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CATALYTIC REDUCTION OF STRATOSPHERIC OZONE BY NITROGEN OXIDES

H.S. Johnston

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Catalytic Reduction of Stratospheric Ozone by Nitrogen Oxides

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Contents

I. Introduction 1

A. History 1

B. Summary 3

II. The Stratosphere 6

A. Structure and Composition 6

B. The Oxides of Nitrogen 9
1. Sources of Natural NO_x 9
2. Artificial Increase in Stratospheric Nitrogen Oxides from SST Exhaust 16

III. Strictly Chemical Considerations 21

A. Oxygen-Ozone Photochemistry 21

B. Nitric Oxide Catalyzed Destruction of Ozone 27
1. The NO_2 Catalytic Cycle 27
2. Other Reactions of the Oxides of Nitrogen 38

C. Other Reactions That Destroy Ozone 39
1. Reactions of Excited Oxygen Species 39
2. Reactions of Free Radicals Based on Water (HO_x) 42

D. Nitrous Acid and Nitric Acid 46
1. Important Reactions 46
2. Thermal Process of Forming HNO_3 48
3. Photochemical Process of Forming HNO_3 51
4. Destruction of HNO_3 54
5. Nitrogen Dioxide-Nitric Acid Steady State Ratio 57

E. The Smog Reactions 59

IV. Steady-State Ozone Profiles 67

A. The Method and Two Examples 67

B. The Effect of Various, Assumed, Non-Uniform NO_x Background Distributions 72

C. The Effect of Various Modes of Distribution of NO_x from SST Exhaust 76

V. Instantaneous Global Reaction Rates 82

VI. Comparison of Natural and Artificial Source Strengths of NO_x in the Stratosphere 90

VII. Conclusions and Comparisons with Other Studies 94

Appendix A 100

Appendix B 106

References 110

I. INTRODUCTION

A. History[4c]

In a 57 page chapter "The Supersonic Transport" in the publication Technical Information for Congress (TIC)[1] dated April 15, 1971, there was extensive discussion of the possible macro-environmental impact of the supersonic transport (SST), including the possible effect on the oxygen balance, excess carbon dioxide, weather modification from water vapor and particulate matter, and the reduction of the ozone shield by water vapor. However, there was no mention of the role of the oxides of nitrogen in the catalytic reduction of ozone. The catalytic destruction of ozone by NO_x (NO and NO_2), now recognized as the major factor in the natural ozone balance, was completely overlooked by both sides of the SST controversy, which reached its climax in the Congressional rejection of the SST in March 1971.

In the summer of 1970 a group sponsored by the Massachusetts Institute of Technology considered some effects of the SST on the stratosphere as a part of its "Study of Critical Environmental Problem" (SCEP).[2a] The SCEP report very briefly touched on the problem of the oxides of nitrogen from the SST exhaust. It concluded that 500 SST (with the properties given by the Federal Aviation Agency) would increase the world average concentration of stratospheric NO_x by 6.8 parts per billion (ppb, parts in 10^9), and there might be high-traffic local situations with 68 ppb of

added NO_x. The SCEP report concluded: "Both carbon monoxide and nitrogen in its various oxide 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" (italics added).

An article by Crutzen[3] in 1970 indicated that the oxides of nitrogen could be important in balancing ozone in the natural atmosphere, but neither TIC nor SCEP referred to this article.

After the stormy debates and the close, dramatic Congressional votes in March 1971, the statement that both sides of the SST controversy had overlooked the most important variable in the global environmental impact of the SST came as an unwanted anti-climax, and there has been considerable reluctance carefully to examine the scientific basis of the arguments. It should be clearly understood that the point of the 1971 articles on NO_x was not to assert that the SST would have this or that specific effect, but rather to assert that an extremely important variable (NO_x from the SST exhaust) had been overlooked or incorrectly dismissed: "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".[4a]

Realistic consideration of this problem requires the determination of the actual NO_x background in the natural stratosphere, the determination of the amount and spatial distribution of the exhaust gases from the SST (a matter of

atmospheric dynamics), and the calculation of the rates of chemical and photochemical reaction rates from accurate, independently evaluated constants. The purpose of this article is not to carry out this very difficult realistic solution of the problem; rather it is to present 1972 as well as 1971 arguments to the effect that the oxides of nitrogen from the SST exhaust are a highly important variable in considerations of the environmental impact of the SST.

B. Summary

In the section on "The Stratosphere" the various levels of the atmosphere are named, and the (24 hour averages) properties are presented as contour maps as a function of elevation and latitude from pole to equator to pole. The concentrations of important natural species are given in detail, and the composition with respect to several minor species is given briefly. The range of variables expected to be encountered from top to bottom of the sun-lit stratosphere is given (for use in the later sections). This range of variables includes the case for full scale operation of fleets of SST.

In the section "Strictly Chemical Analyses", an effort is made to use the smallest possible amount of atmospheric details and the maximum amount of chemistry (this is not to imply that atmospheric motions are unimportant; rather it is an effort clearly to elucidate one component of an exceedingly complex problem). Ozone chemistry in pure air and in an atmosphere

including the oxides of nitrogen, water, and other substances is discussed. The rate (in terms of half-times) of destruction of ozone without and with NO_x catalysts is emphasized. It is concluded that NO and NO_2, as such, in the amounts expected by SCEP would cause major, rapid reductions of ozone. It is further concluded that the large number of reactions by other minor species modify somewhat but do not alter this main conclusions.

The "Strictly Chemical Analyses" neglect an important, self-healing process in the atmosphere, and it requires a model of the structure of the atmosphere and the attenuation of solar radiation through it in order to account for this important buffering process. The simplest model that includes this effect is a static atmosphere and steady-state photochemistry, the section on "Steady-State Ozone Profiles". With such a model including a self-consistent solar energy distribution, the effect of NO_x on ozone is still found to be large if NO_x is greater than one part per billion. Even with this simple model, it is concluded that the <u>distribution</u> of both natural and artificial NO_x is as important a problem as the amount of NO_x.

The section on "Instantaneous Global Reaction Rates" makes maximum use of the structure of the actual atmosphere, including general considerations of atmospheric motions. It concludes that the amount and distribution of ozone in the stratosphere is such that it cannot be explained in terms of "pure air" photochemistry, that is, there is "something else" in the stratosphere besides pure air that plays the major role in the

natural ozone balance. Of all known processes, catalytic destruction of NO_x by the oxides of nitrogen is the only mechanism fast enough to account for the destruction of ozone by "something else".

The section "Comparison of Natural and Artificial Source Strengths of NO_x in the Stratosphere" examines the recognized sources and sinks of NO_x in the natural stratosphere, and it is shown that the artificial source of NO_x from 500 American SST would be equal to or several times greater than the natural source. Since the present stratospheric NO_x generated from the natural sources is the dominant factor in the natural ozone balance, artificially to double (or more) this source strength appears to be a serious matter.

In the final section "Conclusions and Comparisons with Other Studies" there is given a series of quotations from various articles on this subject. There is now a concensus that the oxides of nitrogen are an important variable in the stratosphere (contrary to the position before 1971); to see just how large or small the SST effect would be, and everyone is awaiting the working out of the quantitative details.

II. THE STRATOSPHERE[5-11]

A. Structure and Composition

The earth's atmosphere is conveniently divided into thick vertical shells. The lowest layer is the "troposphere", characterized by fairly rapid vertical mixing, high water content, and a temperature structure that decreases with increase in elevation. The "stratosphere" has a strong temperature inversion, low water content, and very slow vertical mixing rates. Residence half times in the stratosphere vary with elevation[5] and latitude,[6] between one and five years. In broad terms the troposphere extends from zero to 15 kilometers in elevation, and the stratosphere extends from 15 to 50 kilometers. Actually the "tropopause", the boundary between the troposphere and the stratosphere, varies somewhat with latitude and season; it is at 16 or 17 kilometers from 30°N to 30°S and it decreases, with some irregularities, to about 10 kilometers over the poles. The "stratopause", the top of the stratosphere, may be taken to be about 50 kilometers, and the next region above the stratopause is the "mesosphere".

A convenient way to express a global view of stratospheric properties is with a "zonal average" contour map,[7] such as Figure 1. In this figure -90° represents the north pole, 0° is the equator, and +90° is the south pole. The average temperature in belts of constant latitude is given as a function of elevation from 0 to 50 kilometers for the spring equinox. The approximate location of the tropopause is indicated by a dashed line. Figure 2 gives a similar temperature distribution for a winter-summer

situation, namely January 15. Average stratospheric temperatures vary between about 200° to 270°K. This article is addressed primarily to chemists, and thus it is useful to indicate several standard atmospheric quantities in the forms of zonal averaged contour maps. The total gas concentration in molecules per cubic centimeter is given by Figure 3; between 15 and 45 kilometers the gas concentration, [M], varies from 4×10^{18} to 4×10^{16}. The average ozone mole fraction as measured by about 100 stations over the last ten years and as interpreted by Dütsch[11] is given by Figure 4. Dütsch's map was extended from 40 to 50 kilometers by comparison with rocket data.[12] Stratospheric ozone typically varies between 0.5 and 10 parts per million. The maximum ozone mole fraction is between 30 and 35 kilometers above the equator. The average ozone concentration, $[O_3]$, is given in Figure 5. The highest average concentrations of ozone are above the spring polar region. The elevation of maximum concentration is about 25 kilometers at the equator and about 17 kilometers at the poles. The typical range of ozone concentrations is between 1×10^{11} and 5×10^{12} molecules cm^{-3}.

The first 5 figures give average observed experimental data. A number of quantities can be calculated from such data. Ozone absorbs sunlight over a wide range of wave lengths to produce oxygen molecules and oxygen atoms; the electronic states are $O_2(^3\Sigma_g^-)$, $O_2(^1\Delta_g)$, $O_2(^1\Sigma_g^+)$, $O(^3P)$, $O(^1D)$, or $O(^1S)$, depending on wave length. The excited species are fairly quickly deactivated by collision to the stable states. Thus the concentration of ground state oxygen atoms can be calculated by consideration of one photochemical and one chemical reaction

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

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

$$[O]_s = j_c[O_3]/k_b[M][O_2] \qquad (2\text{-}1)$$

(all reactions are collected with standard notation in appendix B; photochemical rate "constants" such as j_c are defined in appendix A). The incoming sunlight is attenuated by nitrogen and oxygen above the stratosphere and by oxygen and ozone in the stratosphere. By calculating the resultant solar intensity at each 5° latitude, at each 15° longitude, and at each kilometer elevation, the steady-state oxygen atom concentrations were calculated and entered on Figures 6 and 7. The zonal average concentration of oxygen atoms is about 10^5 molecules cm^{-3} at the tropopause and about 10^6 molecules cm^{-3} at 20 kilometers; it increases with elevation with a maximum value about 10^{10} molecules cm^{-3}. The oxygen atom concentration is vanishingly low in the polar winter, where there is no sunshine for all 24 hours.

Below 310 nm ozone is photolyzed to give singlet oxygen atoms

(c_3) $O_3 + h\nu$(below 310 nm) $\rightarrow O_2 + O(^1D)$

Although singlet oxygen atoms react with many molecules, its principal reaction is deactivation by nitrogen or oxygen, M:

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

The steady state concentration of singlet oxygen is very rapidly attained

$$[O(^1D)]_s = j_{c3}[O_3]/k_q[M] \qquad (2\text{-}2)$$

A contour map for singlet oxygen atoms is given by Figure 8. Singlet oxygen atoms react with hydrogen, water, and methane to produce hydroxyl radicals

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

(19) $O(^1D) + H_2 \rightarrow HO + H$

(20) $O(^1D) + CH_4 \rightarrow HO + CH_3$

The rate of production of hydroxyl radicals is given by Figure 9. The stratosphere is exceedingly dry,[13] the mole fraction of water is about 5×10^{-6}.

At the tropopause the mole fraction of various species are approximately as follows: CH_4 (5×10^{-6}),[14] H_2 (5×10^{-7}),[14] CO (4 to 8×10^{-8}),[14] N_2O (2.5×10^{-7}).[15-17] These species react with singlet oxygen atoms or with hydroxyl radicals or with both. These reactions discussed in later sections.

B. The Oxides of Nitrogen

1. Sources of Natural NO_x

In the mesosphere and ionosphere, there is a set of reactions involving nitric oxide[18]

(t) $N_2 + h\nu$(below 120 nm) $\rightarrow N + N$
(also various ionization processes $\rightarrow N$)

(u) $N + O_2 \rightarrow NO + O$ temperature dependent

(v) $N + NO \rightarrow N_2 + O$ temperature independent

(w) $NO + h\nu$(below 190 nm) $\rightarrow N + O$

Nitric oxide is both formed and destroyed by nitrogen atoms, with destruction being by far the dominant process at low temperature. Nitric oxide has been observed[19] to be about 50 ppb at 80 km and to increase above 80 km. Diffusion of such nitric oxide into the stratosphere is at best only a minor source of NO_x in the stratosphere.

Crutzen[3b] recently recognized a natural source of NO_x inside the stratosphere. Bacteria in the soil and perhaps in surface ocean waters produce a small amount of nitrous oxide N_2O as a part of the nitrogen cycle.[17] Nitrous oxide resembles carbon dioxide in many respects; it is virtually inert in the troposphere. It has a natural background of 0.25 parts per million in the troposphere, and this value decreases rapidly with elevation in the lower stratosphere. As nitrous oxide diffuses up into the stratosphere, most of it is photolyzed

$$\text{(x)} \quad N_2O + h\nu \rightarrow N_2 + O$$

and about 10% of it reacts with singlet oxygen

$$\text{(y)} \quad N_2O + O(^1D) \rightarrow N_2 + O_2$$

$$\text{(z)} \quad N_2O + O(^1D) \rightarrow NO + NO$$

The flux of NO in the stratosphere from this source, according to Crutzen, is between 0.3×10^8 and 1.5×10^8 molecules cm^{-2} sec^{-1}. The range arises from uncertainties concerning diffusion rates and reaction rate constants.

A calculation of the diffusion of N_2O into the stratosphere and its conversion to NO there has also been carried out by

Nicolet and Vergison[20] and by McElroy and McConnell.[21] Their results and Crutzen's are given in Table 1A. McElroy compared the limited data on the observed N_2O profile in the stratosphere with the prediction made by different values of a vertical eddy diffusion constant. He obtained best agreement between observed and calculated N_2O profile for the low extreme of the vertical flux, that is, 0.25×10^8 molecules cm^{-2} sec^{-1}. The elevation of maximum rate of NO formation was 24 km.

The oxides of nitrogen, NO and NO_2, undergo several reactions with other species in the atmosphere. The sequence of molecules, NO, NO_2, NO_3, and N_2O_5, are rapidly interchanged by photochemical reactions, and these reactions are discussed in a subsequent section. Nitrogen dioxide is slowly converted to nitric acid by hydroxyl radicals[22,23]

$$(1) \quad HO + NO_2 \xrightarrow{M} HNO_3$$

Hydroxyl radicals also destroy nitric acid[22-24]

$$(2) \quad HO + HNO_3 \rightarrow H_2O + NO_3$$

and nitric acid is photolyzed by sunlight (below 325 nm)[25]

$$(3) \quad HNO_3 + h\nu \rightarrow HO + NO_2$$

The recycling of NO_2 in and out of the form of nitric acid is relatively slow (a few days to a few weeks), and in the lower stratosphere a substantial amount of the oxides of nitrogen are temporarily tied up as HNO_3. The nitric acid diffuses downward to be removed by rain in the troposphere and upward to be photolyzed by sunlight to reform NO_2 and NO.

TABLE IA

Natural NO_x Flux in the Stratosphere from the N_2O Mechanism

Range of Calculated NO_x Flux (in units of molecules $cm^{-2}sec^{-1} \times 10^8$	Author	Ref.
0.3 to 1.5	Crutzen	3b
1.5 ± 1.0	Nicolet	20
0.25 to 0.65	McElroy	21
0.35 to 1.5	(average)	

TABLE IB

Observations of NO_2 in the Stratosphere, Reference 26

Elevation km	Mole fraction of NO_2 at sunset $\times 10^9$	$[NO_2]$ molecules cm^{-3} $\times 10^{-9}$
12	(1.5±0.5)	
16	< 1	< 4
21.9	(1.6±0.3)	2.2
23.9	(3.3±1.0)	3.3
25.7	(7.4±2.5)	5.3
27.5	(15 ± 3)	8.0
28.3	(7.8±0.3)	3.5
15 to 29 (ave.)	2.2	3.6

TABLE IC

Observations of Nitric Acid Vapor in the Stratosphere, Reference 27

Elevation km	Mole fraction of HNO_3 $\times 10^9$	$[HNO_3]$ molecules cm^{-3} $\times 10^{-9}$
15	4.5	18
16	7.9	27
17	6.5	19
18	3.6	9
19	3.2	7
20	3.8	7
21	11	17
22	13	18
23	17	19
24	4.1	4
25	4.8	4
26	7.0	5
27	8.1	5
28	9.5	5
29	<2	<1
	<2	<1
15 to 29 (ave.)	6.9	

TABLE ID

Estimates of the Average Amount of NO_x in the Natural Stratosphere

Author	Estimated NO_x, ppb	Reference
Nicolet (1965)	3	18
Crutzen (1970)	12	3a
Park and London (1971)	5	28
Johnston (1971)	6.6	4

Until very recently, there have been no direct measurements of the oxides of nitrogen in the stratosphere. By means of infrared absorption spectra Ackerman[26] has reported direct observation of NO_2 at sunset between 16 and 29 km, Table 1-B. By infrared emission spectra, the concentration of nitric acid vapor has been deduced[27] between 15 and 30 km, Table 1-C. Several older estimates of the average amount of NO_x in the natural stratosphere are given in Table 1-D.

2. Artificial Increases in Stratospheric Nitrogen Oxides from SST Exhaust

The Study of Critical Environmental Problems, SCEP,[2] obtained information from the Federal Aviation Administration and from General Electric Company (the manufacturers of the SST engines) concerning rate of fuel consumption, exhaust composition, anticipated number of SST, and expected amount of flight time. These data, except for the NO_x emission, are given in Tables 2A and B.

There has been considerable discussion and even controversy on the amount of NO_x expected to be emitted from the SST exhaust. A part of the controversy has arisen from ambiguity of the term "parts per million" when referred to jet engine exhausts. An unambiguous measure, however, is the weight of NO emitted in the exhaust per unit weight of fuel burned; the convenient unit here is grams of nitric oxide per kilogram of fuel. The General Electric Company quoted the figure 42 g NO/kg fuel to the SCEP

TABLE II

A. Statistics of Emission from One GE-4 Engines in Cruise Mode (Ref. 3) in Pounds Per Hour

Constituant	Input	Exhaust
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		(see below)
SO_2		33
Soot		5
Hydrocarbons		16.5

B. Anticipated Flight Statistics 500 SST 7 Hours Stratosphere Cruise Time Per Day Per SST

TABLE II-C

C. Grams of NO in Exhaust Per Kilogram of Fuel Burned by Current Models of SST-Type Jet Engines

Value	Identification	Reference
42	G.E. (1970)	2
14.8	Johnston (1971)	4a,b
4.9	G.E. (1971)	29
12.5	Concorde (1972)	30
20-30	McAdams (1971)	31
15-70	Ferri (1972)	32

study group in 1970, but they revised[29] this to 4.9 g/kg in the spring of 1971. Several recent measured values[31] of NO emission have been published for large jet engines that are similar to but not identical with the SST engine. The Concorde is said to emit 12.5 g NO/kg fuel in cruise mode.[30] In my calculations in 1971 I used the figure 14.8 g NO/kg fuel.[4] This number is somewhat lower than recently measured values (Table 2-C), but it is a reasonable value and is used again in this article. At this time the best estimate is perhaps 15±5 g NO/kg fuel for the SST exhaust.

With the large figure of 42 g NO/kg fuel, the SCEP report calculated that 500 SST would fill the stratosphere from top to bottom, all over the world by an increment of nitrogen oxides of 6.8×10^{-9} or 6.8 ppb. From consideration of regions of high traffic and as a safety factor, SCEP also considered a ten-fold higher figure of 68 ppb. If the conservative figure of 14.8 g NO/kg fuel is used,[4a,b] these figures are reduced to 2.4 ppb as the worldwide increment of NO_x and 24 ppb is a possible local maximum including a safety factor. If the NO_x were distributed with a world-wide uniform mole fraction of 2.4 ppb from 15 to 45 kilometers, the increase in concentration of NO_x would be 10^8 molecules cm^{-3} at 45 kilometers and 10^{10} molecules cm^{-3} at 15 kilometers. In a region of high traffic, the (somewhat arbitrary) ten-fold safety factor would give increments of NO_x between 10^9 and 10^{11} molecules cm^{-3}.

It is highly improbable that the NO_x from the SST exhaust would attain a uniform molefraction throughout the stratosphere. In the stratosphere there is rapid horizontal transport, slow vertical diffusion, and periodic (the "spring overturn" near polar regions, once a year) subsidence of some stratospheric air into the troposphere. The exhaust plumes from 500 SST cruising at 20 kilometers would be expected to form an irregular, non-uniform shell all over the world. The thickness of the shell would be a matter of the relative rates of vertical diffusion and sweep-out times through polar (and other local) regions. The full solution to this problem is an exceedingly difficult matter, and at present it is being actively investigated by several groups of atmospheric dynamicists. Meanwhile, model calculations can be made for a range of possible cases. As one extreme, assume that the full two year burden of 500 SST (each flying 7 hours a day) was spread uniformly all over the world for a depth of one kilometer between 20 and 21 kilometers. The concentration of NO_x would be 10^{11} molecules cm^{-3}. If the NO_x was spread uniformly over the world in a 10 kilometer band, the concentration would be 10^{10} molecules cm^{-3}. A uniform world wide spread from 15 to 45 kilometers would constitute an increment of 3×10^{9} molecules cm^{-3}. Nitric acid formation would tend to reduce these figures, but it can be seen from several approaches that increments of NO_x from the SST in the range of 10^{8} to 10^{11} molecules cm^{-3} must be considered as possible results.

III. STRICTLY CHEMICAL CONSIDERATIONS

A. Oxygen-Ozone Photochemistry[4a,11,33]

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

(a) $O_2 + h\nu$ (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 harsh 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)

$$O_3 + h\nu \rightarrow O_2 + O$$

$$O_2 + O + M \rightarrow O_3 + M$$

net: no chemical change

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.

TABLE III

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)	$NO + NO + O_2 \rightarrow NO_2 + NO_2$	$2k_i [NO]^2 [O_2]$
(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)	$NO_3 + h\nu$ (570-700 nm) $\rightarrow NO + O_2$	$j_\ell [NO_3]$

TABLE IV. Values of rate constants.

Rate Constant	k(T)	k(200°K)	k(220°K)	k(240°K)	k(260°K)	Ref
k_b	$1.10\times10^{-34}\exp(1000/RT)$ (cc/particle)^{2}sec^{-1} where M is N_2	1.35×10^{-33}	1.07×10^{-33}	8.9×10^{-34}	7.6×10^{-34}	34
k_d	$3.80\times10^{-30}T^{-1}\exp(-340/RT)$ (cc/particle)^{2}sec^{-1} where M is O_2	8.1×10^{-32}	8.0×10^{-33}	7.8×10^{-33}	7.6×10^{-33}	35
k_e	$1.33\times10^{-11}\exp(-4200/RT)$ cc/particle-sec	3.3×10^{-16}	8.93×10^{-16}	1.99×10^{-15}	3.91×10^{-15}	35-37
k_f	$1.33\times10^{-12}\exp(-2500/RT)$ cc/particle-sec	2.54×10^{-15}	4.36×10^{-15}	7.03×10^{-15}	1.05×10^{-14}	38
k_g	9.2×10^{-12} cc/particle-sec	9.2×10^{-12}	9.2×10^{-12}	9.2×10^{-12}	9.2×10^{-12}	39
k_i	$3.33\times10^{-39}\exp(1046/RT)$					39
k_j	$2.9\times10^{-33}\exp(1870/RT)$					39
k_k	$9.8\times10^{-12}\exp(-7000/RT)$					40
j_ℓ	$> 10^{-3}$					*
j_h	7×10^{-3}					41

* Observed in this laboratory.

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

$$\frac{d[O]}{dt} = 2j_a[O_2] - k_b[M][O_2][O] + j_c[O_3] - 2k_d[M][O]^2 - k_e[O_3][O] \tag{3-1}$$

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

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

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

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

From the rate constants in Table 4 and the stratospheric model of Figures 1-5, 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 50 km). Also ozone is in great excess over oxygen atoms at and below 50 km. Thus as an excellent approximation between 15 and 45 km, one may write

$$\frac{d([O_3]+[O])}{dt} = 2j_a[O_2] - 2k_e[O_3][O] \tag{3-4}$$

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

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 3-4 is integrated subject

to the (unrealistic) assumption of constant oxygen atom concentration

$$\int \frac{d(-2k_e[O][O_3])}{2j_a[O_2]-2k_e[O][O_3]} = -2k_e[O] \int dt \qquad (3\text{-}5)$$

The integral is

$$\ln \frac{(j_a[O_2]-k_e[O][O_3])_o}{(j_a[O_2]-k_e[O][O_3])} = 2k_e[O]t \qquad (3\text{-}6)$$

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

$$j_a[O_2] = k_e[O][O_3]_s \qquad (3\text{-}7)$$

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

$$\Delta = j_a[O_2] - k_e[O][O_3] \qquad (3\text{-}8)$$

is a measure of the departure from the photochemical steady state, and Eq. 3-6 may be written

$$\ln \frac{\Delta_o}{\Delta} = 2k_e[O]t \qquad (3\text{-}9)$$

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

$$\tau_{1/2} = \ln 2/2\ k_e[O] \qquad (3\text{-}10)$$

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. 3-10 provides us with an easily grasped measure of reaction rate for an instantaneous value of oxygen atom concentration (compare the use of a 2 billion year half time for radiactive decay of uranium as a convenient expression of instantaneous rate).

B. Nitric Oxide Catalyzed Destruction of Ozone

1. The NO_2 Catalytic Cycle

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, (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 in 1965, and in the discussion of catalytic cycles it follows an analysis 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

(3-11)

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

Consider the pair of reactions

$$\begin{array}{ll} \text{(f)} & NO + O_3 \rightarrow NO_2 + O_2 \\ \text{(g)} & NO_2 + O \rightarrow NO + O_2 \\ \hline \text{net:} & O_3 + O \rightarrow O_2 + O_2 \end{array} \qquad (3\text{-}12)$$

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

$$\begin{array}{ll} \text{(f)} & NO + O_3 \rightarrow NO_2 + O_2 \\ \text{(h)} & NO_2 + h\nu \rightarrow NO + O \\ \text{(b)} & O + O_2 + M \rightarrow O_3 + M \\ \hline & \text{net: no chemical change} \end{array} \qquad (3\text{-}13)$$

is a "do nothing" cycle, and it acts to reduce the catalytic rate of Eq. 3-12. The catalytic rate is not that of reaction (f), but rather

$$\left\{ - \frac{d([O_3]+[O])}{dt} \right\}_{\text{catalytic}} = k_f [NO][O_3] \frac{k_g[O]}{k_g[O]+h} \qquad (3\text{-}14)$$

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. 3-3. The relation between nitric oxide and nitrogen dioxide is determined by the fast reactions

(f) $NO + O_3 \rightarrow NO_2 + O_2$

(g) $NO_2 + O \rightarrow NO + O_2$

(h) $NO_2 + h\nu \rightarrow NO + O$

The rate of change of nitrogen dioxide is

$$\frac{d[NO_2]}{dt} = k_f[NO][O_3] - k_g[O][NO_2] - j_h[NO_2] \qquad (3\text{-}15)$$

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

$$\frac{[NO_2]}{[NO]} = \frac{k_f[O_3]}{k_g[O]+j_h} \qquad (3\text{-}16)$$

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

$$[NO_2] = \frac{k_f[O_3]}{k_f[O_3]+k_g[O]+j_h} \qquad (3\text{-}17)$$

$$[NO_2] + [NO] = [NO_x] \qquad (3\text{-}18)$$

The differential equation for odd oxygen is

$$\frac{d([O_3]+[O])}{dt} = 2j_a[O_2] + j_h[NO_2] - k_d[M][O]^2 - k_e[O_3][O] - k_f[NO][O_3] - k_g[NO_2][O] \qquad (3\text{-}19)$$

Addition of Eq. 3-15 to Eq. 3-19, with the steady state assumption

for NO_2, gives

$$\frac{d([O_3]+[O])}{dt} = 2j_a[O_2] - 2\{k_d[M][O]^2 + k_e[O_3][O]\} - 2k_g[O][NO_2] \tag{3-20}$$

This differential equation is to be compared with Eq.3-3. The positive term, $2j_a[O_2]$, which forms ozone, is the same in both the catalyzed Eq.3-20 and in the uncatalyzed Eq.3-3; the terms in Eq.3-3 that represent destruction of odd oxygen also appear in Eq.3-20; but in addition, a new destruction term, $-2k_g[O][NO_2]$, appears. If we make the same approximation that was made to obtain Eq. 3-4

$$k_e[O_3][O] \gg k_d[M][O]^2 \tag{3-21}$$

then Eq.3-20 reduces to the form

$$\frac{d([O_3]+[O]}{dt} = 2j_a[O_2] - 2k_e[O_3][O]\left\{1 + \frac{k_g[NO_2]}{k_e[O_3]}\right\} \tag{3-22}$$

It is convenient to give a special name and symbol to the expression in braces in Eq. 3-22

$$\rho = \text{catalytic ratio}$$

$$= \frac{\text{rate of ozone destruction with catalysts}}{\text{rate of ozone destruction without catalysts}} \tag{3-23}$$

$$= \frac{k_e[O_3][O] + k_g[O][NO_2]}{k_e[O_3][O]}$$

$$= 1 + \frac{k_g[NO_2]}{k_e[O_3]}$$

By use of Eq. 3-16, the catalytic ratio may be expressed in an alternative form

$$\rho = 1 + \frac{[NO](k_f k_g / k_e j_h)}{1 + k_g[O]/j_h} \tag{3-24}$$

The expression for catalytic ratio, Eq. 3-24, is closely related to the intuitively derived catalytic rate, Eq. 3-14.

The catalytic ratio ρ may be expressed either in the set of variables [O] and [NO], Eq. 3-24 or in terms of the variables $[O_3]$ and $[NO_2]$, Eq. 3-23. 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

$$k_g[O] << j_h \tag{3-25}$$

then the catalytic ratio assumes the particularly simple form

$$\rho = 1 + \frac{k_f k_g [NO]}{k_e j_h} \tag{3-26}$$

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 all stratospheric temperatures k_g is 9.2×10^{-12} cm^3/particle-sec, h is 7×10^{-3} sec^{-1}, and thus $k_g[O]$ is equal to j_h when the oxygen atom concentration is 7.6×10^8 per cm^3. The catalytic ratio has the simple form of Eq. 3-26

when oxygen atoms are much less than 7.6×10^{8} molecules/cm^3. From Figures 6 and 7 it can be seen that this approximation is valid at all elevations below 35 kilometers. 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, and by use of the rate constants at 220°K in Table 4:

$$\rho = 1 + \frac{(4.36\times10^{-15})(9.2\times10^{-12})10^{10}}{(8.93\times10^{-16})(7\times10^{-3})} \qquad (3\text{-}27)$$

$$= 1 + 64 = 65$$

This simple calculation shows that under these conditions, nitric oxide destroys ozone 65 times faster than pure air; and with $\sqrt{65}$ fold reduction of ozone. The half-time to destroy ozone under these conditions is

$$\tau_{1/2} = \ln 2/2\, k_e [O]\rho \qquad (3\text{-}28)$$

To carry out this calculation a value of oxygen atom concentration must be assigned; the value 10^6 satisfies the condition of Eq. 27 and it is a typical value at 20 kilometers in the stratosphere. The half time is then

$$\tau_{1/2} = 0.693/2(8.9\times10^{-16})(10^6)(65)$$

$$= 6\times10^6 \text{ sec} = 69 \text{ days}$$

These very direct calculations imply a fast (69 day half time), almost total (up to $\sqrt{65}$ fold) destruction of ozone by nitric oxide catalysis for this special case of $[NO] = 10^{10}$ per cc and $[O] = 10^6$ per cc.

TABLE V

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]	10^5	10^6	10^7	10^8	10^9	10^{10}
T°K	[NO]						
200	10^{11}	1011	1010	1000	891	441	72
	10^{10}	102	102	101	90	45	8.2
	10^9	11.1	11.1	11.0	9.9	5.4	1.71
	10^8	2.01	2.01	2.00	1.89	1.44	1.07
220	10^{11}	644	644	637	569	279	46
	10^{10}	65	65	64	58	29	5.5
	10^9	7.4	7.4	7.3	6.7	3.8	1.45
	10^8	1.64	1.64	1.63	1.57	1.28	1.05
240	10^{11}	468	468	461	414	203	43
	10^{10}	48	48	47	42	21	4.3
	10^9	5.7	5.7	5.6	5.1	3.0	1.33
	10^8	1.47	1.47	1.46	1.41	1.20	1.03
260	10^{11}	354	354	351	313	154	26
	10^{10}	36	36	36	32	16	3.5
	10^9	4.5	4.5	4.5	4.1	2.5	1.25
	10^8	1.35	1.35	1.35	1.31	1.15	1.02

TABLE VI

Half times for catalyzed and uncatalyzed decomposition of ozone.

		$\tau_{1/2}$, seconds					
	[O]	10^5	10^6	10^7	10^8	10^9	10^{10}
T°K	[NO]						
200	10^{11}	1.0(7)	1.0(6)	1.0(5)	1.1(4)	2.3(4)	1.4(3)
	10^{10}	1.0(8)	1.0(7)	1.0(6)	1.1(5)	2.2(5)	1.2(4)
	10^9	9.0(8)	9.0(7)	9.0(6)	1.0(6)	1.8(5)	5.8(4)
	10^8	5.0(9)	5.0(8)	5.0(7)	5.3(6)	7.0(5)	9.4(4)
	0	1.0(10)	1.0(9)	1.0(8)	1.0(7)	1.0(6)	1.0(5)
220	10^{11}	6.0(6)	6.0(5)	6.1(4)	6.8(3)	1.4(3)	8.5(2)
	10^{10}	6.0(7)	6.0(6)	6.1(5)	6.7(4)	1.3(4)	7.1(3)
	10^9	5.3(8)	5.3(7)	5.3(6)	5.8(5)	1.0(5)	2.7(4)
	10^8	2.4(9)	2.4(8)	2.4(7)	2.5(6)	3.0(5)	3.7(4)
	0	3.9(9)	3.9(8)	3.9(7)	3.9(6)	3.9(5)	3.9(4)
240	10^{11}	3.8(6)	3.8(5)	3.9(4)	4.3(3)	8.9(2)	4.2(2)
	10^{10}	3.7(7)	3.7(6)	3.8(5)	4.3(4)	8.6(3)	4.2(3)
	10^9	3.2(8)	3.2(7)	3.2(6)	3.5(5)	6.0(4)	1.3(4)
	10^8	1.2(9)	1.2(8)	1.2(7)	1.3(6)	1.5(5)	1.7(4)
	0	1.8(9)	1.8(8)	1.8(7)	1.8(6)	1.8(5)	1.8(4)
260	10^{11}	2.5(6)	2.5(5)	2.5(4)	2.8(3)	5.7(2)	3.4(2)
	10^{10}	2.5(7)	2.5(6)	2.5(5)	2.8(4)	5.5(3)	2.5(3)
	10^9	2.0(8)	2.0(7)	2.0(6)	2.1(5)	3.5(4)	7.0(3)
	10^8	6.5(8)	6.5(7)	6.5(7)	6.7(5)	7.7(4)	8.6(3)
	0	8.8(8)	8.8(7)	8.8(6)	8.8(5)	8.8(4)	8.8(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

From Figures 1 and 2, it can be seen that the four temperatures 200°K, 220°K, 240°K, and 260°K embrace almost all of the stratosphere. From Figures 6 and 7, it can be seen that (24 hour average) oxygen atom concentrations in the stratosphere fall in the range 10^5 to 10^{10} atoms cm^{-1}. From considerations of the natural NO_x background and increments of NO_x from the SST, it was found that the total range of expected nitric oxide concentrations is embraced by 10^8 to 10^{11} molecules cm^{-3}. The catalytic ratio ρ, Equation 3-24, is given for the full range of stratospheric temperature, oxygen atom concentration, and nitric oxide including the maximum SST increment in Table 5. There are 96 entries in Table 5. The incremental rate of ozone destruction by NO_x (relative to pure air) is greater than 10% for 92 cases, greater than a factor of 2 for 71 cases, greater than a factor of 10 for 48 cases, and greater than a factor of 100 for 23 situations. The maximum effect within the domain of expected stratospheric conditions is a factor of 1000. These calculations which cover the full range of the independent chemical variables for all of the stratosphere, show large effects by NO_x under virtually all conditions.

Table 5, however, only gives relative rates, the rate of ozone destruction with NO_x relative to the situation in pure air. If the absolute rate with NO_x is slower than a ten year half-time, then even a relative rate of 100 is not a serious matter. For the full range of independent variables as given in Table 5, the half-time τ (Equation 3-28) for ozone destruction is given by Table 6. For 14 out of the 96 cases including NO_x, the half-time

is greater than two years. For these cases the large ozone reductions indicated by Table 5 will not be realized in the real stratosphere, where residence half-times are from 1 to 5 years,[5,6] averaging about 2 years.

If the catalytic ratios had been large, say larger than 1.10, for all values of all the independent variables as realized in the stratosphere and if the half times for ozone destruction had all been shorter than the two year mean residence time of contaminants in the stratosphere, then one could say from analysis given by Tables 5 and 6 that NO_x is an important problem in the ozone balance of the stratosphere, regardless of air motions. If the effects are both large and fast everywhere, then any wind or atmospheric motion is merely moving a big chemical effect from one place to another. However, as can be seen from Tables 5 and 6, the effects are small for certain ranges of the independent variables and the rates are slow for certain ranges of the independent variables. This makes the problem a very difficult one in which realistic assessment of atmospheric motions and realistic considerations of photochemical and chemical reaction rates must be carried out. For a large region of space the SST exhaust will set up a large catalytic ratio, but whether the rate of ozone destruction is slow or fast is a strong function of oxygen atom concentration, which in turn (Figures 6 and 7) is a strong function of elevation.

It can be seen from Figures 1 and 2 that 220°K is a typical temperature for a large portion of the stratosphere in the range of SST operation. The catalytic ratios and ozone destruction

half-times from Tables 5 and 6 for 220°K are plotted[4e] in Figure 10. The region of small effect is indicated; and where the half-time exceeds two years the region is marked as "slow". The oxygen atom axis of Figure 10 can be translated into elevation and latitude by means of Figures 6 and 7. At the 20 kilometer cruise height of the SST, the 24 hour average oxygen atom concentration is close to 10^6. If the exhaust shell averages 1 kilometer in thickness, the concentration of NO_x in the shell would be 10^{11} cm^{-3} (2 year burden); then the catalytic ratio is greater than 100 and the half time is less than one month. If the exhaust spreads over a 10 kilometer shell in the two year residence time, the catalytic ratio is greater than 10 and the half time varies from about a month of the upper part to more than a year at the lower part of the shell. If the exhaust spreads out over a shell about 20 kilometers thick, then some has passed through the tropopause to be rained out in a few days, some resides in the lowest stratosphere where half times are longer than two years, some has moved up to regions where the oxygen atom concentrations are 10^7 to 10^8 and the rates are fast. These considerations of Figure 10 with comparison to Figures 6 and 7 again show that the full solution of this problem will require extremely detailed and realistic considerations of atmospheric motions and chemistry.

2. Other Reactions of the Oxides of Nitrogen[4a]

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.

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

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

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

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

The NO_3 catalytic cycle may be very important below 22 km[4c]

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

(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) $NO_2 + NO_3 \xrightarrow{M} N_2O_5$

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

(n) $N_2O_5 + M \xrightarrow{M} NO_2 + NO_3$

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

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

(m) $NO_2 + NO_3 \xrightarrow{M} N_2O_5$

net: $2O_3 \rightarrow 3O_2$

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

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

(m) $NO_2 + NO_3 \xrightarrow{M} N_2O_5$

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

where the question mark signifies that the reaction, through plausible, has not been shown to occur as written. Under daylight conditions at the earth's surface, N_2O_5 is photolyzed

(p) $N_2O_5 + h\nu\ (200\text{-}380) \rightarrow 2NO_2 + O$ (?)

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

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

(s) $NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$

$NO_2 + NO_2 \rightleftarrows N_2O_4$

$NO + NO_2 \rightleftarrows N_2O_3$

C. Other Reactions that Destroy Ozone

1. Reactions of Excited Oxygen Species

There are many reactions that involve excited electronic states of oxygen atoms and molecules. This field has been reviewed recently by Wayne[42] and it continues to be an active field of current research. The important reactions are (where O and O_2 represent the stable species and a fuller statement of excited species is $^1\Delta_g$ and $^1\Sigma_g^+$):

(i) Formation of excited species

(c1) $O_3 + h\nu$ (450-650 nm) $\rightarrow O_2 + O$

(c2) (310-340 nm) $\rightarrow O_2(^1\Delta) + O$

(c3) (below 310 nm) $\rightarrow O_2(^1\Delta) + O(^1D)$

(8) $O(^1D) + O_2 \rightarrow O + O_2(^1\Sigma)$

(ii) Deactivation of excited species

(9) $O(^1D) + M \rightarrow O + M$

(10) $O_2(^1\Delta) + M \rightarrow O_2 + M$

(11) $O_2(^1\Sigma) + M \rightarrow O_2 + M$

(iii) Light emission by excited species

(12) $O(^1D) \rightarrow O + h\nu$ (630 nm)

(13) $O_2(^1\Sigma) \rightarrow O_2 + h\nu$ (760 nm)

(14) $O_2(^1\Delta) \rightarrow O_2 + h\nu$ (1270 nm)

(iv) Reaction with ozone

(15) $O(^1D) + O_3 \rightarrow O_2 + O_2$

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

(16) $O_2(^1\Delta) + O_3 \rightarrow O_2 + O_2 + O$

(17) $O_2(^1\Sigma) + O_3 \rightarrow O_2 + O_2 + O$

Under stratospheric conditions the deactivation processes (ii) predominate over the ozone destruction processes (iv). The reactions of $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ with ozone do not lead to loss of odd oxygen. The reaction of $O(^1D)$ with ozone, however, does represent destruction of odd oxygen; and the magnitude of this process is examined below.

The rate equation for $O(^1D)$ is:

$$\frac{d[O(^1D)]}{dt} = j_{c3}[O_3] - k_9[M][O(^1D)] - Q' \qquad (3\text{-}29)$$

where Q' represent reactions of $O(^1D)$ with ozone, water, nitrous oxide, methane, and other minor species. The rate constant for deactivation of $O(^1D)$ by air is very large, $(6\pm3)\times10^{-11}$ cm^3 $molecule^{-1}$ sec^{-1}, and air molecules are in great abundance over the species named above. Thus Q' is negligible compared to the other terms in Equation 3-29. The steady-state concentration of singlet oxygen

$$[O(^1D)] = j_{c3}[O_3]/k_D[M] = j_{c3}\alpha(O_3)/k_9 \qquad (3\text{-}30)$$

where $\alpha(O_3)$ is the mole fraction of ozone and j_{c3} is the photolysis constant for ozone with respect to wavelengths below 310 nm. A global distribution of $O(^1D)$ is given by Figure 8.

The destruction of ozone by singlet oxygen atoms

$$O(^1D) + O_3 \rightarrow O_2 + O_2$$

has a rate constant[42] of about 1.5×10^{-10}.

2. Reactions of Free Radicals Based on Water (HO_x)[4d]

The free radicals based on water are indicated by the symbol HO_x (H, HO, HOO). These free radicals are formed from singlet D oxygen atoms, which are produced by the photolysis of ozone below 310 nm.

(c3) $O_3 + h\nu$ (below 310 nm) $\rightarrow O_2 + O(^1D)$

(9) $O(^1D) + M \rightarrow O + M$

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

(19) $O(^1D) + H_2 \rightarrow HO + H$

(20) $O(^1D) + CH_4 \rightarrow HO + CH_3$

$$\left(\begin{array}{l} CH_3 + O_2 \xrightarrow{M} H_2CO + HO \\ \qquad\qquad \rightarrow CH_3OO \xrightarrow{h\nu} \\ H_2CO + h\nu \rightarrow H_2 + CO \\ \qquad\qquad\quad \rightarrow H + HCO \\ H + O_2 + M \rightarrow HOO + M \\ HCO + O_2 \rightarrow HOO + CO \end{array}\right)$$

From laboratory studies a number of reactions have been shown to occur and rate constants evaluated for HO_x reactions. The known reactions in this system include

(H) (22) $H + O_3 \rightarrow HO + O_2$

(21) $H + O_2 + M \rightarrow HOO + M$

(HO) (23) $HO + O \rightarrow H + O_2$

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

$\rightarrow H_2 + O_2$

(26) $HO + HO + M \rightarrow H_2O_2 + M$

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

(HOO) (28) $HOO + HOO \rightarrow H_2O_2 + O_2$

(H_2O_2) (29) $H_2O_2 + O \rightarrow HO + HOO$

(30) $H_2O_2 + h\nu \rightarrow HO + HO$

(31) $H_2O_2 + HO \rightarrow H_2O + HOO$

(v*) (32) $HO(v \geq 2) + O_3 \rightarrow H + O_2 + O_2$

The rate constants for these reactions are given in reference 4d and in other references cited there. There has been a great deal of activity in this field during the immediate past, and some of the recent estimates have varied rather widely, for example, the ratio of rate constants k_{18}/k_8 for the reactions

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

(8) $O(^1D) + O_2 \rightarrow O + O_2$

has been reported as 10.7 (ref. 43), 4.2 (ref. 44), and 0.12 (ref. 45). In the stratosphere, the important quantity is the ratio of rate constant of $O(^1D)$ with water and with air, since this determines the fraction of $O(^1D)$ that goes to form two hydroxyl radicals. It appears that this important ratio is not yet satisfactorily known, although this situation will probably be corrected very soon, in view of current active interest.

The reaction of $O(^1D)$ with water to form hydroxyl radicals was discovered[46] by McGrath and Norrish in 1960. They then

spectulated that the chain decomposition of wet ozone by ultra-violet light was brought about by the reactions

$$(33) \quad HO + O_3 \rightarrow HOO + O_2 \qquad (?)$$

$$(34) \quad HOO + O_3 \rightarrow HO + O_2 + O_2 \qquad (?)$$

$$\text{net: } 2O_3 \rightarrow 3O_2$$

Kaufman[47] (1964) attempted to measure the first of these reactions, but it was not observed to occur. He was able to set a limit on its rate

$$k_{33} < 5\times10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

Many unsuccessful attempts have been made to measure the rates of these reactions. Recently Langley and McGrath[48] have looked for this reaction in a situation there it would produce a big effect if it was present. They showed that reaction 33 is 5000 times slower than the limit set by Kaufman, that is

$$k_{33} < 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

With this very low limit, the thermal chain reaction based on HO and HOO is ruled out as an important process in the stratosphere.

Hunt[49,50] pointed out the need to consider loss processes for ozone other than those based on pure air, and he adopted McGrath and Norrish's hypothetical reaction chain for model calculations. He replaced Kaufman's inequality, $k_{33} < 5\times10^{-13}$, by an equality

$$k_{33} = 5\times10^{-13}$$

Hunt said: "A rather arbitrary assignment of 10^{-14} was made for the value of k_{34}, but the reaction must be rather slow as the rate has not been measured...The ozone profile was...sensitive to

the value of k_{34}...varying k_{34} from 10^{-13} to 10^{-15} changed the total O_3 amount from 0.1 to 0.35 cm. STP". Thus by adjusting the rate constant of this hypothetical reaction, one can calculate any desired reduction of the total ozone column. In his article, Hunt made model calculations in which he demonstrated that water reactions would be sufficient to explain the ozone deficit if the rate constants were as big as $k_{33} = 5\ 10^{-13}$ and $k_{34} = 10^{-14}$. The demonstration by Langley and McGrath[48] that k_{33} is less than 10^{-16} shows that these water reactions are <u>not</u> sufficient to explain the ozone deficit.

Hydroxyl radicals react with carbon monoxide and with methane at fairly well known rates[51]

(46) $HO + CO \rightarrow CO_2 + H$

(36) $HO + CH_4 \rightarrow H_2O + CH_3$

In terms of known chemical reactions, there are several catalytic cycles involving the HO_x system, but they are very minor in effect below 40 km. Examples of such cycles are

$$\begin{array}{l} HO + O \rightarrow H + O_2 \\ H + O_3 \rightarrow HO + O_2 \\ \hline \text{net: } O + O_3 \rightarrow O_2 + O_2 \end{array}$$

$$\begin{array}{l} HO + O \rightarrow H + O_2 \\ H + O_2 + M \rightarrow HOO + M \\ HOO + O \rightarrow HO + O_2 \\ \hline \text{net: } O + O \rightarrow O_2 \end{array}$$

At high pressures (laboratory conditions) of water and ozone, an energy chain involving vibrationally excited hydroxyl radicals may occur

$$H + O_3 \rightarrow HO(v \leq 9) + O_2$$

$$HO(v \geq 2) + O_3 \rightarrow H + O_2 + O_2$$

net: $2O_3 \rightarrow 3O_2$

Although a number of the rate constants are not well known, it appears that ozone destruction by the "water reactions" is a very small effect below 40 kilometers and the matter of only a few percent between 45 and 50 kilometers.

D. Nitric Acid and Nitrous Acid

1. Important Reactions

Nitrous acid (HNO_2) and nitric acid (HNO_3) are important in the stratosphere as a sink for hydroxyl radicals and as a temporary reservoir for NO and NO_2; in the lowest stratosphere the washout of nitric acid by rain appears to be one of the principal sinks of stratospheric NO_x.

The case for nitrous acid is relatively simple. It is formed from hydroxyl radicals and nitric oxide in a third-order reaction[22]

$$(4) \quad HO + NO + M \rightarrow HNO_2 + M$$

It is destroyed both by hydroxyl radicals and by ultraviolet radiation between 300 and 400 nm

(5) $HO + HNO_2 \rightarrow H_2O + NO_2$

(6) $HNO_2 + h\nu$ (300-400 nm) $\rightarrow HO + NO$

The combination of reactions 4 and 5 constitutes a sink for hydroxyl radicals. However, the photodissociation is so fast ($j \sim 10^{-4}$ to 10^{-3} sec^{-1}) that nitrous acid appears to be of low importance in the stratosphere.

Nitric acid is a much more complicated and more important substance in the stratosphere. Nitric acid may be formed by a thermal process[4a]

(f) $NO + O_3 \rightarrow NO_2 + O_2$

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

(m) $NO_2 + NO_3 \rightarrow N_2O_5$

(7) $N_2O_5 + H_2O \rightarrow 2HNO_3$ (?)

net: $2NO + 3O_3 + H_2O \rightarrow 2HNO_3 + 3O_2$

and it is formed by a photochemical process[4a]

(c3) $O_3 + h\nu$ (below 310 nm) $\rightarrow O_2 + O(^1D)$

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

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

(1) $HO + NO_2 \xrightarrow{M} HNO_3$

net: $O_3 + 2NO_2 + H_2O \rightarrow 2HNO_3 + O_2$

Nitric acid is destroyed by hydroxyl radicals[22-24] and by sunlight[25,54]

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

(3) $HNO_3 + h\nu$ (below 325 nm) $\rightarrow HO + NO_2$

Both the thermal and photochemical processes are discussed below.

2. Thermal Process of Forming HNO_3

The reaction of nitrogen dioxide and ozone produces the free radical NO_3, which is rapidly photolyzed to produce NO and O_2 by day but at night the radical NO_3 is capable of entering into a series of reactions

(r) $NO_3 + NO \rightarrow 2NO_2$

(s) $NO_3 + NO_2 \rightarrow NO_2 + O_2 + NO$

(m) $NO_3 + NO_2 \xrightarrow{M} N_2O_5$

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

At night, ozone reduces NO to such a low value that the rate of the first reaction is very low. 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.

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

(m) $NO_3 + NO_2 \xrightarrow{M} N_2O_5$ (night)

net: $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$ (night)

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

$$\tau_k = \ln 2/2k_k[O_3] \qquad (3\text{-}31)$$

These half times vary over the stratosphere between 0.5 and 120 nights.[4a]

The dinitrogen pentoxide so formed undergoes both thermal and photochemical reactions

$$(n) \quad N_2O_5 \xrightarrow{M} NO_2 + NO_3$$

$$(p) \quad N_2O_5 + h\nu \rightarrow 2NO_2 + O \quad (?)$$

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

$$(7) \quad N_2O_5 + H_2O \rightarrow 2HNO_3 \quad (?)$$

At 300°K, the rate constant k_7 has been tentatively reported[55] to have the value of 1.7×10^{-18} cm^3/molecule-sec. 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 7 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 $k_7 = 10^{-12}$ exp-(8.0/RT)cc/molecules sec. On the other hand, measurements in this laboratory by Calamore[56] using a large (22 liter) bulb has shown that the rate constant for reaction 7 is less than 2×10^{-19} at 323°K. Thus, the rate constant under homogeneous conditions is limited by the inequality $k_7 < 10^{-12}$ exp(-5000/T) cm^3 $molecule^{-1}$ sec^{-1}. At 220°K the rate constant is less than 10^{-22}, and thus it is quite negligible. However, it is conceivable that reaction 7 occurs on the surface of particulate matter in the stratosphere, and until that possibility is quantitatively worked out, it is well to retain reaction 7 as a possibility.

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

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

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

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

(7) $N_2O_5 + H_2O \rightarrow 2HNO_3$

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

$$\frac{d[NO_2]}{dt} = -2k_k[O_3][NO_2] \tag{3-32}$$

$$\frac{d[N_2O_5]}{dt} = k_k[O_3][NO_2] - k_7[H_2O][N_2O_5]$$

$$\frac{d[HNO_3]}{dt} = 2k_7[H_2O][N_2O_5]$$

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:

$$[HNO_3] = [NO_2]_o \left\{(1 - e^{-\beta t}) - \frac{\beta}{\gamma}(1 - e^{-\gamma t})\right\} \tag{3-33}$$

where $\beta = 2k_7[H_2O]$ and $\gamma = 2k_7[H_2O] + 2k_k[O_3]$. 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.

Eq. 3-33 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 (using the old value of k_7) were calculated. 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.[4a] Below 25 km the half-time ranges from one to twenty years. Using Calamore's value[56] for k_7 the rates are about one hundred fold slower.

The absorption spectrum of N_2O_5 was obtained by Jones and Wulf.[57] 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

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

is $j_p = 2.2\ 10^{-5}\ sec^{-1}$. 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.

3. Photochemical Process of Forming HNO_3

Hydroxyl radicals, produced photochemically, add to nitrogen dioxide to form nitric acid

$$(1) \quad HO + NO_2 \xrightarrow{M} HNO_3$$

This reaction has been studied over a wide range of pressure, temperatures, and identity of foreign gases M at temperatures[23,24] above 600°K; and recently the reaction has been studied near room temperature.[22] The reaction is a bimolecular association, it shows strong effects of non-equilibrium distribution over vibrational states of HNO_3, at stratospheric pressures it is in the middle of its "fall-off" region, and the rate is neither third order nor second order but a variable order between these limits.

The shape of the curve of empirical second-order rate constant was determined at high temperature. The values of the rate constants as a function of helium pressures has been determined over a wide pressure range at room temperature. The curve expected to have the correct shape has been inserted in the observed experimental points at room temperature, Figure 11. Actual stratospheric conditions involve a different foreign gas M (N_2 and O_2 instead of He) and a different temperature. One cannot say a priori whether air would be more or less efficient than helium, compare experimental results for four similar cases including HNO_3 in Table 7. The rate constant for bimolecular associations increase slowly with a decreasing temperature. Thus the experimental points and the full curve given in Figure 11 probably underestimate the rate for stratospheric temperatures and gas composition.

TABLE VII

Relative efficiency, k_M/k_A, of various foreign gases as measured at the low-pressure limits of the unimolecular decomposition

M \ A	N_2O	NO_2Cl	HNO_3	N_2O_5
A	1.00	1.00	1.00	1.00
He	0.66	0.25	-	0.12
Ar	0.20	0.21	0.16	0.14
N_2	0.24	0.29	-	0.23
O_2	0.23	0.26	0.16	0.30
CO_2	1.3	0.39	0.29	0.40
H_2O	-	-	1.05	-
Reference	58	59	53	60

58. M. Volmer and M. Bogdan, Z. Phys. Chem. 21B, 257 (1933); M. Volmer and H. Froehlich, Z. Phys. Chem. 19B, 89 (1932).

59. M. Volpe and H.S. Johnston, J. Am. Chem. Soc. 78, 3903 (1956).

60. D.J. Wilson and H.S. Johnston, J. Am. Chem. Soc. 75, 5673 (1953); H.S. Johnston, J. Am. Chem. Soc. 75, 1567 (1953).

4. Destruction of HNO_3

The reaction of HO with HNO_3 has been studied at high temperature (700°K) and at room temperature (300°K) by different investigators. The observed rate constants were very nearly the same, Table 8. The indication is that this reaction has a very small activation energy. The best present estimate of the rate constant appears to be 1.5×10^{-13} cm^3 $molecule^{-1}$ sec^{-1} at all temperatures.

The absorption spectrum of nitric acid vapor as a function of wave length is given by Table 9. Berces and Forgeteg[29] studied the quantum yield of the photolysis of nitric acid vapor at 253.7 nm and at 265 nm. They found a quantum yield for the formation of NO_2: 0.3 at 253.7 and 0.1 at 265 nm. Preliminary studies in this laboratory give a primary quantum yield of about one at 200 nm and about 0.3 at 300 nm. The shape of the absorption spectrum indicates two or more electronic transitions are involved; a strong absorption beginning at 280 nm and increasing to a very large value at 190 nm; a weak absorption centered at about 260 nm, extending out to 325 nm. It may be that absorption in the short-wave length band has unit quantum yield and absorption in the long-wave length band has a variable, low quantum yield.

By the methods presented in appendix A, the rate constant j_3 was calculated

$$j_3 = \sum_{\lambda} \sigma(\lambda)\phi(\lambda)I(\lambda,h) \qquad (3\text{-}34)$$

TABLE VIII

Observed values of the rate constant for HO + HNO_3 at various temperatures

Temperature °K	k cm^3 $molecule^{-1}$ sec^{-1}	Reference
698	1.8×10^{-13}	24
670	2.0×10^{-13}	23
639	1.9×10^{-13}	53
300	1.3×10^{-13}	22
298	1.7×10^{-13}	54

TABLE IX

Absorption cross section of nitric acid for ultraviolet radiation[52]

λ nm	σ cm^2	λ nm	σ cm^2
190	1.32(-17)	260	1.90(-20)
195	9.10(-18)	265	1.80(-20)
200	5.50(-18)	270	1.63(-20)
205	2.55(-18)	275	1.40(-20)
210	9.70(-19)	280	1.14(-20)
215	3.28(-19)	285	8.77(-21)
220	1.44(-19)	290	6.34(-21)
225	8.51(-20)	295	4.26(-21)
230	5.63(-20)	300	2.76(-21)
235	3.74(-20)	305	1.68(-21)
240	2.60(-20)	310	9.5(-22)
245	2.10)-20)	315	4.7(-22)
250	1.95(-20)	320	1.8(-22)
255	1.94(-20)	325	2(-23)

1.32(-17) means 1.32×10^{-17}

$\ln(I_o/I) = \sigma[HNO_3]L$, with L in cm and concentration in units of molecules cm^{-3}.

where σ is the light absorption cross section, ϕ is the primary quantum yield, and I is the light intensity as a function of wave length and elevation. The light intensity depends on all light absorbing species above the elevation h and on latitude and time of day. Table 10 gives these photochemical rate constants at 45° latitude, solar equinox, noon, and 24 hour average. The "light absorption constant" is given by Equation 3-34 with $\phi = 1$; the "photolysis constant" takes a variable quantum yield from 1.0 to 0.3 between 210 and 310 nm.

5. Nitrogen Dioxide-Nitric Acid Steady-State Ratio

The important reactions in setting the steady-state ratio of nitrogen dioxide to nitric acid are

(1) $HO + NO_2 \xrightarrow{M} HNO_3$

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

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

The ratio of nitrogen dioxide to nitric acid is

$$\frac{[NO_2]}{[HNO_3]_s} = \frac{k_2}{k_1} + \frac{k_3}{k_1[HO]} \qquad (3\text{-}35)$$

The half-time to approach the steady-state is

$$\tau_{1/2} = \ln 2/(k_1[HO] + k_2[HO] + k_3) \qquad (3\text{-}36)$$

Between 20 and 25 kilometers, k_1 is about 10^{-12}, k_2 is about 10^{-13}, and k_3 is between 10^{-7} and 10^{-6} sec^{-1}. Thus the ratio of NO_2 to HNO_3 is

TABLE X

Rate of absorption of sunlight and preliminary estimate* of photolysis constant for nitric acid vapor, 45° latitude, solar equinox

Elevation km	Rate of absorption* of sunlight, sec^{-1}		Photolytic** rate constant, sec^{-1}	
	noon	24 hr. ave.	noon	24 hr. ave.
50	1.3(-4)	5.5(-5)	1.2(-4)	5.0(-5)
45	1.1(-4)	4.2(-5)	9.7(-5)	3.9(-5)
40	7.6(-5)	2.7(-5)	7.2(-5)	2.5(-5)
35	4.1(-5)	1.2(-5)	3.8(-5)	1.1(-5)
30	1.4(-5)	3.5(-6)	1.3(-5)	3.0(-6)
25	2.8(-6)	6.8(-7)	1.9(-6)	4.2(-7)
20	7.7(-7)	2.3(-7)	2.8(-7)	8.1(-8)
15	5.1(-7)	1.5(-7)	1.7(-7)	5.1(-8)

* Equation 3-34 with $\phi = 1$.

** Primary quantum yield taken to be 1.0 at 210 nm and 0.3 at 310 nm.

$$([NO_2]/[HNO_3])_s \simeq 0.1 + (10^5 \text{ to } 10^6)/[HO] \qquad (3\text{-}37)$$

If hydroxyl radicals are less than 10^5 molecules cm^{-3}, nitrogen dioxide will exceed nitric acid, and the half-time is determined by the photolysis rate, about 6 to 60 days. If the hydroxyl radicals exceed 10^6 molecules cm^{-3}, then nitric acid exceeds nitrogen dioxide, and the half time to reach the steady state is less than 6 days. At higher elevations k_1 decreases, k_3 increases, and [HO] increases; the net effect is for NO_2 to become increasingly important relative to HNO_3, and the steady state between NO_2 and HNO_3 is rapidly attained. Although all the numbers are not yet established, it appears probable that the ratio, $[NO_2]/[HNO_3]$, is about 0.1 at 15 kilometers, about 1 in the vicinity of 25 kilometers, and much larger than 1 above 35 kilometers. At all elevations, the half-time to establish the steady state between NO_2 and HNO_3 appears to be 2 months or less.

E. The Smog Reactions[41,51,61]

As A.J. Haagen-Smit[61] demonstrated 20 years ago, the oxides of nitrogen in sunlight produce ozone if organic gases of almost any sort are present. The activity of the organic gases in this respect is widely variable.[51] In urban air the concentrated pollutants are swept away by horizontal winds or vertical convection within a few hours, and thus only those organic gases that are so active that they undergo the smog reaction within an hour or two are regarded as important. Methane is the least active of all tested organic gases in the smog reaction, and in

general methane is regarded as inactive in photochemical air pollution. However, with the long residence times in the stratosphere (years) and with the intense radiation field producing $O(^3P)$, $O(^1D)$ and HO radicals, the role of methane in the photochemical smog reaction must be considered. The full details of the smog reaction are still not known, but the broad outlines have been clear for many years.[41,51,61] There is the basic, inorganic cycle, the organic contribution to the inorganic cycle, and the manifold reactions of the intermediates and products of these reactions. The inorganic cycle is simply

$$\text{(h)} \quad NO_2 + h\nu \ (300\text{-}400 \text{ nm}) \rightarrow NO + O(^3P)$$

$$\text{(b)} \quad O + O_2 + M \rightarrow O_3 + M$$

$$\text{(f)} \quad NO + O_3 \rightarrow NO_2 + O_2$$

net: no reaction

Although there is no net reaction, there is a small steady-state concentration of ozone, which is reached within a few minutes even at sea level

$$[O_3]_s = j_h[NO_2]/k_f[NO] \tag{3-38}$$

The ozone derived from the inorganic cycle alone cannot exceed the amount of NO_x. The organic materials are attacked by ozone (or by $O(^1D)$ or HO derived from the near 300 nm photolysis of ozone) to produce peroxyl free radicals (or other intermediates) that reconvert NO to NO_2 with the net production of one ozone molecule. For a relatively simple smog reactant like propylene, there are a large number of branching reactions, some of which

produce peroxyl radicals, $CH_3(CO)OO$, CH_3OO, HOO, etc. These radicals, ROO, presumably react with nitric oxide either directly or indirectly

$$ROO + NO \rightarrow RO + NO_2$$

In general about one atom of carbon in a complex hydrocarbon converts one NO to NO_2 and thus makes one molecule of ozone. The organic material is not a catalyst; it is a reactant consumed or at least degraded when it forms ozone by this mechanism.

On the long time scale of the stratosphere methane also enters the smog reaction. There is a large natural background of methane whereas the concentration of all other organic materials is very low in the natural atmosphere. A possible (not unique) set of reactions whereby the consumption of methane produces ozone is

(c3) $O_3 + h\nu$ (below 310 nm) $\rightarrow O_2 + O(^1D)$

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

(36) $HO + CH_4 \rightarrow H_2O + CH_3$

(39) $CH_3 + O_2 \xrightarrow{M} CH_3OO \xrightarrow{h\nu} H_2CO + HO$ (?)

(43) $H_2CO + h\nu \rightarrow H + HCO$

(21) $H + O_2 + M \rightarrow HOO + M$

(44) $HCO + O_2 \rightarrow HOO + CO$

(47) $HOO + NO \rightarrow HO + NO_2$

(h) $NO_2 + h\nu \rightarrow NO + O$

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

net: $2CH_4 + 9O_2 \rightarrow H_2O + 6HO + 2CO + 3O_3$

The hydroxyl radicals could produce more HOO and thus O_3 via

$$\begin{array}{ll} (46) & HO + CO \rightarrow CO_2 + H \\ (21) & H + O_2 + M \rightarrow HOO + M \\ (47) & HOO + NO \rightarrow HO + NO_2 \\ (h) & NO_2 + h\nu \rightarrow NO + O \\ (b) & O + O_2 + M \rightarrow O_3 + M \\ \hline \text{net:} & CO + 2O_2 \rightarrow CO_2 + O_3 \end{array}$$

On the other hand, there is a large inefficiency (branching) in the steps involving the reactants CH_4, CH_3, and H_2CO.

The formation of ozone from methane can be initiated by hydroxyl radicals formed in the photolysis of nitric acid

$$HNO_3 + h\nu \rightarrow HO + NO_2$$

in the photolysis of hydrogen peroxide

$$H_2O_2 + h\nu \rightarrow 2HO$$

or in the photolysis of formaldehyde

$$\begin{array}{l} H_2CO + h\nu \rightarrow H_2 + CO \\ \qquad\qquad\quad \rightarrow H + HCO \xrightarrow{O_2} 2HOO + CO \\ HOO + NO \rightarrow NO_2 + HO \end{array}$$

These substances, HNO_3, H_2O_2, and H_2CO, provide delayed sources of HO_x radicals in the stratosphere.

With consideration to the amplification factor inherent in the HOO reactions, the inefficiency factor following from branching

of the organic reactants, and the uncertainty of several key rate constants, it can be said that methane probably produces about two molecule of ozone per molecule of methane lost. According to Erhalt and Heidt,[62] the average global production rate of methane is between (1.5 to 4.7)$\times 10^{11}$ molecules cm^{-2} sec^{-1}. The average global transport[62] to the stratosphere was estimated to be between (0.25 to 0.5)$\times 10^{11}$ molecules cm^{-2} sec^{-1}. The average global rate of production of ozone from the photolysis of oxygen in the stratosphere is 100×10^{11} molecules cm^{-2} sec^{-1}. Thus natural methane by way of the diffuse widespread smog reactions may produce about 1 to 2 per cent of the stratospheric ozone (assuming 2 ozone molecules are formed for each methane lost). The rest of the methane, (1 to 4)$\times 10^{11}$, presumably reacts with hydroxyl radicals in the troposphere[14] to produce up to (2 to 8)$\times 10^{11}$ molecules cm^{-2} sec^{-1} of ozone in the troposphere from the nitrogen dioxide-methane smog reaction. This amount of ozone is equal to or larger than the amount transported from the stratosphere to the troposphere (Crutzen[3d]), and thus it appears that ozone in the troposphere is not an inert tracer, but it is coupled to an active chemical source (CH_4, NO_2) and sink (NO_2 + O_3).

It is well established that the oxides of nitrogen catalytically destroy ozone in the stratosphere, but the oxides of nitrogen form ozone from hydrocarbons near the earth's surface. At what elevation is the crossover point separating the zone of ozone formation and destruction by the oxides of nitrogen? Order of magnitude calculations establish that it is in the lowest stratosphere or upper troposphere

and that it depends strongly on the concentration of nitrogen dioxide. The dominant reactions forming ozone are

(c3) $O_3 + h\nu(\text{below } 310) \rightarrow O_2 + O(^1D)$

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

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

(1) $HO + NO_2 \xrightarrow{M} HNO_3$

(36) $HO + CH_4 \rightarrow H_2O + CH_3 \rightarrow\rightarrow 2O_3 + \ldots$

The rate-determining step is reaction 36. The fastest mode of destruction of ozone by the oxides of nitrogen at low elevations[4c] is

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

(ℓ) $NO_3 + h\nu\ (\text{red}) \rightarrow NO + O_2$

(f) $NO + O_3 \rightarrow NO_2 + O_2$

net: $2O_3 + h\nu\ (\text{red}) \rightarrow 3O_2$

Here reaction k is the rate determining step. The rate of destruction relative to the rate of formation is

$$\eta = \frac{k_k[NO_2][O_3]}{k_{36}[CH_4][HO]} = \frac{\text{rate of ozone destruction}}{\text{rate of ozone formation}} \qquad (3\text{-}39)$$

By making the steady-state assumption for $O(^1D)$, one finds

$$[O(^1D)] = \frac{j_{c3}[O_3]}{k_9[M]} \qquad (3\text{-}40)$$

The steady-state for the hydroxyl radical gives

$$[HO] = \frac{2j_{c3}k_{18}[O_3][H_2O]}{k_9k_1[NO_2][M]} \qquad (3\text{-}41)$$

Thus the destruction-formation ratio is independent of ozone and given by

$$\eta = \frac{k_k k_9 k_1 [NO_2]^2}{2j_{c3} k_{18} k_{36} [CH_4] \alpha_{H_2O}} \tag{3-42}$$

At 15 kilometers, 220°K, the various parameters are

$j_{c3} = 1.1\times10^{-5}$ $\alpha_{H_2O} = 5\times10^{-6}$

$k_9 = 4\times10^{-11}$ $\alpha_{CH_4} = 1.5\times10^{-6}$

$k_{18} = 2\times10^{-10}$ $[CH_4] = 6\times10^{12}$

$k_1 = 3\times10^{-12}$

$k_{36} = 8.7\times10^{-16}$

$k_k = 10^{-18}$

The destruction-formation ratio is then

$$\eta = [NO_2]^2/10^{18} \tag{3-43}$$

AT 15 kilometers, the formation and destruction of ozone by NO_x would be balanced if the concentration of nitrogen dioxide is 10^9 molecules cm^{-3}, that is, for a mole fraction of 0.25 ppb. It is probable that the background mole fraction of NO_x is about one parts per billion at 15 kilometers (Table 1-B) and thus the crossover point is indicated to be below 15 kilometers. There is enough uncertainty in the values of the rate constants and in the completeness of the set of reactions considered that one should only say that the crossover point is very sensitive to the

concentration of nitrogen dioxide (varies as $[NO_2]^2$), and it probably occurs in the middle or upper troposphere.

It has sometimes been suggested that the hydrocarbons released by the SST in the stratosphere would undergo the smog reactions to restore the ozone destroyed by NO_x catalysis, or it has been suggested that extra hydrocarbons could be vented into the stratosphere to reform ozone. A simple calculation[4c] shows that "if the smog reaction goes with complete efficiency in the stratosphere, the hydrocarbons that would have to be released into the stratosphere to mend the catalytic destruction of ozone by NO_x would be about twice as much as the total fuel consumed by the SST itself". Thus it appears highly unlikely that the ozone depletion can be cured by hydrocarbon releases or by the native methane already in the stratosphere.

IV. STEADY-STATE OZONE PROFILES

A. The Method and Two Examples

The consideration of catalytic ratios and ozone half times, Tables 5 and 6 and Figure 10, overstates the importance of the oxides of nitrogen, in part because it overlooks one important buffering process. Both O_2 and O_3 absorb ultraviolet radiation below 242 nm. When oxygen absorbs such radiation, ozone is formed

(a) $O_2 + h\nu \rightarrow O + O$

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

net: $3O_2 + h\nu \rightarrow 2O_3$

When ozone absorbs such radiation, there is no net change in ozone concentration

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

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

net: u.v. radiation → heat

Suppose a large increment of NO_x is suddenly introduced at, say, 35 kilometers. Ozone at 35 kilometers would be rapidly reduced to some lower value, and some radiation below 242 nm that formerly was absorbed at 35 kilometers would now pass to lower elevations in part to be absorbed by ozone (change in heat input) and in part to be absorbed by oxygen, which would generate more ozone at a lower elevation. The new ozone generated at lower elevations would be less than that destroyed at 35 kilometers, but even so this is an important, partial self-healing mechanism.

The simplest computational device that will assess the magnitude of the effect of NO_x on stratospheric ozone including this self-healing, radiation-transfer mechanism is that of the photochemical steady state in an assumed static atmosphere.[4a,b] The computational procedures for making the steady-state calculations are given in appendix A. The differential equation for odd oxygen (essentially ozone) is

$$\frac{d[O_3]}{dt} = 2j_a[O_2] - \frac{2j_c k_e \rho [O_3]^2}{k_b [M][O_2]} - Q \tag{4-1}$$

where Q involves small terms involving excited oxygen reactions, "water" reactions, and reactions i, j, k, ℓ, etc; ρ is the catalytic ratio, Eq. 3-23. Neglecting the term Q, the steady state for ozone is

$$[O_3]_s = \left(\frac{j_a k_b [M]}{j_c k_e \rho}\right)^{\frac{1}{2}} [O_2] \tag{4-2}$$

and the half-time to go from zero ozone to one-half the steady state concentration is

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

By multiplying numerator and denominator by steady state concentrations, this equation may be modified to the form:

$$\tau = \frac{\ln 3}{4}\left\{\frac{(k_b [M][O_2][O]_s) \quad [O_3]_s^{\,2}}{(j_c [O_3]_s)(j_a [O_2])\rho (k_e [O]_s [O_3]_s}\right\}^{\frac{1}{2}} \tag{4-4}$$

$$\approx \frac{\ln 3}{4} \frac{[O_3]_s}{j_a [O_2]} \tag{4-5}$$

since rate b is equal to rate c and at the steady state rate eρ is equal to rate a.

The principal shortcoming of the steady-state calculation is that there is a large gradient in photochemical reaction rates between the top and the bottom of the stratosphere. Photochemical relaxation times are fast at the top of the stratosphere and slow at the bottom, relative to the time scale of atmospheric motions. The quantitative aspects of this problem of time scales will be given for two particular distributions of NO_x in the stratosphere.

Park and London[28] proposed two NO_x distributions in the stratosphere, one as a natural background and one as the stratosphere might be perturbed by SST operation. These distributions were articulated to the known (Meira, 1971) NO distribution in the mesosphere and to the troposphere. Park and London's distributions of NO_x in the stratosphere are given as Figure 12, and the steady state ozone profiles are given in Figure 13. The steady state ozone concentrations and photochemical half times are given in Table 11. With the natural background of NO_x given by Park and London, the half-times are 1.3 years at 15 kilometers and 5 months at 20 kilometers. There is substantial horizontal transport of ozone in times as long as these, and there is also some vertical spreading. Thus photochemical steady-state calculations based the model of a static atmosphere are expected to be badly distorted in the lower stratosphere. In the middle and upper stratosphere where photochemical relaxation times are a matter of a few days or less, the photochemical steady-state calculation should be quite good. With the NO_x distribution given by Park and London

TABLE XI

Half-times for ozone photochemistry with NO_x distributions of Park and London[28]

Elevation km	15	20	25	30	35	40	45
T °K	220	217	222	227	235	250	260
log $[M]/cm^3$	18.60	18.27	17.93	17.58	17.26	16.92	16.60
			Natural background				
$\alpha = [NO_x]/[M]$, ppb	3.00	4.47	5.96	7.94	9.12	10.5	12.9
$[O_3]$ units of 10^{12} cm^{-3}	0.49	2.78	4.90	4.87	2.73	0.91	0.28
log $j_a[O_2]$	3.51	4.74	5.50	6.07	6.44	6.60	6.59
$\tau_{1/2}$ sec	4.2(7)	1.8(7)	4.3(6)	1.1(6)	2.8(5)	6.3(4)	2.0(4)
$\tau_{1/2}$	1.3 yr	6 mo	2 mo	13 day	3 day	1 day	6 hr
			With SST operation				
α ppb	35	40	45	50	50	50	50
$[O_3]$	0.30	1.65	2.76	2.26	1.07	0.39	0.18
log $j_a[O_2]$	4.43	5.55	6.17	6.56	6.73	6.72	6.62
$\tau_{1/2}$ sec	3.06(6)	1.28(6)	5.1(5)	1.71(5)	5.5(4)	2.04(4)	1.2(4)
$\tau_{1/2}$ days	36	15	6	2	0.6	0.2	0.14

for SST operations, the photochemical half-times are reduced to 36 days at 15 kilometers and 15 days at 20 kilometers.

The vertical column of ozone given by the natural background of Park and London is 0.33 cm (STP) using the recent photochemical constants of Ackerman[63] and the chemical constants of Davis,[34] Figure 12. The column is 0.28 cm (STP), calculated on the basis of somewhat older photochemical and chemical constants, summarized in references 64,65. For the NO_x distribution based on SST operation, the steady-state ozone column is 0.17 cm (new photochemical constants) and 0.165 cm (old photochemical constants). The change in ozone brought about by the SST, according to Park and London's NO_x distributions and my steady state calculations, is a 40% reduction based on 1971 photochemical data and a 49% reduction based on 1972 photochemical constants. Park and London failed to discover this enormous effect coming from their own NO_x distributions because they included reaction i

$$2NO + O_2 \rightarrow 2NO_2$$

in their reaction scheme with the wrong rate constant; they used $k_i = 1\times10^{-33}$ cm^6 $molecule^{-2}$ sec^{-1} instead of the correct value of 4×10^{-38}. With this spuriously high rate constant, the following catalytic cycle generates ozone from NO_x at a fast rate

$$2NO + O_2 \rightarrow 2NO_2$$

$$(NO_2 + h\nu \rightarrow NO + O) \quad \text{Twice}$$

$$(O + O_2 + M \rightarrow O_3 + M) \quad \text{Twice}$$

$$\text{net: } 3O_2 + h\nu \rightarrow 2O_3$$

Although steady-state ozone profiles are undoubtedly distorted at lower elevations by atmospheric motions, they are, nevertheless, a valuable tool in assessing the first-order effects of certain parameters, such as added NO_x. A series of steady-state ozone profiles are given in Figure 14A for various uniform mole fractions of NO_x, zero, 1, 3, 10, 30, and 100 ppb. Similarly, Figure 14B shows a series of ozone profiles for uniform NO_x concentrations, zero, 0.3, 1, 3, and 10×10^9 molecules cm^{-3}. In these calculations, correction has been made for the redistribution of stratospheric radiation for every change of any variable. The radiation field is self-consistent with the chemical composition derived from it. These profiles show that stratospheric ozone is very sensitive to oxides of nitrogen at mole fractions above 1×10^{-9} or at concentrations above 1×10^9 molecules cm^{-3}.

B. The Effect of Various, Assumed, Non-Uniform NO_x Background Distributions[4a,b]

Although the steady-state ozone profiles are expected never to be precisely correct, because of the effect of air motions, the steady-state calculation itself remains a powerful, simple method for the identification of <u>important variables</u>. If a perturbation has a very small effect even after the time to reach the photochemical steady state, then usually it can be expected to have an even smaller effect in the finite residence time of gases in given regions of the stratosphere. On the other

hand, if a perturbation has a large effect on the photochemical steady state, then it is an important variable that must be examined by methods more realistic than the steady-state calculation; after such a detailed examination, including atmospheric motions, the perturbation may be found to have a large or a small effect.

In order to explore for the important variables in this problem, a large number of steady-state calculations were made for various distributions of NO_x in the stratosphere. The standard conditions were 45° latitude, a standard temperature profile, and 24 hour average radiation intensity at each kilometer from 15 to 50 kilometers. Several hundred such calculations were made, and the results for 17 examples are briefly given here. Non-uniform NO_x profiles are given in Table 12. The profiles are summarized in terms of five numbers: integrated vertical column of ozone, N_x; maximum concentration of ozone, X_m; elevation of the maximum concentration of ozone and the two elevations where the ozone concentration is one-tenth that of the maximum value. These data are given in Table 13.

For the progression of cases (12-14, 15-17) where log α varied linearly with elevation, the ozone column decreases strongly with increasing magnitude of the oxides of nitrogen. For fixed distributions of NO_x in the lower stratosphere (1-4, 5-8, 9-11) the ozone vertical column changes rather slowly with increasing oxides of nitrogen above 30 kilometers. These calculations indicate that the <u>distribution</u> of NO_x in thee stratosphere is as important a variable as the magnitude of the total burden of NO_x.

TABLE XII

Models for NO_x natural background: non-uniform distribution of oxides of nitrogen in terms of log α, where $\alpha = [NO_x]/[M]$

km / Number	15	20	25	30	35	40	45	50
A. Irregular distributions of log α								
(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
B. Linear variation of log α								
(12)	-10							-9
(13)	-9							-8
(14	-8							-7
(15)	-11							-9
(16)	-10							-8
(17)	-9							-7

TABLE XIII

Ozone vertical column N_x, maximum ozone concentration X_m for non-uniform mole fraction of NO_x, elevations at 10% points

	$10^{-18}N_x$ molecules cm^{-2}	$10^{-12}X_m$ molecules cm^{-3}	Elevation (km) X_m		$X_m/10$
A. Irregular fractions of NO_x as given in Table 12					
Number					
(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
B. Linear variation with elevation of log α between 15 to 50 km					
(12)	10.88	6.60	30	17	44
(13)	8.90	5.94	30	18	44
(14)	5.61	4.04	30	18	42
(15)	11.59	6.69	29	16	44
(16)	10.58	6.51	30	17	44
(17)	8.00	5.61	30	18	42

C. The Effect of Various Modes of Distribution of NO_x from SST Exhaust[4a,b]

If 500 American SST flew 7 hours per day at 20 kilometers elevation, the exhaust gases would be laid down as relatively narrow wakes in an irregular criss-cross pattern over the world. These wakes are expected rapidly to be transported and mixed in horizontal directions, to be slowly mixed in vertical directions, and to be bodily removed from the stratosphere through the spring "polar overturns" and through breaks in the tropopause over temperate zones. If the horizontal mixing is slow compared to the mean stratospheric residence time, one would expect local maximum of exhaust concentrations much higher than the global average; the SCEP report recommended consideration of a local maximum of up to 10 times the world-wide average (also this factor of 10 had some aspects of a safety factor). If the vertical mixing is slow compared to the horizontal "sweep-out" processes, then the average thickness of the layer of exhaust gases would be quite narrow.

How important is it whether the exhaust gases are constrained vertically or horizontally?

The full answer to this question requires simultaneous solution of all the problems of atmospheric motions in 3 dimensions, all of the photochemistry, and all energy balances, including radiation at all wave lengths. It may require 10 years or much longer for this total problem to be solved.

An approximate, semi-quantitative answer to this question can easily be provided by a few simple steady-state calculations. Each of the first eleven non-uniform distributions in Table 12 was taken as a natural NO_x background. The steady state (equal to 2 year input) accumulation of NO_x from SST operation (4.5×10^{34} molecules) was distributed in a number of arbitrary manners, but these distributions were selected so as to imitate the effect of restricted vertical spread or restricted horizontal spread of the exhaust. For one set of calculations, the exhaust was distributed uniformly all over the world (maximum horizontal spread, zero horizontal constraint), and it was assigned various uniform thicknesses: 20 to 21 km (maximum vertical constraint), 19 to 23 km, 18 to 25 km, 17 to 27 km, 16 to 29 km, and 15 to 31 km (successively less and less vertical constraint). The ozone vertical columns, relative to that for no artificial NO_x, are given for each degree of vertical spread in Table 14A. The 11 background distributions represent widely different total NO_x, but results are remarkably similar for the 11 cases. When the world-wide spread is only one kilometer thick, the ozone column is reduced to 96 to 98 per cent of its background value. Consider entry 5 for discussion; the per cent reduction of the ozone column increases with increasing vertical spread of the fixed amount of NO_x: 3%, 12%, 19%, 23%, 21%, and 20%. The reduction of ozone is a maximum with a 10 kilometer vertical spread, and it decreases with further vertical dilution. All 11 cases show very nearly parallel behavior. The highly vertically constrained (20 to 21 km) exhaust gases "overkills" the ozone in its shell, but relatively little of the total vertical column of ozone is contacted by the

TABLE XIV-A

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 12

	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	96	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

artificial NO_x. The minimally vertically constrained NO_x is so dilute that its effect is less than that of the intermediate case, a vertical spread of about 10 kilometers.

The effect of both horizontal and vertical constraints is given by Table 14B. A 10 fold "local maximum" or horizontal constraint gives only a small (2 to 4%) reduction of the ozone column if there is also maximum vertical constraint. The maximum reduction of ozone, occurring with a vertical spread of 16 kilometers, represents a reduction of ozone between 48 and 52%.

These calculations (steady-state, assumed natural backgrounds, arbitrary uniform thicknesses of spread) clearly show that the distribution of SST exhaust in the stratosphere is an important variable in this problem, every bit as important as the amount of NO_x from the exhaust. For a fixed number (4.5×10^{34}) of NO_x molecules, the reduction of the ozone column at a given location is only 3% with a highly constrained vertical distribution, but it is a 50% ozone reduction with a highly constrained horizontal distribution. Each of these highly constrained distributions appears much less probable than a wide range intermediate cases (vertical spread of several kilometers, horizontal contraint no more than a factor of two), for which the calculated ozone reduction is 20±10%.

The qualitative conclusions of this section are regarded as firm: the distribution (vertical and horizontal) of exhaust gases from the SST is an essential factor in this problem. The quantitative conclusions are merely the first approximation,

TABLE XIV-B

Local maximum of NO_x is assumed to be ten times as high as that for A

Number		O_3 column in units of 10^{18}, molecules/cm^2						
		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	52

subject to revision (up or down) as quantitative considerations of atmospheric motions are brought to bear on the problem.

The role of atmospheric motions is crucial in shaping the distribution of background and artificial oxides of nitrogen in the stratosphere. Crutzen[3c] has found that some modes of atmospheric motion result in much more severe lowering of ozone by NO_x than static models, but it is to be expected that the opposite effect will apply to some situations.

V. INSTANTANEOUS GLOBAL REACTION RATES[66]

This section does not use the steady-state method for ozone. The only part of this article that uses the steady-state method for ozone is Section IV above. This section is complementary to Section II, which made maximum use of chemistry and minimum use of the structure of the stratosphere. This section also makes maximum use of chemistry, but it also makes heavy use of the detailed, observed composition of the stratosphere. In this section, world wide reaction rates are calculated for one second of time, starting with the observed atmosphere and incoming solar flux. The distribution of atmospheric species cannot be perturbed very much by atmospheric motions in one second. Thus this approach is an effort to say something meaningful about world-wide photochemical balances without having to work out the vast complexities of the detailed motions nor does it neglect these motions. The global stratosphere as it now exists was produced by coupled atmospheric motions, photochemistry, and radiation balance. This analysis takes the atmosphere as it exists and asks about the instantaneous rates of the various elementary reactions and about certain rates of atmospheric transport.

The world-wide average transport of ozone from the stratosphere to the troposphere has been estimated by several authors,[67,68] and the upper limit of these estimates is about 5×10^{29} molecules sec^{-1} for the average world-wide vertical turbulent diffusion, including the "spring overturn" in polar regions. Horizontal motions inside the stratosphere are very much greater than the motions leading to these vertical losses. Both

horizontal and vertical motions distort the steady-state calculations. It was desired to find a method of computation that would help identify the important photochemical variables in the stratosphere which would not be distorted by the extensive, complicated, difficultly analyzed horizontal motions. The scheme is as follows: Start with the actual, measured, average distribution of ozone (Figure 5, for example) in the atmosphere. Set up an extensive grid all over the globe (every 5° latitude, every 15° longitude, and every kilometer from zero to 50, which gives 43,200 volume elements). Let a planar wave of sunlight impinge on the spherical earth. Calculate the radiation density for each nanometer of solar radiation above 190 nm in each of the volume elements, taking account of all absorbing species in the light path before it reaches the volume element. Calculate steady-state concentrations of oxygen atoms (Figures 6, 7, and 8) and the steady-state ratio of NO to NO_2. In this way, the radiation intensity as a function of wave length and the local concentrations of O_2, O_3, $O(^3P$, $O(^1D)$, NO, and NO_2 are known quantities. Then calculate the instantaneous reaction rates for the separable, elementary reactions

(a) $O_2 + h\nu \rightarrow O + O$

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

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

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

(f) $NO + O_3 \rightarrow NO_2 + O_2$

(g) $NO_2 + O \rightarrow NO + O_2$

(h) $NO_2 + h\nu \rightarrow NO + O$

(15) $O(^1D) + O_3 \quad O_2 + O_2$

in units of molecules cm^{-3} sec^{-1} in all of the volume elements. Carry out a zonal average (that is, average the rates all around the globe for each 5° band of latitude at each elevation) of all the rates. Present the instantaneous rates and certain sums and differences of them as contour lines on the zonal average maps. This procedure was carried out for two global situations, January 15 and March 22. These are referred to as the "winter-summer" and "spring-fall" conditions.

The zonal averaged instantaneous rate of oxygen photolyses for January 15 is given by Figure 15. This figure may be interpreted as the "gross rate of ozone formation" if the rate is multiplied by two. From Figure 5 it can be seen that ozone concentrations are 10^{12} or somewhat more in the lower stratosphere. There are 3×10^{7} seconds per year, and thus a rate of 3×10^{4} molecules cm^{-3} sec^{-1} would just produce 10^{12} molecules cm^{-3} in a year if there were no loss processes. There are large zones in the upper temperate and polar regions where the concentration of ozone greatly exceeds 10^{12} (Figure 5) and where the local production of ozone (Figure 15) is far less than 3×10^{4} molecules sec^{-1}. This discrepancy is explained in terms of massive transport of "clouds of ozone" from the formation region (Rate a 10^{5} greater) downward and poleward.[11]

The instantaneous rate of photolyses of ozone is given for winter-summer in Figure 16. Except in and near the region of polar night, this rate is surprisingly uniform all over the stratosphere. The rate of destruction of ozone by the Chapman mechanism

($O + O_3 \rightarrow O_2 + O_2$) is given by Figure 17 for the winter-summer situation.

For each volume element ($\Delta\theta = 5°$, $\Delta\phi = 15°$, $\Delta\Omega = 1$ km) the net rate of change of odd oxygen (ozone) is

$$\frac{d([O_3]+[O])}{dt} = 2j_a[O_2] - \text{chemical loss} - \text{transport loss} \quad (5\text{-}1)$$

The loss by transport can be either positive or negative for any given volume element. The integral of this rate over the entire stratosphere may be interpreted as

$$\begin{matrix}\text{Global rate}\\ \text{of ozone increase}\end{matrix} = 2\int \text{rate a} - \int \begin{matrix}\text{chemical}\\ \text{loss}\end{matrix} - \begin{matrix}\text{transport to}\\ \text{troposphere}\end{matrix} \quad (5\text{-}2)$$

The global ozone inventory is known as a function of time of year from the integral over a series of data such as Figure 5. The average rate of transport of ozone to the troposphere is known, as discussed above. The total rate of reaction a is readily found by integrating data such as Figure 15 over the entire stratosphere, and the value is 500×10^{29} molecules ozone produced per second. Thus one is able, by difference, to evaluate any model for "chemical loss" of ozone in the stratosphere. In particular, this approach gets around the very complicated problem of transport inside the stratosphere; all motions of ozone between one part of the stratosphere and another give a net change of zero to the instantaneous, globally integrated rates.

First, this method is used to see if the Chapman reactions alone, a, b, c, and e, are adequate to explain the chemical loss of ozone. The zonal average map for the net formation of ozone

$$\frac{d[O_3]}{dt} = 2j_a[O_2] - 2k_e[O][O_3] \qquad (5\text{-}3)$$

is given as Figures 18 and 19. Where this figure is positive, ozone is being formed faster than it is being destroyed by the Chapman reaction e. This quantity is positive for most of the stratosphere. The integral of this quantity over the entire global stratosphere is 414×10^{29} molecules ozone sec^{-1}. The transport of ozone to the troposphere is equal to or less than 5×10^{29} molecules sec^{-1}. If all chemical destruction of ozone is by the Chapman reactions, then the change of global ozone should be about 409×10^{20} molecules sec^{-1}. The integrated global inventory of ozone as a function of month of year is given by Figure 20, and the vectors at January 15 and March 15 give the calculated rate of increase of global ozone on the basis of the Chapman reactions, the integral over Figure 18. The discrepancy between the slope of the vectors and the slope of the global ozone inventory is enormous. The integrated, instantaneous, global, gross rate of formation of ozone ($2j_a[O_2]$) is 500×10^{29}; twice Rate e is 86×10^{29}. Thus the Chapman model removes ozone by one-fifth as fast as it is formed. This five-fold discrepancy is a world-wide average, and the same discrepancy is found at every season (spring, summer, fall, or winter). As a chemist fairly familiar with the literature of this field, I regard it is very unlikely that this discrepancy can be explained in terms of uncertainties in the values of the rate constants for the Chapman reactions. It is concluded therefore that some chemical process other than the Chapman reactions is very active in destroying stratospheric ozone.

Brewer and Wilson[67] carried out an analysis similar to that given above, except they had not quite so fine a grid and they were less sure of their rate constants. They attempted, unsuccessfully, to explain the discrepancy in terms of errors in the Chapman rate constants, errors in the intensity of the solar ultraviolet radiation, and in terms of the "water reactions". The "water reactions" have been discussed in an earlier section, and it can be said that they are quite inadequate to explain the discrepancy between the instantaneous rate of formation of ozone and the rate of destruction of ozone.

Following the evidence of Figures 8, 10, 11, and 12, we turn now to the question of how much oxides of nitrogen in the natural stratosphere would be required to remove the discrepancy between the rate of formation and destruction of ozone. It is desirable to have a simple, one-dimensional variation function. Maps such as Figure 19 were prepared and integrated for various assumed concentrations of NO_x, uniform from 15 to 50 kilometers and uniform with latitude and longitude (It is recognized, of course, that such a uniform distribution is not "realistic", but these calculations are made to see what order of magnitude of NO_x is required and to see what other effects NO_x would have on maps such as Figure 19). As expected, the addition of NO_x increases the rate of ozone destruction. A uniform concentration of 4.2×10^9 for spring-fall and 4.4×10^9 molecules cm^{-3} for winter-summer reduces the unbalanced rate of ozone production down to the rate of transport from stratosphere to troposphere. At concentrations of NO_x greater than 4.2×10^9, global ozone is destroyed faster than it is formed, and thus

the global ozone inventory would decrease. At about 8.4×10^9 molecules cm^{-3} of NO_x, the vectors in Figure 20 have about the same magnitude, but they point down instead of up, indicating a very strong decrease in the global ozone inventory.

Now it is of interest to see what the detailed effects (all over the globe) are of the assumed uniform concentration of NO_x that balance the global ozone rate. For this purpose, define the "odd oxygen ratio"

$$\gamma = \frac{\text{rate of odd oxygen production}}{\text{rate of odd oxygen destruction}} \tag{5-4}$$

$$= \frac{2j_a[O_2] + j_h[NO_2]}{2k_e[O][O_3] + k_f[NO][O_3] + k_g[O][NO_2]}$$

This expression, γ, is greater than one if ozone (odd oxygen) is locally, photochemically produced faster than it is destroyed. Conversely it is less than one if ozone is destroyed chemically faster than it is being made. It is precisely one at the photochemical steady state. Figure 21 gives the map of the odd oxygen ratio for the Chapman reactions. There is large region in the lower, tropical stratosphere where ozone is produced more than 1000 times faster than it is destroyed and the positive region embraces most of the stratosphere. The odd oxygen ratio for the case of $[NO_x] = 4.2\times10^9$ molecules cm^{-3} (the value that achieves an integrated global balance) is given by Figure 22. Most of the stratosphere is brought close to instantaneous local balance. Whereas the Chapman reactions alone had odd oxygen ratios higher than 1000, the added NO_x has leveled out to 1.0 ± 0.2 for most of the stratosphere and to 1.0 ± 0.4 for all of the stratosphere.

The uniform concentration of oxides of nitrogen at 4.2×10^9 molecules cm^{-3} brings about a global balance between the instantaneous production of ozone and its destruction by all processes. The instantaneous global rates of the individual reactions are given as follows: $NO + O_3 \rightarrow NO_2 + O_2$, Figure 23; $NO_2 + h\nu \rightarrow NO + O$, Figure 24; and $NO_2 + O \rightarrow NO + O_2$, Figure 25.

The conclusion at this section is that the Chapman reactions alone are grossly unable to explain the ozone balance in the stratosphere. Some other chemical agent is very active in destroying ozone in the stratosphere. About 4.2×10^9 molecules cm^{-3} of NO_x are sufficient to remove the global disbalance and to smooth out local, anomalous, unbalanced rates (compare ref. 3a).

VI. COMPARISON OF NATURAL AND ARTIFICIAL SOURCE STRENGTHS OF NO_x IN THE STRATOSPHERE[4d,e,f]

In section II it was shown that the oxides of nitrogen are very powerful catalysts for the destruction of ozone under stratospheric conditions. In section III it was shown that the total vertical column of ozone in the stratosphere is sensitive to NO_x at one part per billion or more, and a major reduction is to be expected if NO_x is as much as 10 ppb. In section IV it was shown that the existing ozone distribution in the stratosphere requires some powerful chemical inhibitor of ozone, and the only agent known capable of this action is nitric oxide and nitrogen dioxide. On a world-wide basis, ozone is destroyed by NO_x about four times faster than by all other mechanisms put together. Since stratospheric ozone varies as the square root of the destruction rate, global ozone is now a factor of two less than it would be if there were no oxides of nitrogen in the stratosphere.

Supersonic transport planes fly in the stratosphere and emit oxides of nitrogen from their exhaust. One asks how much the natural NO_x level of the stratosphere would be increased by full scale operation of a fleet of SST. This question is a difficult one. The exhaust would be laid down in a long thin ribbon at the cruise height, it would be strongly transported by horizontal winds, it would be slowly shifted by vertical components of wind, it would be subject to large horizontal and weak vertical turbulence, and it would eventually be removed from the stratosphere. The removal processes include vertical eddy diffusion to the top

of the stratosphere where NO is photodissociated[18b] to N and NO, vertical diffusion to the bottom of the stratosphere where (largely in the form of nitric acid) it would be removed by rain-out in the troposphere, it would be swept out by horizontal motions (with small vertical components) through breaks in the tropopause in temperate and polar regions, and it would be released by the "spring overturn" in polar regions. While in the stratosphere the NO is converted to NO_x every night and photochemically reformed every day. During the night about 5 per cent of the nitrogen dioxide is converted to dinitrogen pentoxide (N_2O_5), which is largely photolyzed again the next day. Also, N_2O_5 may react with water on the surface of particulate matter to form nitric acid. Hydroxyl radicals produced during the day mostly add to nitrogen dioxide to produce nitric acid, add to nitric oxide to produce nitrous acid, or abstract a hydrogen atom from nitric or nitrous acid to reform the active oxides of nitrogen and water. The nitric acid diffuses down to be removed as rain in the troposphere, and it diffuses up to be photolyzed back to NO_2. Throughout these complicated chemical reactions, the oxides of nitrogen move very extensively under the influence of horizontal winds. The net burden and distribution of NO_x from the SST in the stratosphere, subject to all these chemical and meteorological complexities, are very complex problems. It may take 10 years of concentrated effort by chemists and meteorologists to solve this extremely difficult problem, although certain large aspects of the problem may be cleared up in two years.[69]

It is not necessary to solve this extremely difficult problem to get a good insight into the magnitude of the threat of the SST to stratospheric ozone. Both the natural and the artificial (SST) source strengths of NO_x in the stratosphere are fairly well known, Tables 1A and 2. On a global basis, the natural sources of NO in the stratosphere is from the reaction $O(^1D) + N_2O \rightarrow 2NO$ at 25±5 km, and it is estimated to be

$$\text{Natural source of NO} = (0.35 \text{ to } 1.5)\times10^{8}\ \frac{\text{molecules}}{\text{cm}^2\ \text{sec}} \times 5\times10^{18}\ \frac{\text{cm}^2}{\text{world}}$$

$$= (1.8 \text{ to } 7.5)\times10^{26}\ \frac{\text{molecules}}{\text{sec}}$$

On a global basis the artificial source strength of NO_x from 500 SST can be calculated from Table 2

$$\text{Artificial source of NO} = 500\ \text{SST}\times\frac{7\ \text{hr flight}}{\text{day}}\times\frac{1\ \text{day}}{8.6\ 10^{4}\ \text{sec}}$$

$$\times132000\ \frac{\text{lb fuel}}{\text{hr flight}}\times 0.15\ \frac{\text{lb NO}}{\text{lb fuel}}$$

$$\times452\ \frac{\text{g}}{\text{lb}}\times\frac{1}{30}\ \frac{\text{moles}}{\text{g}}\times6\times10^{23}\ \frac{\text{molecule}}{\text{mole}}$$

$$= 7.3\times10^{26}\ \frac{\text{molecules}}{\text{sec}}$$

Thus 500 American SST as conceived in 1971 would constitute a source of NO at 20 km equal to or several times greater than the natural flux of NO 500 Concordes[30] would emit about one-third as much NO at elevations between 17 and 19 km.

The natural flux of NO from N_2O is subject to all of the complexities of stratospheric motions and photochemistry, including the formation and destruction of nitric acid. In spite of all these complexities, the natural NO_x reduces global ozone by about a factor of two below the value it would have in the absence of NO_x. Addition of 500 SST to the stratosphere would double or more the source strength of NO in the stratosphere, and it then faces all of the complexities of the stratosphere (motions, minor species, HNO_3, etc.) just like the natural NO_x. Unless positive evidence is developed to the contrary, one should assume that the artificial NO_x would play a role similar to the natural NO_x in the stratosphere, namely, it would reduce ozone by a large amount.

It is possible that the distribution of NO_x from SST flying at 20 km will be different from the natural distribution of NO_x from N_2O formed at 25±5 km. The effect of NO_x on ozone is strongly affected by the distribution of NO_x, not just the amount. It is not clear, however, whether this different distribution of artificial NO_x would reduce ozone more or less than an equal amount of natural NO_x.

In summary, the oxides of nitrogen now appear to be (by far) the most important ingredient in the natural balance of ozone, and 500 SST promise to double or more the present source of NO_x in the stratosphere.

VII. CONCLUSIONS AND COMPARISONS WITH OTHER STUDIES

The conclusions to my principal 1971 report are quoted in full here (reference 4a, pp. 105-106, 114):

"Conclusions

"(1) If NO and NO_2, as such, build up in the stratosphere to the expected [SCEP, 1970; ref. 2; Park and London, 1971, ref. 28] 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 the 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.

"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."

To date (August, 1972) no articles have been published that contradict or substantially alter any of the conclusions quoted above or the detailed chemical arguments[4a,d] upon which they are based. Several recent articles or reports on this subject will be briefly reviewed:

The Australian Academy of Science[30] in a special report "Atmospheric Effects of Supersonic Aircraft" included the following statements in its conclusions and recommendations: "...The aircraft industry should take all possible steps to minimize nitrogen oxide emission from engines". [compare with SCEP (1970) "...NO_x...may be neglected"] "...the possibility of deleterious changes cannot be totally dismissed...". However, this committee's

first statement of conclusion was: "On the basis of the data available to us we would not expect significant adverse climatic effects to derive from supersonic aircraft assumed by us to be flying in 1985". I have discussed this report in an article in Search.[4e] In the same issue of Search,[70] there are several quotations adverse to my case, although these quotations include a certain amount of personal feelings and hearsay.

The Department of Commerce Panel on Supersonic Transport Environmental Research[29] "concludes that in certain critical areas of information, reliable data are lacking and further, directed, mission-oriented research must be performed in order to provide a basis for decision making". The Department of Transportation under its Climatic Impact Assessment Program[69] has initiated a broad program of research that more or less parallels the general recommendations of this panel. An insight into the detailed thinking of this panel is given by the quotation "...it was felt that the most important uncertainty associated with the environmental consequences of SST operation was that of the currently existing concentration of NO..."

A.A. Westenberg[71] was among the first to point out the effect of the oxides of nitrogen on ozone under stratospheric conditions. He stated: "A strongly catalytic effect of NO_x in reducing O_3 is indicated...The possible effects of the artificial addition of NO_x (as by large scale SST operations) is considered, and it is emphasized that the relative importance of this is crucially dependent on the amount of NO_x already present naturally".

P. Crutzen has published technical articles[3a,b] on this subject and one general[3c] article SST's-A Threat to the Earth's Ozone Shield, which includes the statement: "Although it is not possible to assess at this stage the real environmental consequences of future supersonic air transport, present knowledge indicates that there exists a real possibility of serious decreases in the atmospheric ozone shield due to the catalytic action of the oxides of nitrogen, emitted from supersonic aircraft".

E. Hesstvedt[72] carried out calculations of the effect of NO_x on stratospheric ozone, including atmospheric motions. Assuming a uniform background of 10 ppb of NO_x he found that doubling the oxides of nitrogen would decrease the vertical column of ozone by 18 per cent. For a factor of 2 increase above the same background of NO_x, a steady-state calculation with a static atmosphere gives a decrease of ozone by 20 per cent (Figure 9, ref. 4a; Figure 6, curve A, ref. 4c). This computation with atmospheric motions and global circulation gives very nearly the same ozone reduction as the static model.

An ad hoc panel of the U.S. National Academy of Sciences, National Research Council under the chairmanship of Herbert Friedman reviewed the work of references 3a and 4a,b of this article.[71] The report of this panel included the statement: "There was general agreement with the conclusions of Johnston and Crutzen that the introduction of nitrogen oxides from SST exhausts in the stratosphere can have important effects on the ozone concentration..." The report then reviewed some of the uncertainties in the field

and made recommendations for research in several areas. It stated: "...the possibility of serious effects on the normal ozone content cannot be dismissed".

In March 1971 the concensus[1,2] of atmospheric scientists and SST planners was that the oxides of nitrogen in the stratosphere "...may be neglected".[2] In August 1972 the concensus[29,30,69,79,73] of the same group is that "...NO_x is a highly important variable in this problem and it must be given realistic consideration".[4a] My detailed calculations[4a,b,d] were designed only to convince people that NO_x is an important variable; they never pretended to be the required "realistic consideration". My calculated ozone reduction (3 to 50 per cent for 500 American SST, depending on atmospheric motions and distributions of NO_x) was an unexaggerated statement of the possible effects within the range of uncertainty. In view of the "realistic consideration" being given to the NO_x problem,[69] I regard the contention of the 1971 articles[4a,b,3a,b] already to have been generally accepted.

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Appendix A

Computational Procedure for Steady-State Ozone Profiles

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

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

The expression for the general iteration is

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

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

$$
V_{n+1} = \frac{\alpha M F X_n \left(1 + \frac{2IW_n}{FX_n} + \frac{JY_n}{FX_n}\right)}{FX_n + (G+J)Y_n + H + 2IW_n}
$$

$$
W_{n+1} = \alpha M - V_{n+1}
$$

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

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

$$j_a(S) = \sum_{\lambda} Q(\lambda)\ \sigma(\lambda)\ L(S,\lambda) \qquad \text{(A-3)}$$

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. The rate constants j_a, j_c, and j_h are calculated here directly from modern values of incoming solar radiation and absorption cross sections for O_2, O_3, and NO_2.

The solar radiation at the top of the atmosphere was obtained from Ackerman

$$L_o = L_o(\lambda) \qquad \text{(A-4)}$$

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

$$L(\lambda,S,\phi) = L_o \exp-(\sigma_x N_x + \sigma_z N_z + \sigma_v N_v)\,\text{secant}\phi \qquad \text{(A-5)}$$

where N is the vertical column of a species above elevation S in units of molecules/cm^2. The cosine of the solar angle is

$$\cos\phi = \cos\Lambda\cos\theta\cos\Delta + \sin\Lambda\sin\Delta \qquad \text{(A-6)}$$

where Λ is the latitude on the earth, θ is the local solar angle where $\theta = 0$ corresponds to local solar noon, and Δ is the solar declination. The 24 hour average intensity $\overline{L(\lambda,s)}$ is found for a given latitude by summing Eq. (A-5) over every 5 degrees of solar angle

$$\overline{L(\lambda,s)} = \sum L(\lambda,s,\phi) \qquad \text{(A-7)}$$

in increments of 5° each

The photolysis rate constants are

$$\underline{A} = j_a[O_2]\sum_{190}^{242} \overline{L(\lambda,S)}\sigma_z[O_2] \qquad \text{(A-8)}$$

$$C = j_c = \sum_{190}^{350} \overline{L(\lambda,S)}\sigma_x + \sum_{450}^{650} \overline{L(\lambda,S)}\sigma_x$$

$$\underline{H} = j_h = \sum_{260}^{400} \overline{L(\lambda,S)}\ \sigma_v$$

Since $\underline{a}$ and $\underline{c}$ both involve radiation between 190 and 242 nm, each of these constants at an elevation $\underline{S}$ depends on the total column of both O_2 and O_3 above $\underline{S}$. 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; which is estimated by integration of the profiles given by the classic rocket probes for ozone. The constants A, C and H at 50 km are evaluated from Eq. (A-8). 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. (A-1) to (A-2), 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. (A-4) to (A-8), 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, effect of NO_x, life-times, etc., it is necessary to be as realistic as possible. The method used here averages the radiation intensity every 5 degrees of solar angle (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 below 200 nm, where the sharp intense Schman-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;

0 0 0 0 3 8 0 0 2 1

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 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.

Appendix B

Chemical and Photochemical Reactions

A. The Chapman or "pure air" reactions

a. $O_2 + h\nu$ (below 242 nm) $\rightarrow O + O$

b. $O + O_2 + M \rightarrow O_3 + M$

c. $O_3 + h\nu \rightarrow O_2 + O$

d. $O + O + M \rightarrow O_2 + M$

e. $O_3 + O \rightarrow O_2 + O_2$

B. Reactions of the oxides of nitrogen that enter the catalytic cycles for ozone formation and destruction

f. $NO + O_3 \rightarrow NO_2 + O_2$

g. $NO_2 + O \rightarrow NO + O_2$

h. $NO_2 + h\nu$ (below 400 nm) $\rightarrow NO + O$

h'. $NO_2 + h\nu$ (below 245 nm) $\rightarrow NO + O(^1D)$

i. $NO + NO + O_2 \rightarrow 2NO_2$

j. $NO + O + M \rightarrow NO_2 + M$

k. $NO_2 + O_3 \rightarrow NO_3 + O_2$

ℓ. $NO_3 + h\nu$ (red light) $\rightarrow NO + O_2$

m. $NO_2 + NO_3 \xrightarrow{M} N_2O_5$

n. $N_2O_5 \xrightarrow{M} NO_2 + NO_3$

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

p. $N_2O_5 + h\nu$ (below 380 nm) $\rightarrow 2NO_2 + O$ (?)

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

r. $NO_3 + NO \rightarrow 2NO_2$

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

C. Sources and sinks of the active oxides of nitrogen, NO and NO_2

t. $N_2 + h\nu$ (below 120 nm) $\rightarrow N + N$

u. $N + O_2 \rightarrow NO + O$

v. $N + NO \rightarrow N_2 + O$

w. $NO + h\nu$ (below 190 nm) $\rightarrow N + O$

x. $N_2O + O(^1D) \rightarrow N_2 + O_2$

y. $N_2O + O(^1D) \rightarrow N_2 + O_2$

z. $N_2O + O(^1D) \rightarrow NO + NO$

(1) $HO + NO_2 \xrightarrow{M} HNO_3$

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

(3) $HNO_3 + h\nu$ (below 325 nm) $\rightarrow HO + NO_2$

(4) $HO + NO + M \rightarrow HNO_2 + M$

(5) $HO + HNO_2 \rightarrow H_2O + NO_2$

(6) $HNO_2 + h\nu$ (below 400 nm) $\rightarrow HO + NO$

(7) $N_2O_5 + H_2O$ (on particles) $\rightarrow 2HNO_3$ (?)

D. Reactions of excited oxygen species

(c1) $O_3 + h\nu$ (450-650 nm) $\rightarrow O_2 + O$

(c2) (310-340 nm) $\rightarrow O_2(^1\Delta) + O$

(c3) (below 310 nm) $\rightarrow O_2(^1\Delta) + O(^1D)$

(8) $O(^1D) + O_2 \rightarrow O + O_2(^1\Sigma)$

(9) $O(^1D) + M \rightarrow O + M$

(10) $O_2(^1\Delta) + M \rightarrow O_2 + M$

(11) $O_2(^1\Sigma) + M \rightarrow O_2 + M$

(12) $O(^1D) \rightarrow O + h\nu$ (630 nm)

(13) $O_2(^1\Sigma) \rightarrow O_2 + h\nu$ (760 nm)

(14) $O_2(^1\Delta) \rightarrow O_2 + h\nu$ (1270 nm)

(15) $O(^1D) + O_3 \rightarrow O_2 + O_2$

(16) $O_2(^1\Delta) + O_3 \rightarrow O_2 + O_2 + O$

(17) $O_2(^1\Sigma) + O_3 \rightarrow O_2 + O_2 + O$

E. Reactions of free radicals based on water (HO_x)

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

(19) $O(^1D) + H_2 \rightarrow H + HO$

(20) $O(^1D) + CH_4 \rightarrow CH_3 + HO$

(21) $H + O_2 + M \rightarrow HOO + M$

(22) $H + O_3 \rightarrow HO(v \leq 9) + O_2$

(23) $HO + O \rightarrow H + O_2$

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

(25) $\rightarrow H_2 + O_2$

(26) $\xrightarrow{M} H_2O_2$

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

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

(29) $H_2O_2 + O \rightarrow HO + HOO$

(30) $H_2O_2 + h\nu \rightarrow HO + HO$

(31) $H_2O_2 + HO \rightarrow H_2O + HOO$

(32) $HO(v \leq 2) + O_3 \rightarrow H + O_2 + O_2$

(33) $HO + O_3 \rightarrow HOO + O_2$ (?)

(34) $HOO + O_3 \rightarrow HO + O_2 + O_2$ (?)

F. Reactions related to methane

(35) $O + CH_4 \rightarrow CH_3 + HO$

(36) $HO + CH_4 \rightarrow H_2O + CH_3$

(37) $CH_3 + O_2 \rightarrow H_2CO + HO$

(38) $CH_3 + O_2 \xrightarrow{M} CH_3OO$

(39) $CH_3OO + h\nu \rightarrow H_2CO + HO$ (?)

(40) $CH_3OO + NO \rightarrow CH_3O + NO_2$ (?)

(41) $CH_3OO + NO \xrightarrow{M} CH_3OONO \xrightarrow{h\nu} ?$ (?)

(42) $CH_3OO + NO_2 \rightarrow CH_3OONO_2 \xrightarrow{h\nu} ?$ (?)

(43) $H_2CO + h\nu \rightarrow H_2 + CO$

$\rightarrow H + HCO$

(44) $HCO + O_2 \rightarrow CO + HOO$

(45) $H_2 + HO \rightarrow H_2O + H$

(46) $CO + HO \rightarrow CO_2 + H$

(47) $HOO + NO \rightarrow NO_2 + HO$

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Titles to Figures

Figure 1. Zonal average temperature °K (March 22) as a function of latitude and altitude. The tropopause is indicated by the dashed line. -90 to 0, northern hemisphere; 0, equator; 0 to +90, southern hemisphere.

Figure 2. Temperature (January 15).

Figure 3. Air concentration (N_2, O_2, Ar) in molecules cm^{-3} as a function of elevation and average latitude. 5(E16) ≡ 5×10^{16}.

Figure 4. Mole fraction of ozone based on average observations over several years, in parts per million.

Figure 5. Concentration of ozone, molecules cm^{-3}, average observations.

Figure 6. Concentration of oxygen atoms calculated from observed ozone (Figure 5) and local light intensity as of March 22. The calculated concentrations were averaged over longitude (15° grid) to give world-wide average value, or these concentrations may be interpreted as the 24 hour average [O] at each point.

Figure 7. Same as Figure 6, but for January 15.

Figure 8. Concentration of singlet oxygen atoms, $O(^1D)$, zonal average, March 22.

Figure 9. Rate of production of hydroxyl radicals (molecules cm^{-3} sec^{-1}) from the reaction of $O(^1D)$ with water and methane, March 22.

Figure 10. Ratio for rate of destruction of ozone by the catalytic cycle ($NO + O_3 \rightarrow NO_2 + O_2$, $NO_2 + O \rightarrow NO + O_2$) to the rate of destruction in pure air ($O + O_3 \rightarrow O_2 + O_2$) as a function of the full range of the independent variables, [NO] and [O], at one temperature, 220°K: -----. Half time for ozone destruction ———.

Figure 11. Rate of formation of nitric acid from the reaction $HO + NO_2 \overset{M}{\rightarrow} HNO_3$, 300°K, M is He. Observed points and theoretical curve (adjusted to observations at 1 atm).

Figure 12. Proposed distributions for the oxides of nitrogen in the stratosphere (Park and London, 1971), natural background and maximum expected perturbation by supersonic transports.

Figure 13. Steady state distribution of stratospheric ozone as calculated from Park and London's distributions (Figure 12). A. With correct value of k_i. B. With Park and London's value of k_i.

Figure 14. A. Steady-state ozone profiles calculated on the basis of no oxides of nitrogen and with various assumed values for uniform mole fractions (parts per billion) of NO_x.
B. Same as Figure 14A, but with various assumed values for uniform concentration of NO_x.

Figure 15. The rate of elementary reaction a ($O_2 + h\nu \rightarrow O + O$) as an instantaneous average around the world or as a 24 hour average at one position. If multiplied by 2 this may be interpreted as the gross rate of ozone formation, January 15.

Figure 16. The global rate of the elementary reaction c ($O_3 + h\nu \rightarrow O_2 + O$).

Figure 17. The global rate of the elementary reaction e ($O_3 + O \rightarrow O_2 + O_2$).

Figure 18. Net rate of formation of ozone according to the Chapman mechanism (2 Rate a minus 2 Rate e), January 15.

Figure 19. Same as Figure 18, March 22.

Figure 20. Seasonal change of global ozone inventory compared to instantaneous net rate of ozone production, January 15 and March 22.

Figure 21. Odd oxygen ratio: the rate of ozone formation divided by the rate of ozone destruction, Chapman mechanism, January 15.

Figure 22. Same as Figure 21, but with 4.4×10^9 molecules cm^{-3} of NO_x added throughout the stratosphere. This relatively small amount of NO_x is sufficient to remove the major discrepancies of Figure 21.

Figure 23. The rate of the elementary reaction f ($NO + O_3 \rightarrow NO_2 + O_2$) under conditions of Figure 22.

Figure 24. The rate of the elementary reaction h ($NO_2 + h\nu \rightarrow NO + O$), as in Figure 22.

Figure 25. The rate of the elementary reaction g ($NO_2 + O \rightarrow NO + O_2$), as in Figure 22.

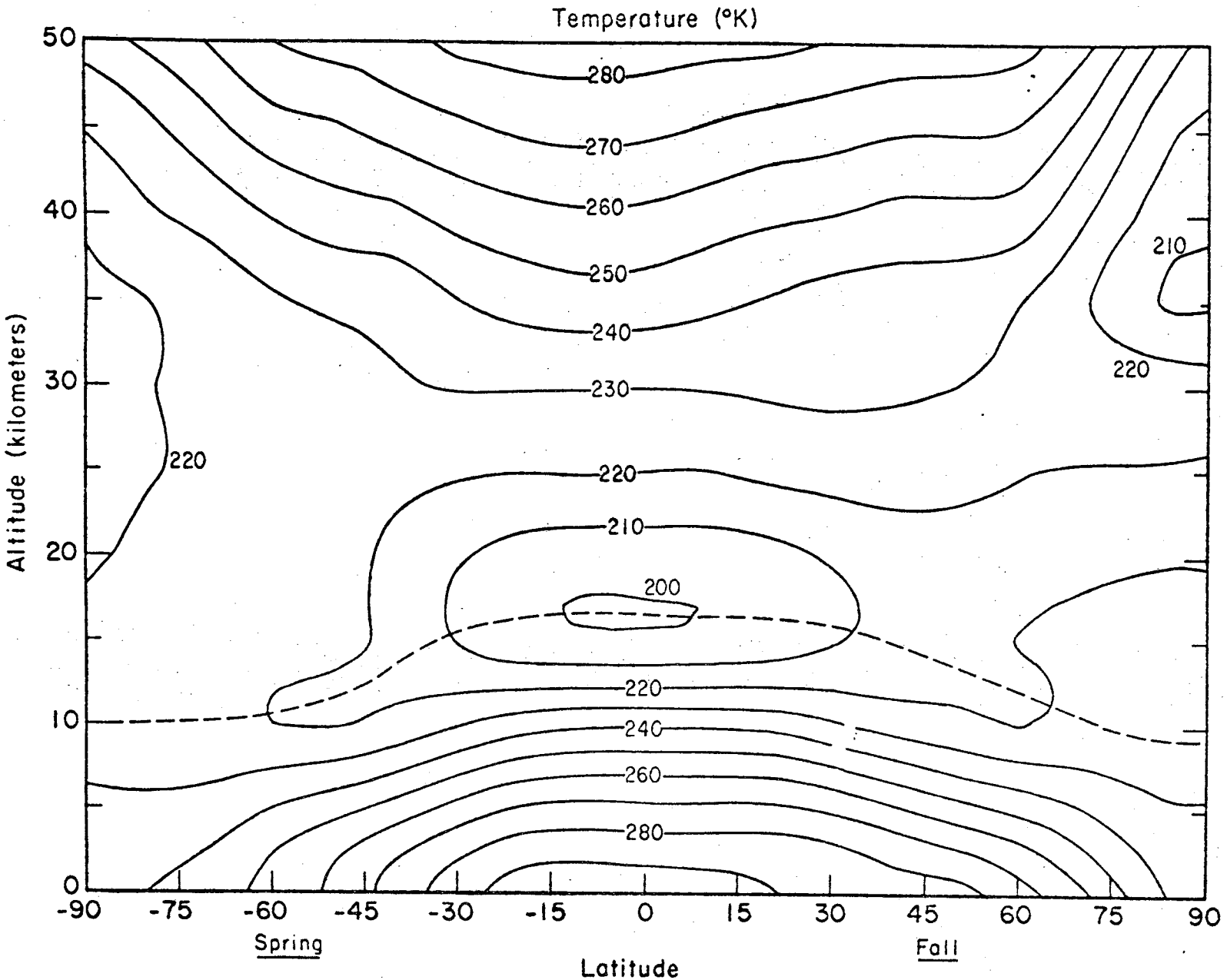

Fig. 1

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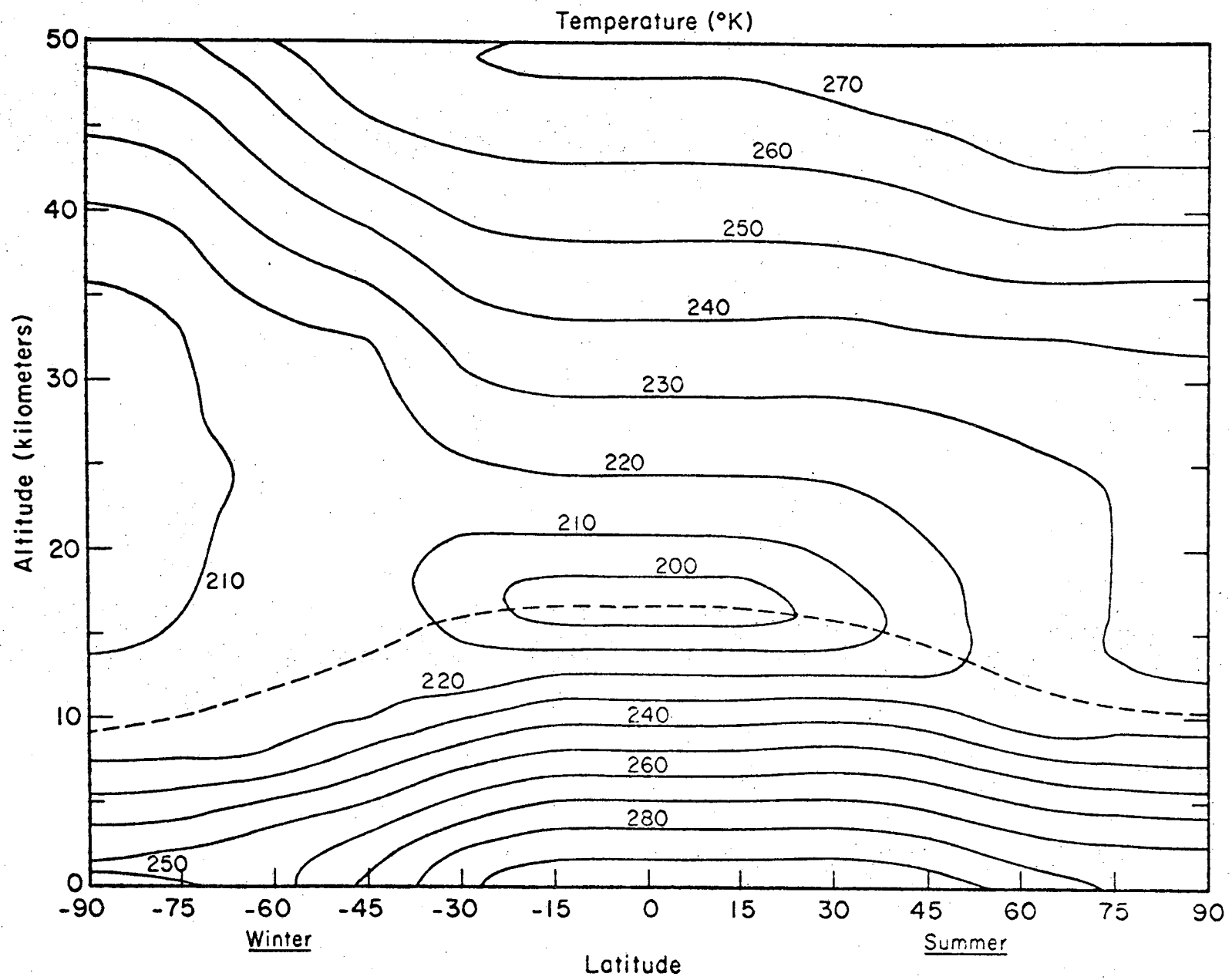

Fig. 2

XBL 726-6734

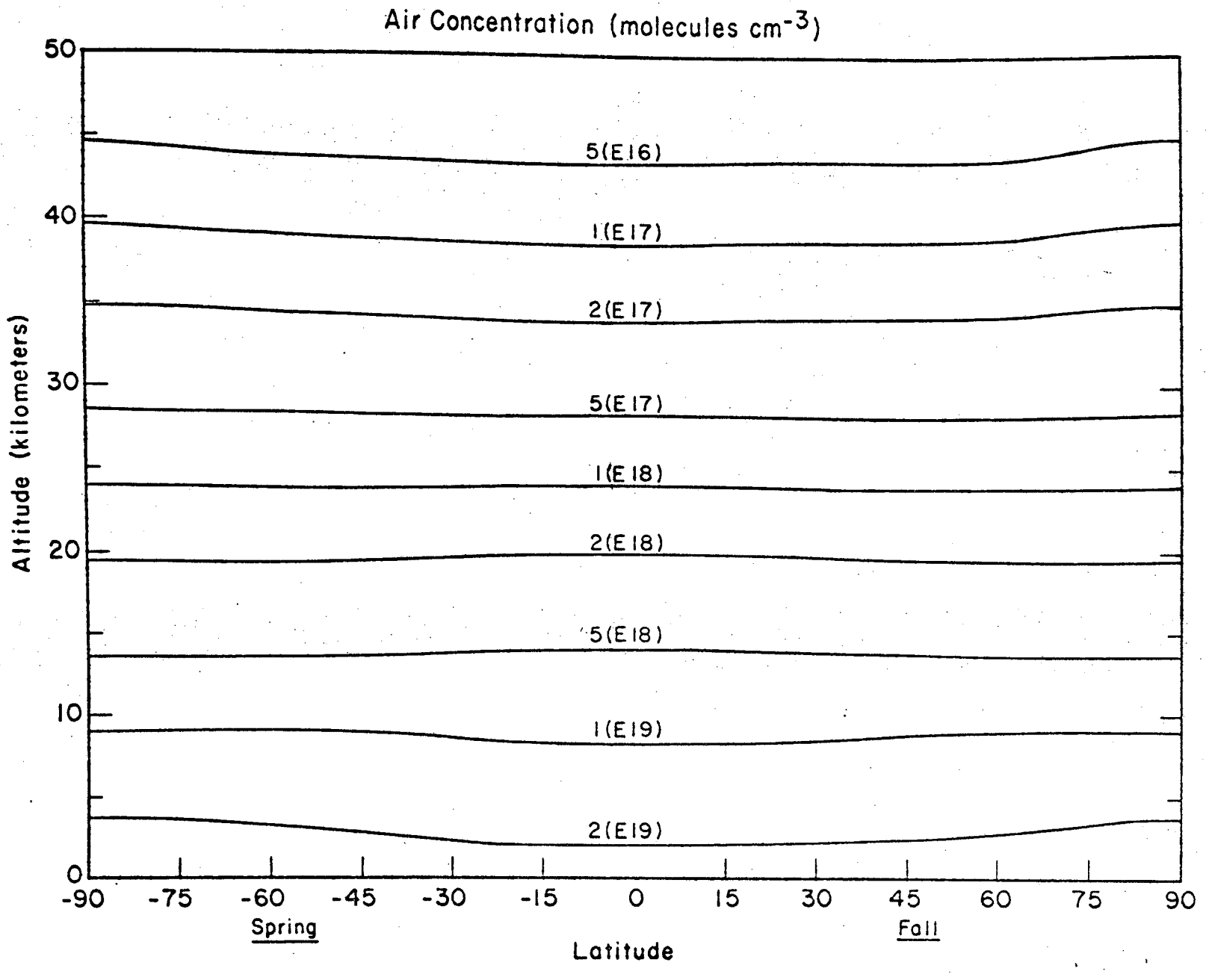

Fig. 3

XBL 728-6733

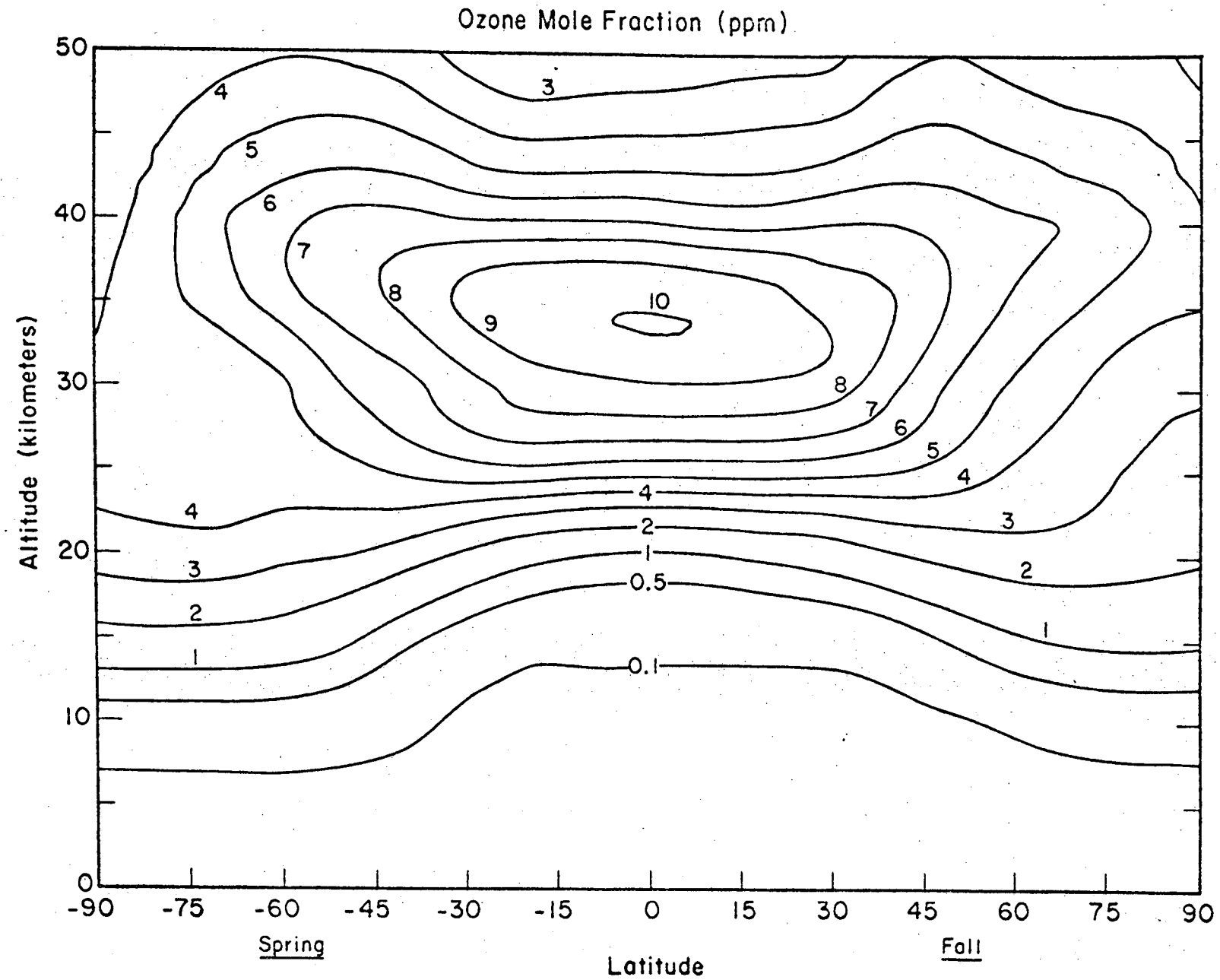

Fig. 4

XBL 728-6742

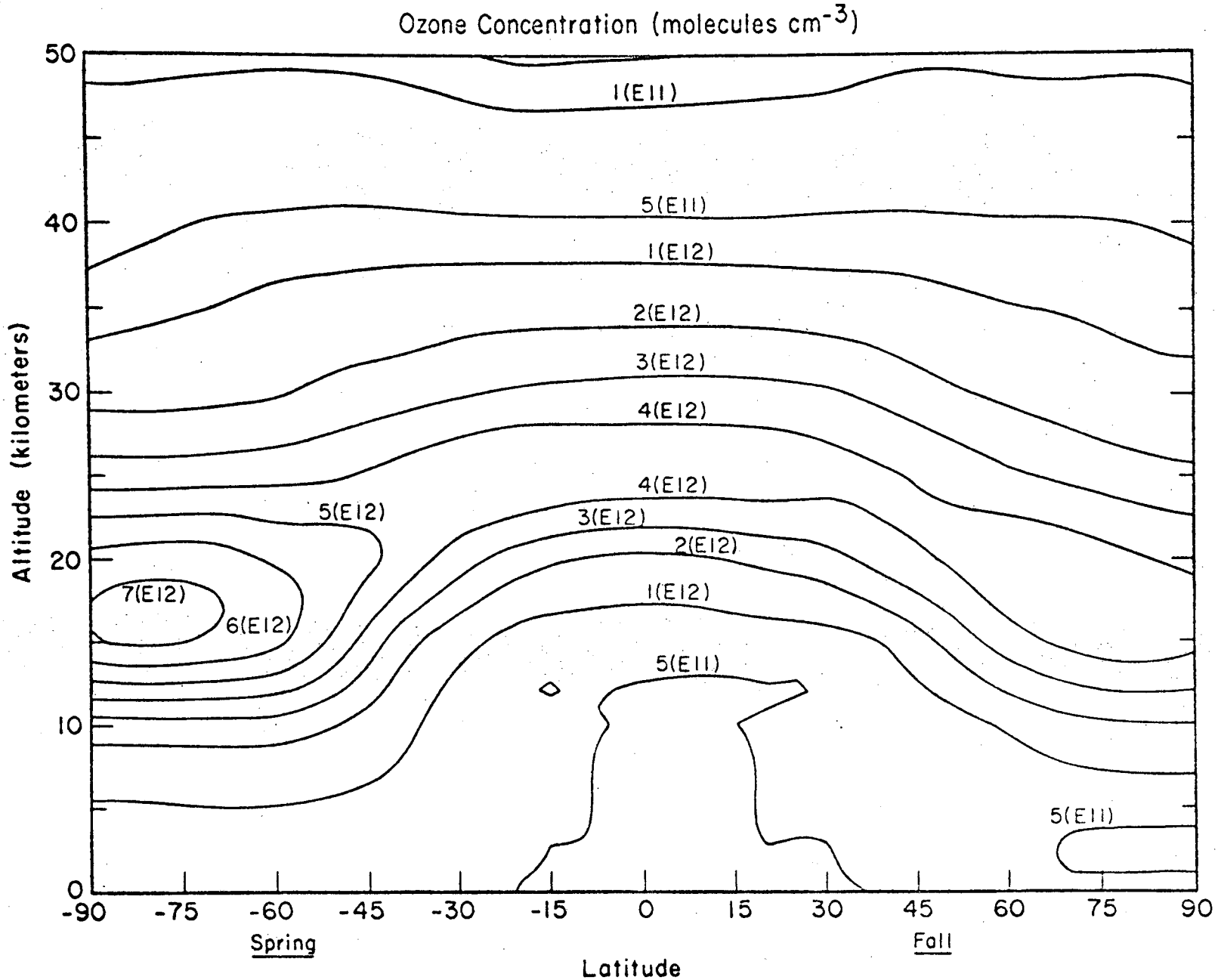

Fig. 5

XBL 728-6735

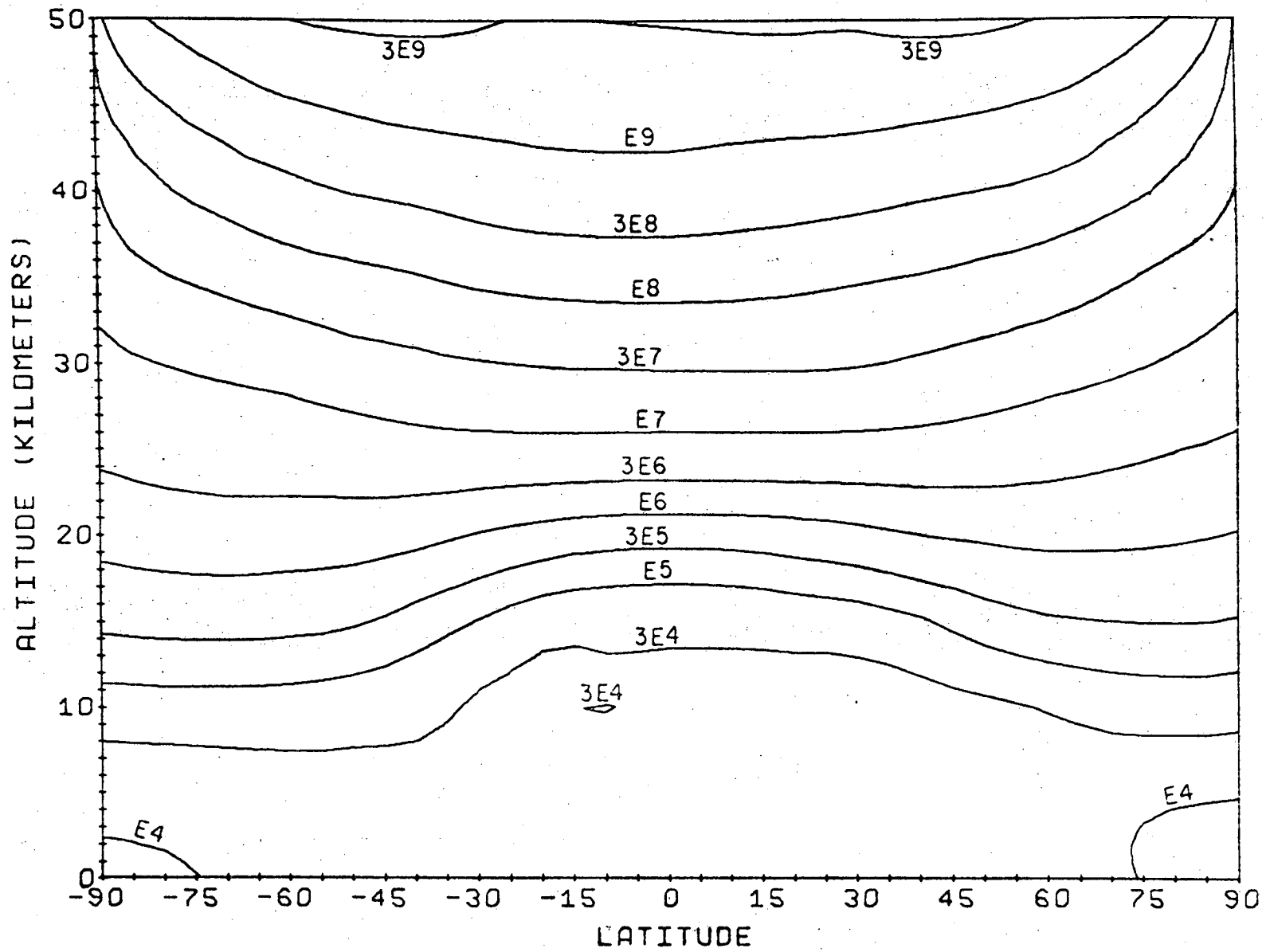
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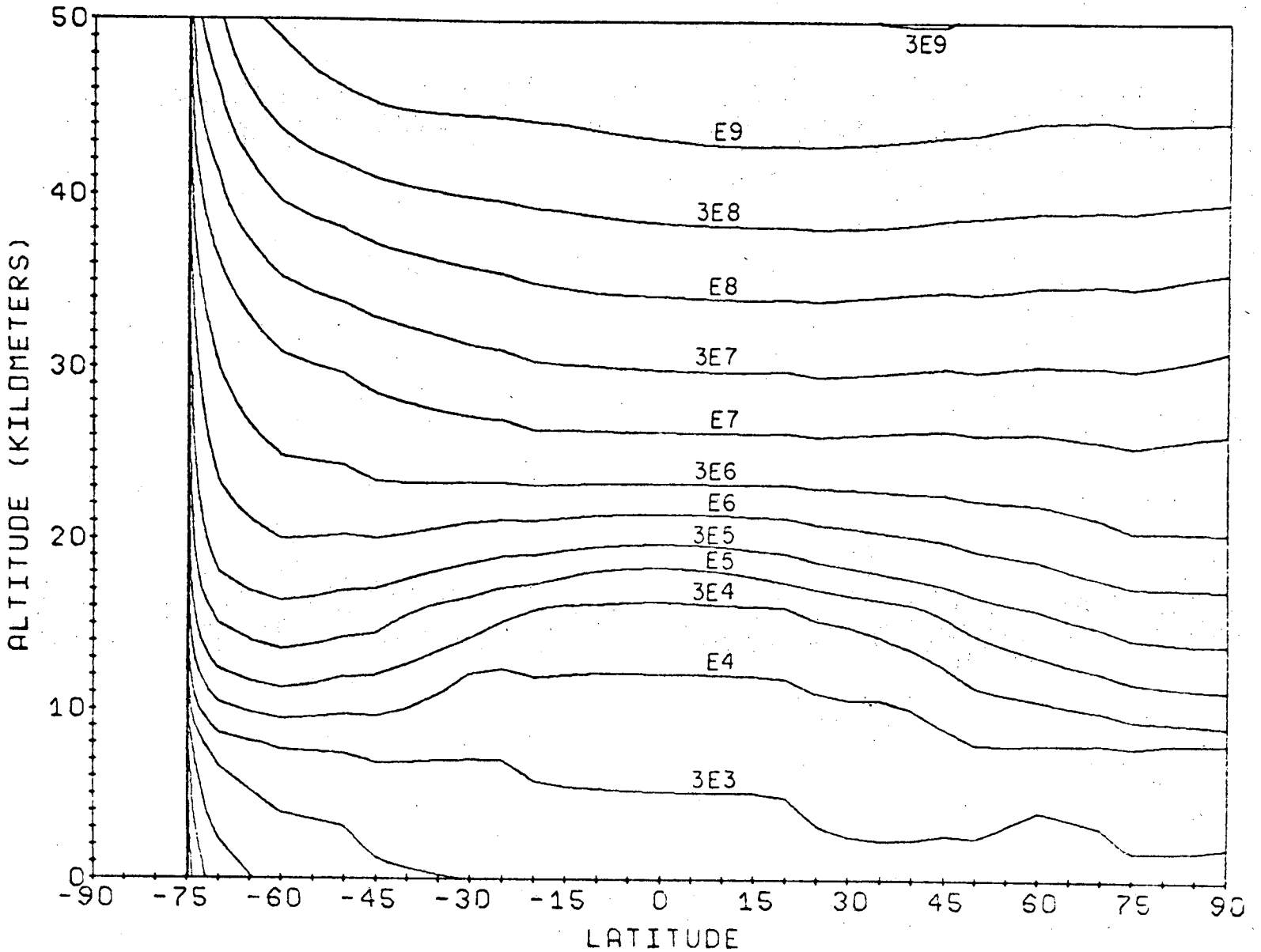
Fig. 6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3E3

Fig. 7

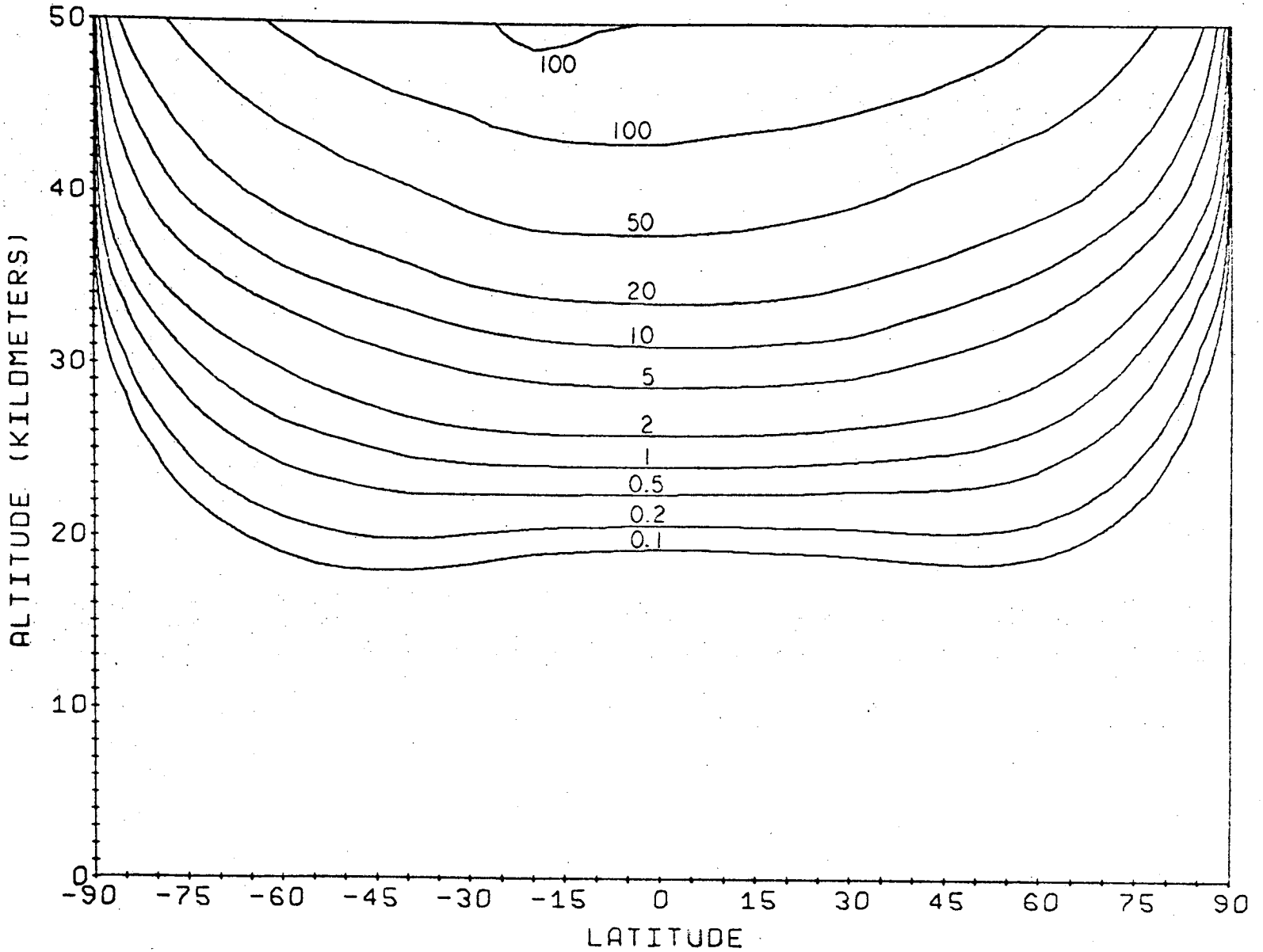

ALTITUDE (KILOMETERS)
50
40
30
20
10
0
-90
-75
-60
-45
-30
-15
0
15
30
45
60
75
90
LATITUDE
100
100
50
20
10
5
2
1
0.5
0.2
0.1

Fig. 8

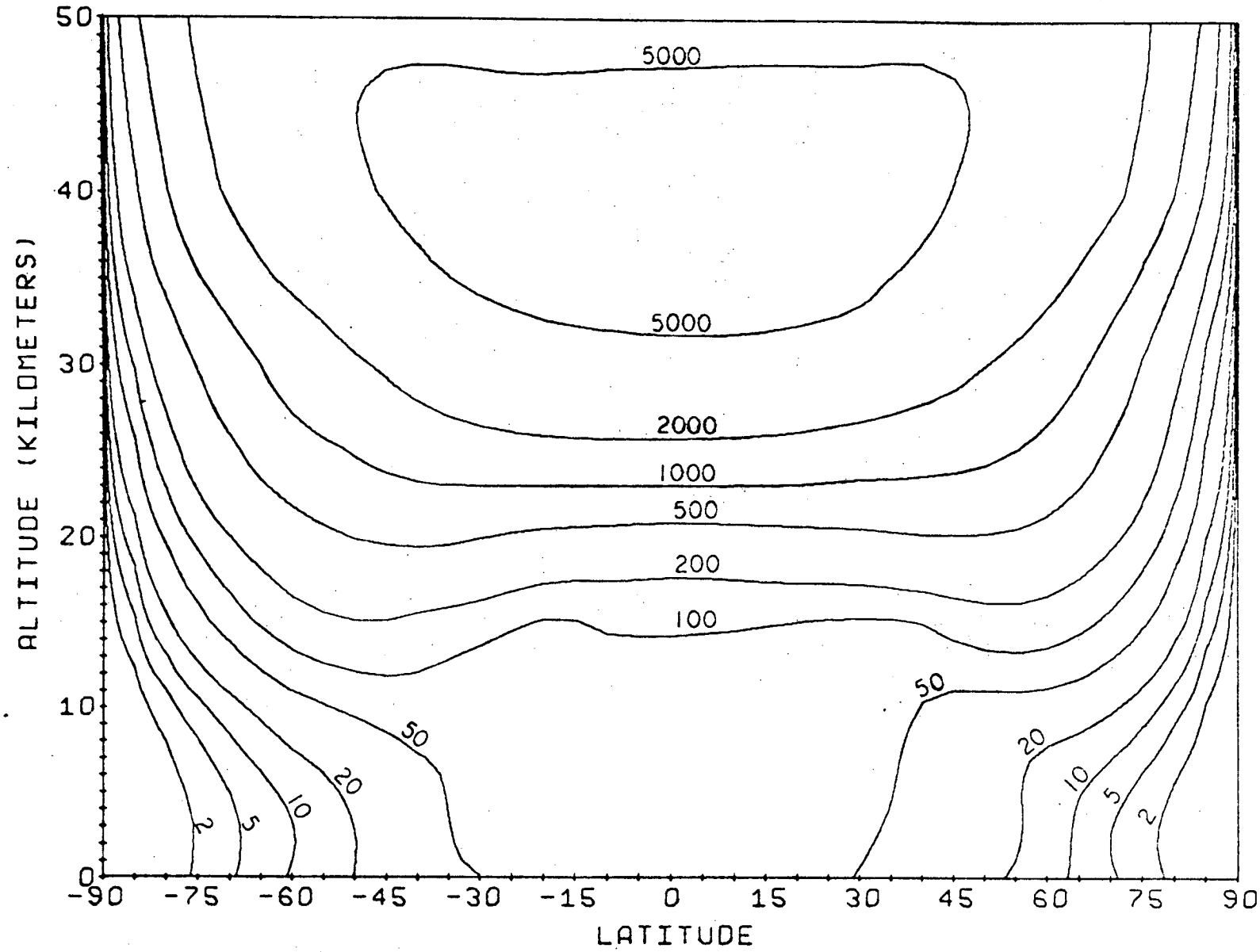

ALTITUDE (KILOMETERS)
LATITUDE
0
10
20
30
40
50
-90
-75
-60
-45
-30
-15
0
15
30
45
60
75
90
5000
5000
2000
1000
500
200
100
50
20
10
5
2
50
20
10
5
2

Fig. 9

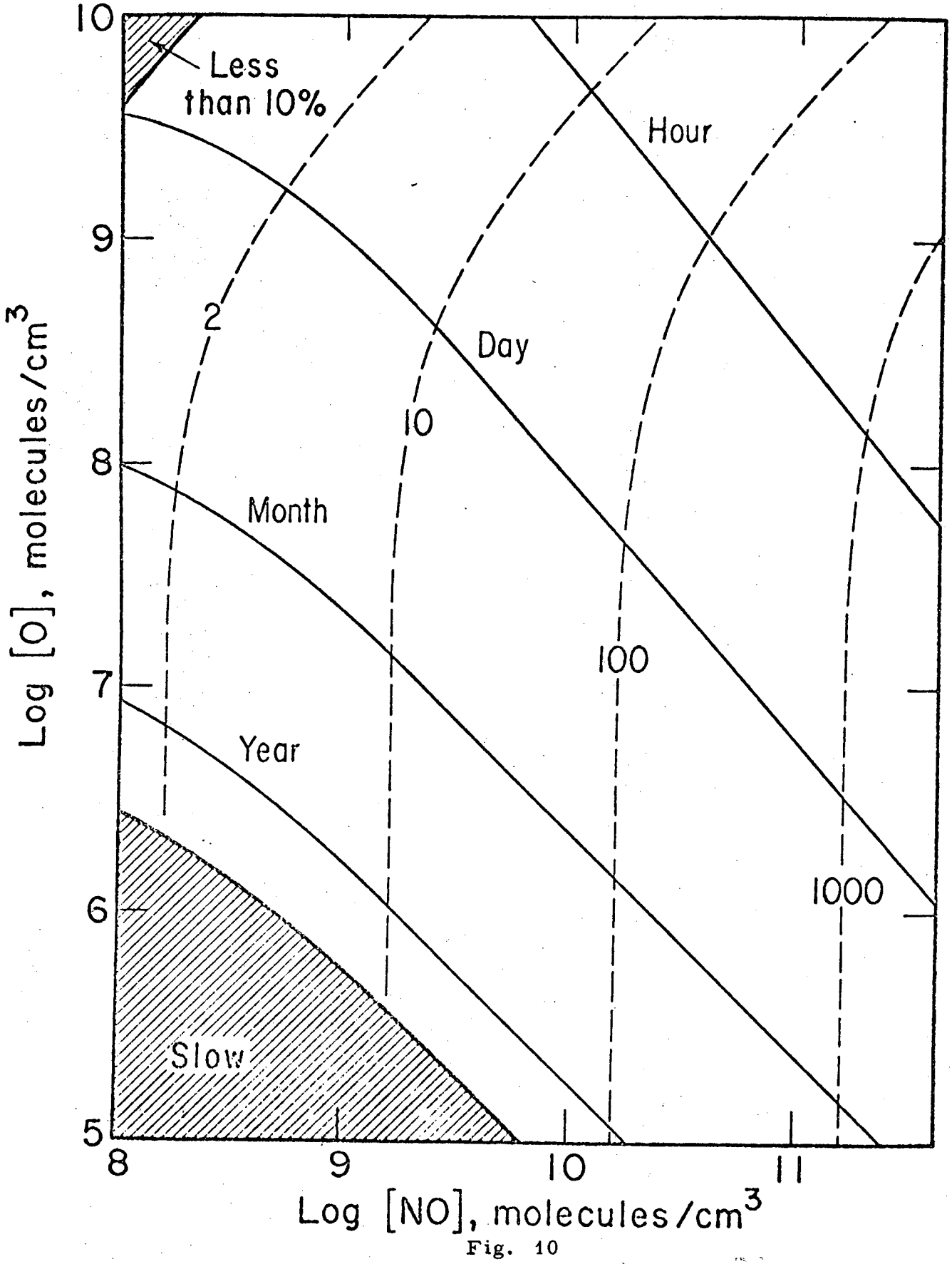
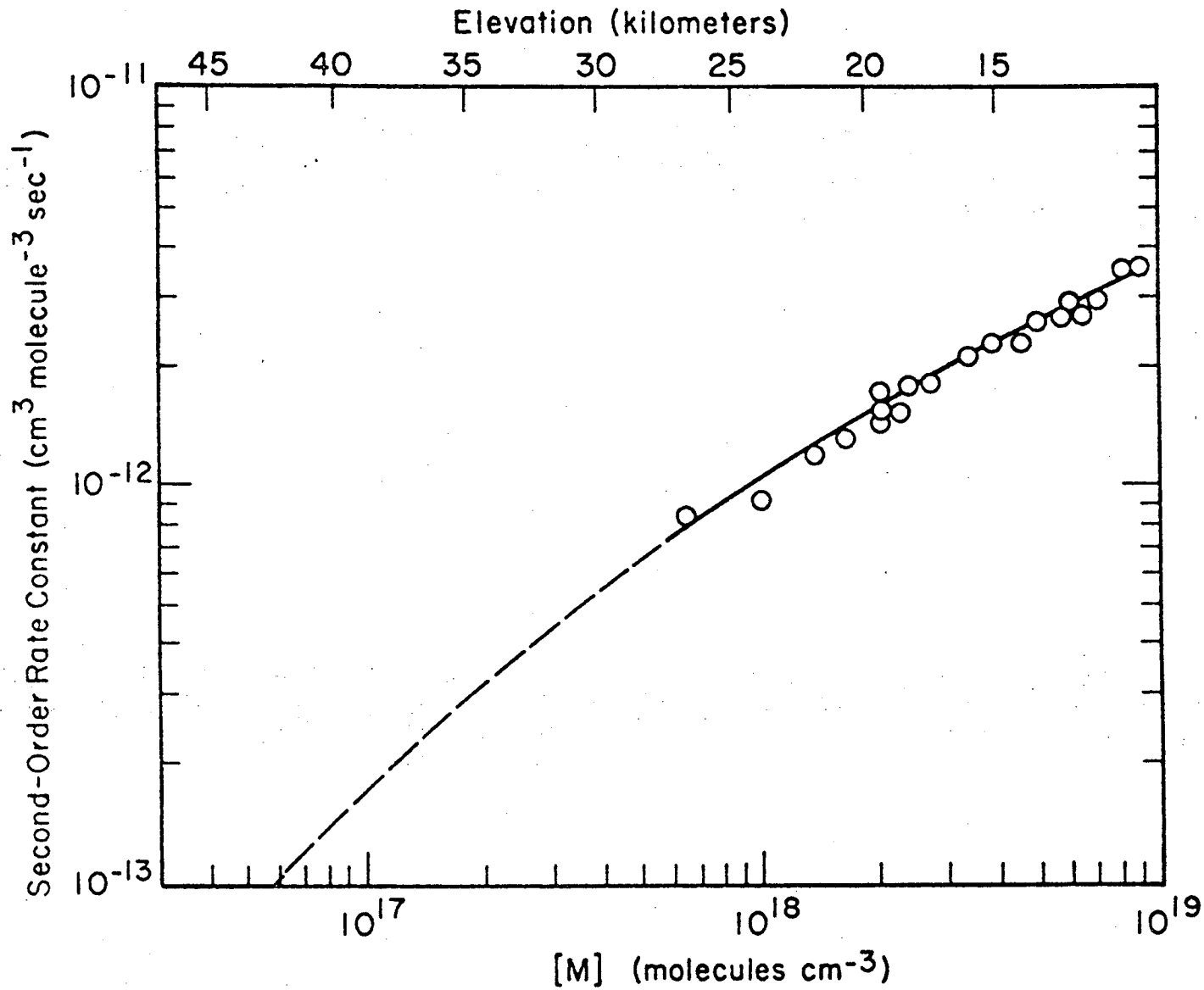
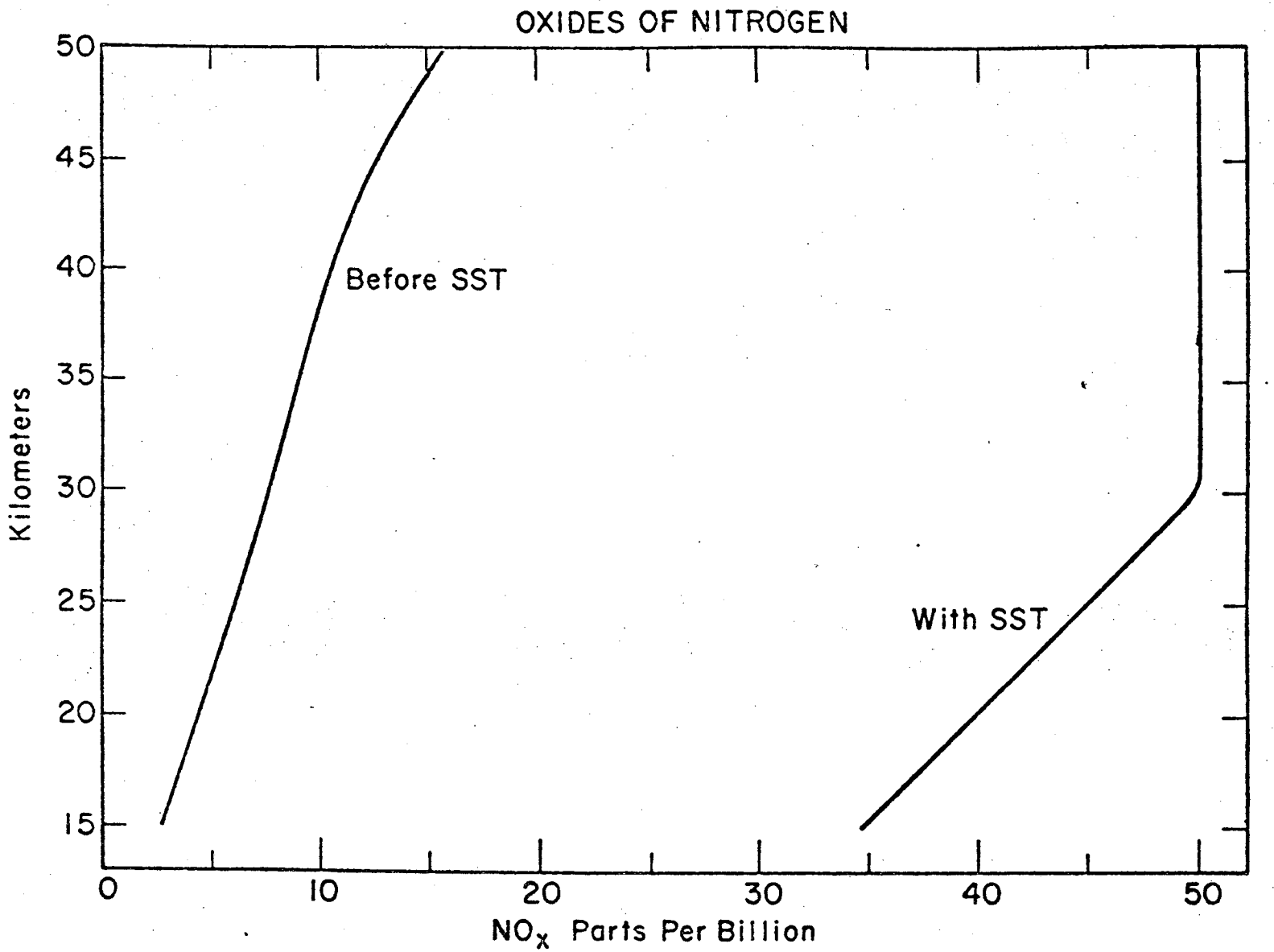

Less than 10%
Hour
Day
Month
Year
Slow
2
10
100
1000
10
9
8
7
6
5
8
9
10
11
Log [O], molecules/cm3
Log [NO], molecules/cm3

Fig. 10



XBL 728-6870

Fig. 11



XBL 728-6821

Fig. 12

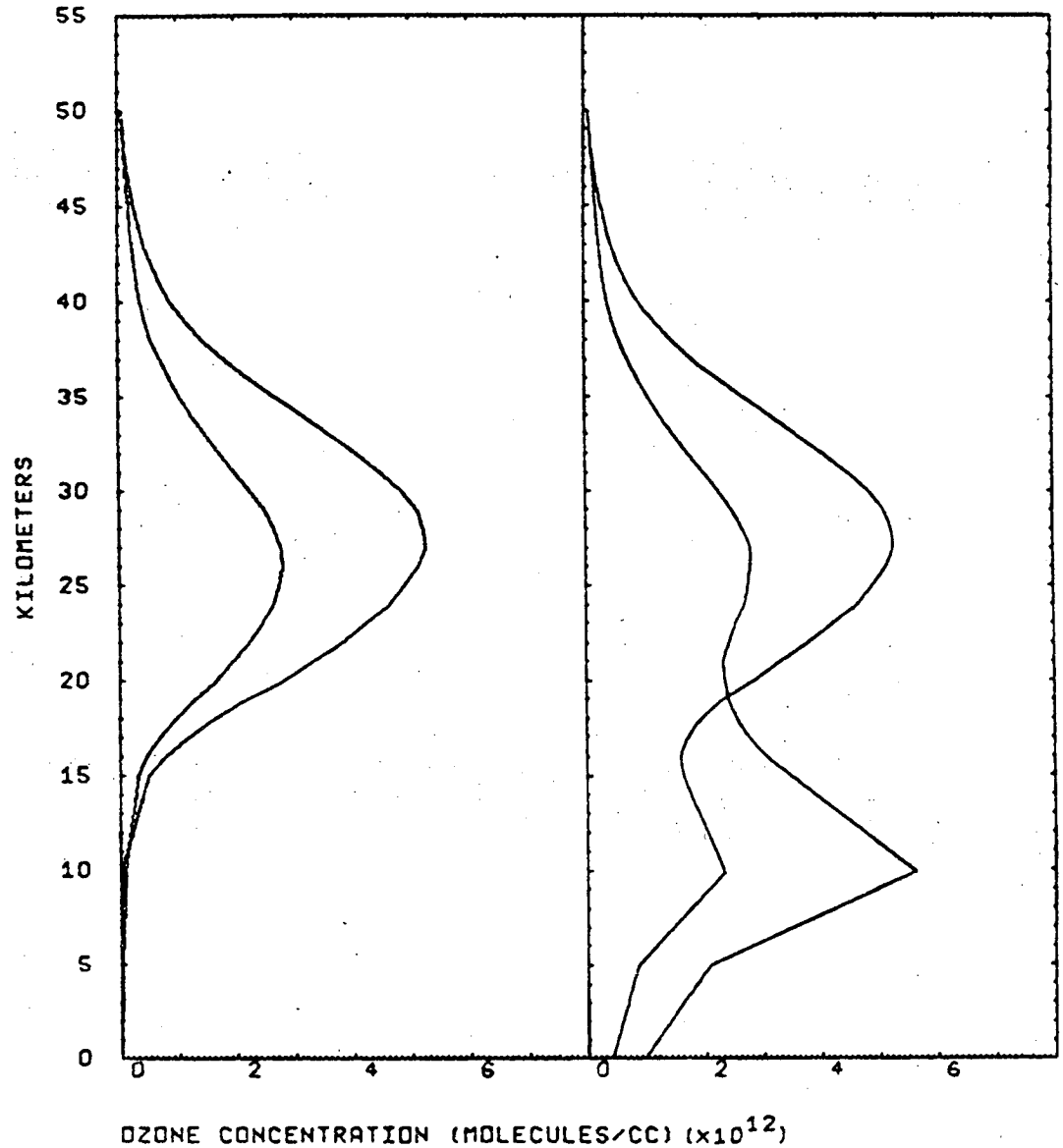

55
50
45
40
35
30
25
20
15
10
5
0
KILOMETERS
0
2
4
6
0
2
4
6
OZONE CONCENTRATION (MOLECULES/CC) (x10^12)

Fig. 13

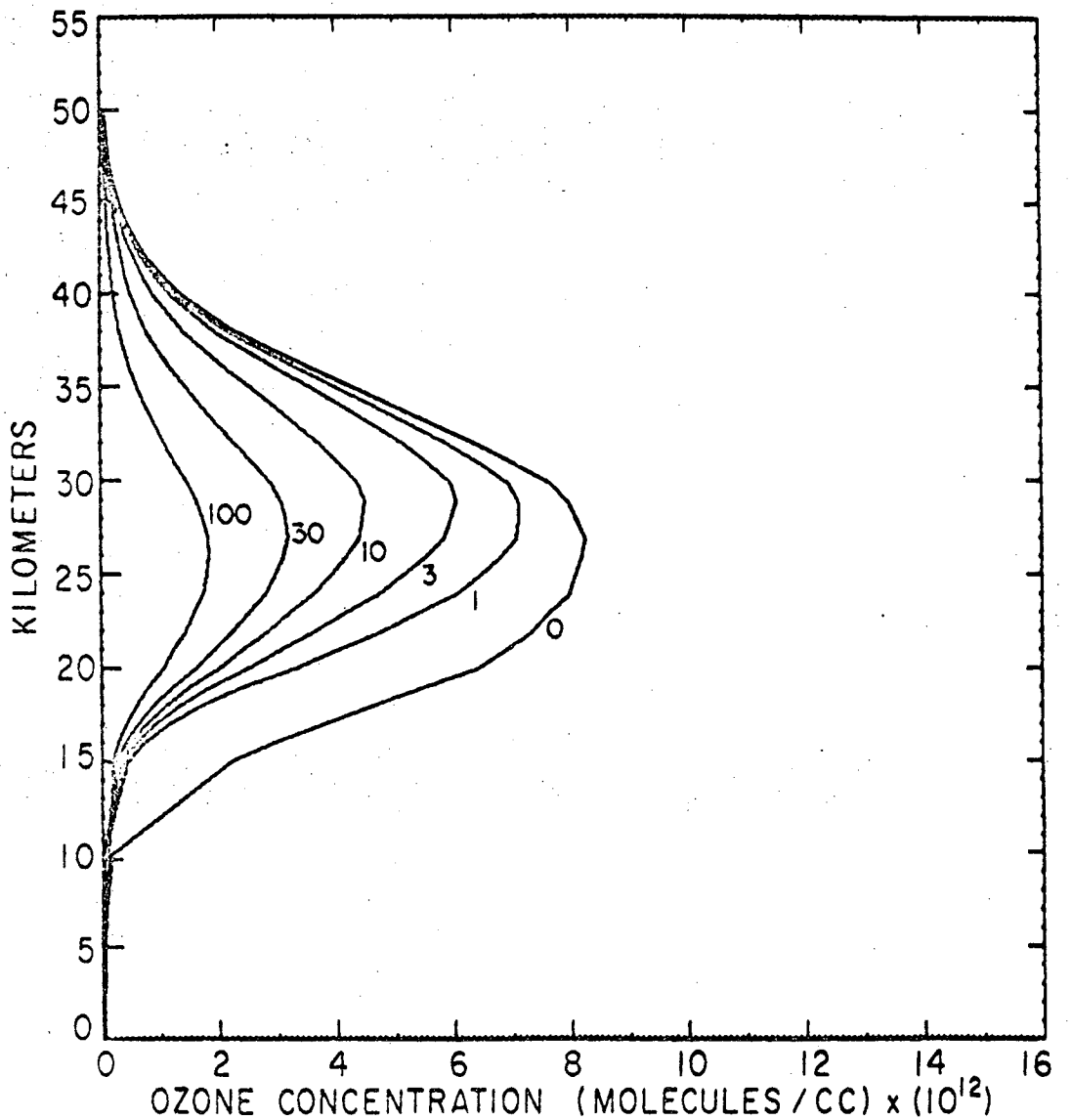

KILOMETERS
55
50
45
40
35
30
25
20
15
10
5
0
100
30
10
3
1
0
0
2
4
6
8
10
12
14
16
OZONE CONCENTRATION (MOLECULES / CC) x (10^{12})

Fig. 14

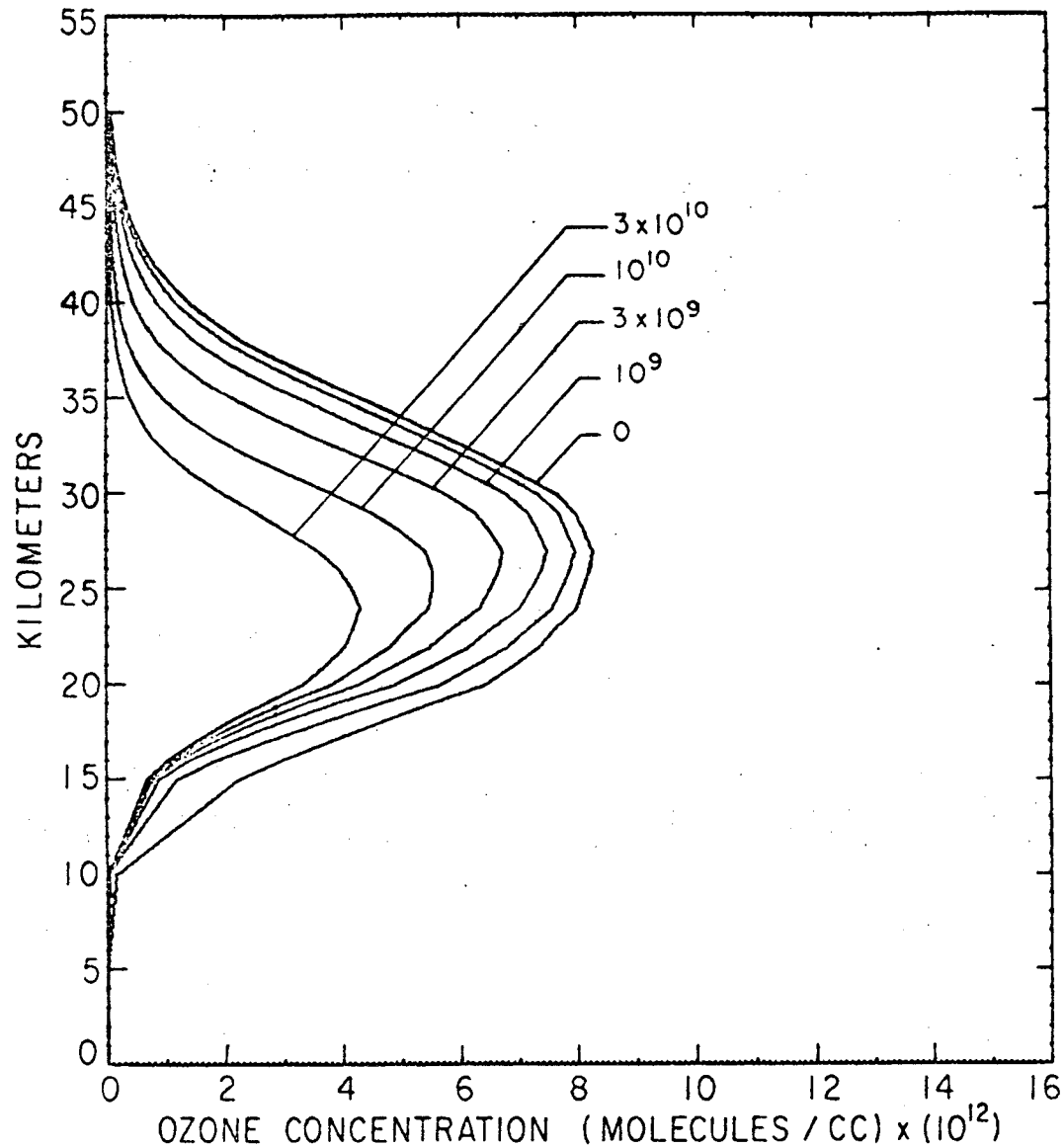

KILOMETERS
55
50
45
40
35
30
25
20
15
10
5
0
0
2
4
6
8
10
12
14
16
OZONE CONCENTRATION (MOLECULES / CC) x (10^{12})
3×10^{10}
10^{10}
3×10^{9}
10^{9}
0

Fig. 15

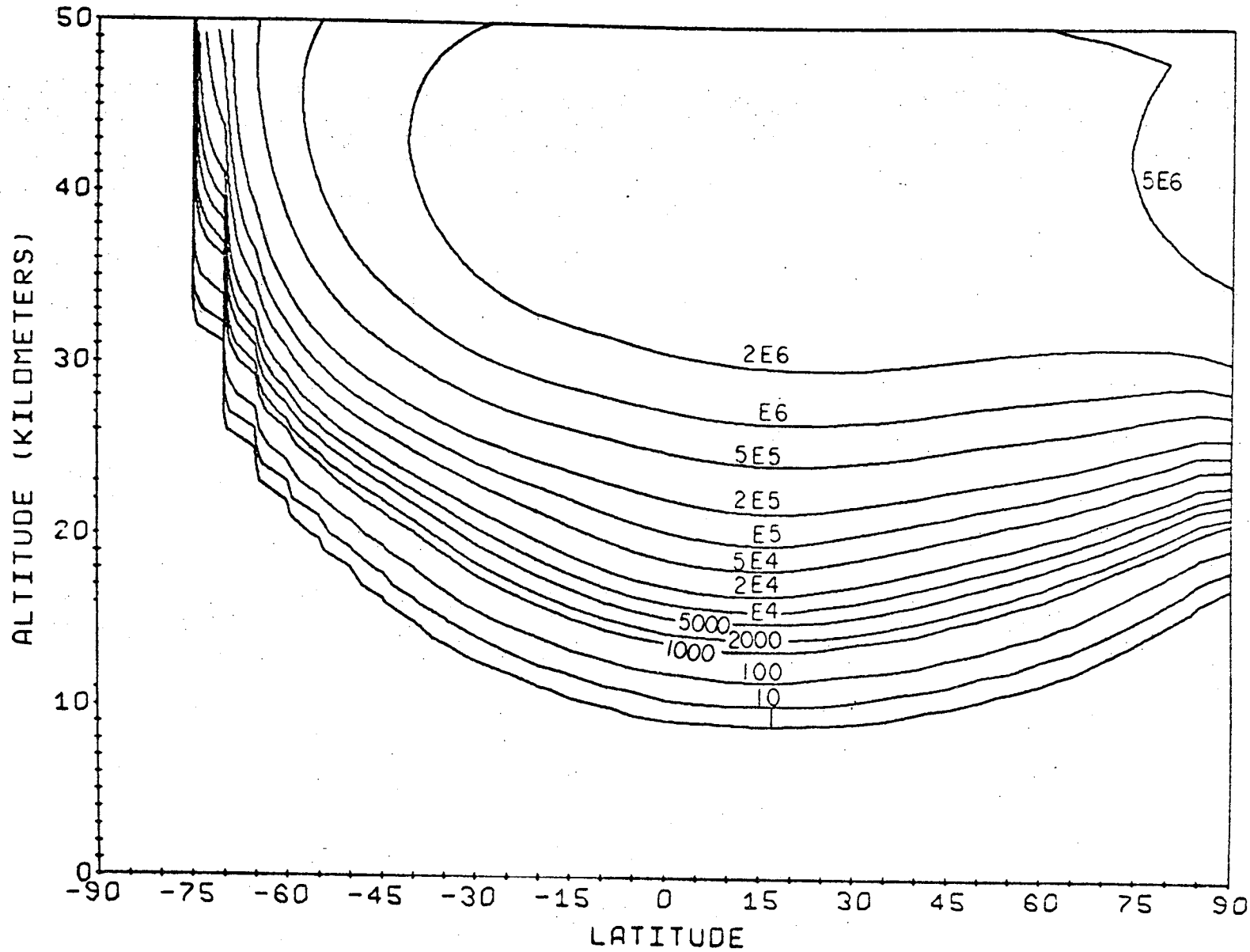

ALTITUDE (KILOMETERS)
50
40
30
20
10
0
-90
-75
-60
-45
-30
-15
0
15
30
45
60
75
90
LATITUDE
5E6
2E6
E6
5E5
2E5
E5
5E4
2E4
E4
5000
2000
1000
100
10

Fig. 16

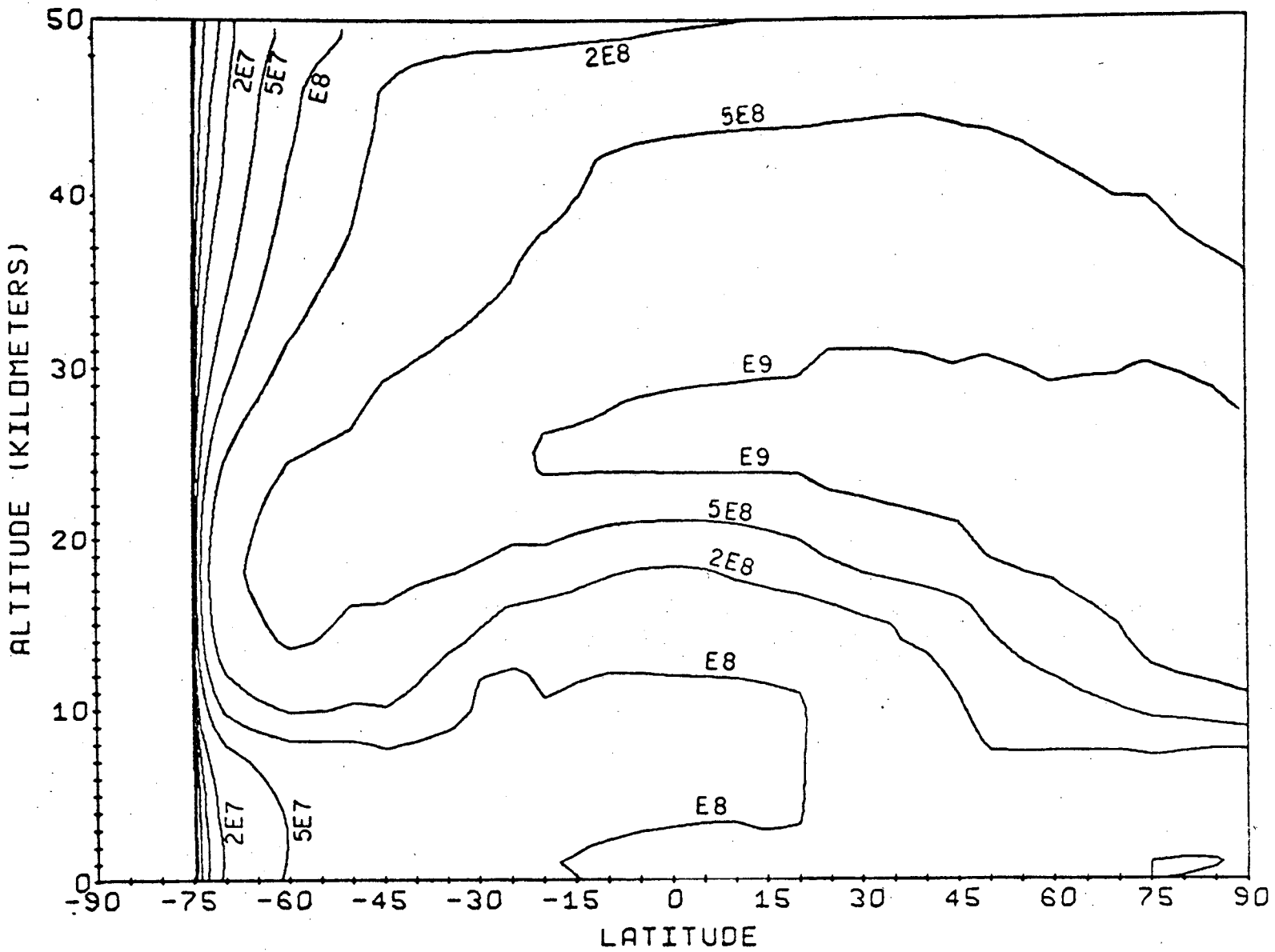

ALTITUDE (KILOMETERS)
LATITUDE
50
40
30
20
10
0
-90
-75
-60
-45
-30
-15
0
15
30
45
60
75
90
2E8
5E8
E9
E9
5E8
2E8
E8
E8
2E7
5E7
E8
2E7
5E7

Fig. 17

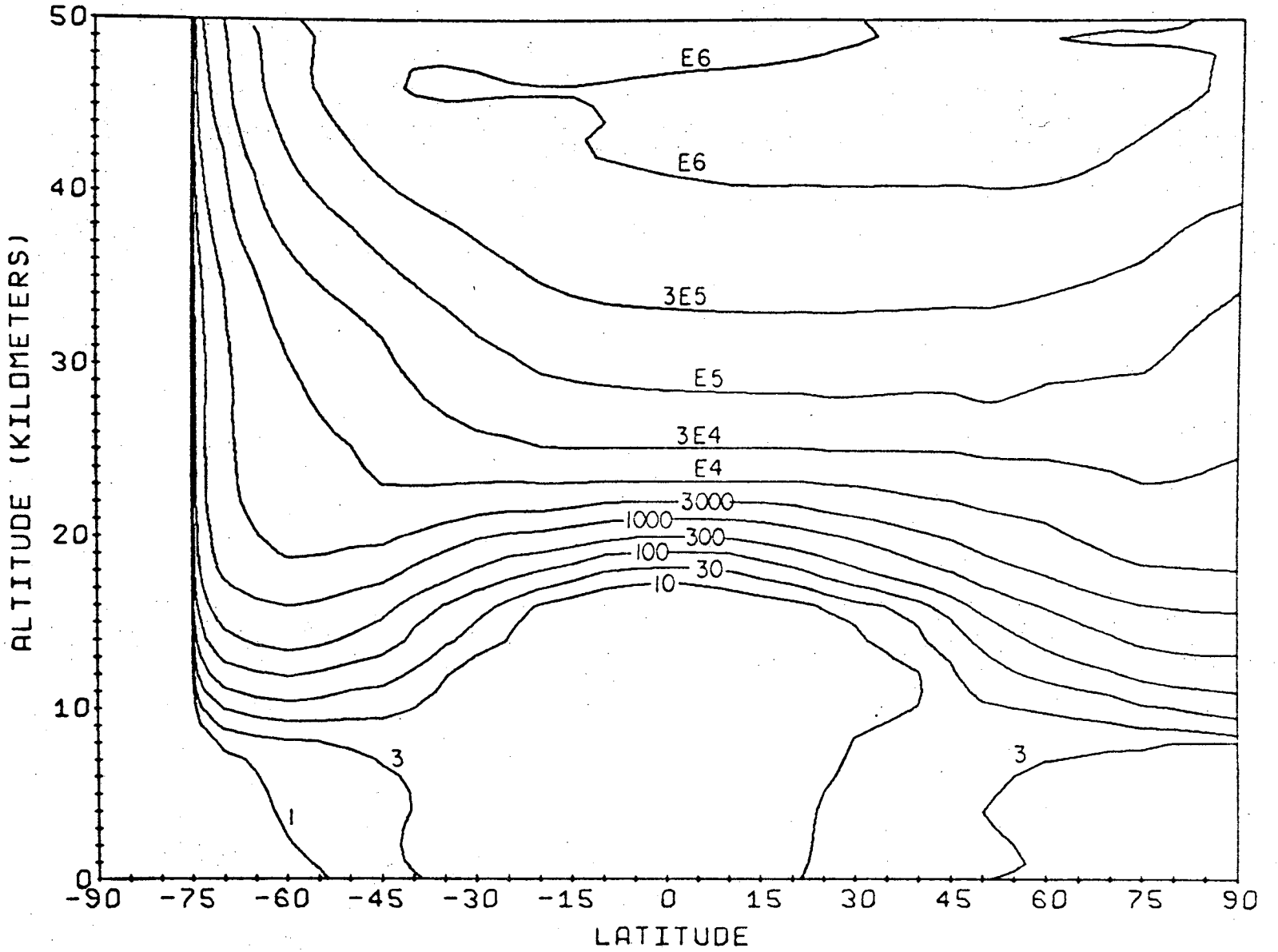

ALTITUDE (KILOMETERS)
LATITUDE
50
40
30
20
10
0
-90
-75
-60
-45
-30
-15
0
15
30
45
60
75
90
E6
E6
3E5
E5
3E4
E4
3000
1000
300
100
30
10
3
3
1

Fig. 18

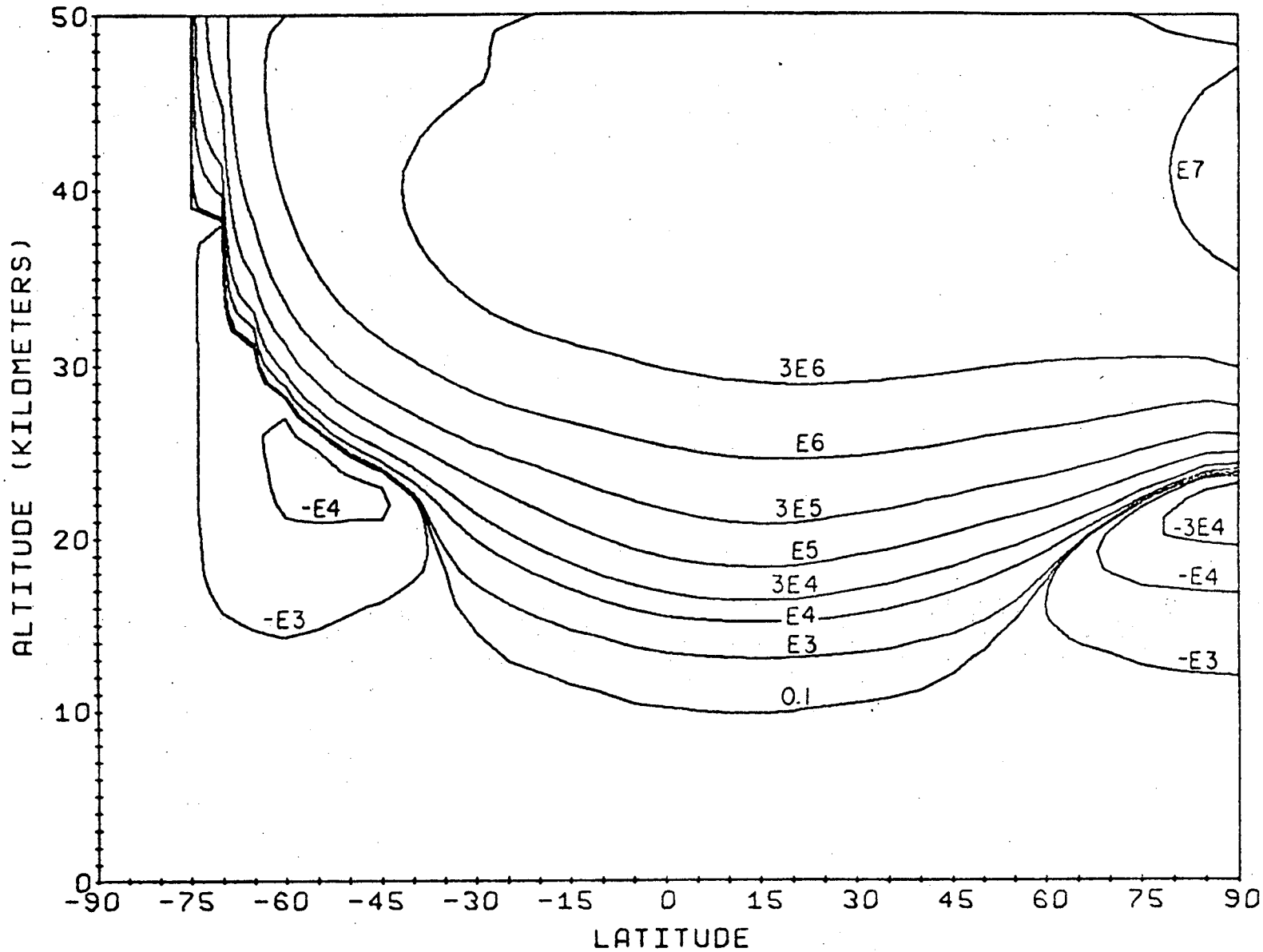

ALTITUDE (KILOMETERS)
LATITUDE
50
40
30
20
10
0
-90
-75
-60
-45
-30
-15
0
15
30
45
60
75
90
E7
3E6
E6
3E5
E5
3E4
E4
E3
0.1
-E4
-E3
-3E4
-E4
-E3

Fig. 19

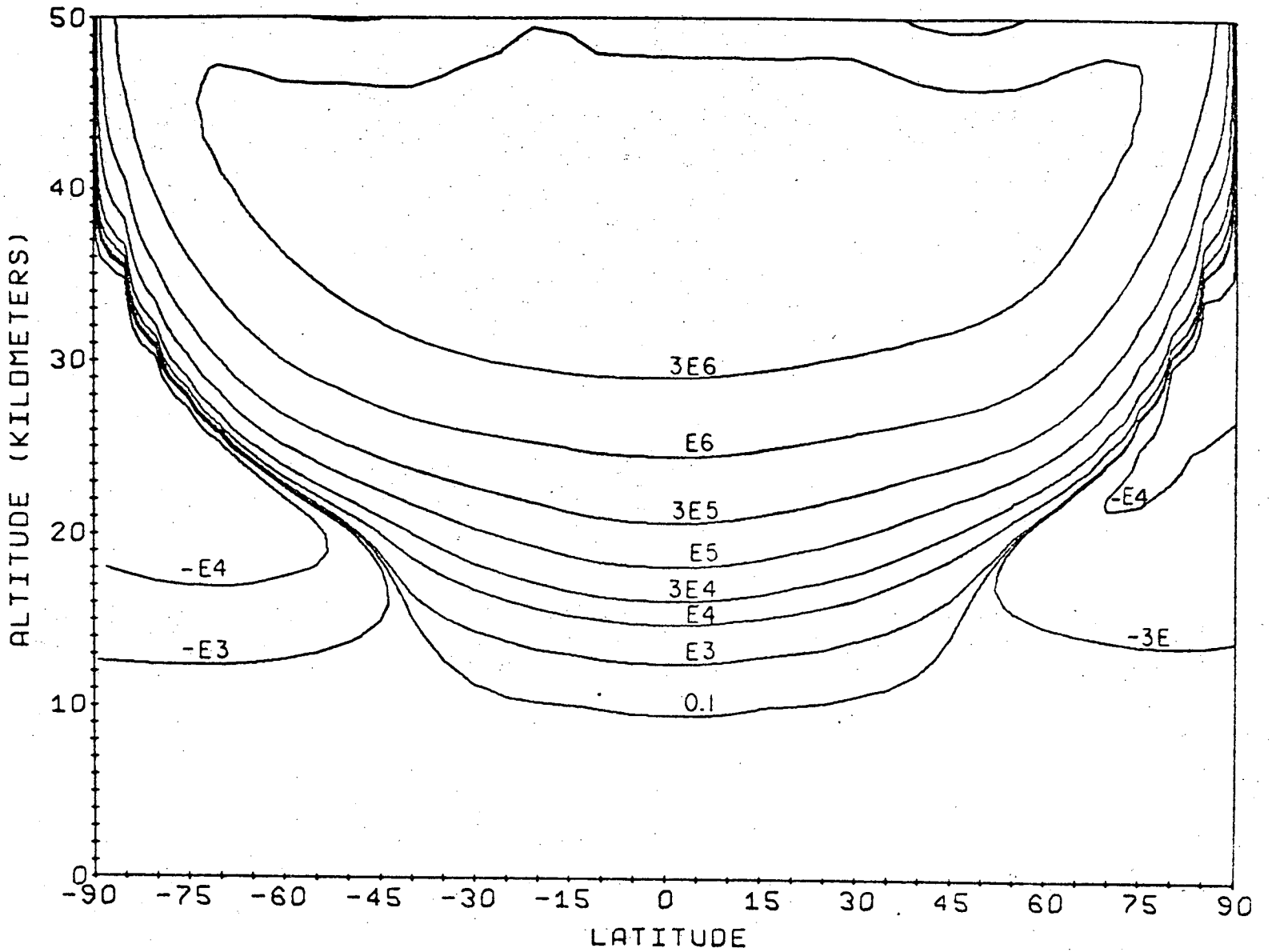

ALTITUDE (KILOMETERS)
50
40
30
20
10
0
-90
-75
-60
-45
-30
-15
0
15
30
45
60
75
90
LATITUDE
3E6
E6
3E5
E5
3E4
E4
E3
0.1
-E4
-E3
-E4
-3E

Fig. 20

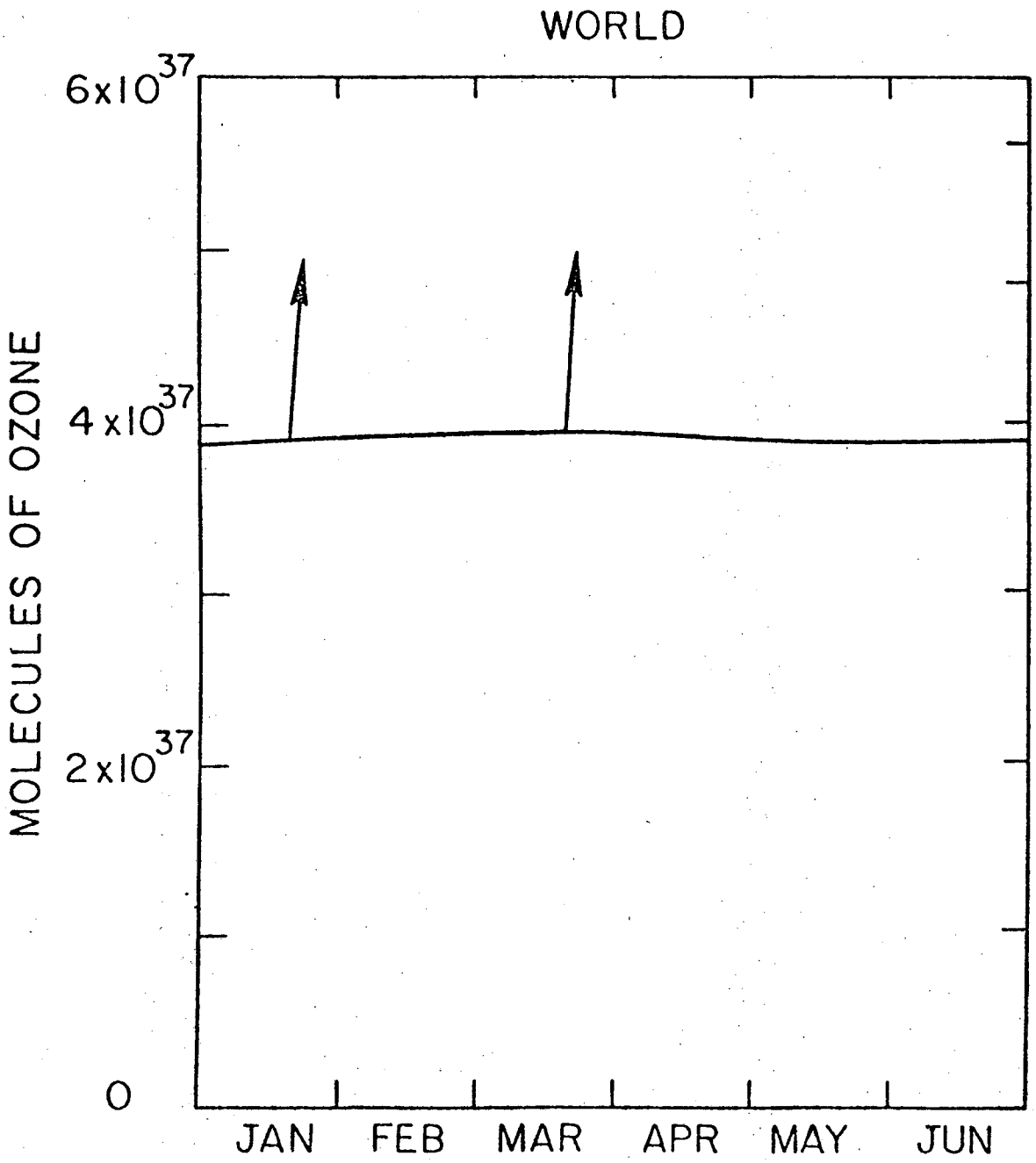

WORLD
6x10^37
4x10^37
2x10^37
0
MOLECULES OF OZONE
JAN
FEB
MAR
APR
MAY
JUN

Fig. 21

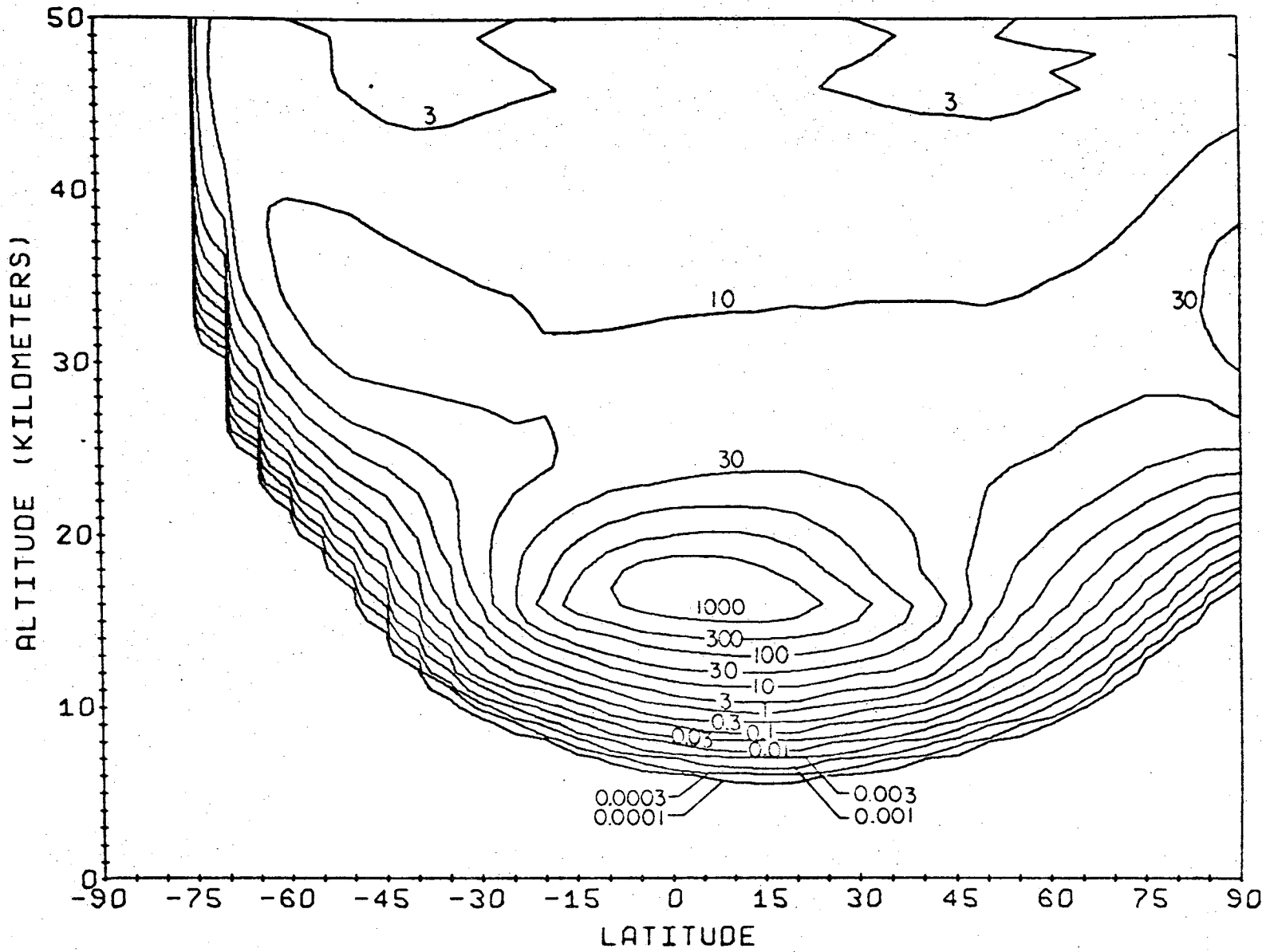

ALTITUDE (KILOMETERS)
LATITUDE
50
40
30
20
10
0
-90
-75
-60
-45
-30
-15
0
15
30
45
60
75
90
3
3
10
30
30
1000
300
100
30
10
3
1
0.3
0.1
0.03
0.01
0.0003
0.0001
0.003
0.001

Fig. 22

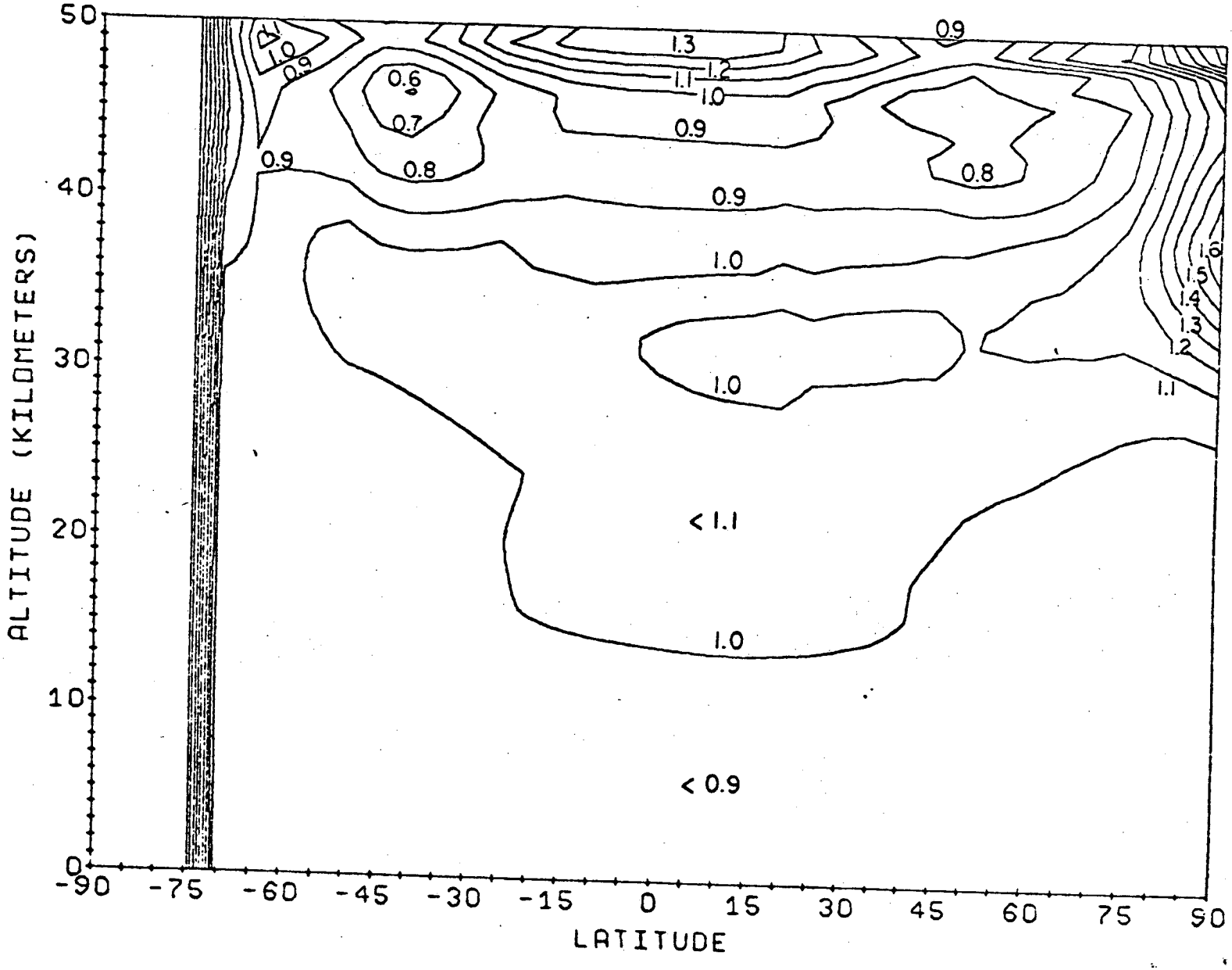

ALTITUDE (KILOMETERS)
LATITUDE
50
40
30
20
10
0
-90
-75
-60
-45
-30
-15
0
15
30
45
60
75
90
1.3
1.2
1.1
1.0
0.9
0.6
0.7
0.8
1.6
1.5
1.4
< 1.1
< 0.9

Fig. 23

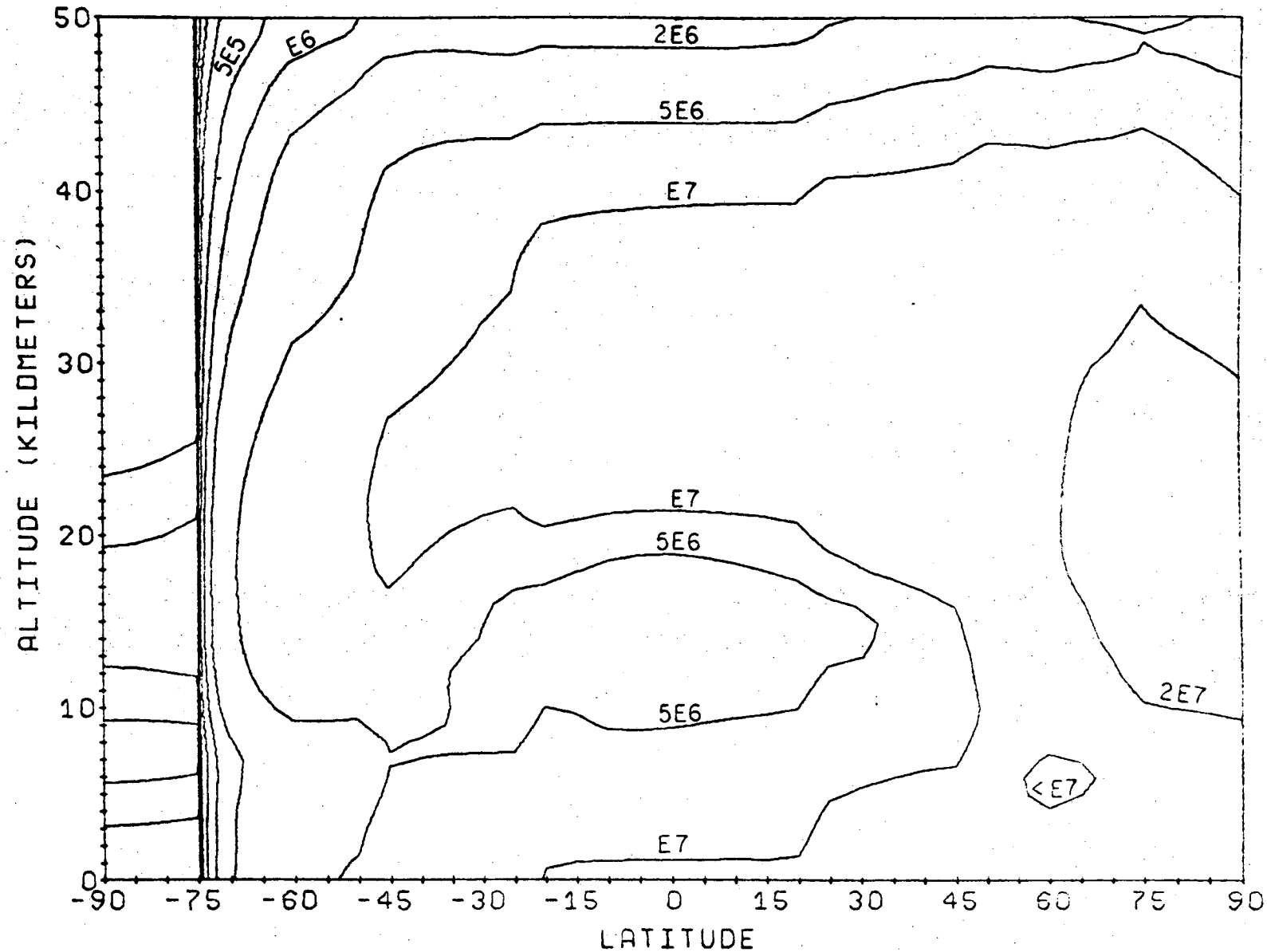

ALTITUDE (KILOMETERS)
LATITUDE
50
40
30
20
10
0
-90
-75
-60
-45
-30
-15
0
15
30
45
60
75
90
5E5
E6
2E6
5E6
E7
E7
5E6
5E6
E7
2E7
<E7

Fig. 24

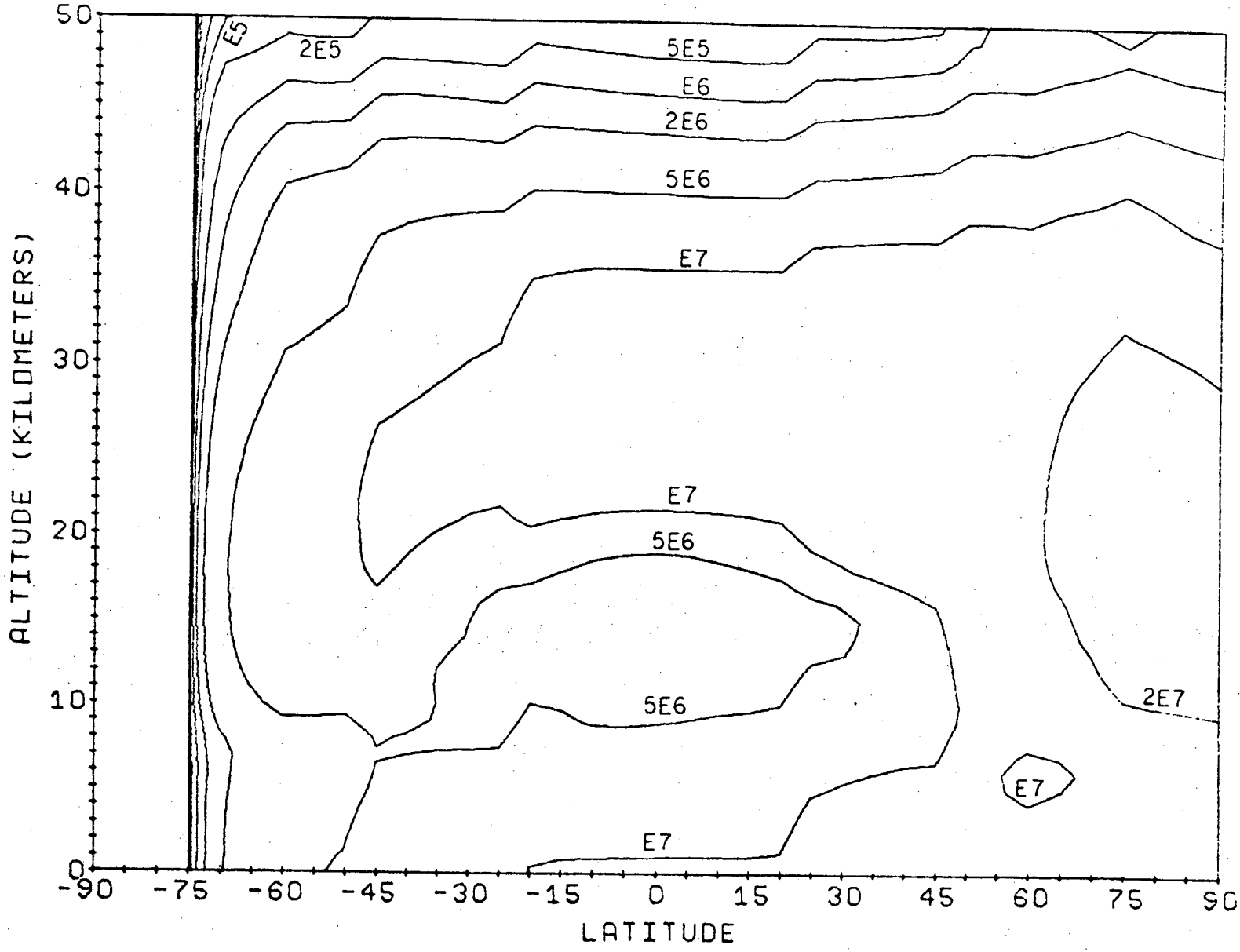

ALTITUDE (KILOMETERS)
LATITUDE
50
40
30
20
10
0
-90
-75
-60
-45
-30
-15
0
15
30
45
60
75
90
E5
2E5
5E5
E6
2E6
5E6
E7
E7
5E6
5E6
E7
E7
2E7

Fig. 25

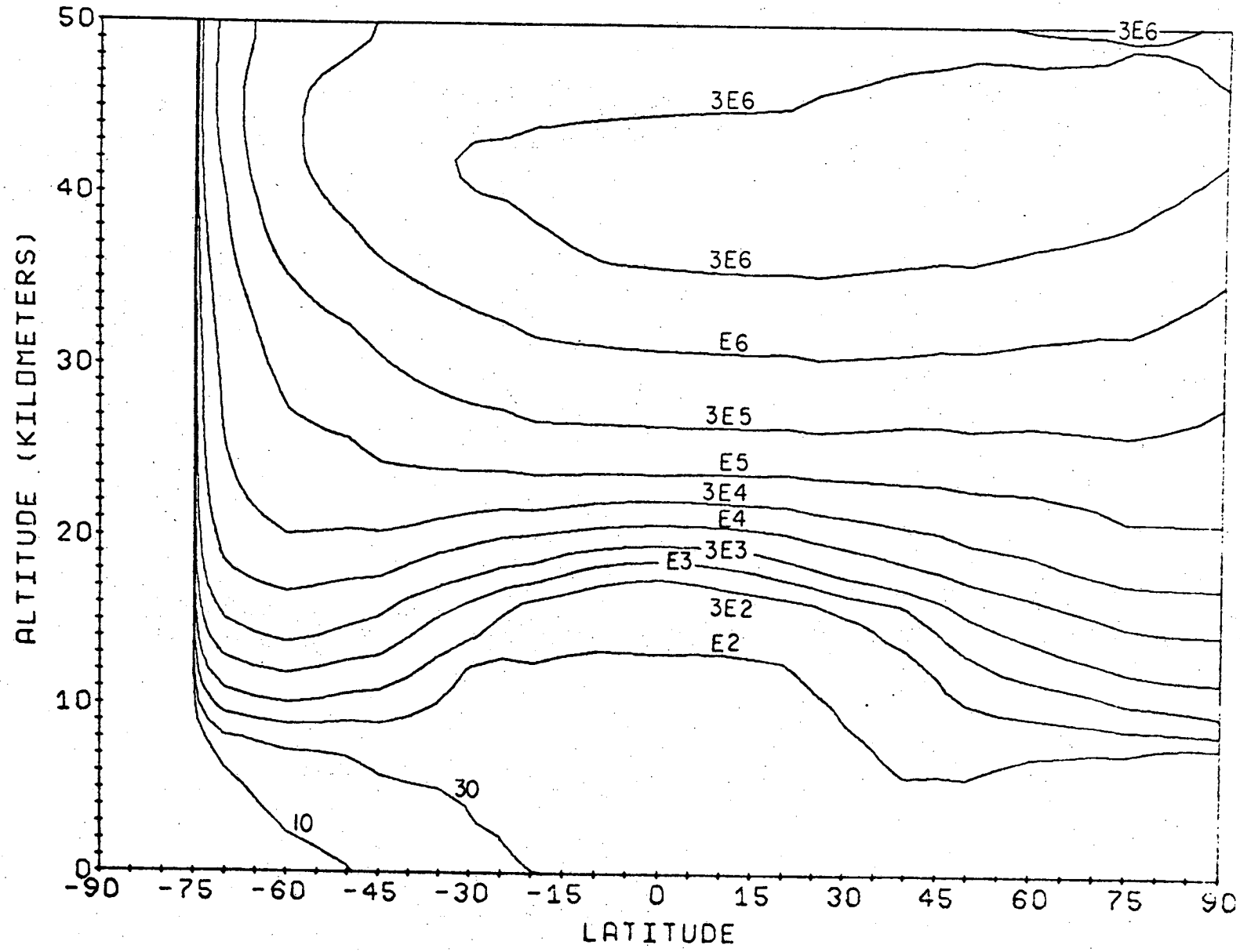

ALTITUDE (KILOMETERS)
LATITUDE
50
40
30
20
10
0
-90
-75
-60
-45
-30
-15
0
15
30
45
60
75
90
3E6
3E6
3E6
E6
3E5
E5
3E4
E4
3E3
E3
3E2
E2
30
10

Fig. 26

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