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Global Ozone Balance in the Natural Stratosphere

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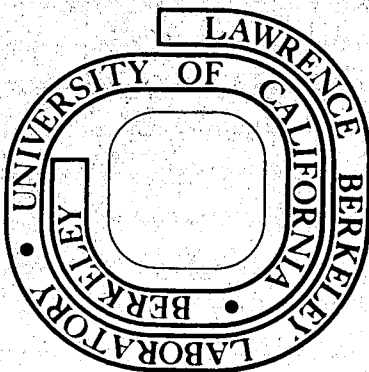
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ABSTRACT

The method of instantaneous rates is a three-dimensional model that takes the observed distribution of atmospheric species and temperature as input data. The distribution of radiation, photochemical rate constants, and reaction rates are evaluated in each cell of the three dimensional grid. For certain problems of restricted scope, definite answers can be given by this approach. For example, it is shown that the Chapman reactions and air motions are insufficient to give a global ozone balance; these factors account for only about 20 percent of the ozone produced below 45 kilometers. There must be other photochemical or chemical reactions that destroy natural stratospheric ozone. The water reactions (H, HO, HOO radicals) balance about 10 percent of the ozone produced below 45 kilometers. Recently observed concentrations of nitrogen dioxide up to 36 kilometer elevations are close to those required to destroy the remaining 70 percent of naturally produced ozone. Until enough measurements are made to characterize the vertical, latitudinal, and seasonal distribution of nitrogen dioxide, it will not be known whether yet other substances (such as chlorine, bromine, or metallic oxide particles) play a significant (10 percent or more) role in the natural ozone balance.

1. INTRODUCTION

Are the photochemical reactions of oxygen species (O_2, O, O_3) and air motions $\underline{sufficient}$ to account for the natural ozone balance in the stratosphere? If not, what other photochemical reactions or other processes contribute strongly to the formation or destruction of stratospheric ozone? This problem has been recognized and discussed over a long period of time and by many investigators; including Chapman [1930], Dütsch [1961, 1969], Hunt [1966], Crutzen [1970]. During the past few years, new information and new approaches to this problem have been developed. This review emphasizes the method of global instantaneous rates [Johnston and Whitten, 1973a, 1973b, 1975; Johnston, 1974b] and brings together the results of these studies.

A zonal-average temperature distribution [Crutcher, 1969] for a "standard" March 22 is illustrated by Figure 1. With the replacement of longitudinal variations by a 24-hour average at each latitude and elevation, a zonal-average contour map depicts the global state of any property of the atmosphere. The northern hemisphere is represented by -90° to 0° latitude, and the southern hemisphere is 0° to +90° latitude. The atmosphere from sea level to 50 kilometer elevation is given by the greatly exaggerated vertical scale. This convenient representation can be used to give standard global distributions of atmospheric properties, such as temperature, Figure 1, of atmospheric composition, such as standard ozone concentration, [Dütsch, 1969; Krueger, 1973; Johnson, Purcell, and Tousey, 1954], Figure 2, and of photochemical reaction rates such as the photolysis of oxygen to produce ozone, Figure 3:

a. $O_2 + h\nu \ (< 244 \text{ nm}) \rightarrow O + O$

b. $O + O_2 + M \rightarrow O_3 + M$ (twice)
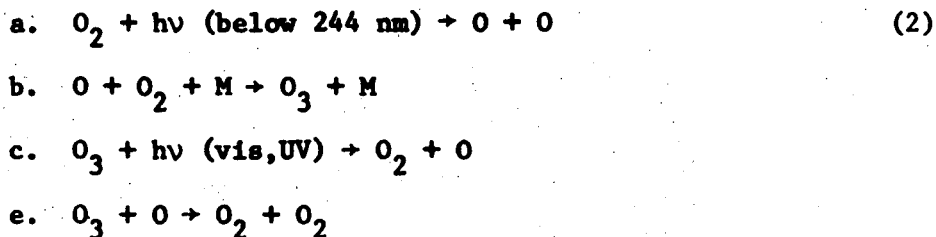
net: $3 O_2 \rightarrow 2 O_3$
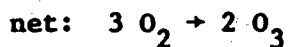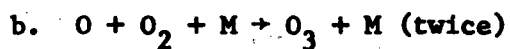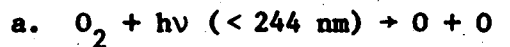
The nature and the subtlety of the question as to whether pure oxygen photochemistry is sufficient are brought out by a superposition [Johnston, 1974a] of the contour maps of ozone concentration (Figure 2) and the rate of ozone formation (Figure 3). This superposition is given by Figure 4, where the number of contour lines is reduced for the sake of clarity. The "ozone formation region" may be taken to be that where the rate of ozone production is 10^5 molecules cm^{-3} sec^{-1} or faster. The maximum ozone concentration is in the spring polar region, well outside the ozone formation region; and large concentrations of ozone are in the temperate zones of each hemisphere at elevations below the locus of significant photochemical formation. As has been recognized for decades, this discrepancy between the distributions of ozone location and ozone formation is caused by transport of ozone by air motions in the stratosphere [Dütsch, 1961].

Further air motions remove ozone from the stratosphere, especially at gaps in the tropopause at temperate and near-polar regions. The rate of ozone destruction at the ground is deduced from the observed gradients of ozone in the troposphere [Aldaz, 1969; Fabian and Junge, 1970; Tiefenau and Fabian, 1972]. There is concensus that the global average rate of this process is the order of magnitude of 10^{29} molecules sec^{-1}, and the rate of destruction of ozone at the ground is probably not more than 6×10^{29} molecules sec^{-1} [Brewer and Wilson, 1968].

There are two quite different approaches to the question of whether air motions and pure oxygen chemistry are sufficient to account for the global ozone balance. One approach is to model the total global problem of air motions and ozone photochemistry [Cunnold et al, 1973, 1974; Dickinson, 1973; London and Park, 1973; Mahlman, 1973]. Another approach is to take the observed standard distributions of ozone and to calculate the three-dimensional instantaneous rates of formation and destruction of ozone.

2. GLOBAL RATES OF THE CHAPMAN REACTIONS

The pure air or Chapman [1930] reactions are

$$
\begin{array}{lll}
\text{a.} & O_2 + h\nu \text{ (below 244 nm)} \rightarrow O + O & \text{(2)} \\
\text{b.} & O + O_2 + M \rightarrow O_3 + M & \\
\text{c.} & O_3 + h\nu \text{ (vis,UV)} \rightarrow O_2 + O & \\
\text{e.} & O_3 + O \rightarrow O_2 + O_2 &
\end{array}
$$

(A fifth reaction, $O + O + M \rightarrow O_2 + M$, is very slow in the stratosphere). The rates (R) of the reactions are expressed as

$$
\begin{array}{ll}
R_a = j_a[O_2] & \text{(3)} \\
R_b = k_b[O][O_2][M] & \\
R_c = j_c[O_3] & \\
R_e = k_e[O][O_3] &
\end{array}
$$

The photolysis constants are written as j and the chemical rate constants are expressed as k. Concentrations are expressed by square brackets and in units of molecules cm^{-3}. The rate of formation of ozone is $2 R_a$ as given by Equation (1). The rate of destruction of

ozone is 2 R_e as seen from the reaction couple

c. $O_3 + h\nu \rightarrow O_2 + O$ (4)

e. $O_3 + O \rightarrow 2\ O_2$

net: $2\ O_3 \rightarrow 3\ O_2$

With the method of instantaneous rates the atmosphere is divided into a grid of every 15° longitude, 5° latitude, and 1 kilometer elevation from 0 to 50 kilometers - to give 43200 volume elements distributed over the globe. A planar wave of solar radiation at wavelengths above 190 nm [Ackerman, 1971] impinges on the atmosphere. The distribution of radiation is calculated in each sunlit volume element, taking into account the vertical path of ozone and oxygen between the sun and the volume element. The photolysis rate constants, j_a for O_2 and j_c for O_3, are calculated in each volume element. These calculations have been carried out for two standard distributions of ozone and temperature. The March 22 distribution corresponds to spring in the northern hemisphere and to fall in the southern hemisphere. The January 15 distribution corresponds to winter and summer.

Figures 3 and 4 are zonal averages based on the method of instantaneous rates. Figure 4 demonstrates the great importance of air motions in redistributing stratospheric ozone, and yet this method employed no explicit treatment of air motions. By use of the observed distribution of ozone, the

pattern of instantaneous rates reveals the occurrence and direction of air

transport in the stratosphere. A map similar to Figure 4 for the time 6

months later shows a reversal between northern and southern hemispheres

in the location of the region of high ozone concentration, although the

hemispheres are not fully symmetric. Thus it is seen that a large amount

of horizontal north-south transport occurs in the lower stratosphere in

a time scale of a few months. The photochemical time scale can be esti-

mated by a calculation of the local "ozone replacement time", which is

defined as the concentration of ozone divided by its local rate of

formation, $[O_3]/2 \, j_a [O_2]$. These times are measures of instantaneous rate;

compare the use of a 4 billion year half-time as a measure of the

instantaneous rate of radioactive decay of uranium-238. The zonal average

ozone replacement times for a standard January 15 are illustrated by

these replacement times. Photochemical rates are faster than large scale

horizontal air transport in the upper stratosphere and slower in the lower

stratosphere. The separation between "ozone formation region" and the

"detached ozone region" may be regarded as that where the photochemical

replacement time is about 4 months.

The zonal-average distribution of the rate of photolysis of oxygen

is given by Figure 2. The global rate of photolysis of ozone (Figure 6)

is quite different from that of oxygen, because ozone is dissociated to

a significant extent by everywhere-abundant visible and near ultraviolet

radiation.

If the simultaneous rate equations for the four Chapman reactions

are solved for the concentration of oxygen atoms, it is found that the

oxygen atoms build up to a steady-state concentration in much less than one second in the lower stratosphere and within a hundred seconds at the top of the stratosphere. The steady-state concentration of oxygen atoms is

$$[O] = j_c[O_3]/k_b[M][O_2] \qquad (5)$$

The zonal-average, global distribution of oxygen-atom concentrations is shown in Figure 7. The oxygen-atom concentrations are highly stratified, reflecting the relatively uniform rate of photolysis of ozone (Figure 6) and the strongly altitude-dependent product, $[O_2]$ $[M]$ in Equation 4. The oxygen-atom concentrations in Figure 7 are zonal averages around the globe, which is equivalent to a 24 hour average at one location. The essentially zero night-time concentrations are included in the average. The day-time averages are twice as great, and the noon-time values are higher still.

The instantaneous, global, zonal-average rate of ozone destruction, 2 R_e, Equation 4, is given by Figure 8. The instantaneous, net, local rate of production of ozone is the difference between the rate of ozone formation and destruction in each volume element of the atmosphere; this rate is

$$\text{net production} = 2 \, j_a[O_2] - 2 \, k_e[O] \, [O_3] \qquad (6)$$

The zonal-average distribution of this net ozone production according to the Chapman mechanism is given by Figure 9. Throughout the ozone formation region the production of ozone is substantially faster than the destruction of ozone by Reaction e. In the "detached ozone region",

Figure 4, where the concentration of ozone is high and where the concentration of oxygen atoms is also fairly high (Figure 7), there is net destruction of ozone, as can be seen from the negative rates in Figure 9. The ratio Γ of ozone fromation to destruction according to the Chapman mechanism is

$$\Gamma = \frac{\text{ozone formation rate}}{\text{ozone destruction rate}} = \frac{2j_a[O_2]}{2k_e[O][O_3]} \tag{7}$$

This ratio for the sunlit half of the globe is given by Figure 10. This ratio is larger than one throughout the ozone formation region, and it is very large in the lower tropical stratosphere.

With due weight given to the quantity of air in each volume element, the instantaneous rate of formation of ozone (Equation 1) was integrated over the stratosphere, and the instantaneous rate of ozone destruction (Equation 4) was integrated over the stratosphere. The range of integration was from the tropopause as indicated by the dashed line in Figure 1 to 45 kilometers. The integrated global reaction rates of ozone formation, ozone destruction at the earth's surface, and ozone destruction according to the Chapman mechanism for standard January 15 and March 22 are given in Table 1. The difference Δ in global ozone formation and destruction is the unbalanced ozone formation, which is about 80 percent of the rate of formation.

$$\Delta = \text{global rate of ozone formation minus global} \tag{8}$$
$$\text{rate of ozone destruction}$$

$$= \int 2\, j_a[O_2] - \int 2\, k_e[O][O_3]$$

If this unbalanced rate of ozone formation persisted, it would double the present quantity of global ozone in less than two weeks. Figures 9 and 10 show large regional imbalance in ozone formation.

These calculations take the observed distributions of stratospheric ozone and temperature. These distributions are the resultant of natural air motions, radiation balance, and photochemistry. For the limited question examined here, it is not necessary to calculate the course of atmospheric motions; it is satisfactory to use the observed consequent distribution of ozone. Instantaneous rates, based on the observed ozone distribution, show that global ozone is being produced five times faster than it is being destroyed by the Chapman mechanism. This ratio is very nearly the same for each of the four seasons, spring, summer, fall, and winter in terms of hemispherical average. The conclusion is one of the following:

1.   _Something else_ besides the Chapman reactions is very important in destroying ozone in the natural stratosphere, or

2.   The calculated imbalance is due to errors or misassignments of parameters in the computation itself.

3.   EXPERIMENTAL ERRORS AND UNCERTAINTIES

This computation that concludes that the Chapman mechanism and air motions are insufficient to account for the natural ozone balance depends on the following input parameters:

(i)   Distribution of oxygen, $[O_2]$

(ii)   Distribution of temperature, T

(iii) Distribution of ozone, $[O_3]$

(iv)   Intensity of solar radiation above the atmosphere as a function of wavelength, $I_o(\lambda)$.

(v)   Cross section of oxygen for solar radiation, $\sigma_2(\lambda)$.

(vi)   Cross section of ozone for solar radiation, $\sigma_3(\lambda)$

(vii) Rate constant for combination of oxygen atoms and oxygen, k_b.

(viii) Rate constant for the reaction of oxygen atoms with ozone, k_e.

(ix)   Neglect of Rayleigh scattering and albedo effects in calculating the distribution of radiation.

There appears to be a discrepancy of a factor of five between ozone formation and destruction by the Chapman mechanism. What is the chance that this factor of five is due to experimental error or uncertainty in one or more of these nine quantities? It is easy for one to recall cases for which a rate constant was uncertain by a factor of five and one must be skeptical about the parameters used in any computation. In this section, these nine quantities will be discussed one-by-one, and then the combined role of several sources of error and uncertainty will be examined.

(i). The concentration and distribution of molecular oxygen is known, and it is not regarded as a significant source of error or uncertainty.

(ii). The temperature is variable from day to day and from season to season. On any one day the temperature will not be the standard temperature. The calculations discussed above were repeated with various

perturbations of the standard temperature (Johnston and Whitten, 1973b). The standard temperature was decreased everywhere by 10°C, 20°C, and 30°C, but the imbalance between ozone production and destruction according to the Chapman mechanism became larger. The standard temperature distribution was increased everywhere by steps of 10°C up to +60°C. The ozone imbalance decreased non-linearly with an increase in temperature, and there was a global ozone balance if the temperature was increased everywhere by 50°C. For small changes in temperature, the calculated imbalance changed equally and oppositely for perturbations above and below the standard value, and thus spatial non-uniformities of temperature with longitude are not expected to cause a systematic error in the calculation.

(iii). The calculations were repeated with the entire body of ozone displaced downward or upward by 1,2,3,4,5 of 6 kilometers. The calculated ozone imbalance is very sensitive to this perturbation. The Chapman mechanism alone would give a global ozone balance if the body of ozone were 4.5 kilometers higher than it actually is. The radiation that forms stratospheric ozone (190 to 244 nm) is absorbed by both oxygen and ozone. Ozone is formed if the radiation is absorbed by oxygen, Equation 1; but, to the first approximation, ozone is neither formed nor destroyed, Reactions c and b, if the radiation is absorbed by ozone. Thus if ozone were 4.5 kilometers higher, it would reduce ozone formation and as a secondary effect it would increase ozone destruction (higher T, larger [0] enough to produce a global ozone balance.

Although it is out of the question that the elevation of ozone is uncertain by a matter of 4.5 kilometers, there is a large amount of

irregularity in the vertical ozone distribution. The vertical profiles

of ozone at 9°N, 35°N, 47°N, and 76°N on May 1, 1963 [Hering and Borden,

1964] are given as Figure 11. The calculations of global ozone balance

were repeated with imposition of a "zebra effect" on the ozone distribu-

tion. In every even vertical shell (that is, with an even number of kilo-

meters at the lower edge), all ozone was removed and half assigned to the

shell above and half to the shell below. The calculation was repeated

emptying the odd vertical shells. The calculations were repeated

removing ozone from alternate shells two kilometers thick and reassigning

it up and down. In these calculations the total amount of ozone was

preserved, the total column was maintained at each point, and the height

of average ozone was unchanged. These extreme layerings of ozone did not

cause a significant change in the instantaneous ozone balance.

(iv). The observed intensity of solar radiation above the atmosphere

is given by Figure 12 [Ackerman, Frimout, and Pastiel, 1968; Bonnet, 1968;

Detwiller et al, 1961; Ackerman, 1971]. The average line through the

points [Ackerman, 1971] was displaced up and down by various amounts, and

the global ozone balance was re-evaluated. If the distribution of

radiation corresponded to the line in Figure 12 instead of to the experi-

mental data, then there would be a global ozone balance with the Chapman

mechanism. For this calculation, the intensity of radiation above 300 nm

was not varied, since this quantity is directly observable at the ground

and is not uncertain.

(v). The cross section σ_3 of ozone for the absorption of ultra-

violet radiation is large and easily measured in the laboratory. There

is good agreement between different investigators, [Ackerman, 1971;

Inn and Tanaka, 1953; Hearn, 1961; Vigroux, 1953; Ny and Choong, 1933],
Figure 13. The heavy line displaced far above the experimental points is
what σ_3 would have to be for uncertainties in this quantity to produce a
global ozone balance with the Chapman mechanism.

(vi). The cross section σ_2 for absorption of ultraviolet radiation
by oxygen is very small, and laboratory measurements are readily dis-
torted by formation of trace amounts of ozone by the radiation being used
to measure σ_2. Observed values [Shardanand, 1969; Ackerman, 1971;
Ditchburn and Young, 1961; Ogawa, 1971] of σ_2 are given in Figure 14; the
line through the points is that used in the calculations of the global
ozone balance; and the heavy line displaced far below the line is what
σ_2 would have to be to give global ozone balance with the Chapman
mechanism.

(vii). The observed rate constants k_b for reaction b as a function
of temperature are shown in Figure 15 [Huie et al, 1972; Stuhl and Niki,
1971; Hippler and Troe, 1971; Kaufman and Kelso, 1967; Johnston, 1968;
Slanger and Black, 1970]. To account for a global ozone balance with
the Chapman mechanism, this rate constant would have to be given by the
heavy line far below the experimental points.

(viii). Rate constants, k_e, including values from 1906 to 1972, for
reaction e are given in Figure 16 [Davis et al, 1973a; McCrumb and
Kaufman, 1972; Krezenski et al, 1971; Jones and Davidson, 1962; Garvin,
1954; Jahn, 1906; Glissman and Schumacher, 1933]. The line through
the points was used in these calculations, except when k_e was varied as
a sensitivity test. The data would have to be represented by the heavy
line high above the experimental points if a change of this rate constant

is to explain a global ozone balance subject to the Chapman mechanism.

(ix). Rayleigh scattering or reflection from clouds or the earth's surface has no effect on reaction $\underline{a}$, the photolysis of oxygen, because the radiation involved is at very short wavelengths and it is strongly absorbed. Radiation weakly absorbed by ozone (that above 310 nm) can be back-scattered into the stratosphere by Rayleigh scattering in the troposphere or by reflection from clouds or ground. Such scattering would act to increase the photolysis of ozone, to increase the concentration of oxygen atoms, to increase the rate of ozone destruction by reaction $\underline{e}$, and thus reduce the discrepancy Δ between ozone formation and destruction in the Chapman mechanism. These calculations neglected this effect. Luther and Gelinas [1974] carried out calculations of the increase of the rate of reaction $\underline{c}$ as a function of solar angle and albedo of the earth. The rate of reaction $\underline{e}$ could be increased up to 20 percent from this effect that is, the Chapman loss terms in units of Table 1 could be as large as -103 and -107. In this case, the Chapman reactions account for 21 to 22 percent of the loss of global ozone instead of 17 to 18 percent.

An examination of Figures 12-16 shows that it is highly unlikely that errors or uncertainty in any one of the parameters I_o, σ_2, σ_3, k_b, k_e can account for the failure of the Chapman mechanism to give a global ozone balance. Another question is whether a combination of errors and uncertainties in each of the five parameters could be reasonably expected to account for the calculated imbalance. For the large perturbations of the parameters, as given by the heavy lines in Figures 12-16, the ozone imbalance was non-linear in the assumed perturbation, and thus straightforward combination of error terms cannot be carried

out. A Monte Carlo calculation was used to estimate the effect of random combinations of the expected error and uncertainty in the five parameters.

In the Monte Carlo calculation, an estimate was made of the standard error of each quantity in a fractional form.

Parameter	Figure	Fractional standard error	$|E|$
I_o	12	± 0.15	.15
σ_2	14	± 0.20	.20
σ_3	13	± 0.05	.05
k_b	15	± 0.18	.18
k_e	16	± 0.26	.26

Each parameters P was randomly varied subject to the equation

$$P = P_o \ (1 + |E|)^x \qquad (9)$$

where P_o is the central value of each parameter, $|E|$ is the absolute value of the error, and x random number between −6 and +6 with a standard deviation of ±1. The entire calculation was repeated 200 times, with use of 1000 random numbers. The global difference in ozone formation and destruction is defined as Δ. The results of these 200 calculations of are given by Figure 17 where the values of Δ are accumulated in groups of width 20×10^{29} molecules $\sec^{-1}$. The average value for this Monte Carlo distribution is 422×10^{29} molecules $\sec^{-1}$ and twice the standard deviation is 186×10^{29} molecules.

Unless there is a very large systematic error in one of the 5 parameters such as those illustrated by the heavy lines in Figures 12-16, then it is highly improbable (Figure 17) that the failure of the Chapman

mechanism to give a proper global ozone balance is a false impression due to errors in the the input parameters. The conclusion is reached that the Chapman reactions plus air motions are insufficient to account for the global ozone balance.

The next sections examine whether the so-called "water reactions" or the reactions of the oxides of nitrogen

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) $\rightarrow NO + O$
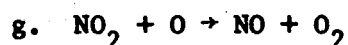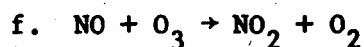
are sufficient to account for the global ozone balance.

4. WATER REACTIONS

The free radicals based on water, HO_x (H, HO, HOO) react with ozone and with oxygen atoms to destroy ozone (a more detailed review of these reactions is given by Nicolet and in this volume). The rates for several of these reactions have been determined for the first time during the past two or three years. However, the rates are still not satisfactorily known for at least two important reactions ($HO + HOO \rightarrow H_2O + O_2$ and $HOO + O \rightarrow HO + O_2$).

Below 310 nm the photolysis of ozone leads to singlet oxygen atoms

c1. $O_3 + h\nu$ (below 310 nm) $\rightarrow O_2 + O\ (^1D)$
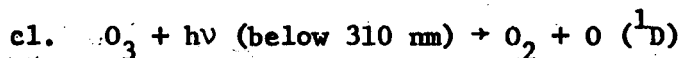
The singlet oxygen atoms are very rapidly deactivated by nitrogen or oxygen to form ground-state triplet oxygen atoms
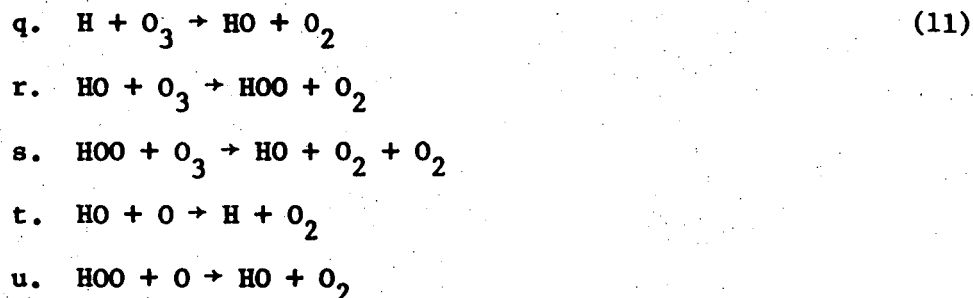
m. $O(^1D) + M \rightarrow O(^3P) + M$

The steady-state concentration of singlet oxygen atoms is established at times much less than one second throughout the stratosphere

$$[O(^1D)] = j_{c1}[O_3]/k_m[M] \tag{10}$$

Zonal average contours of singlet oxygen atom concentration are given by Figure 18. Singlet oxygen, unlike stable triplet oxygen, reacts rapidly with water or with methane to produce hydroxyl radicals

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

p. $O(^1D) + CH_4 \rightarrow HO + CH_3$
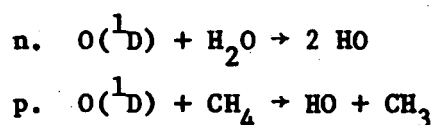
The oxidation of the methyl radical produces two to three additional HO_x radicals with CH_3OO, CH_3O, and H_2CO as intermediates. The following reactions destroy odd oxygen (ozone or oxygen atoms) with no destruction of HO_x as a group

q. $H + O_3 \rightarrow HO + O_2$ $\qquad$ (11)

r. $HO + O_3 \rightarrow HOO + O_2$

s. $HOO + O_3 \rightarrow HO + O_2 + O_2$

t. $HO + O \rightarrow H + O_2$

u. $HOO + O \rightarrow HO + O_2$

The HO_x group is destroyed by recombination of HO and HOO radicals

v. $HO + HO \rightarrow H_2O + O$

w. $HO + HOO \rightarrow H_2O + O_2$

x. $HOO + HOO \rightarrow H_2O_2 + O_2$
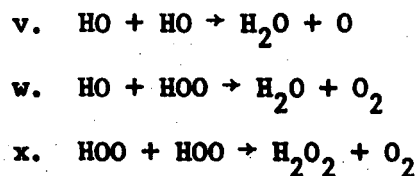
Hydrogen peroxide, H_2O_2, is photodissociated to two hydroxyl radicals, and it is attacked by HO to give water and HOO.

It is difficult to carry out quantitative calculations on the global rate of ozone destruction by the HO_x free radicals, because of uncertainty about the rate constants for reactions $\underline{u}$ and $\underline{w}$ and because of the role of H_2CO and H_2O_2 as delayed sources of these radicals. The procedure used was to assign to the atmospheric volume elements along one latitude line: temperature, ozone concentration, water concentration, methane concentration, and a tentative value for the concentration of hydrogen peroxide. Rate constants were obtained from the compilation by Garvin and Hampson [1974]. The photochemistry in each volume element was followed for 24 hours by a chemical kinetics program [Chang, Hindmarsh, and Madsen, 1973] based on the Gear routine. If the hydrogen peroxide at the end of 24 hours was different from what it was at the beginning, the initial value of ozone was restored and that for H_2O_2 was readjusted, and the 24 hour run was repeated. When the final value was sufficiently close to the initial value, the calculated values of HO, HOO, H, H_2CO, H_2O_2 were assigned to the various longitude bands around the world as initial condition. The instantaneous rates of reactions $\underline{g}$ to $\underline{u}$ were evaluated and the global integral evaluated for the standard January 15. The global rate of ozone destruction by the water reactions was found to be 56×10^{29} molecules sec^{-1}, or about 11 percent of the rate of formation.
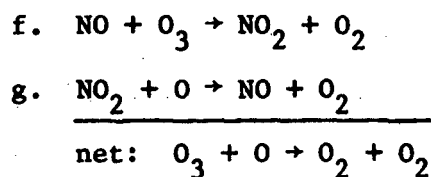
The destruction of ozone by the HO_x radicals occurs in two regions, reactions $\underline{r}$ and $\underline{s}$ in the lowest stratosphere and reactions $\underline{t}$ and $\underline{u}$ in the upper stratosphere. The profiles of ozone formation and destruction reaction rates, according to McElroy $\underline{et\ al}$ [1974] are given for mid-latitude in Figure 19.

Thus, considering the species whose global distributions are fairly well known (O_2, O_3, H_2O, CH_4), one finds that the discrepency Δ between ozone formation and destruction is a matter of about 70 percent, Table 1.
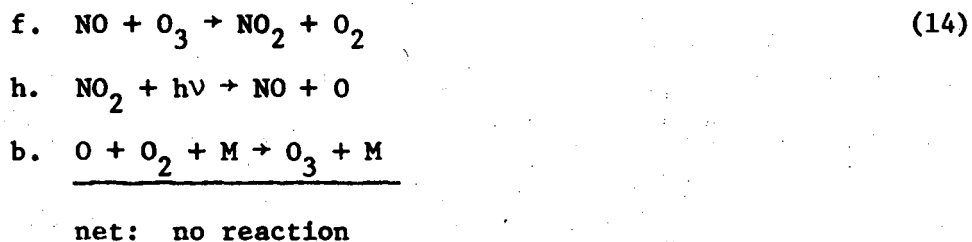
5. REACTIONS OF THE OXIDES OF NITROGEN

Ozone is destroyed by nitrogen oxide in the catalytic cycle [Crutzen, 1970, 1971; Johnston, 1971]

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

$$\underline{\text{g.} \quad NO_2 + O \rightarrow NO + O_2}$$

$$\text{net:} \quad O_3 + O \rightarrow O_2 + O_2$$

The first step does not always result in ozone destruction; it is usually followed by NO_2 photolysis and regeneration of ozone

$$\text{f.} \quad NO + O_3 \rightarrow NO_2 + O_2 \tag{14}$$

$$\text{h.} \quad NO_2 + h\nu \rightarrow NO + O$$

$$\underline{\text{b.} \quad O + O_2 + M \rightarrow O_3 + M}$$

$$\text{net:} \quad \text{no reaction}$$

Thus reaction g is the rate-determining step, and every time it occurs two molecules of ozone are converted to oxygen. Nitrogen dioxide is reversibly tied up as nitric acid

$$HO + NO_2 \overset{M}{\rightleftarrows} HNO_3 \tag{15}$$

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

The relaxation time for nitric acid is the order of magnitude of 10 days. At night a substantial fraction of NO_2 is converted to nitrogen pentoxide

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

$$NO_2 + NO_3 \overset{M}{\rightleftharpoons} N_2O_5$$
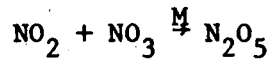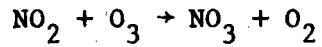
During the day the N_2O_5 is largely photolysed to give back NO_2.

There are insufficient observations of the oxides of nitrogen in the stratosphere to define a standard distribution. There are measurements of nitric acid from Alaska to southern South America [Lazrus and Gandrud, 1974]. Most reported measurements of nitric oxide and nitrogen dioxide are in the temperate zone [Hard, 1974]. There are large variations from time to time and from place to place (compare the irregularities of observed ozone, Figure 11). Observations of nitrogen dioxide are given in Figure 20 [Ackerman et al, 1974; Farmer et al, 1974; Fontanella et al, 1974; Murcray, 1974; Harries, 1974], which will be discussed later.

In the absence of enough observations to define a standard distribution of nitrogen oxides, model calculations were made of the global ozone balance with various assumed distributions. The sum of nitric oxide and nitrogen dioxide was defined as NO_x

$$[NO_x] = [NO] + [NO_2]$$

Nitric acid and nitrogen pentoxide are not included in this discussion. Model calculations were made for concentrations of NO_x, uniform in latitude and altitude throughout the stratosphere. The Chapman reactions were included, but the water reactions were omitted. The ratio of nitric oxide to nitrogen dioxide is

$$\frac{[NO]}{[NO_2]} = \frac{k_g[O] + j_a}{k_f[O_3]} \tag{16}$$

It was found that 4.2×10^9 molecules cm^{-3} of NO_x was sufficient to give a global ozone balance. The ratio Γ of odd-oxygen production and destruction in this system is defined as

$$\Gamma = \frac{2\ j[O_2] + j_k[NO_2]}{2\ k_e[O][O_3] + k_f\ [NO][O_3] + k_g[O][NO_2]} \quad (17)$$

The odd-oxygen ratio for the case of ozone balance by 4.2×10^9 molecules $NO_x\ cm^{-3}$ is given by Figure 21. The great irregularities of Figure 10 are removed. However, there is too much ozone destruction in the upper stratosphere. Inclusion of the water reactions and reduction of total NO_x would improve this irregularity.

In the absence of enough observations to define the standard distribution of natural NO_x, these calculations can be turned around to give the local concentration of NO_2, as such, that would destroy ozone at 70 percent of its rate of formation (compare Table 1). In each volume element of the sunlit atmosphere, the concentration of NO_2 required to destroy ozone at 70 percent of its local rate of formation is

$$[NO_2] = \frac{(2\ j_a[O_2])\ (0.70)}{(2\ k_g[O])} \quad (18)$$

Figure 3 gives the global distribution of the rate of formation of ozone, $2\ j_a[O_2]$. Figure 7 gives the distribution of oxygen atoms. The rate constant k_g is 9.1×10^{-12} molecules $cm^{-3}\ sec^{-1}$ at all temperatures [Davis et al, 1972]. The zonal average concentration of nitrogen dioxide required to destroy ozone at 70 percent of the rate of formation is given by Figure 22, for a standard January 15.

It is possible that NO_2 destroys 70 percent of the ozone formed over the entire stratosphere, but it is not necessary that it be precisely 70 percent at every point. A comparison between the limited observed data on NO_2 and the amount required to destroy ozone at 70 percent of its local rate of formation is given in Figure 20. Calculated NO_2 profiles for 45°N are given for January 15, March 22, and July 15 (actually, January 15 in the southern hemisphere). Most observations were made between 33°N and 51°N, and the band of high-level observations labelled A in Figure 20 were made at 44°N in May 1974. On the basis of Figure 20, it appears that the observed NO_2 destroys ozone at about 70 percent of the formation rate between 25 and 30 km, somewhat faster than 70 percent below 25 km, and somewhat slower than 70 percent above 30 km.

Both NO and NO_2 have been observed simultaneously and over a wide range of altitude [Ackerman et al, 1974]. The total NO_x, NO + NO_2, is plotted in Figure 23. The total NO_x concentrations vary only by a factor of two over the range 20 to 36 kilometers. A calculation of the global ozone balance [Johnston and Whitten, 1973a] found that 4.2×10^9 molecules cm^{-1} of NO_x destroyed 81 percent of the ozone formed. The water reactions destroy 11 percent, so that an ozone balance would be obtained if NO_x destroyed 70 percent of the ozone formed in the stratosphere, reducing 4.2×10^9 to 3.6×10^9 molecules cm^{-3} sec^{-1}. This quantity is plotted as a vertical dashed line in Figure 23, and it passes close to the center of the observations. If these observations of NO_x are representative of the entire stratosphere, it appears that natural stratospheric NO_x can account for most (perhaps all) of the missing 70 percent in the global ozone balance.

The large quantity of ozone outside the ozone formation region, Figure 4, arrived in its position by air transport, and there must be some regions of the stratosphere where ozone is produced faster than it is photochemically destroyed. Furthermore, the ozone in the "detached ozone region" is in a region of fairly high oxygen atom concentration, Figure 7, and non-negligible rate of destruction. The zonal-average concentration of nitrogen dioxide that would destroy ten percent of the local ozone per year (in the absence of replenishment by photochemistry or transport) is given by Figure 24. The heavy dashed line corresponds to the rate of O_2 photolysis of 10^5 molecules cm^{-3} sec^{-1}, Figure 3. The region above the line may be regarded as the "ozone formation region" and that below the line as the "detached ozone region". A large amount

of ozone is in the detached region, and the concentrations of observed NO_2 between 15 and 25 km in Figure 20 would cause substantial photochemical ozone destruction in the detached ozone region. To calculate the global ozone balance, one must integrate over this region of ozone destruction as well as over the ozone formation region.

6. OTHER OZONE-DESTROYING CATALYSTS?

It appears that the Chapman reactions, the water reactions, transport to the earth's surface, and the NO_x reactions are sufficient to balance the rate of formation of ozone from solar radiation and sunlight, if the global distribution of nitrogen oxides is comparable to that of Figures 20 and 23. There is, of course, great uncertainty in the global distribution of nitrogen oxides; and there is room, within this uncertainty, for other ozone-destroying catalysts in the natural stratosphere. Such possibilities include heterogeneous catalysis on the metal oxide [Johnston, 1968] particles from meteors, natural chlorine compounds [Hoshizaki et al, 1973; Molina and Rowland, 1974; Stolarski and Cicerone, 1974; Wofsy and McElroy, 1974] and natural bromine compounds [Watson, 1974]. It is important to obtain substantially more measurements of stratospheric nitrogen dioxide to see if further imbalances are indicated and specifically to continue research on solid particles, chlorine, and bromine in the stratosphere.

TABLE 1.   Global Instantaneous Rates of Change of Ozone

(Rates in Units of 10^{29} molecules $\sec^{-1}$)

	January 15	March 22
Integrated gross rate of O_3 formation	500	486
Transport to troposphere, average	6	6
Actual rate of chemical loss (by difference)	494	480
Rate of chemical loss from Chapman mechanism (twice rate e)	86	89
Rate of chemical loss of ozone from chemical processes other than the Chapman reactions	408	391
Rate of chemical loss to water reactions	56	54
Unbalanced ozone production	352	337
Percent unbalanced ozone production	70	69

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TITLES TO FIGURES

Fig. 1. Standard temperature contours (March 22) $-90°$, north pole; $0°$, equator; $+90°$, south pole. Dotted line is approximate location of average tropopause. Zonal average.

Fig. 2. Standard (March 22) ozone concentration in units of molecules. cm^{-3} expressed as zonal-average contour lines (7E12 means $7x10^{12}$). The variation of the ozone maximum with latitude can be read from the figure. The large concentration in the lower, spring, polar stratosphere is noteworthy .

Fig. 3. Zonal average rate of formation of ozone from the photolysis of oxygen:

$$O_2 + h\nu \text{ (below 242 nm)} \rightarrow O + O$$
$$\underline{O + O_2 + M \rightarrow O_3 \text{ (twice)}}$$
$$\text{net:} \quad 3 O_3 + h\nu \rightarrow 2O_3$$
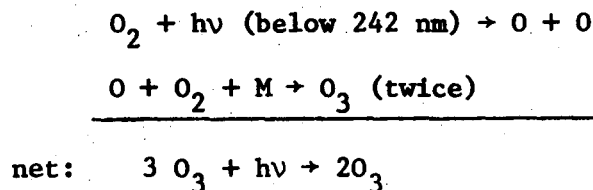
Fig. 4. Zonal average ozone concentration (heavy lines) in units of molecules cm^{-3} (6E12 = $6x10^{12}$) and zonal average production rate (light lines) in units of molecules cm^{-3} sec^{-1}. Note: $3x10^4$ molecules cm^{-3} sec^{-1} produces $1x10^{12}$ molecules cm^{-3} in one year.

Fig. 5. The rate of photolysis of ozone. Standard January 15 .

Fig. 6. Zonal-average ozone-replacement time, that is, local ozone concentration divided point-by-point by ozone formation rate. January 15.

Fig. 7. Zonal average contour maps of triplet oxygen atom concentration, molecules cm^{-3}. Note the strong stratification of these concentrations and the rapid decrease with decreasing elevation. January 15 .

Fig. 8.   Zonal average reaction rate of the destruction of ozone by the pure oxygen reactions:

$$O_3 + h\nu \rightarrow O_2 + O$$
$$\underline{O_3 + O \rightarrow O_2 + O_2}$$
$$\text{net:} \quad 2O_3 + h\nu \rightarrow 3O_2$$
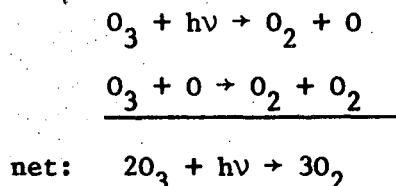
Fig. 9.   The net rate of production of ozone on the basis of the Chapman model, Equation 14,   January 15 .

Fig. 10.   The ratio of the rate of photochemical ozone formation to its rate of destruction according to the Chapman mechanism, $2j_a[O_2]/k_e[O][O_3]$ for a standard January 15.

Fig. 11.   Ragged vertical ozone profile in temperate and polar regions as seen by high-resolution Regener method in an ascending balloon.

Fig. 12.   Observed intensity I_o of solar radiation above the atmosphere. I, Ackerman et al, 1968; O, Bonnet, 1968; ⊢——⊣ , Detweiler et al, 1961; average value used, Ackerman, 1971.   The heavy line displaced from the data is how much I_o must be reduced to give balanced global ozone with the Chapman mechanism, that is, $\Delta = 0$, Equation 8.

Fig. 13.   Ultraviolet-radiation absorption cross-section for ozone, σ_3, with experimental points, a curve through the experimental points, and a curve displaced from the points such that $\Delta = 0$.   □, Ackerman, 1971; ● Inn and Tanaka, 1953; △, Ny and Choong, 1933; ◊, Hearn, 1961; O, Vigroux, 1953.

Fig. 14.   Ultraviolet-radiation absorption cross-section for molecular oxygen. O, Shardanand, 1969; □, Ackerman, 1971; ◊, Ditchburn, 1961; , Ogawa, 1971.

Fig. 15. Rate constants for the reaction $O + O_2 + M \rightarrow O_3 + M$. O, Huie et al, 1972; □,Stuhl and Niki, 1971; ◊, Hippler and Troe, 1971, ∇, Slanger and Black, 1970; Δ, Kaufman and Kelso, 1967; ---, $Kk_{reverse}$, high temperature, Johnston, 1968.

Fig. 16. Rate constants for the reaction $O + O_3 \rightarrow O_2 + O_2$. O, Davis et al, 1973; + McCrumb and Kaufman, 1972; Δ, Krezenski and Heicklen, 1971; □, Jones and Davidson, 1962; ∇, Garvin, 1954; ◊, Jahn, 1906; ----, Glissman and Schumacher, 1933.

Fig. 17. Results of Monte Carlo calculation of the global ozone balance according only to the Chapman mechanism. Random multiples of the standard deviation (Equation 9) were dealt into each of five experimental quantities (I_o, σ_2, σ_3, k_b, k_e). The calculated quantity is the global rate of ozone formation minus the global rate of ozone destruction by reaction e between the tropopause and 45 km.

Fig. 18. Zonal average contour maps of singlet oxygen atom, $O\ (^1D)$, concentration. March 22.

Fig. 19. Relative photochemical rates in the natural stratosphere: A. Photochemical formation of ozone, $2\ j_a[O_2]$; B. the NO_2 catalytic cycle, $2\ k_g[O][NO_2]$; C. the elementary reaction $O + O_3 \rightarrow O_2 + O_2$; D. $HO + O \rightarrow H + O_2$; E. $HOO + O \rightarrow HO + O_2$; F. $HO + O_3 \rightarrow HOO + O_2$; G. $H + O_3 \rightarrow HO + O_2$; H. $HO_2 + O_3 \rightarrow HO + 2\ O_2$.

Fig. 20. Observed stratospheric nitrogen dioxide as summarized by Hard (1974). A. Ackerman et al, 1974; B. Murcray et al, 1974; C. Fontanella et al, 1974; D. Harries et al, 1974; E. Farmer et al, 1974. Lines represent the concentration of NO_2 required to destroy ozone at 70 percent of the rate of formation at 45°N at the indicated dates.

Fig. 21. The ratio of odd-oxygen formation/destruction, Equation 17, with a water-free stratosphere and with 4.2×10^9 molecules cm^{-3} of NO plus NO_2 added throughout the stratosphere. This quantity of NO_x gives a global ozone balance, but there is too much ozone destruction at high levels. Inclusion of the water reactions gives a global ozone balance for about 3.6×10^9 molecules cm^{-3}. January 15 .

Fig. 22. The distribution of nitrogen dioxide (molecules cm^{-3}) required to destroy ozone at 70 percent of the rate of formation from sunlight (January 15).

Fig. 23. A. Simultaneously measured NO and NO_2 over a wide range of elevations in the stratosphere (Ackerman et al, 1974) with error range as estimated by the authors. B. The uniform concentration of NO and NO_2 required to give a global ozone balance, where the Chapman reactions, the water reactions, and transport to the troposphere destroy 30 percent of the ozone formed from sunlight.

Fig. 24. The distribution of nitrogen dioxide that would destroy ozone at a local, instantaneous rate of 10 percent per year, if there were no replacement of ozone by sunlight or transport. This figure, compared to Figure 4, shows that detached ozone can be destroyed at a significant rate if the concentration of NO_2 is high enough. Calculations of the global ozone balance must include this contribution.
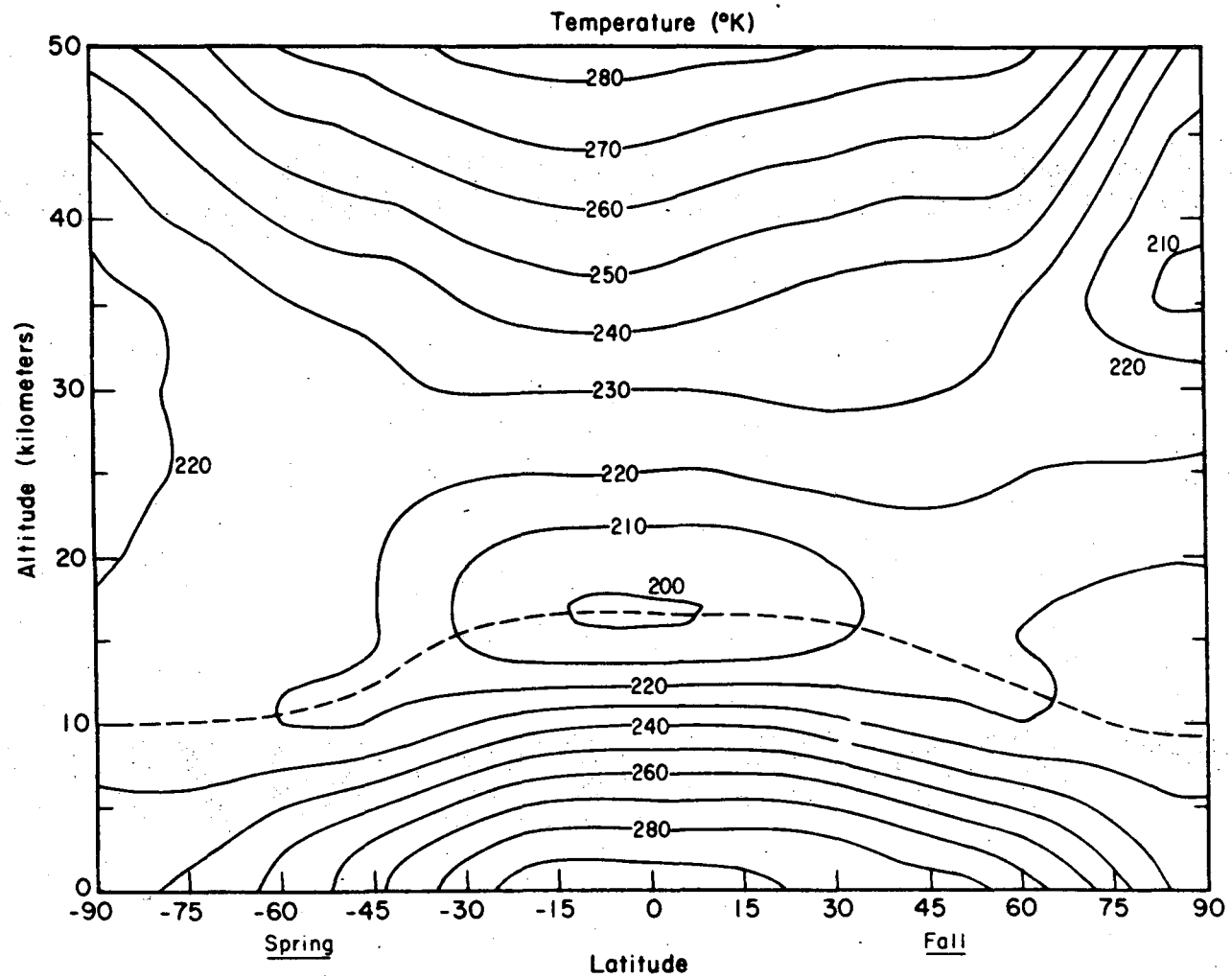
FIGURE 1

Ozone Concentration (molecules cm^{-3})

FIGURE 2

Instantaneous Local Ozone Production Rate (molecules $cm^{-3} sec^{-1}$)

FIGURE 3

XBL 741-5461
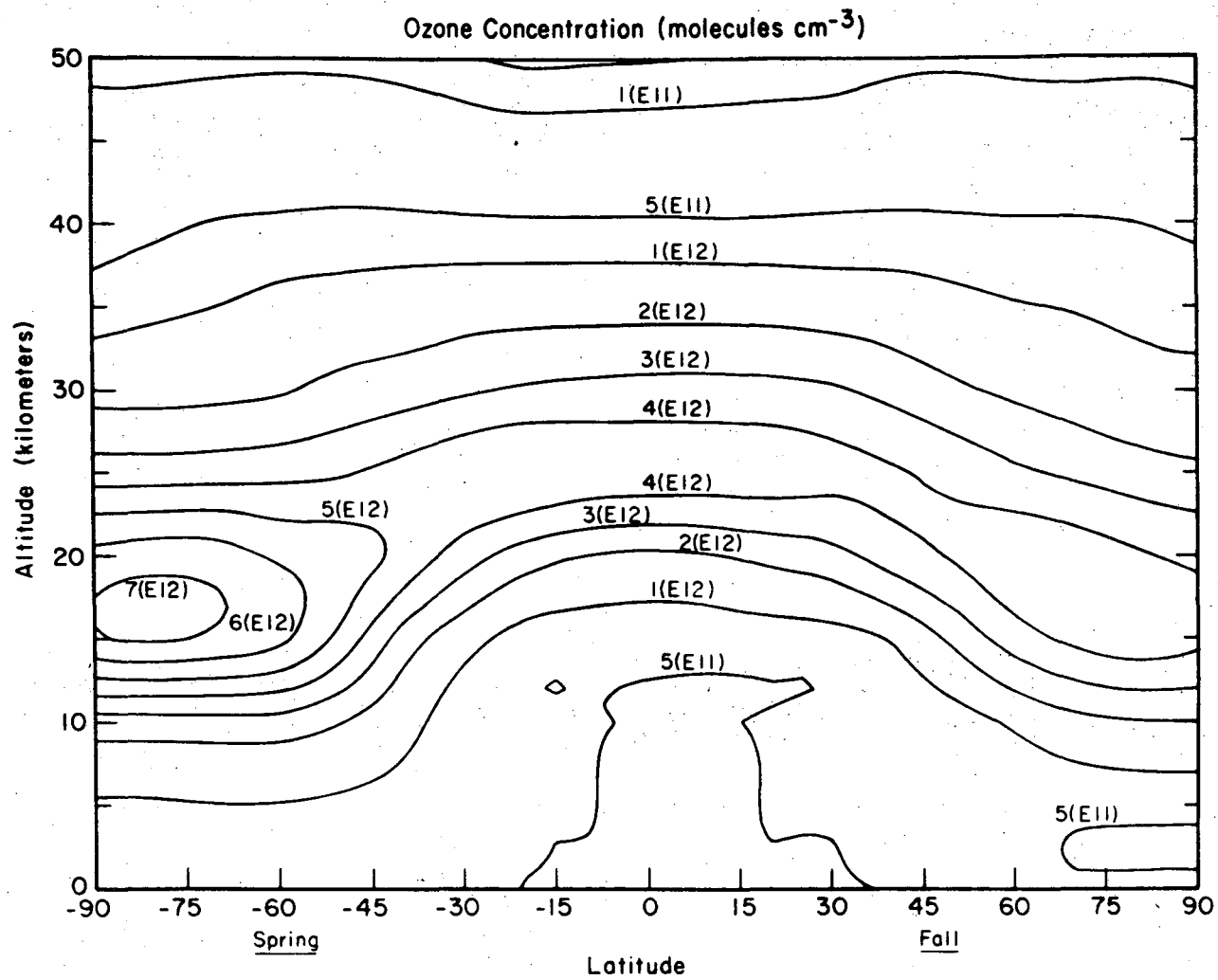
OZONE PRODUCTION RATE, MOLECULES cm^{-3} sec^{-1}
and
OZONE CONCENTRATION, MOLECULES cm^{-3}
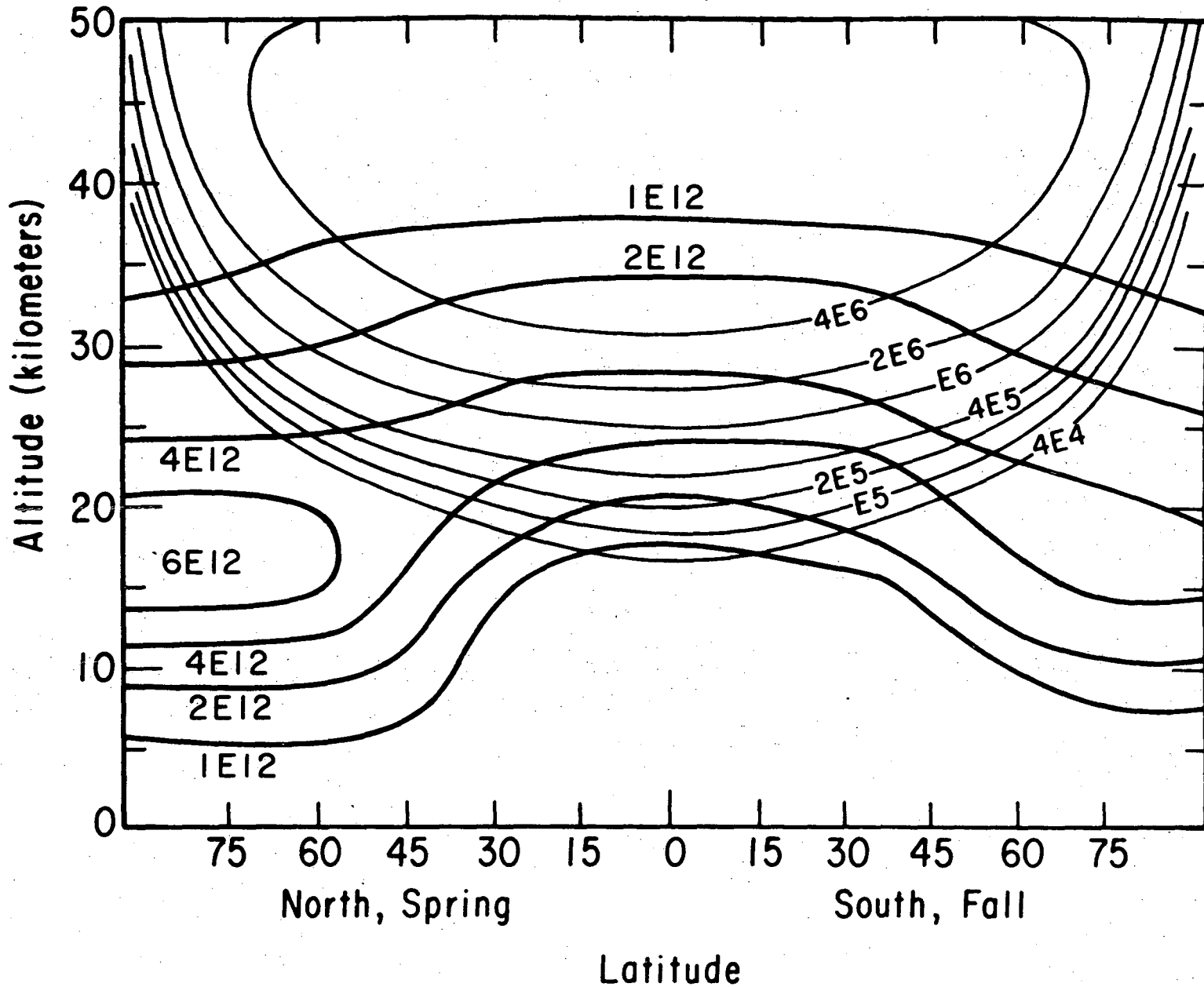
FIGURE 4

OZONE REPLACEMENT TIME, JANUARY 15 (LOCAL OZONE CONCENTRATION DIVIDED BY LOCAL OZONE FORMATION RATE)
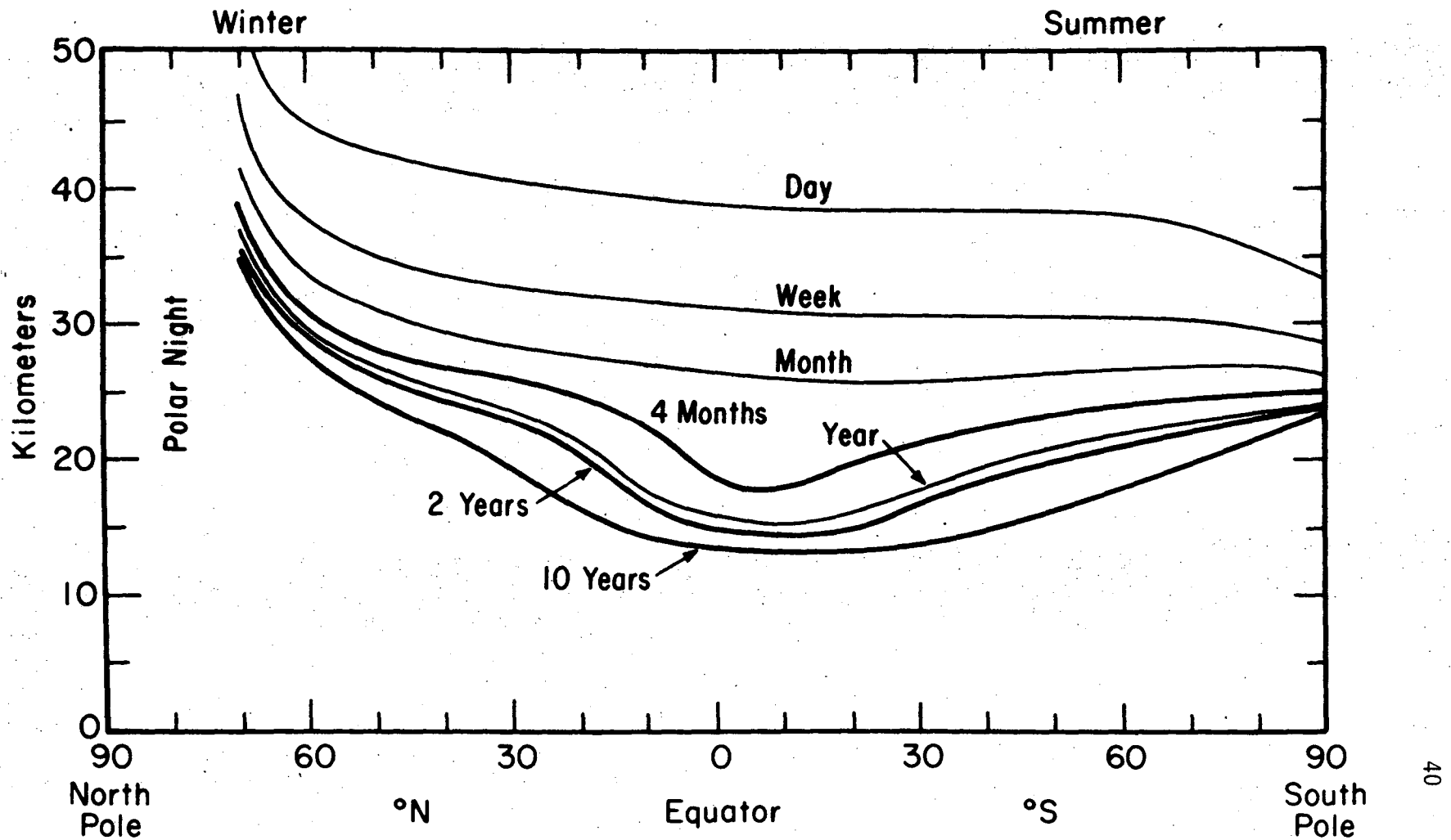
FIGURE 5

XBL 7310-5506

$O_3 + h\nu \longrightarrow O_2 + O$, Rate (molecules cm^{-3} sec^{-1})

Figure 6

XBL-754-6034

FIGURE 7

XBL 748-6946

42
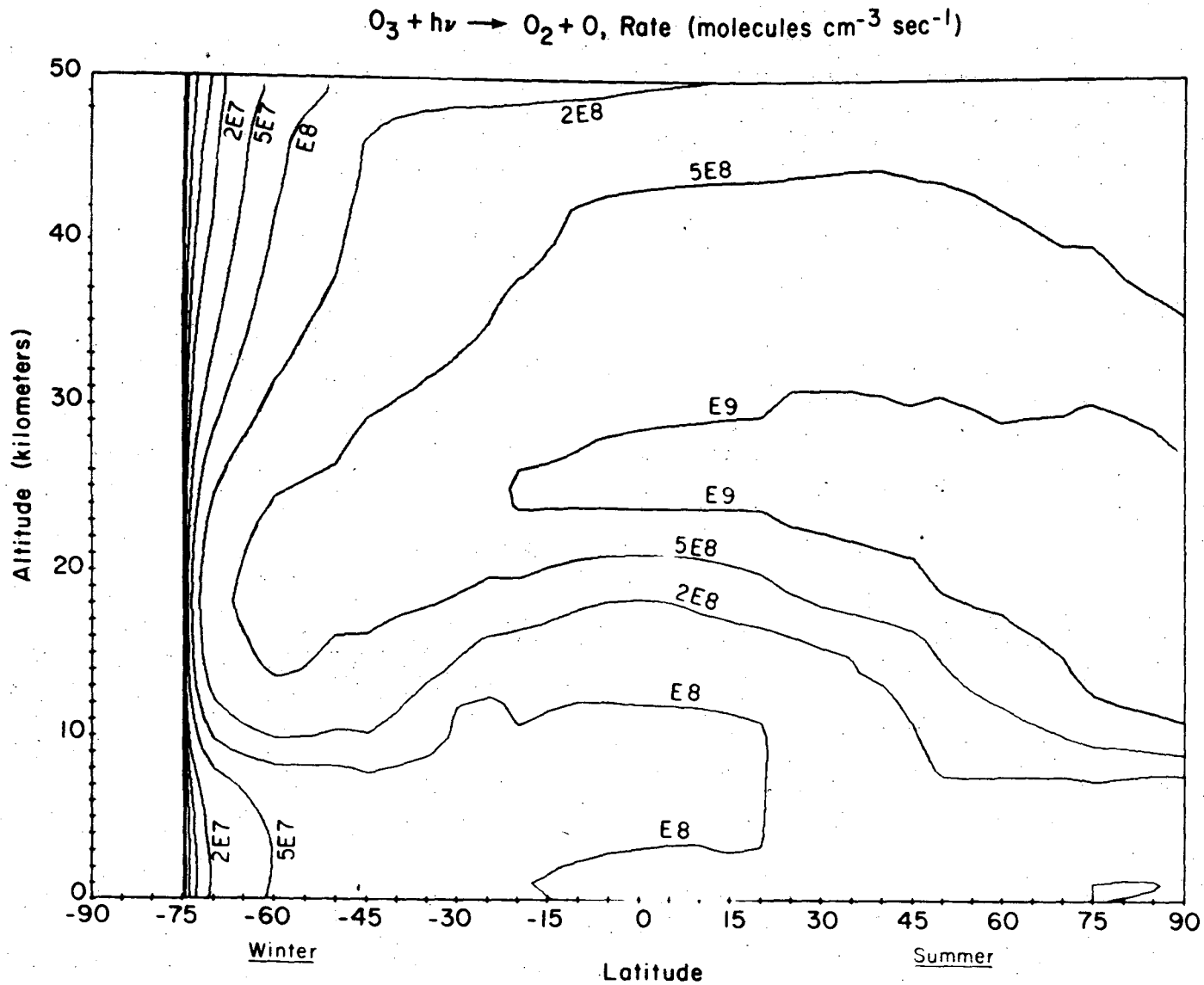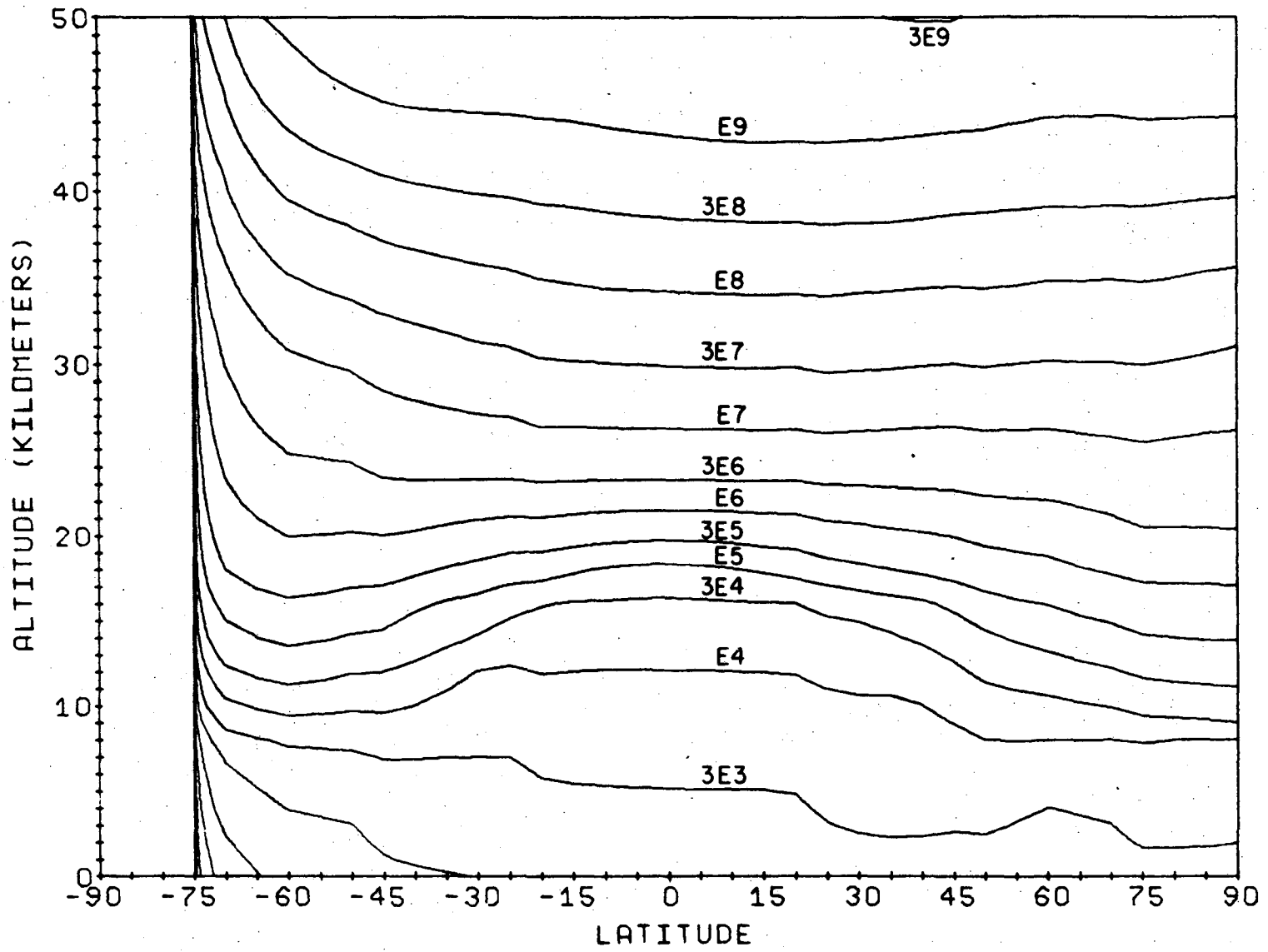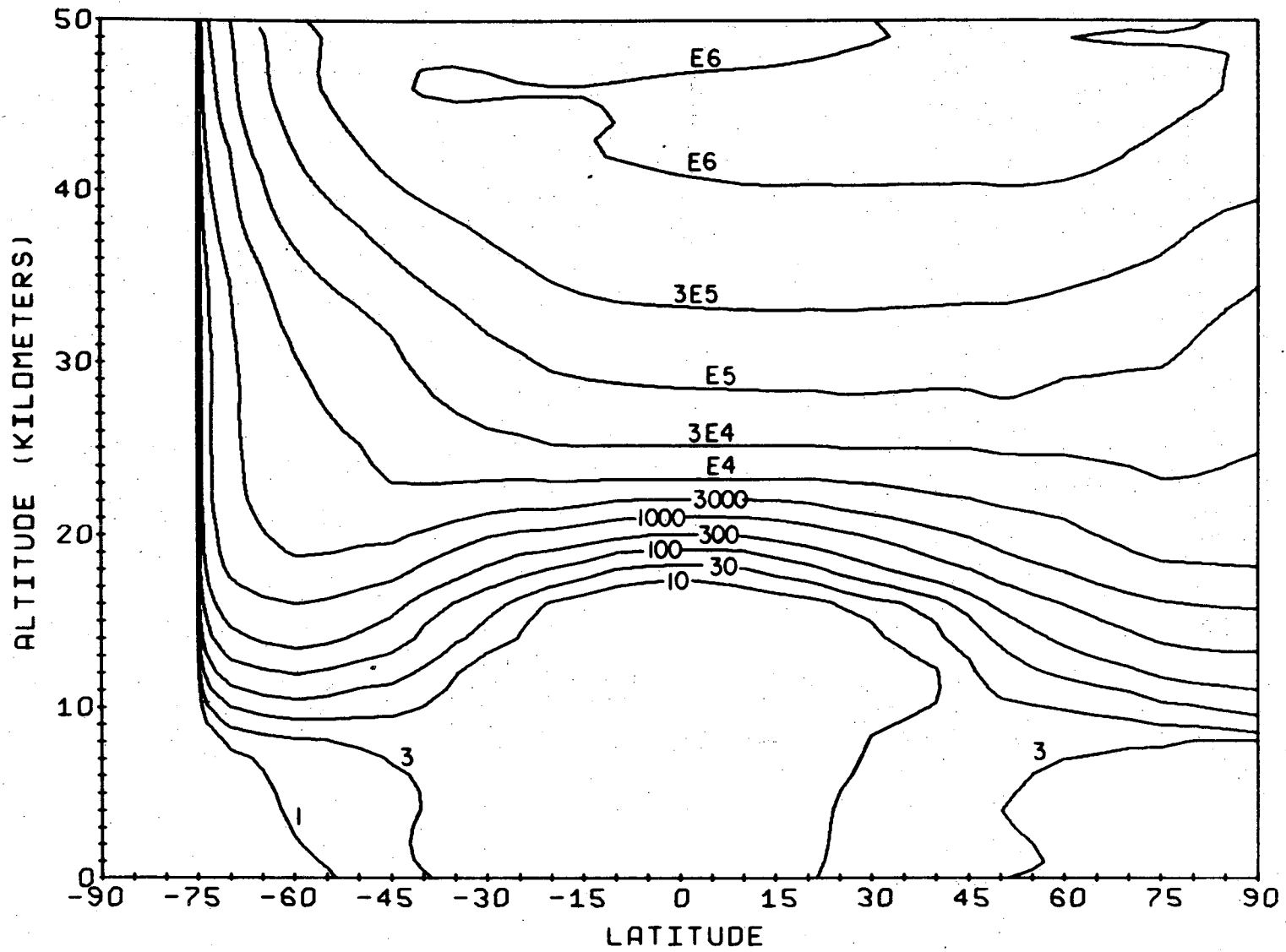
FIGURE 8

FIGURE 9

XBL-754-6035

44

FIGURE 10

Thule, Greenland 76° N   Seattle, Wash. 47° N   Albuquerque N.M. 35° N   Panama Canal 9° N

Partial pressure of ozone (μmb)
May 1, 1963
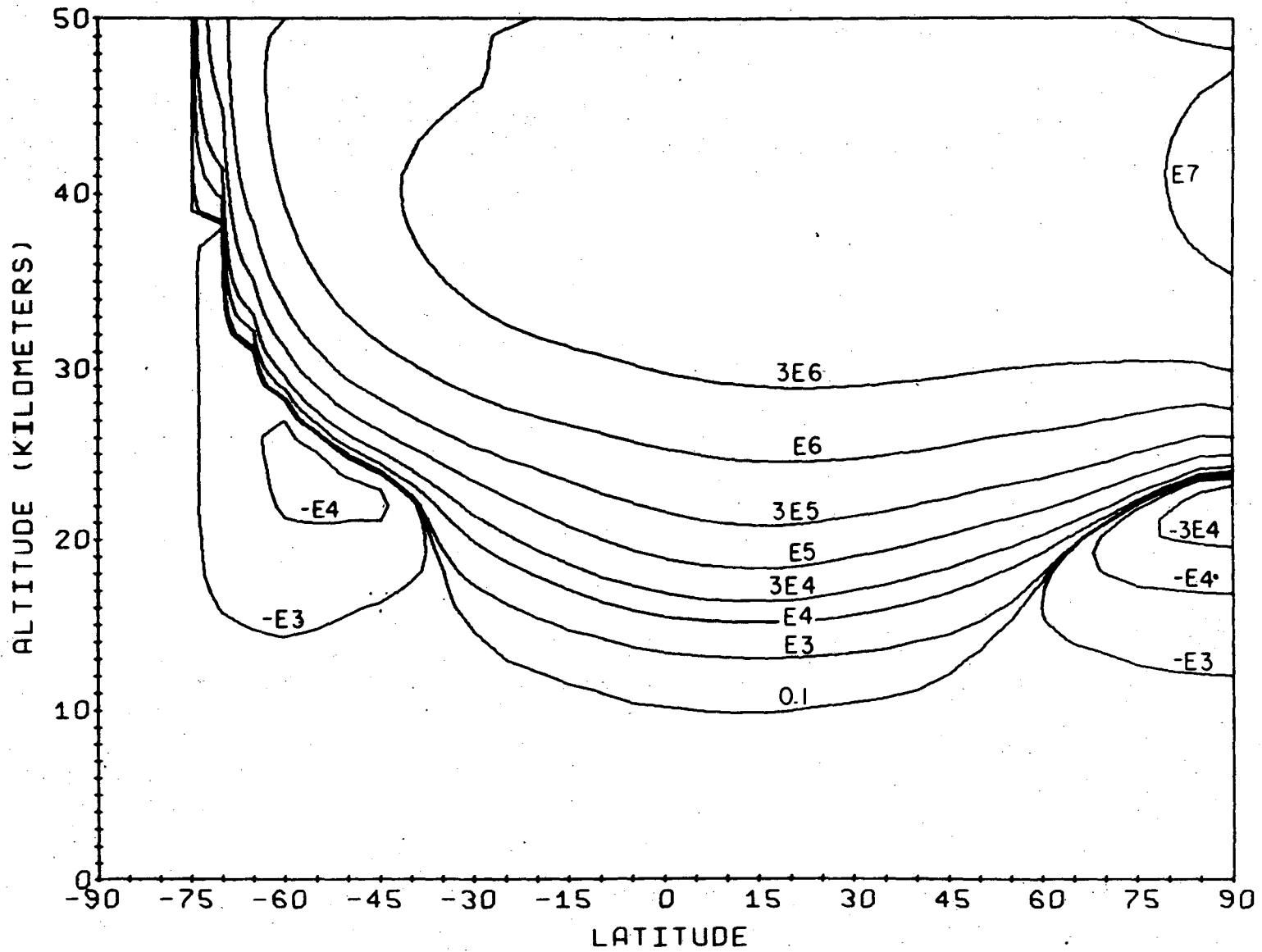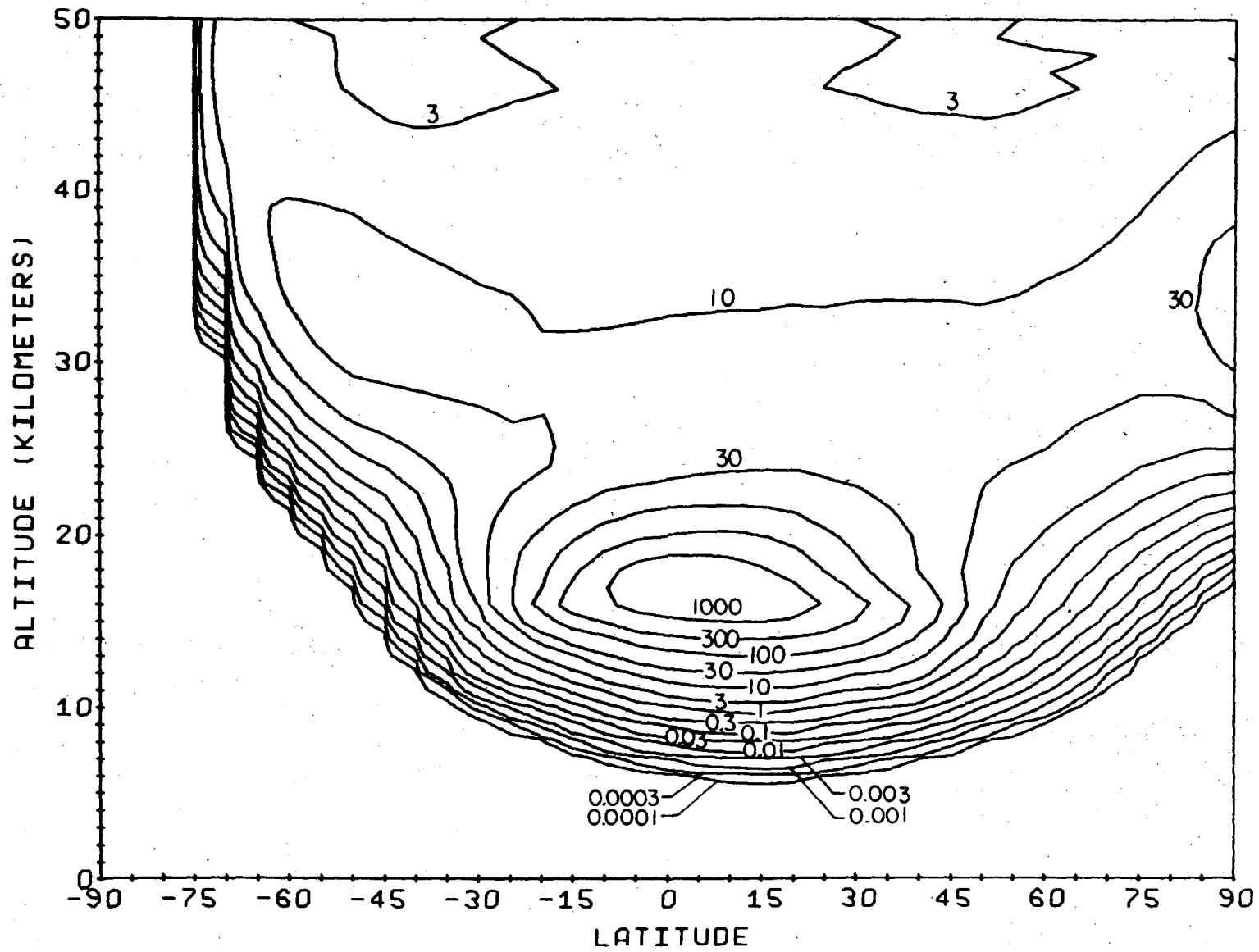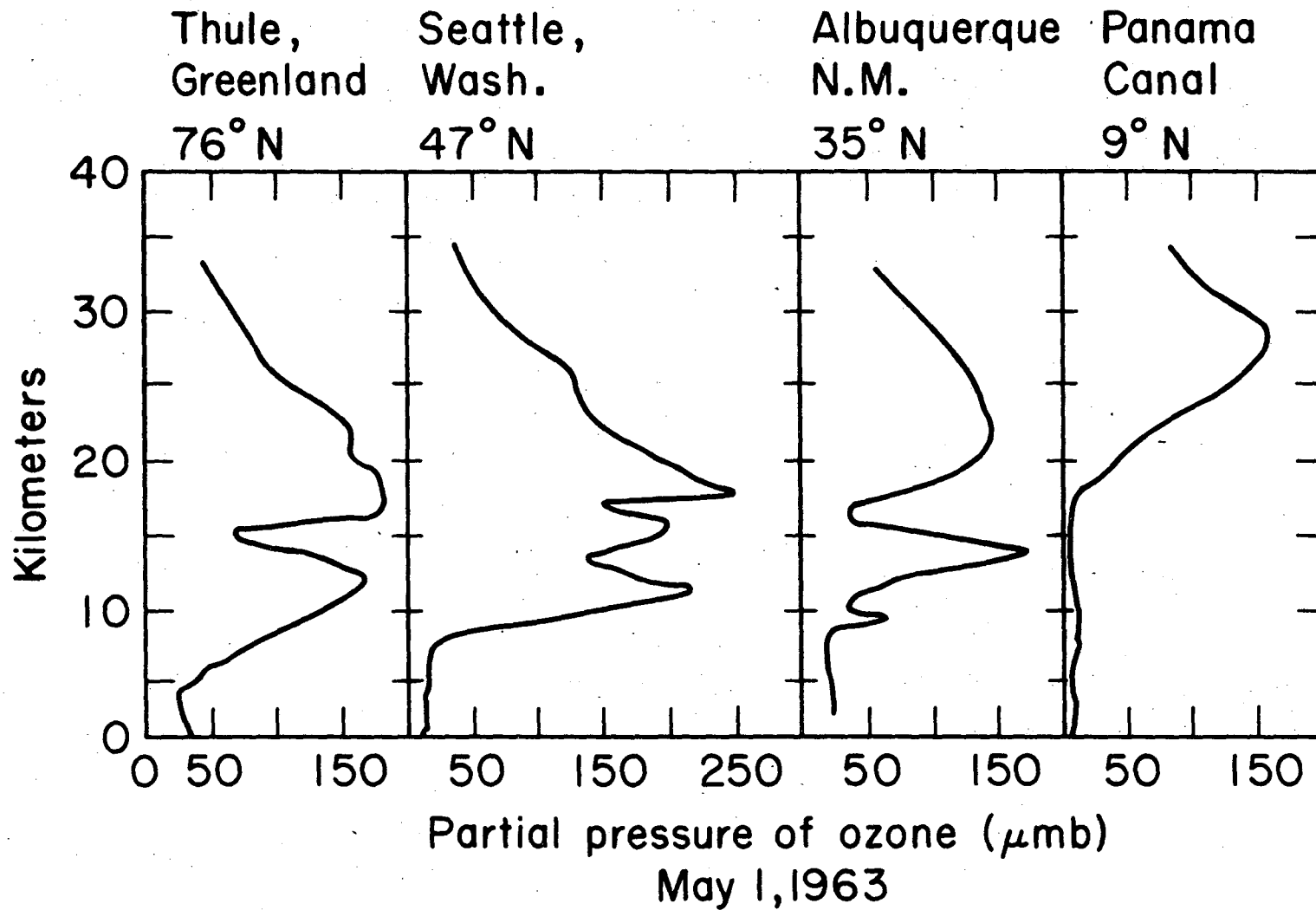
XBL 748-3816

46
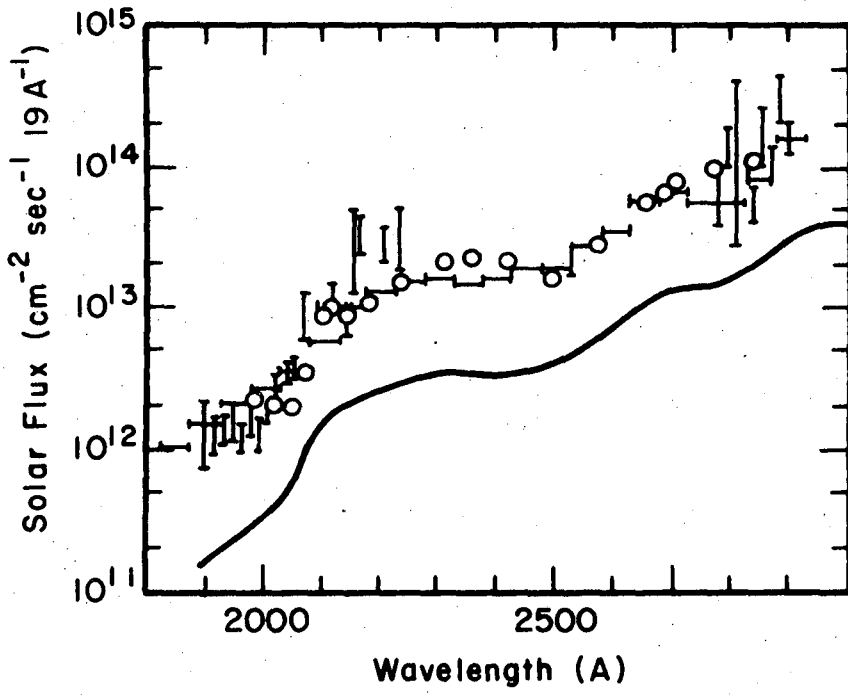
FIGURE 11

FIGURE 12

XBL-754-6036
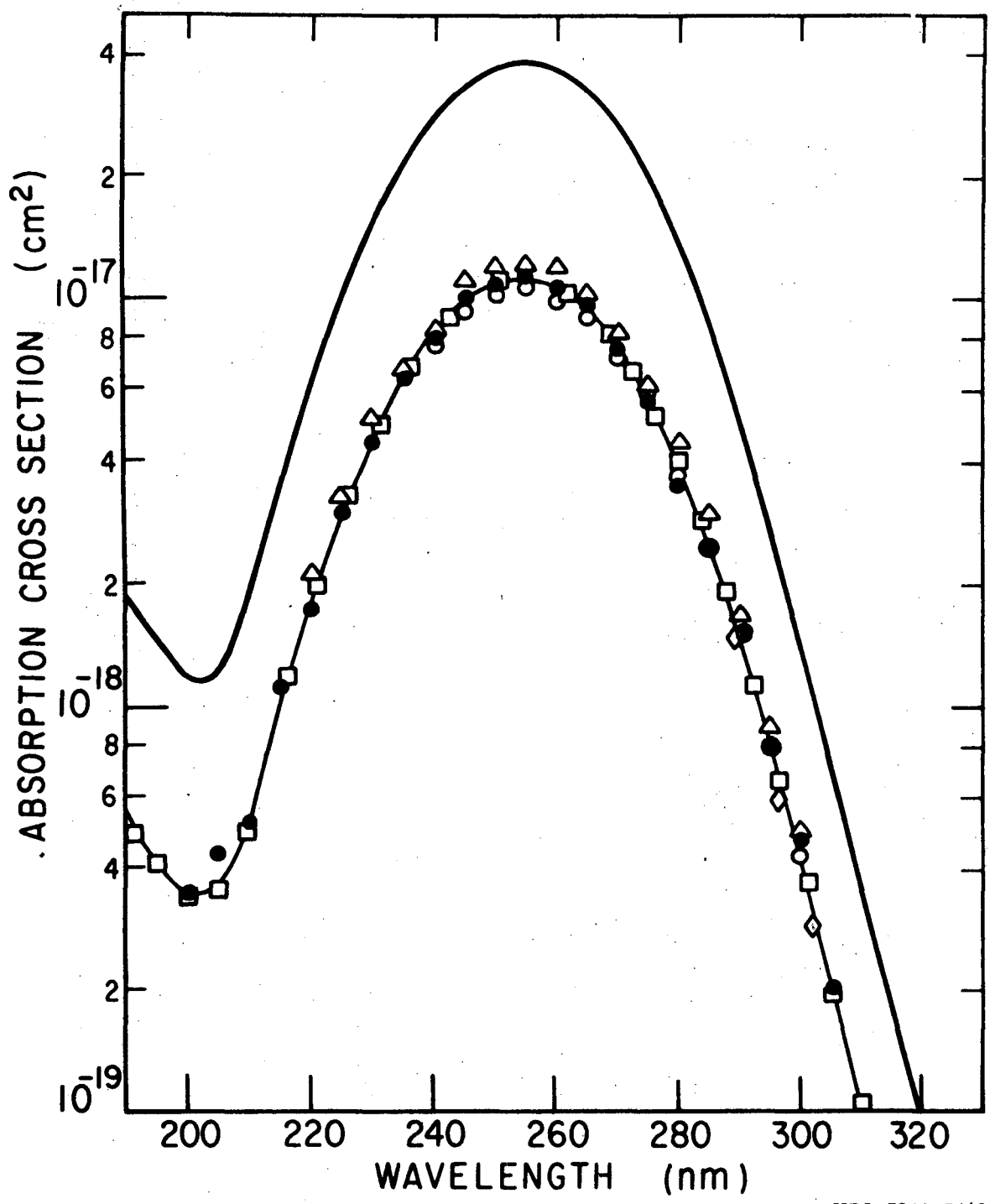
Figure 13.

XBL 7211-7469
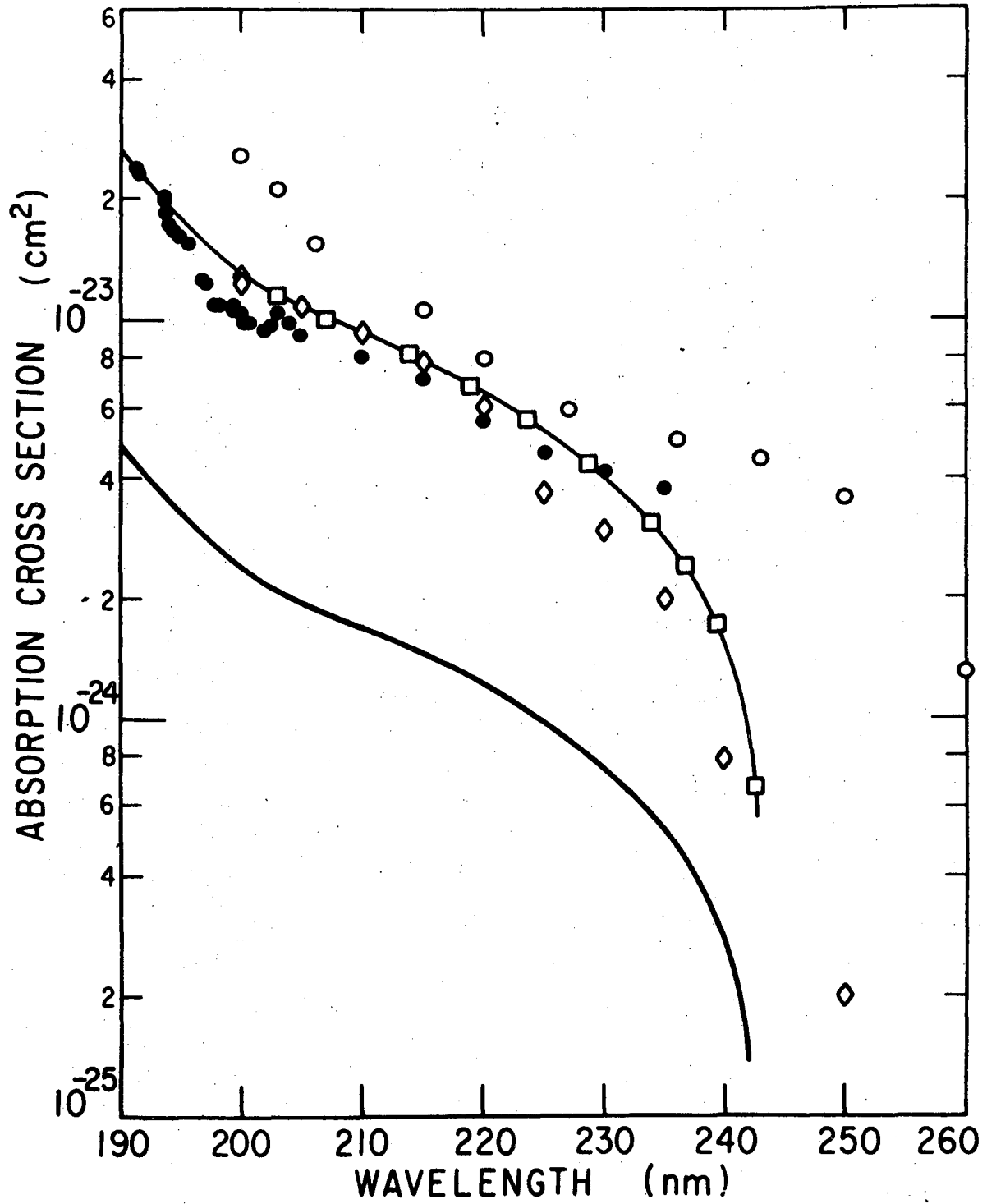
Figure 14

XBL 7211-7470
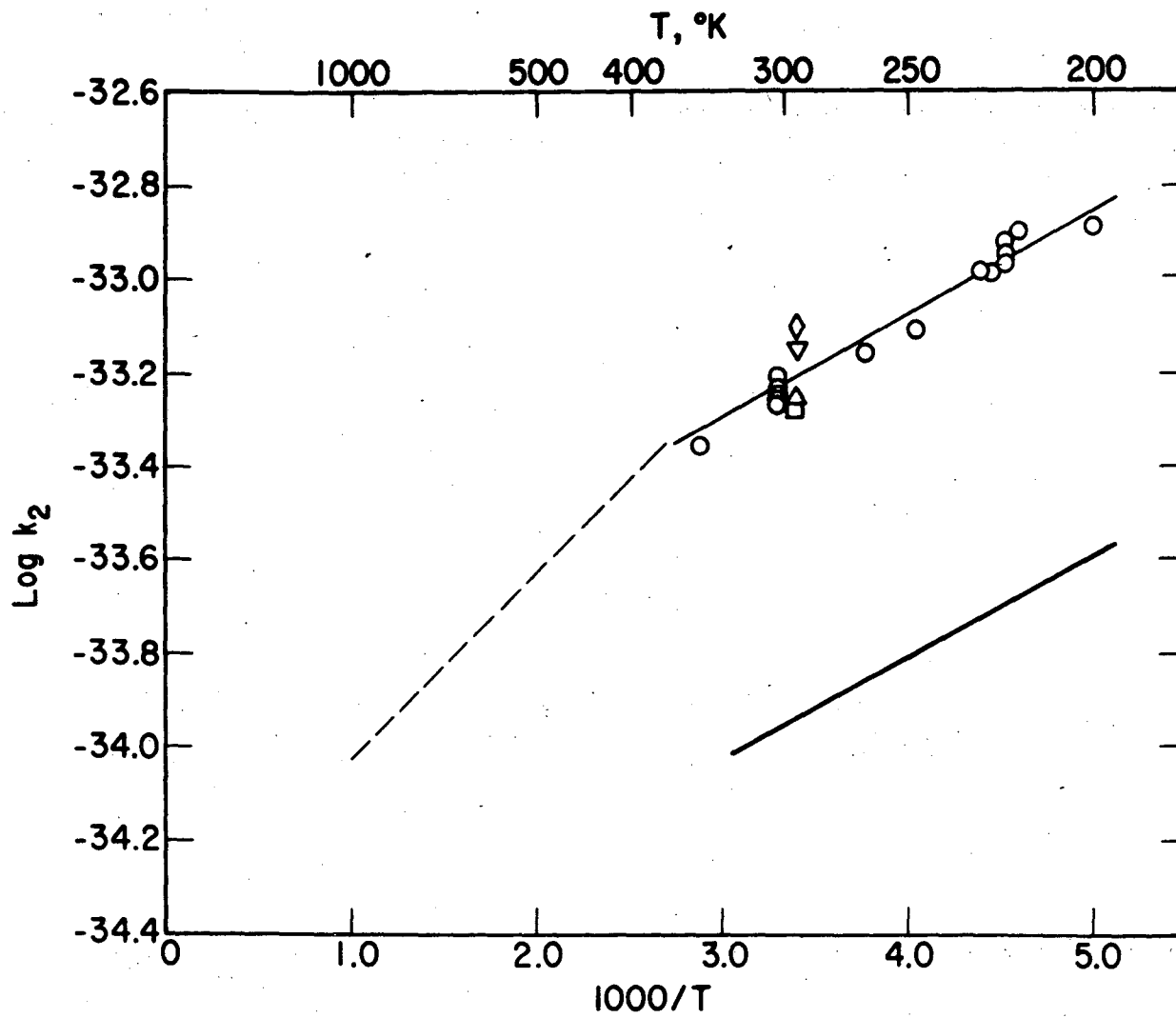
Figure 15
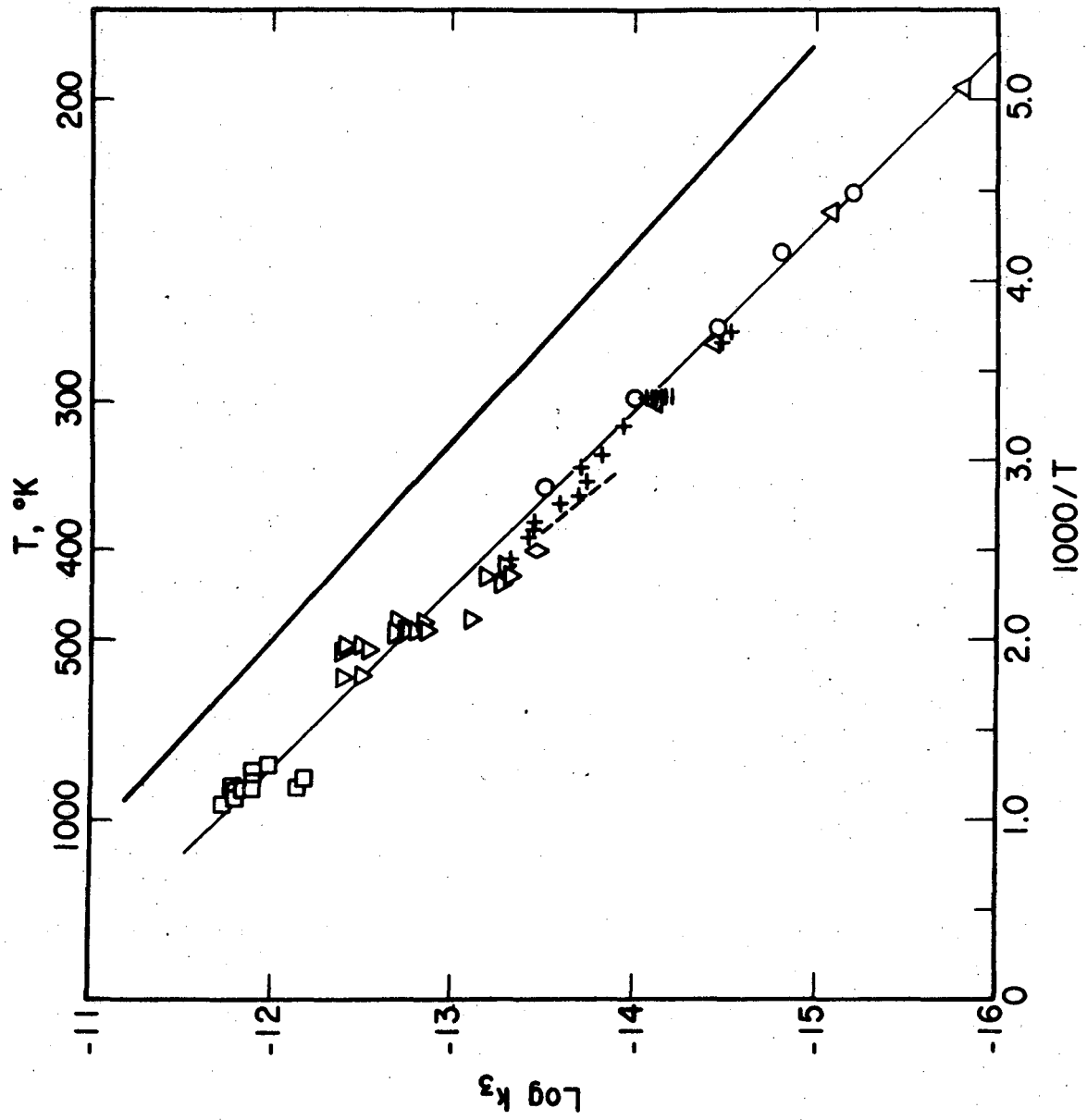
Figure 16

XBL 7211-7311

UNBALANCED OZONE PRODUCTION (CHAPMAN MECHANISM) WITH
MONTE CARLO ASSIGNMENT OF EXPERIMENTAL ERRORS

Figure 17

XBL 745-6397

LATITUDE

ALTITUDE (KILOMETERS)
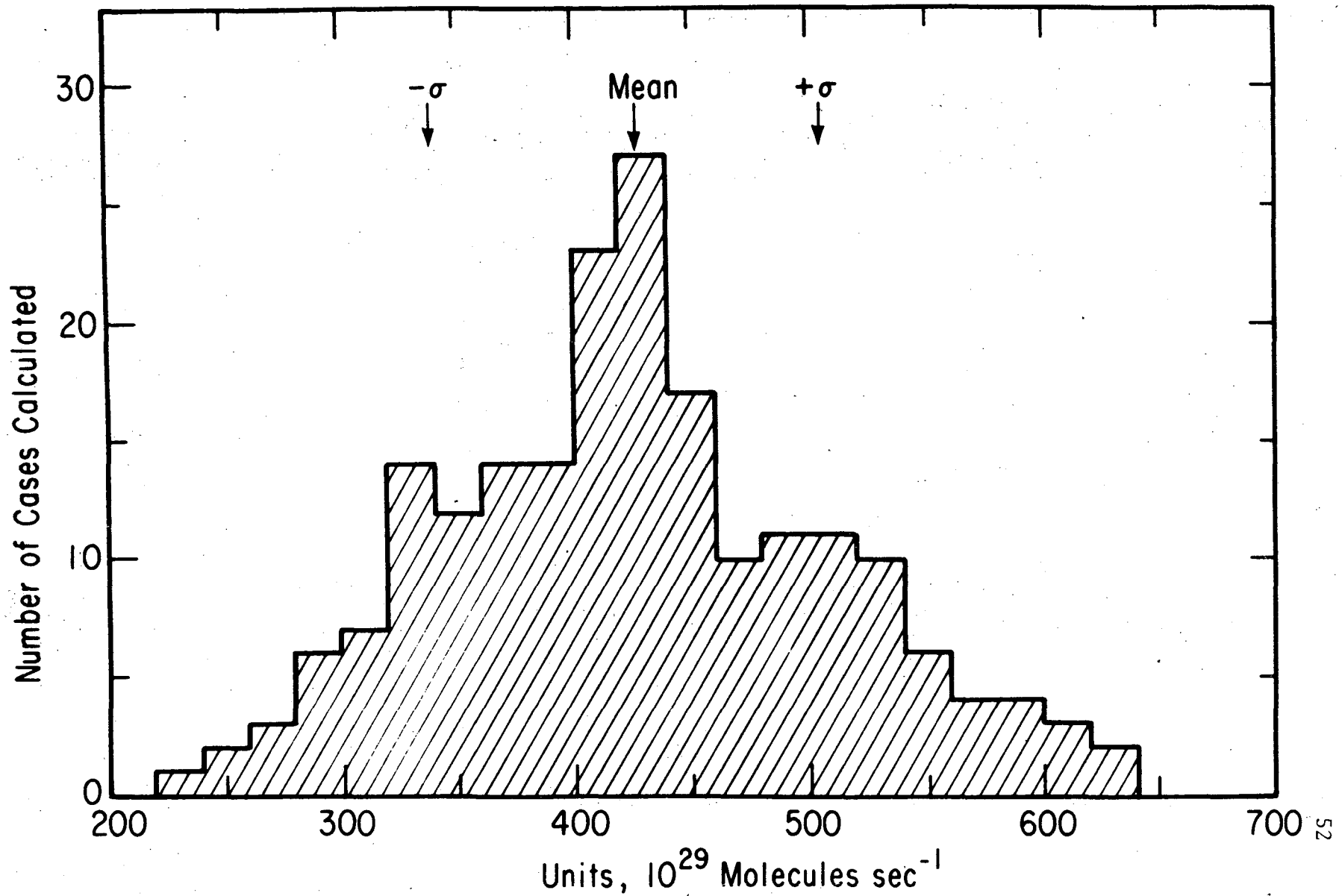
XBL 748-6947
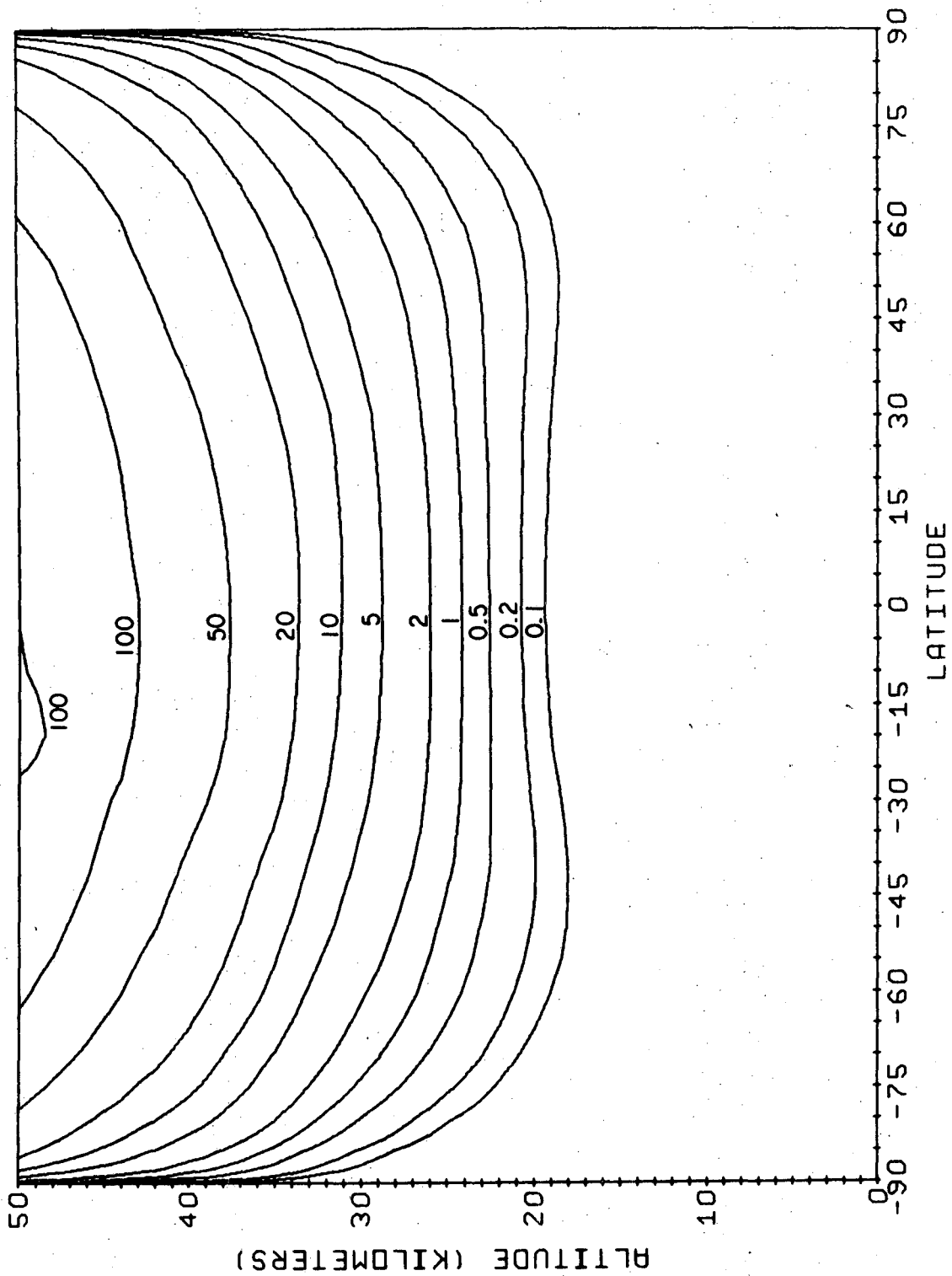
Figure 18
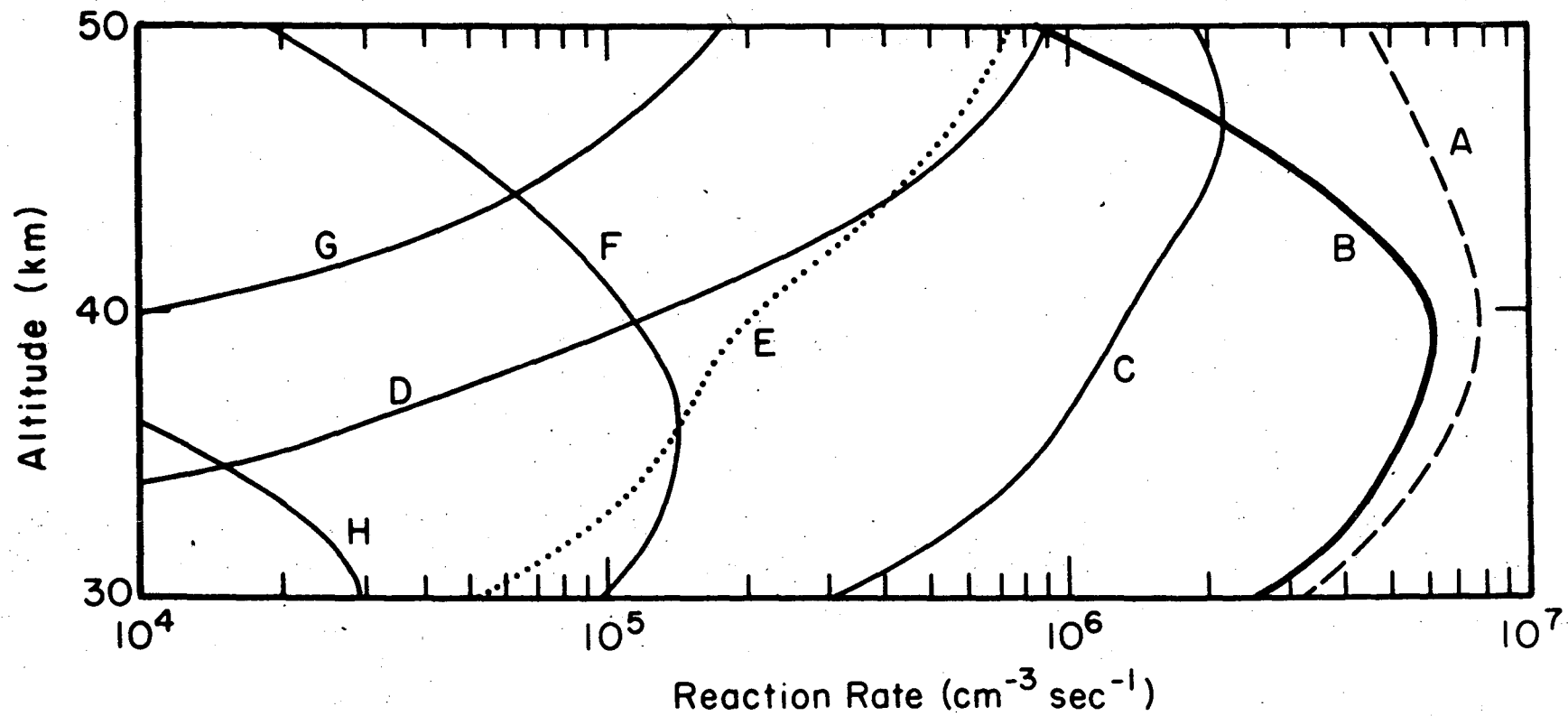
Figure 19
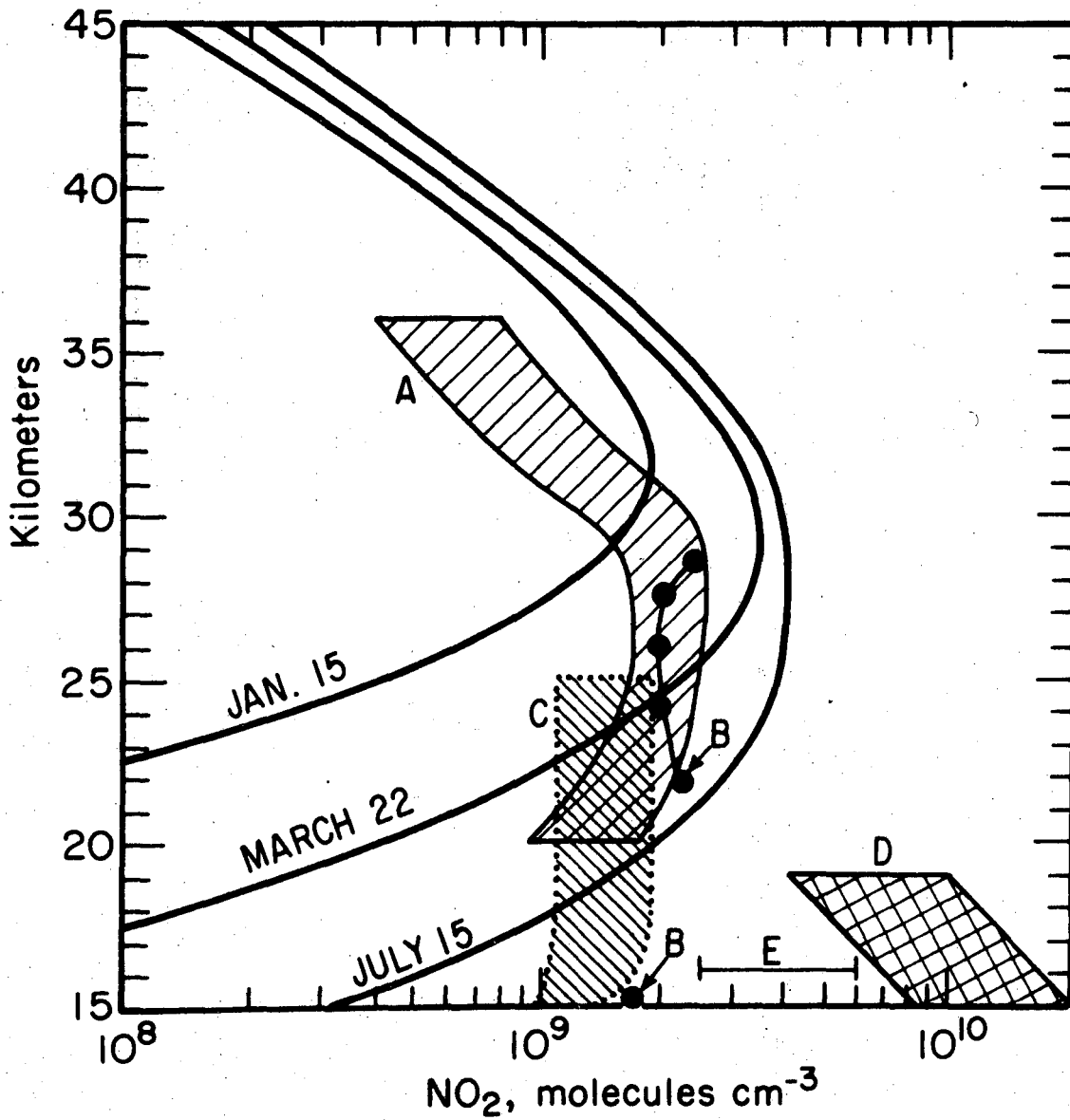
XBL-754-6038

XBL 753-5982

Figure 20
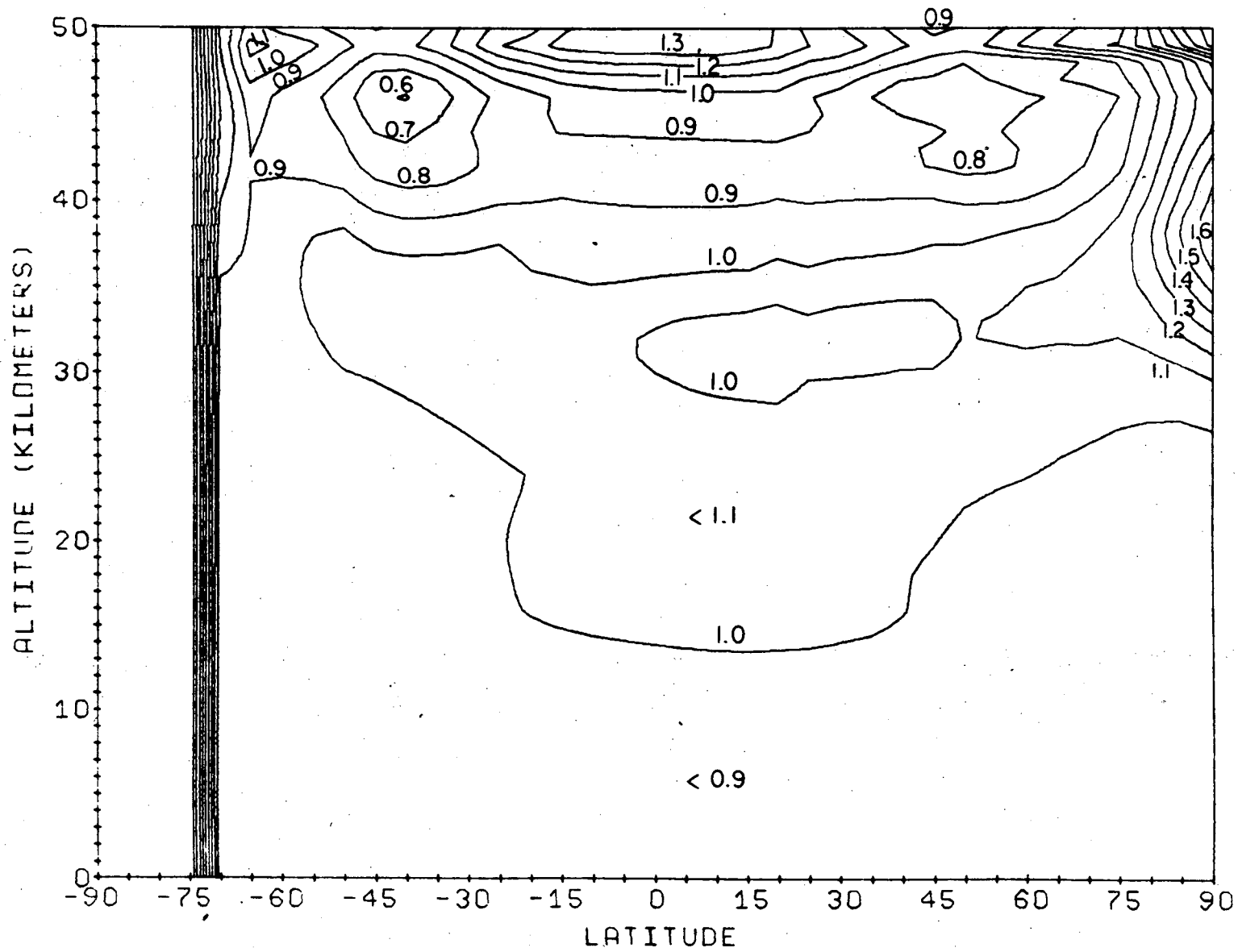
Figure 21

XBL-754-6039

Nitrogen Dioxide Required to Destroy Ozone at 70% of the Rate of Formation From Sunlight.
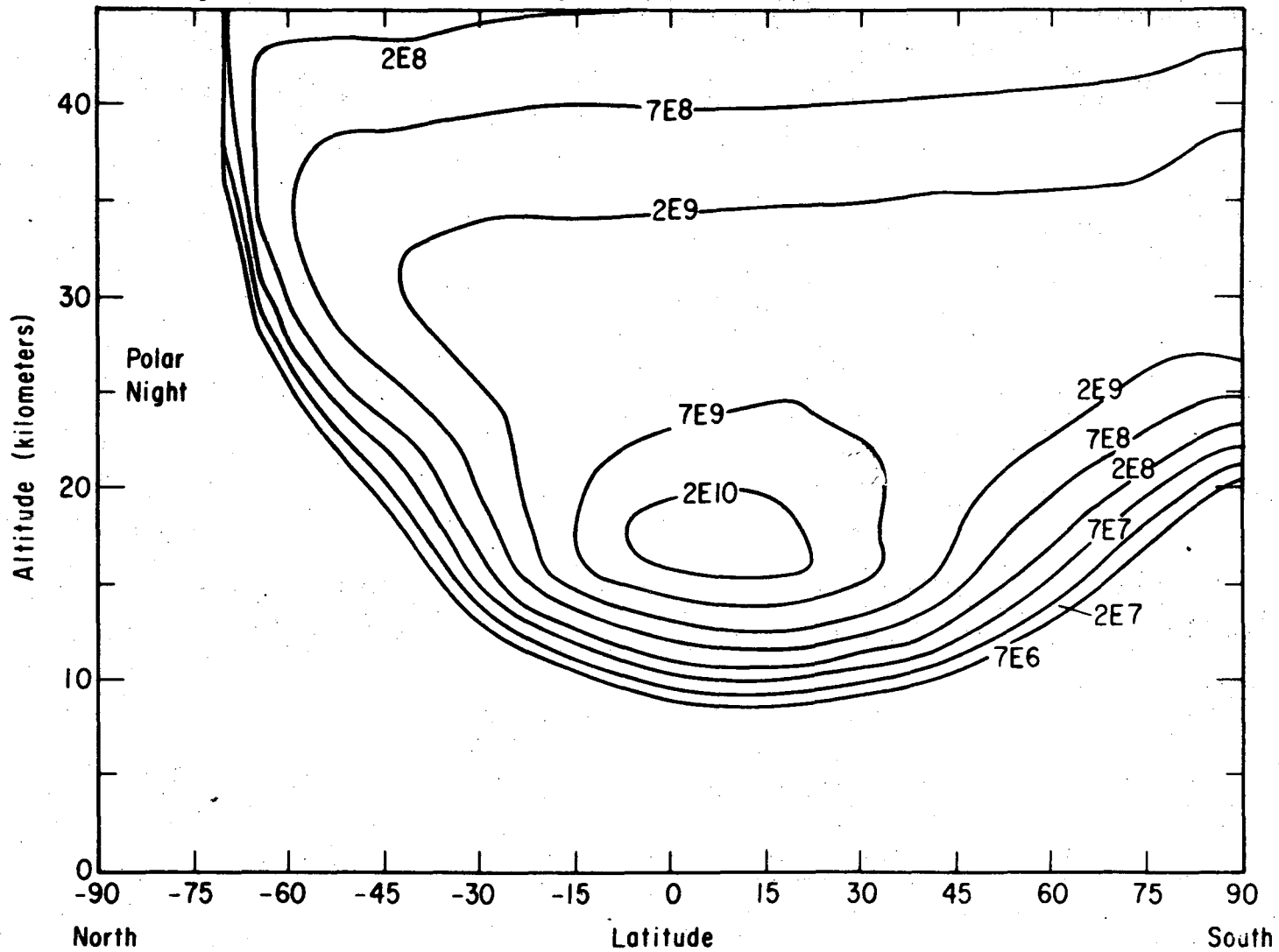
Figure 22

XBL 745-6206a

NITRIC OXIDE PLUS NITROGEN DIOXIDE
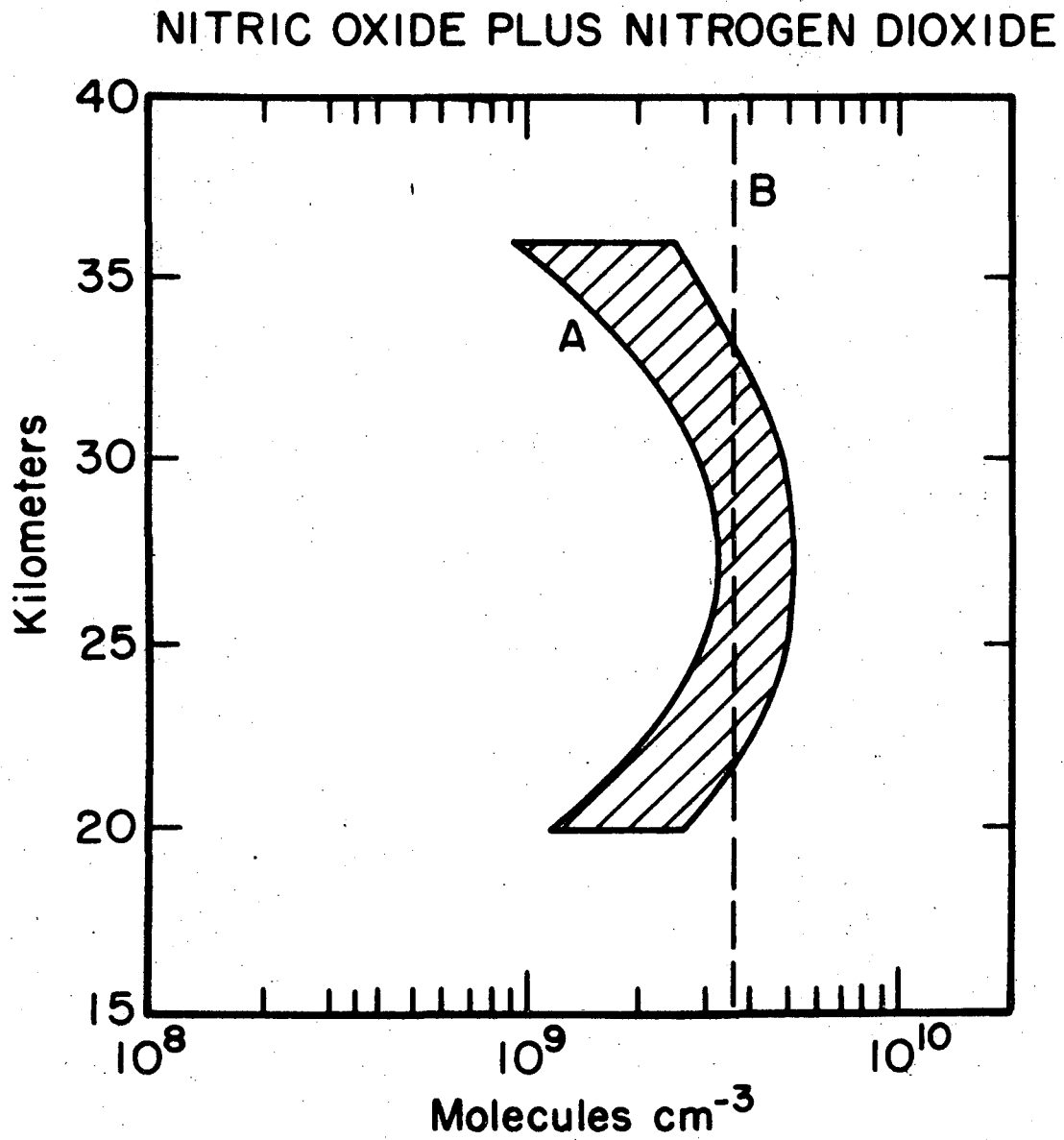
Figure 23

Nitrogen Dioxide Required to Destroy 10% of Local Ozone Per Year.

Figure 24

XBL 745-5204a