O])/dt$, of Eq. (31) may be approximated by $d[O_3]/dt$. The oxygen atom concentration in Eq. (31) may be approximated by Eq. (62). In this case the differential equation for ozone is

$$\frac{d[O_3]}{dt} = 2\, j_a[O_2] - \frac{2\, j_c\, k_e \rho\, [O_3]^2}{k_b\, [M][O_2]} \qquad (72)$$

Since this is a second-order equation the half time is not a constant but depends on initial ozone concentration. The half-time to go from zero ozone to half the steady-state concentration of ozone is

$$\tau_{1/2} = \frac{\ln 3}{4} \left(\frac{k_b[M]}{j_a j_c k_e \rho} \right)^{\frac{1}{2}} \qquad (73)$$

where ρ is the catalytic ratio, Eq. (25). For the standard photochemical conditions used in Part II, the half-times for zero NO_x and for a mole fraction of 10^{-8} are given in Table 19. With no NO_x, the ozone half-time at is 700 years at 15 km, 27 years at 20 km, 2.7 years at 25 km, decreasing to 11 hours at 45 km. Even for $\alpha = 10^{-8}$, the halftime is 12 years at 15 km and 1.4 years at 20 km. For $\alpha = 10^{-9}$ the half times below 25 km exceed those for $\alpha = 10^{-8}$ by about a factor of three.

Near the cruising height of the SST there an four processes of about the same, long lifetime:

(1) The accumulation of NO_x from the exhaust would occur with a half-time of about 2 years, as limited by vertical mixing to the top and to the bottom of the stratosphere (Table 1).

(2) The transport from the equatorial region toward the polar region and the waves of subsidence in the temperate and polar regions are driven by the annual cycles of the earth.

(3) The photochemical relaxation time for odd oxygen is about 2 ± 1 years at 20 km (depending on the concentration of NO_x there) and much longer at lower elevations.

(4) The conversion of NO and NO_2 to HNO_3 in the stratosphere probably (Tables 9 and 10) occurs with a half-time between $\frac{1}{2}$ and 3 years.

Table 19. Time for ozone to reach one-half the steady-state value, starting with zero ozone (45° latitude, solar equinox).

Elevation km	15	20	25	30	35	40	45	α
log M	18.60	18.27	17.93	17.50	17.26	16.92	16.60	
log k_b	-32.61	-32.58	-32.63	-32.67	-32.73	-32.85	-32.92	
log k_e	-15.06	-15.10	-15.01	-14.92	-14.78	-14.55	-14.41	
log k_g	-11.38	-11.38	-11.37	-11.36	-11.34	-11.30	-11.28	
log j_a	-17.02	-14.49	-12.98	-11.67	-10.65	-9.91	-9.44	0
	-15.79	-13.66	-12.41	-11.37	-10.51	-9.85	-9.42	10^{-8}
log j_c	-3.74	-3.73	-3.72	-3.68	-3.58	-3.33	-2.80	0
	-3.71	-3.70	-3.69	-3.66	-3.54	-3.28	-2.77	10^{-8}
log $\tau_{\frac{1}{2}}$/sec	10.34	8.94	7.94	6.99	6.21	5.37	4.61	0
	8.59	7.65	7.12	6.55	5.96	5.20	4.51	10^{-8}
$\tau_{\frac{1}{2}}$ yr	700	27	2.7					0
day				113	19	2.7	0.47	0
$\tau_{\frac{1}{2}}$ yr	12	1.4						10^{-8}
day			150	42	11	1.8	0.38	10^{-8}
ρ	178	52	10.8	3.53	2.12	1.68	1.36	10^{-8}

With four superimposed, slow processes, all with half-times the order of magnitude of a year or so, it becomes an exceedingly difficult problem to calculate the exact effect of SST flights on the stratosphere. It was pointed out in Part I that for all values of temperature and concentrations of NO and O (or on the other hand concentrations of NO_2 and O_3) NO_x increased the rate of destruction of ozone relative to no NO_x, and thus diffusion and transport of NO_x in the stratosphere primarily carries a serious problem from one place to another; diffusion and transport does not remove the problem altogether nor even diminish it appreciably. It was pointed out in Part II that steady-state calculations all indicated a large reduction in ozone by added NO_x. There may not be time to achieve the steady state at low elevations in the stratosphere, but the time (Table 6) for added NO_x to destroy O_3 is short. In all cases the direction of change is that of reduction of ozone by added NO_x. Since NO_x reduces ozone everywhere in the stratosphere, diffusion and transport complicate but do not eliminate the problem.

What is the degree of certainty of these calculations? What alternatives would make NO_x from the SST a less serious problem? What would make the situation worse than indicated here? If the chemical species nitric oxide and nitrogen dioxide, NO and NO_2 as such, build up in the stratosphere to the amounts expected by the SCEP report or as reduced by the factor 0.35 (the four cases of Table 1), then it is virtually a certainty that there would be a major reduction of ozone; the rate constants are so well known and the elementary reactions are so nearly independent of the environment that the species NO and NO_2 as such would have a large destructive effect on ozone. However, if chemical reactions convert NO and NO_2 to other chemical species, for example, nitric acid, then the situation depends on the properties of HNO_3, not NO and NO_2. There are at least two mechanisms that convert NO_2 to HNO_3, as discussed in Part I. The rate constants are very poorly determined in each case. Present knowledge indicates these rates to have half lives of about six months in the middle stratosphere and considerably longer in the lower stratosphere. A careful determination of the appropriate rate constants might show these rates to be faster or slower than expected. Further study of this system may discover additional reactions that convert NO and NO_2 to relatively inert forms. The actual NO_x emission from the SST is uncertain, it may be less than indicated here, and it might be further reduced by engine modifications. The number of planes and flights given in Table 2 may be an overestimate. A possibility that the SST would have a greater impact on ozone than indicated here concerns the great stability and sluggishness of the stratosphere at 20 km. A world-wide shell of NO_x at 20 km would tend to cut off diffusion of ozone from above 20 km to below 20 km. If a large bulk of O_3 now below 20 km arrived there by diffusion (as contrasted with subsidence), the ozone below 20 km would fade out as it mixed with the troposphere and it would not be replaced because of the catalytic barrier at 20 km.

Physiological effects

Although the physiological effect of ultraviolet radiations below 300 nm is quite outside my field of competence, I give here two references that invite a detailed, quantitative study by biological scientists: (1) Donald G. Pitts[47] made an extensive study (with rabbits) of the threshold and wavelength dependence of "snow blindness" by ultraviolet radiation. His study was background for the space helmets to be used by

astronauts on the moon. The wavelength limit is about 310 or 315 nm, and the effect increases rapidly with decreasing wavelength with maxima at 290 and 270 nm. Quantitative data were given for the amount of radiation below 310 nm that causes various degrees of eye damage and temporary blindness. (2) W. Tranquillini[48] wrote a review about the physiology of plants at high altitudes and the effect of natural and unnatural (below 300 nm) ultraviolet radiation on plants. His interpretation of a study by Pirschle[49] is as follows:

> "Pirschle studied the growth of plants from various elevations in growth chambers at constant temperature, moisture, and light, with and without the addition of artificially produced long-wave or middle-wave ultraviolet light. It was apparent that the plants which received long-wave ultraviolet light were indeed somewhat inhibited in their elongation compared to those receiving only visible light, but no damage was suffered by any of the plants. Irradiation with middle-wave ultraviolet...(280-315 mμ) resulted in death after a short time of plants from sea level, whereas alpine plants remained alive."

Tranquillini went on to say that later experiments showed that the killing of the plants was caused exclusively by the radiation not now reaching the earth, which, of course is what would reach the earth if the ozone shield were greatly reduced. I think that plant physiologists should consider the quantitative problem here, namely, how much ozone reduction would have what effect on plants?

Conclusions

(1) If NO and NO_2, as such, build up in the stratosphere to the expected[3] concentrations from SST operation, the ozone shield would be reduced by a large amount, about a factor of two.

(2) If NO and NO_2 are converted to HNO_3 (or other inert molecules) at a rate faster than is indicated by present knowledge, then the effect of NO_x from SST exhaust would be less than expected in (1) above. The chemistry of the stratosphere is sufficiently complicated that one should look for new, unexpected chemical reactions.

(3) A large reduction in stratospheric ozone would be expected to change the temperature, structure, and dynamics of the stratosphere, which may modify the quantitative aspects of conclusion (1). These effects are outside the scope of this report.

(4) In the reduction of ozone, the oxides of nitrogen at low concentrations exhibit a threshhold effect, and at high concentrations the oxides of nitrogen reduce ozone according to the square root of NO_x.

(5) Transport by air motions has a major effect in shaping the vertical profile of ozone in the lower half of the stratosphere; the catalytic chemical action of NO_x in destroying ozone is a large effect under all conditions of temperature, pressure, composition, and radiation distribution in the lower half of the stratosphere. Transport by air motions is an action that moves the large catalytic effect of NO_x from one part of the world to another, but it does not cancel this strong catalytic effect.

(6) In the present stratosphere, oxides of nitrogen act to limit the concentration and partly to shape the distribution of ozone; the indicated mole fraction of NO_x is about 10^{-9} at 20 km increasing to substantially higher values at higher elevations.

(7) At all levels of the stratosphere water vapor has less effect on ozone than the effect of natural NO_x on ozone. The most important effect on ozone by water in the stratosphere is its role in converting NO_2 to HNO_3, not the role of its free radicals (HO_x) in directly destroying ozone. NO_x from SST is a much more serious threat than water vapor with respect to reducing the ozone shield.

(8) Further experimental studies, especially chemical analyses in the stratosphere and photochemical and kinetic studies in the laboratory are needed to clear up the uncertainties under (2) above.

(9) Quantitative physiological studies should be made of what would happen to plants, animals, and people if the ozone shield should be reduced by various amounts up to a full tenfold reduction.

(10) Even though it may be too complicated for a complete theoretical treatment, the stratosphere is vulnerable to added oxides of nitrogen, and forethought should be given to this hazard before the stratosphere is subjected to heavy use.

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APPENDIX

Since this report was completed, I have received advice from several people as to the level of oxides of nitrogen to be expected from a large jet engine. Opinions have varied from estimates (verbally transmitted) as low as 50 ppm to as high as 1600 ppm. The 1600 ppm figure was quoted to me on the basis of published work, which I have not yet seen: T. Durrant, "The Control of Atmospheric Pollution from Gas Turbine Engines", SAE Paper No. 680347, and it was with respect to the Rolls-Royce Spey engine. It should be noted that there is a great difference in NO_x emission depending on whether the engine is idling, cruising, or exerting maximum power.

I am very grateful to Professor R. F. Sawyer for pointing out the following: (1) The engines discussed in reference 7 are quite different from the SST engines and should not be brought into the discussion one way or another. (2) There are no published data on NO emissions under cruise-mode conditions for engines such as those designed for the SST. (3) Based on his experience, Professor Sawyer believes that the actual performance of the SST engine at cruise mode would be about one pound of NO per hundred pounds of fuel. The number I used is 1.48 pounds of NO per hundred pounds of fuel.

In summary, the SCEP report quoted GE engineers to the effect that NO would be 1000 ppm of the exhaust, but SCEP gave a footnote that it might be lower. In the absence of definite information, I lowered the GE estimate from 1000 to 350 ppm. Meanwhile, I have statements that the number might be as low as 50 ppm or as high as 1600 ppm, with expert advice (Professor Sawyer) that the number 240 ppm is very reasonable. Most calculations made in this report cover a wide range of NO_x, mole fractions from 10^{-11} to 10^{-6}. When we get definite values for NO_x

emission from various engines, the expected concentration of NO_x in the stratosphere can be scaled up or down from the reference points I used. However, the point of this report is not to assert that SST flights will reduce the ozone shield by some precise factor; rather the point is that NO_x is a highly important variable in this problem and it must be given realistic consideration.

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