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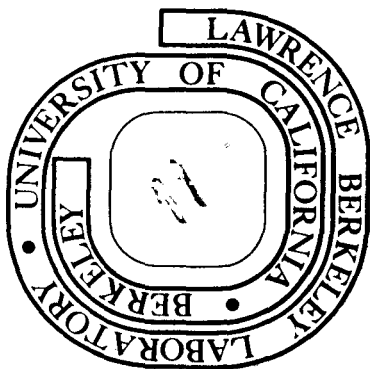
Harold S. Johnston and Gary Whitten

September, 1974

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Chemical Reactions in the Atmosphere As Studied
by the Method of Instantaneous Rates

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Abstract

Some definite statements about chemical reactions in the atmosphere can be made on the basis of instantaneous rates of reaction, regardless of the state of atmospheric motions. This method is illustrated here for several topics in the stratospheric ozone problem. By a Monte Carlo method, it is shown that it is very improbable that random experimental errors in the basic kinetic constants are responsible for the failure of the classic Chapman mechanism and air transport to account for the natural ozone balance. It is probable that the observed concentrations of nitrogen dioxide in the stratosphere is sufficient to account for the natural ozone balance. There appears to be a strong latitude dependence on the sensitivity of stratospheric ozone to catalytic destruction by the oxides of nitrogen. Considerations based on the classic photochemical sector method show that there is no average intensity over the diurnal cycle that is appropriate for stratospheric ozone. The crossover point between ozone formation from the methane-NO_x-smog reaction and ozone destruction by NO_x catalysis occurs at about 13 kilometers in temperate latitudes.

Introduction

It is easy to emphasize the complexity of photochemical reactions in the moving atmosphere with diurnal and seasonal cycles of sunlight; there are direct reactions, feedback mechanisms, and interactions between solar radiation, infrared radiation, chemistry, and atmospheric motions. No theoretical model in the foreseeable future will be able to handle realistically all of the actions and interactions, in three dimensions, and including all temporal cycles. At best, atmospheric models contribute answers to only a part of the problem. Thus it is desirable to develop and promote any model that illuminates any component of the problem. In this laboratory, emphasis has been given to methods that give definite answers to chemical questions, regardless of the state of atmospheric motions; and several such methods have been developed. These methods do not neglect atmospheric motions; they develop components of the problem that are orthogonal to those of atmospheric motions. The "method of instantaneous rates" takes the composition of the atmosphere as it is observed to be; it starts with the distribution of species in the atmosphere as set up by nature, including atmospheric motions. The distribution of solar radiation is calculated, and the instantaneous rates of reactions of interest are computed. This method is reviewed in this article and extended to new cases.

In the atmosphere somewhat different sets of species and reactions are involved in different regions. Four examples are: (1) photochemical smog in urban air; (2) photochemistry

of methane in the global troposphere; (3) photochemistry of ozone in the stratosphere; and (4) reactions of gaseous ions in the mesosphere and higher. This article largely, but not entirely, takes the photochemistry of ozone in the stratosphere as its example of studying chemistry in the atmosphere by the method of instantaneous rates.

1. Sources of Data

The National Bureau of Standards [1] has collected rate constants for chemical and photochemical reactions in the stratosphere. There are approximately 250 elementary reactions in the list. The known ionic reactions in the stratosphere number over 200 [2]. Approximately a score of substances undergo photolysis in the stratosphere. Stratospheric ozone has been the subject of several reviews during the past year [3].

2. Properties of the Stratosphere

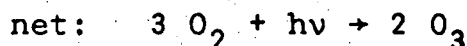
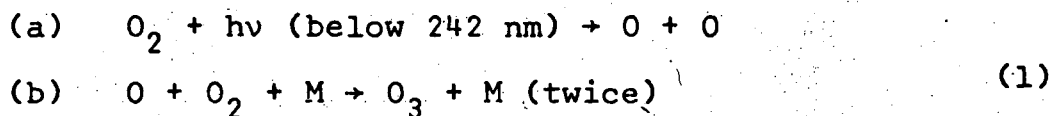
A standard distribution of temperature in the troposphere and stratosphere is given by a zonal average contour map [4a] in Figure 1. Temperature decreases with altitude in the troposphere and increases with elevation in the stratosphere; the approximate boundary is indicated by the dashed line in Figure 1. The temperature distribution in the stratosphere arises from a dynamic balance between in situ photochemical heating, absorption and emission of infrared radiation by carbon dioxide and water and other minor species, heat conduction, and heat transport by air motions. There are complex interactions and feed-back mechanisms between thermal, photochemical, and mechanical effects.

3. Chemistry and Photochemistry

The most important chemistry in the stratosphere is that of ozone. A standard distribution of ozone concentration in the

troposphere and stratosphere [4b] is given by Figure 2. The elevation of maximum concentration of ozone as a function of latitude varies from about 17 km in polar regions to about 25 km in equatorial regions. The absorption spectrum of ozone above 265 nm very nearly parallels that of DNA [5] and stratospheric ozone thus shields the biosphere from lethal and mutating radiation below about 300 nm [6].

In the stratosphere there is only one important source of ozone, the photolysis of molecular oxygen and the subsequent addition of the product atoms to other molecules of oxygen



A zonal-average contour for the rate of oxygen photolysis, as found by the method of instantaneous chemical reactions [7], is given by Figure 3. The rate of formation of ozone is twice the rate shown in Figure 3. The short wavelength radiation that can dissociate oxygen is absorbed by both ozone and oxygen, and it is screened out in the upper and middle stratosphere.

The local "ozone replacement time" is defined as the concentration of ozone divided by the rate of formation of ozone

$$\begin{aligned} \tau &= \frac{\text{ozone concentration}}{\text{rate of ozone formation}} \\ &= [\text{O}_3] / 2 j_a [\text{O}_2] \end{aligned} \quad (2)$$

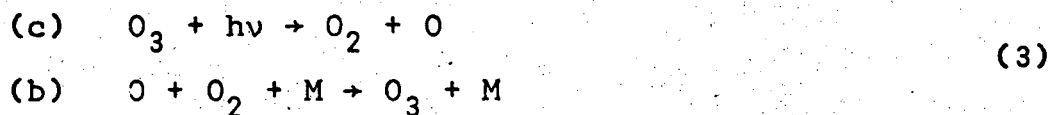
where j_a is the first-order rate constant for the photolysis of oxygen, reaction a.

For a standard (January 15) distribution of ozone, the instantaneous, zonal-average, ozone-replacement times are given by Figure 4. The replacement times are a few hours at the top of the stratosphere, a few days at about 30 km; a few months at about 23 km, and several years below 15 km in the tropics or below 20 km in temperate zones.

Many mechanisms have been recognized for the destruction of ozone. About one-half of one percent of the ozone formed in the stratosphere is transported to the troposphere and destroyed at the earth's surface [8,9,10]. Ozone is destroyed by a series of chemical mechanisms [3]: the O_x system, the NO_x system, the HO_x system, the ClO_x system [11,12], and perhaps others.

The photolysis of ozone does not constitute ozone destruction, since this process is rapidly reversed by reaction

b

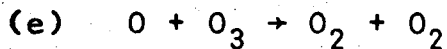
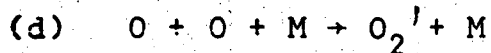


net: solar energy converted to heat in the atmosphere

The zonal average rate of ozone photolysis is given by Figure 5. This distribution of reaction rates is quite different from that of the photolysis of oxygen, Figure 3. In part, ozone is photolyzed by ultraviolet radiation below 300 nm, which is strongly screened out by ozone, so that the distribution of this rate is similar to that in Figure 3. Also, ozone is photolyzed by radiation above 300 nm and by visible light (450-700 nm), but

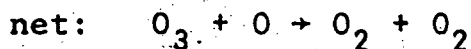
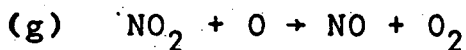
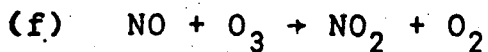
this radiation is only weakly absorbed by ozone and not significantly absorbed by other atmospheric substances. Thus this photolysis occurs almost uniformly from top to bottom of the atmosphere as soon as the sun rises. The photolysis and recombination of ozone, Equation 3, rapidly sets up a small, steady-state concentration of oxygen atoms, a zonal-average contour map of which is given by Figure 6. At a given elevation, the concentration of oxygen atoms is almost uniform with latitude in the sunlit atmosphere, but it increases rapidly with altitude, largely by virtue of the decrease of the rate b.

The destruction of ozone in the O_x mechanism occurs indirectly by reactions of oxygen atoms, which thereby do not reform ozone, and by reactions of oxygen atoms with ozone



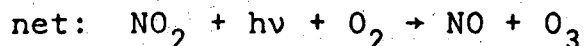
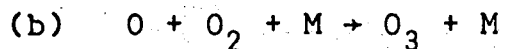
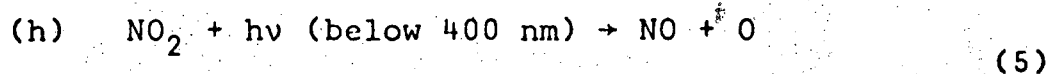
In the troposphere and stratosphere, reaction d is very slow compared to reaction e, and it may be neglected. There are many reactions involving excited electronic states of atomic and molecular oxygen, but these are not important in the direct destruction of ozone.

Nitric oxide and nitrogen dioxide destroy ozone in a number of catalytic cycles [13], but only one of these is important in the stratosphere [13d]



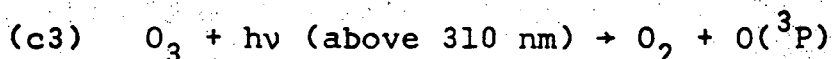
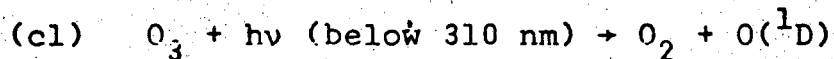
(4)

Reaction f is usually reversed by photolysis of nitrogen dioxide

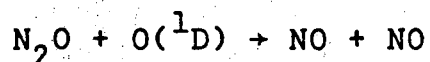


so that reaction g is the rate-determining step in the catalytic cycle (4). The rate constants for reactions a-h are rather well known [1], and quantitative comparisons between these rates can be made if the concentrations of ozone and nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) are known.

Ozone photolysis has important features not given by reaction c as written above

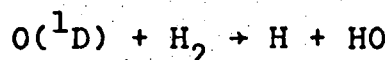
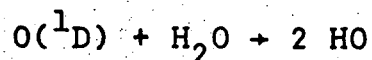


Singlet oxygen atoms, $\text{O}({}^1\text{D})$, are very much more reactive than triplet oxygen atoms, $\text{O}({}^3\text{P})$. Reaction of singlet oxygen with the rather inert nitrous oxide, N_2O

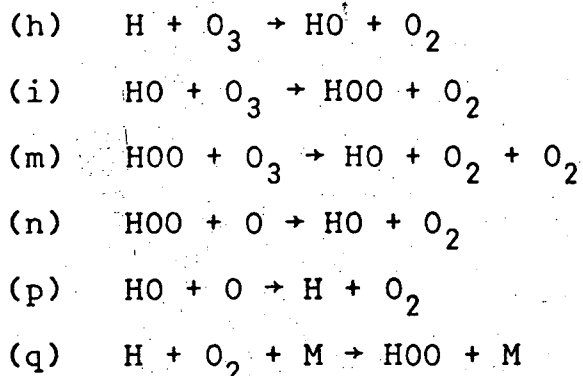


is the primary source of NO_x in the natural stratosphere [14].

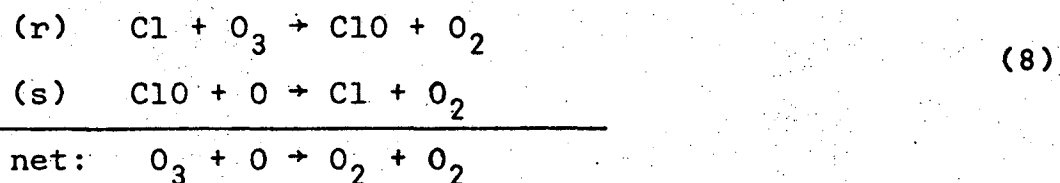
Reaction of singlet oxygen atoms with water or with methane or with hydrogen produce active free radicals in the atmosphere



The free radicals H, HO, and HOO, collectively referred to as HO_x, rapidly interchange with each other and destroy ozone



Although the natural level of chlorine - containing gases in the stratosphere [15] is so low that the chlorine system (ClO_x = Cl + ClO + ClOO) seems now not to be important in the global ozone balance, reaction rate constants [1b] are such that stratospheric ozone is vulnerable [12] to chlorine because of the catalytic cycle



The active ClO_x species interact with methane, hydroxyl radicals, and nitric oxide.

The hundreds of reactions recognized in the stratosphere concern the interactions of the O_x, NO_x, HO_x, and ClO_x systems. These hundreds of reactions are not equally important. A set of about 50 reactions seems to be sufficient to account for the essential chemistry of the oxygen-nitrogen-hydrogen families. These reactions have been reviewed in several recent articles [3], and the details will not be discussed here.

4. Air Motions

Chemistry and photochemistry are only half the story of the stratospheric ozone distribution. The other half concerns atmospheric motions [16]. East-west winds circle the globe in several days or a few weeks. North-south air movement typically takes a few months for horizontal spreading from the equator to a pole. Vertical mixing in the stratosphere is inhibited by the strong temperature inversion (Figure 1) and requires a matter of years. The importance of air motions in shaping the distribution of stratospheric ozone is simply demonstrated by superimposing the zonal average contours of ozone replacement time (Figure 4) on the zonal average contours of ozone concentration (Figure 2). Such a superposition [17] is given by Figure 7. The contour lines for ozone-replacement time in Figure 4 were reduced to two, that for 4 months and that for 10 years; and the number of contour lines in Figure 2 were reduced for the sake of clarity in Figure 7. The "ozone formation region" is defined as that where the ozone photochemical replacement time is 4 months or less, and ozone is regarded as being detached from its formation region if the ozone replacement time is 10 years or more. In the summer hemisphere, the ozone formation region lies above 20 to 25 km, and it is sharply cut off in the winter hemisphere. The global maximum ozone concentration is 6×10^{12} molecules cm^{-3} in the north polar region, and the locus of the maximum elsewhere is indicated by the dotted line. The location of maximum ozone and maximum ozone formation rate (compare Figure 3) are quite different. The high ozone

concentration in the north polar region accumulated over the winter by means of air motions that transported ozone poleward and downward.

This brief review of atmospheric chemistry and atmospheric motions shows that a realistic model of stratospheric ozone should involve three-dimensional motion and about 50 photochemical reactions. A realistic theory involving a three dimensional atmosphere, photochemistry, radiation, heat, and interactions between all of these factors appears to be at least several years in the future, although several groups are carrying out a powerful assault on this full problem [16].

5. The Method of Instantaneous Rates

In order to answer some of the questions of atmospheric photochemistry, Johnston and Whitten [7] devised a global, three-dimensional, instantaneous model. This method starts with observed, standard temperature (such as Figure 1), ozone concentrations (such as Figure 2) and solar radiation above the atmosphere, Figure 8. The atmosphere was divided into a grid using spherical polar coordinates: $\Delta r = 1$ km from 0 to 50 km above sea-level; $\Delta \theta = 5^\circ$ latitude from pole to pole; $\Delta \phi = 15^\circ$ longitude for 360° . This grid gives 43200 volume elements, half of which are in sunlight and half on the dark side of the earth. The 21600 volume elements facing the sun present different angles to incoming sunlight and thus different shielding columns of overhead oxygen and ozone. In each of these volume elements the intensity of radiation was calculated at each nm

between 190 and 400 nm. Light intensity from 400 to 700 nm is constant in the sunlit stratosphere. The photochemical rate constants for photolysis of oxygen, j_a , and photolysis of ozone, j_c , were calculated in each volume element, and the rate of photolysis of oxygen and ozone was evaluated. The steady-state concentration of oxygen atoms was evaluated in each volume element

$$[O]_s = j_c [O_3] / k_b [M] [O_2] \quad (9)$$

After all photochemistry of interest was evaluated in each volume element, then averaging of various sorts were carried out. Averaging around the full 360° circle of the earth gives zonal averages of various rates and concentrations: Figure 3, zonal-average, instantaneous rate of oxygen photolysis; Figure 5, ozone photolysis; Figure 6, oxygen atom concentration; Figure 4, ozone replacement times. Further integration gives global rates of various kinds.

This method does not neglect atmospheric motions. Atmospheric motions were important in shaping the observed distributions of temperature and ozone concentration, which are used in the "instantaneous reaction" method.

This method was used to answer the question whether the pure air or Chapman [17] reactions, a, b, c, e, and air motions are sufficient to give a global ozone balance. This treatment is reviewed and extended here. Also this method is applied to other problems.

6. Are the Chapman Reactions Sufficient
to Account for the Natural Ozone Balance?

The mechanism proposed by Chapman [17] in 1930 for stratospheric ozone concerns only the pure oxygen species and reactions a, b, c, d, e. The rates of these reactions were calculated in each volume element given by the grid indicated in Figure 8, and integration of these rates over the entire stratosphere gave instantaneous global rates for each reaction a-e. The results of this calculation is given by Table 1.

Table 1. Instantaneous, global rates (in units of 10^{29} molecules sec^{-1}) in the stratosphere in terms of the Chapman mechanism.

Process	Global reaction rate		Ref.
	Jan. 15	Mar. 22	
Ozone formation	500	486	7
Transport to troposphere	-5±3	-5±3	8
Chemical loss	-86	-89	7
Unbalanced ozone production	409	392	7

Approximately 80 percent of the ozone produced by sunlight fails to be balanced by the Chapman reactions and by transport to the troposphere. Thus each second (and for any second) ozone is produced over five times as fast as it is destroyed by the Chapman mechanism, and at this rate global ozone would double in less than two weeks. Therefore, the Chapman mechanism and air motions appear not to be sufficient to account for the natural ozone balance.

The large unbalance of ozone shown in Table 1 is based on the central values of a number of experimental quantities. The primary data for the calculation are temperature (Figure 1), ozone concentration (Figure 2), solar radiation intensity I_0 above the atmosphere, the cross section for light absorption by oxygen σ_2 , the cross section for light absorption by ozone σ_3 , the rate constant for reaction b , and the rate constant for reaction c . The experimental quantities have a range of uncertainty, and one asks whether the calculated unbalance of ozone could be due to experimental error in the rate constants or other data. To answer this question, Monte Carlo calculations were made whereby random values and signs of error were assigned to five quantities above, and the global, three-dimensional, instantaneous calculation was repeated. The difference Δ between ozone formation and destruction for the globe was evaluated for each assignment of errors to the five experimental quantities.

In the Monte Carlo calculation, the fractional standard deviation E in each quantity was deduced to be:

$I_0(\lambda)$	± 0.15	
σ_2	± 0.20	
σ_3	± 0.05	(10)
k_b	± 0.18	
k_c	± 0.26	

The parameters were randomly varied by means of the formula:

$$P = P_N (1 + |E|)^x \quad (11)$$

where P is the varied quantity, P_N is the normal or central value, $|E|$ is the absolute value of the error (Equation 10), and x is a random number. The random numbers were produced by the CDC7600 computer from a list of 5.8×10^{12} random numbers between +6 and -6 with a standard deviation of ± 1 .

The quantity Δ is the integrated global difference between instantaneous ozone production from sunlight and destruction by reaction e. The standard (January 15) calculation with all parameters having their central values P_N gave an unbalanced ozone production of 414×10^{29} molecules sec^{-1} . The calculation was repeated 200 times based on 1000 random numbers. For each calculation each parameter had a random chance of positive or negative deviation by an amount properly weighted by its own standard deviation (Equation 11).

The results of these 200 calculations with a bin size of 20×10^{29} molecules sec^{-1} are presented in Figure 9. The average value calculated was 422×10^{29} molecules sec^{-1} , and the standard deviation was $\pm 83 \times 10^{29}$ molecules sec^{-1} . The quantity plus or minus twice the standard deviation is

$$\Delta = (422 \pm 186) \times 10^{29} \text{ molecules sec}^{-1}$$

This range gives approximately the 95% confidence limit. Thus one can say to a high degree of confidence that random experimental errors in the 5 experimental quantities do not cause a false impression of the failure of the Chapman mechanism.

7. Are the Oxides of Nitrogen Sufficient to Account
for the Natural Ozone Balance?

The pair of reactions, f and g , Equation (3) involving nitric oxide and nitrogen dioxide is a very potent mechanism for ozone destruction under stratospheric conditions. The relative rate of ozone destruction with the oxides of nitrogen and without is given by the catalytic ratio [13c]

$$\begin{aligned}\rho &= \{k_e [O][O_3] + k_g [O][NO_2]\} / k_e [O][O_3] \\ &= 1 + k_g [NO_2] / k_e [O_3]\end{aligned}\quad (12)$$

At typical stratospheric temperatures, the rate constant k_g is 10^3 to 10^4 greater than k_e . Thus nitrogen dioxide at about 10^9 molecules cm^{-3} catalytically destroys ozone (Figure 2), faster than the Chapman reactions.

From Table 1 it can be seen that the Chapman reactions account for about 20 percent of the ozone balance: Similar calculations [17] show that the free radicals based on water destroys about 10 percent of the ozone produced. If the nitrogen oxides in the stratosphere are responsible for the remaining 70 percent, then NO_x must destroy ozone 3.5 times faster, on the average, than the O_x reactions. In other words, the catalytic ratio, Equation 12, must be 4.5 on a global-average basis. It is simple to calculate the concentration of NO_2 that would give a catalytic ratio of 4.5. A profile of the required NO_2 concentration to give the value of the catalytic ratio is entered on Figure 10 for 45 degrees latitude in the spring. Figure 10

also includes the range of measured NO_2 , as reported through July 1974 (15,18,19). The observed NO_2 appears to be somewhat more than the minimum required in the lower and middle stratosphere at this latitude, but NO_2 observations for higher elevations and other than temperate latitudes are not yet available. The tentative conclusion is that natural nitrogen oxides are sufficient to account for the global ozone balance, but further data are needed to confirm or modify this conclusion.

Although the concentration of nitrogen dioxide has not been observed over a wide range of elevation, latitude, and season, it is interesting to calculate how much nitrogen dioxide would be required to destroy 70 percent of the ozone produced. However, a distinction needs to be made between the effect of NO_2 in the ozone source region and in the region where ozone is detached from its photochemical source, Figure 4.

In this article the distribution of nitrogen dioxide required to destroy ozone at a prescribed rate in each of these regions is examined for the three-dimensional atmosphere by the method of "instantaneous rates".

Inside the "ozone source region", the interesting comparison is the rate of ozone destruction by nitrogen dioxide relative to the rate of ozone formation. The concentration of nitrogen dioxide that destroys ozone at 10% the rate of formation is

$$[\text{NO}_2]_{0.1}^F = \frac{(0.10) 2 j_a [\text{O}_2]}{2 k_g [\text{O}]} \quad (13)$$

The quantity 10% is chosen for convenience, and it can be linearly scaled to include 70% or 100% or any other percent relative rate of ozone destruction by the NO_x and O_x mechanisms. This comparison of two instantaneous rates was made for 43,200 volume elements of the global atmospheric grid, and a zonal average is presented in Figure 11. At low elevations, the required NO_2 concentration is very low, but the rate of ozone formation is vanishingly slow there, Figure 3. This comparison is useful only in regions when the ozone replacement time (Figure 4) is one year or less.

In the "detached ozone region" where the ozone replacement time is one year or longer, the ozone residence half time is approximately two years (based on radioactive carbon-14 from the nuclear bomb test series of 1961-62). The interesting question to ask in this region is how much nitrogen dioxide is required to destroy local ozone at an instantaneous rate of 10% per year

$$[\text{NO}_2]_{0.1}^D = \frac{(\frac{1}{10}) [\text{O}_3]}{2 k_g [\text{O}] (3.15 \times 10^7 \text{ sec yr}^{-1})} \quad (14)$$

This concentration of nitrogen dioxide was evaluated in each volume element, and the zonal average is given by Figure 12. Even in the detached ozone region, ozone can be significantly destroyed by NO_x catalysts if the quantity of catalyst is equal to or greater than the values indicated in Figure 12, for example, 10^9 molecules $\text{NO}_2 \text{ cm}^{-3}$ at 20 km. It appears that very little nitrogen dioxide is needed at high elevations, but this appearance is not valid since ozone is rapidly replaced there.

The two definitions of $[\text{NO}_2]_{0.1}$ become identical where the ozone replacement time is one year. The interesting contour map is the composite one shown in Figure 13. Where the

ozone replacement time is one year or less, $[\text{NO}_2]_{0.1}$ is that required to destroy ozone one-tenth as fast as it is formed, and where the ozone replacement time is longer than one year, $[\text{NO}_2]_{0.1}$ is that which would destroy one-tenth of the ozone in one year. These two superimposed functions give the global distribution of nitrogen dioxide required to contribute 10% ozone destruction. Including the effect of the HO_x reactions (H, HO, HOO), the Chapman reactions, and air motions, about 30 percent of the ozone balance can be accounted for. If the oxides of nitrogen account for the remaining 70 percent, then the concentration of nitrogen dioxide must average about 7 times the values given by Figure 13, especially in the ozone formation region. If consideration is given to the spread of the Monte Carlo calculation, Figure 9, then nitrogen dioxide must average between 4 and 11 times as much as that shown in Figure 13, above the 20 km level. It will be interesting to see if future observations of stratospheric NO_2 fall within this range.

8. Latitudinal Variation of Ozone Sensitivity to Nitrogen Dioxide

A notable feature of Figure 13 is that at constant altitude there are some strong latitudinal variations of ozone sensitivity. At a height of 23 km, ozone is ten times as sensitive to nitrogen dioxide in the polar summer region as in the equatorial region. In the winter temperate zone, there is a region of high sensitivity between 25 and 35 km. In the equatorial stratosphere between 17 and 25 km, ozone is

exceptionally resistant to NO_x catalytic destruction. In this section, the reasons for this variable sensitivity of ozone to nitrogen oxides are explored. Also, it is pointed out that other three-dimensional model calculations have detected this feature, and there is experimental data based on cosmic rays that tend to confirm the high sensitivity of the middle polar stratosphere to NO_x.

The reason for the latitudinal variation of sensitivity of ozone to nitrogen dioxide is given by the various figures of this article. Some of these features will be reviewed in terms of just this question. There are regions of the stratosphere where both oxygen (Figure 3) and ozone (Figure 4) absorb solar radiation; there are regions where solar radiation capable of dissociating oxygen and forming ozone has all been screened out. In this latter region, oxygen atom concentrations may still be high (Figure 6); and ozone may be destroyed by the reaction $O + NO_2$ even though none is regenerated in situ from oxygen. Air transport tends to move ozone away from the equatorial region and to the polar regions. At an elevation of 20 km, for example, there is still significant ozone formation above the summer equator, and it requires about 3×10^9 molecules NO₂ cm⁻³ to destroy ozone one-tenth as fast as it is formed (Figure 11). At the same elevation over the summer pole, the rate of ozone formation from oxygen (Figure 3) is very low, but there is abundant radiation above 300 nm that forms oxygen atoms and destroys ozone in the presence of NO_x. Thus merely 3×10^8 molecules NO₂ cm⁻³ destroys ozone at a rate of 10 percent per year.

These comparisons point up the importance of two, or preferably three, dimensional models for the study of the perturbation of stratospheric ozone by supersonic transports (SST). A number of one-dimensional models [20] and a few two

dimensional models [21] have recently produced results on the effect of artificial NO_x on stratospheric ozone.

One three-dimensional photochemical model of air motions and photochemistry has been applied to perturbation of stratospheric ozone by supersonic transports, the MIT general circulation model [22]. The projected future size of SST fleets in terms of mass of fuel burned is given by Figure 14, according to Grobecker [23] in 1974. The circled point corresponds to the year 1997 when 10^{11} kg fuel per year are expected to be burned at 20 km nominal cruising height. With current rates of NO_x emission, this corresponds to 1.8×10^{12} grams NO_2 per year injected at 20 km. The MIT group took this rate of emission, and they placed it between 40 and 50° north latitude. One result of their calculations is given by Figure 15, where zonal average values of natural ozone and SST perturbed ozone are given. They calculated a global average ozone reduction of 12 percent, and the local maximum near the traffic corridor was 25 percent. Although they found more NO_x at the equator than in the southern hemisphere, the reduction of ozone is greater in the southern hemisphere than at the equator (Figure 15), which is of course, consistent with the much simpler calculations by the method of "instantaneous rates", Figure 13. It can be seen (Figure 14), that the projected SST's after 1997 correspond to greatly increased fleet sizes and thus to much greater ozone depletions than that calculated by the MIT three-dimensional, general-circulation model in Figure 15.

There is fairly direct experimental confirmation of the great sensitivity of the high-latitude mid-stratosphere to NO_2 that is indicated by Figure 13. For many years there has been noted a statistical correlation of overhead ozone with sunspot cycle [24]. Recently a physical explanation of this effect has been given by Ruderman and Chamberlain [25]. Cosmic rays are steered into the polar atmosphere by the earth's magnetic field, and the flux of cosmic rays is strongly modified by the solar eleven-year cycle, one symptom of which is the number of sunspots. Thus cosmic rays enter the earth's atmosphere in a localized region, and the signal undergoes about a 50 percent modulation with the eleven year sunspot cycle, Figure 16. This figure is based on directly measured ionization in the atmosphere [26] and a constant factor relating the formation of nitric oxide and ion pairs. The correlation of measured ozone and sunspot cycle for the two long-term stations is given by Figure 17. A year ago (September 1973) it appeared anomalous that such small changes of nitric oxide as is caused by cosmic rays (Figure 16) could have so large an effect on stratospheric ozone (Figure 17), since this sensitivity of ozone to NO_x was greater than that predicted by one-dimensional models of stratospheric ozone [20d]. However, this perturbation of ozone by nitric oxide from cosmic rays is consistent with the instantaneous rate calculations, which gives a great sensitivity of ozone to NO_x in high-elevation, polar regions (Figure 13).

9. Average Solar Radiation and the Diurnal Cycle

In the atmosphere the light intensity at any location has a strong diurnal variation and usually a lesser annual

variation. By dint of major effort, some one-dimensional models of stratospheric motions and photochemistry [27] have included the effect of diurnal variation of sunlight, but such a refinement appears to be several years in the future for models including three dimensional motions. Thus one comes to the question: "What is the appropriate average intensity to use for day and night changes of solar radiation?" The essence of this question was answered decades ago by the photochemical method of rotating sectors [28] and more recently by the method of molecular modulation [29]. The starting point of the old photochemical method of rotating sectors or the more recent method of molecular modulation spectrometry is that in a photochemical experiment with intermittent light the concentration of an intermediate species is strongly dependant on the chemical kinetic lifetime of the intermediate. If the photolyzing light turns on and off at a rate slow compared to the lifetime of the intermediate, then the intermediate quickly attains its steady state concentration, R_S , in the light and it quickly drops to zero in the dark, as illustrated by Figure 18. For equal periods of light and dark, the average concentration \bar{R} is the time-weighted average of the value in the light R_S and the value in the dark, zero

$$\bar{R}_{FAST} = \frac{1}{2}\{R(I) + R(0)\} \quad (15)$$

This case is that of a "fast intermediate". On the other hand, if the photolyzing light turns on and off at a rate fast compared to the chemical relaxation time of the intermediate there is a slow build-up to the case for the "slow intermediate"

in Figure 18. When the light is on, the intermediate increases by a small amount. When the light is off, the intermediate concentrations slowly drops off; but long before it reaches zero, the light comes back on again. The average concentration is as if the light of intensity at all times had the average value between illuminated and dark periods

$$\bar{R}_{\text{SLOW}} = R(I/2) \quad (16)$$

If the intermediate varies in proportion to light intensity, the two averages, \bar{R}_{FAST} and \bar{R}_{SLOW} , will be the same. However, if the intermediate is not proportional to light intensity, the fast and slow averages are not the same. A frequently encountered case is that where the radicals are destroyed in a reaction second order in radicals

$$\frac{dR}{dt} = jI - k R^2 \quad (17)$$

In this case the steady-state concentration of radicals in light of intensity I is

$$R_S = (j I/k)^{1/2} \quad (18)$$

The average concentration in intermittent light for the fast intermediate is

$$\bar{R}_{\text{FAST}} = R_S/2 \quad (19)$$

but the average concentration of the slow intermediate is the substantially larger value

$$\bar{R}_{\text{SLOW}} = R_S/(2)^{1/2} \quad (20)$$

Some substances in the stratosphere have chemical relaxation times that are very short compared to the length of one day: singlet oxygen atoms, triplet oxygen atoms, the ratio NO/NO_2 , and others. Some substances or families of substances respond very slowly compared to the diurnal cycle, for example, the formation of NO_x from nitrous oxide N_2O and its loss by transport and washout as nitric acid in the troposphere. The formation and destruction of dinitrogen pentoxide N_2O_5 occurs with very nearly the same frequency as the diurnal cycle.

Ozone responds to solar radiation in a very strongly non-linear way, approximately:

$$\begin{aligned}\frac{d[\text{O}_3]}{dt} &= 2 j_a [\text{O}_2] - 2 k_e [\text{O}] [\text{O}_3] - 2 k_g [\text{O}] [\text{NO}_2] \\ \frac{d[\text{O}]}{dt} &= j_c [\text{O}_3] - k_b [\text{O}] [\text{O}_2] [M] = 0 \\ \frac{d[\text{NO}_2]}{dt} &= k_f [\text{NO}] [\text{O}_3] - k_g [\text{O}] [\text{NO}_2] - j_h [\text{NO}_2]\end{aligned}\quad (21)$$

Thus it is very important to use the proper average light intensity for photochemical, atmospheric calculations. The key to proper average is the chemical relaxation time of ozone relative to the duration of daylight. The characteristic times of ozone are given by Figure 4. The ozone replacement times in daylight vary from four hours at the top of the stratosphere to several years at the base of the stratosphere. Relative to the diurnal cycle, ozone is a "fast" photochemical substance at the top of the stratosphere, and a "slow" photochemical substance in the lower stratosphere. Since the proper average light

intensity depends on the ratio of chemical relaxation time to the duration of daylight, there is no averaging procedure suitable for all elevations. For the indefinite future, complex models of atmospheric motions and photochemistry will be forced to accept the rather severe approximation of some average light intensity.

The method of "instantaneous photochemical reactions" is a three-dimensional model that does not require an average light intensity. It replaces an average over time with an average of instantaneous rate over three dimensional space. Of course, the method of instantaneous rates is quite limited in the questions it can consider. However it has some distinct advantages over all other models for some problems.

10. The General Method of "Instantaneous Rates"

Applied to Atmospheric Methane Chemistry

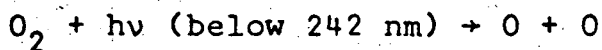
The previous sections have discussed in detail the application of the method of instantaneous rates to simple reaction mechanisms. The general method considers any number of chemical reactions and any number of species. Photolysis constants are calculated in each volume element indicated by Figure 8: Assumed or observed concentrations of air, ozone, water, NO_x , etc. assigned to each volume element. The Gear routine adapted for photochemical reactions [30,] is operated for a time long enough to let fast intermediates build up to a steady state but short enough to avoid any significant change of the major reactants. At that time, the computer prints

out the instantaneous rates of all reactions. These instantaneous rates can then be compared with each other or integrated over the hemisphere or globe. The program can be subscripted to give the rate of production or loss of a species by a specified process.

This method was used to examine the rates of ozone production from the methane- NO_x smog reaction and the rate of ozone destruction by the NO_x catalytic cycle, [3g], Figure 19. At 45° latitude in the spring, ozone is formed from methane and NO_2 by the smog reaction below 13 km at a rate faster than it is destroyed by NO_2 . However, above 13 km, the reverse is the case. At 30 km, NO_x destroys ozone one hundred times faster than methane- NO_x forms ozone.

TITLES TO FIGURES

1. Standard temperature contours (January 15) -90° , north pole; 0° , equator; $+90^{\circ}$, south pole. Dotted line is approximate location of average tropopause. Zonal average.
2. Standard (January 15) ozone concentration in units of molecules cm^{-3} expressed as zonal-average contour lines (7E12 means 7×10^{12}). The variation of the ozone maximum with latitude can be read from the figure.
3. Zonal average rate of the photolysis of oxygen ($\text{ja}[\text{O}_2]$) for the process:



(Standard January 15).

4. Zonal average ozone replacement time, that is, local ozone concentration (Fig. 2) divided point-by-point by ozone formation rate. January 15.
5. Zonal average rate of the photolysis of ozone ($\text{jc}[\text{O}_3]$) for the process:
$$\text{O}_3 + \text{h}\nu \rightarrow \text{O}_2 + \text{O}$$

(Standard January 15).
6. 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)
7. Illustration of the role of horizontal air motions in moving ozone from the ozone formation region to the polar regions. This figure is a partial superposition of Figs. 2 and 4.

TITLES TO FIGURES, CONT.

8. Three dimensional model and grid of volume elements for the calculation of instantaneous photochemical rates. Starting with observed (standard) distributions of temperature and ozone, the distribution of radiation is calculated in each volume element and chemical and photochemical rates are calculated in each volume element. Then these rates are integrated to give zonal average rates, and further integrated to give instantaneous global rates.
9. Results of Monte Carlo calculation of the global ozone balance according only to the Chapman mechanism. Random multiples of the standard deviation (Equation 11) were dealt into each of five experimental quantities (I_0 , 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 ($3 E9 = 3 \times 10^9$, etc.)
10. Vertical profiles of observed NO_2 . The curve $\rho = 4.5$ is the amount of NO_2 that would destroy ozone 3.5 fold faster than the elementary reaction $O + O_3 \rightarrow O_2 + O_2$ destroys ozone, which is the amount of NO_2 required to destroy 70% of the ozone formed from solar radiation. The various observations were made by: AM, Ackerman and Muller (1972; 1973); B, Brewer et al. (1973, 1974); FT, Farmer et al. (1974); M. Murcray et al. (1974). Diagonal lines, NO_2 mole fraction.
11. The concentration of nitrogen dioxide (molecules cm^{-3}) required to destroy ozone at 10 percent of the rate of formation of ozone from sunlight (Equation 13)

$$[NO_2]_{0.1}^F = 0.10 j_a [O_2] / k_g [O]$$

TITLES TO FIGURES, CONT.

12. The concentration of nitrogen dioxide (molecules cm^{-3}) required to destroy local ozone at an instantaneous rate of 10 percent per year (Equation 14)

$$[\text{NO}_2]_{0.1}^D = 0.05[\text{O}_3]/3.15 \times 10^7 k_g [O]$$

13. The concentration of nitrogen dioxide (molecules cm^{-3}) to have a 10 percent effect on ozone everywhere. $[\text{NO}_2]_{0.1}$ is the larger of $[\text{NO}_2]_{0.1}^F$ or $[\text{NO}_2]_{0.1}^D$. To be sufficient to account for the global ozone balance, nitrogen dioxide in the natural stratosphere must on the average be between 4 and 11 times these values. Artificial NO_x , as from SSTs, would increase the rate of ozone destruction by 10 percent if the amount is equal to these concentrations. If NO_2 is high enough ozone is destroyed even in the detached ozone region (compare Figure 7).
14. Fuel burned in various altitude bands by supersonic aircraft (exclusive of hypersonic transport, HST) as projected (Groebcker, 1974) to the year 2025. The NO_x produced is the product of the fuel burned and the NO_2 produced per mass of fuel. At Concorde rate of NO_2 production the mass of NO_2 produced would be:

1990	$0.18 \times 10^{12} \text{ g yr}^{-1}$
1997	$1.8 \times 10^{12} \text{ g yr}^{-1}$
2020	$18 \times 10^{12} \text{ g yr}^{-1}$

15. Latitude dependence of ozone reduction when all SST flights occurred between 40 and 50° North, according to MIT three dimensional model. The rate of injection corresponds to 500 Boeing SST as projected in 1971 (but with reduced

TITLES TO FIGURES, CONT.

15. (continued)

NO_x emission index, 15 g NO per kg fuel) or to the point circled in Figure 14. The world-wide average ozone reduction is 12%; the local maximum near the flight corridor is 25%. One Dobson unit is 2.68×10^{16} molecules cm⁻².

16. Formation of nitric oxide from cosmic rays. The rate of production of atmospheric ions and nitric oxide from cosmic rays varies by about a factor of two as a function of the eleven year solar cycle. This figure gives the magnitude of NO produced per year (molecules cm⁻³) at the minimum of the eleven year cycle, or it can be interpreted as the modulation amplitude of the periodic signal.

17. The variation of total ozone at Tromso (70°N) and Arosa (47°N) as a function of sunspot number, according to Angell and Korshover (reference 23a). Note the decreasing amplitude as one moves away from the polar source (Figure 16).

18. Relation of a photochemically produced substance to frequency of modulated light as a function of its chemical relaxation time. A fast intermediate closely follows the exciting light, and the appropriate average is one half the concentration produced by the full light. A slow intermediate oscillates with small amplitude and 90° phase shift about an intermediate value corresponding to a steady light of half the full intensity. If the concentration of intermediate varies non-linearly with light intensity, these two averages are different.

TITLES TO FIGURES, CONT.

19. Vertical profiles of the rate of formation of ozone from the methane - NO_x - smog reaction and of rate of ozone destruction from the NO_2 catalytic cycle. The former reaction increases with background O_3 , CH_4 , H_2O and the latter reaction is proportional to the concentration of oxygen atoms and NO_2 . For a given set of 36 reactions, there is a cross-over at about 13 km between ozone destruction and ozone formation so far as NO_x is concerned.

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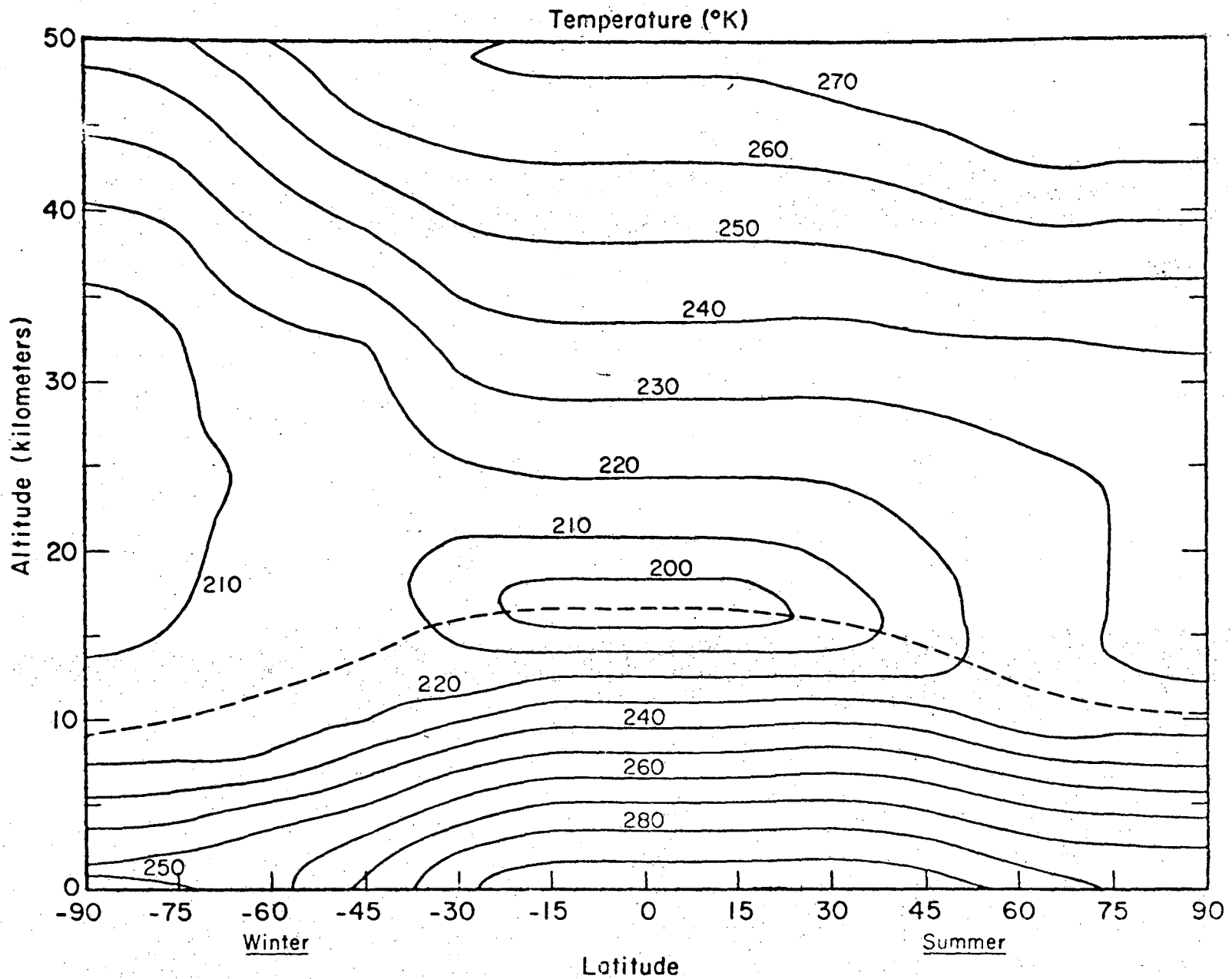


Fig. 1

XBL 728-6734

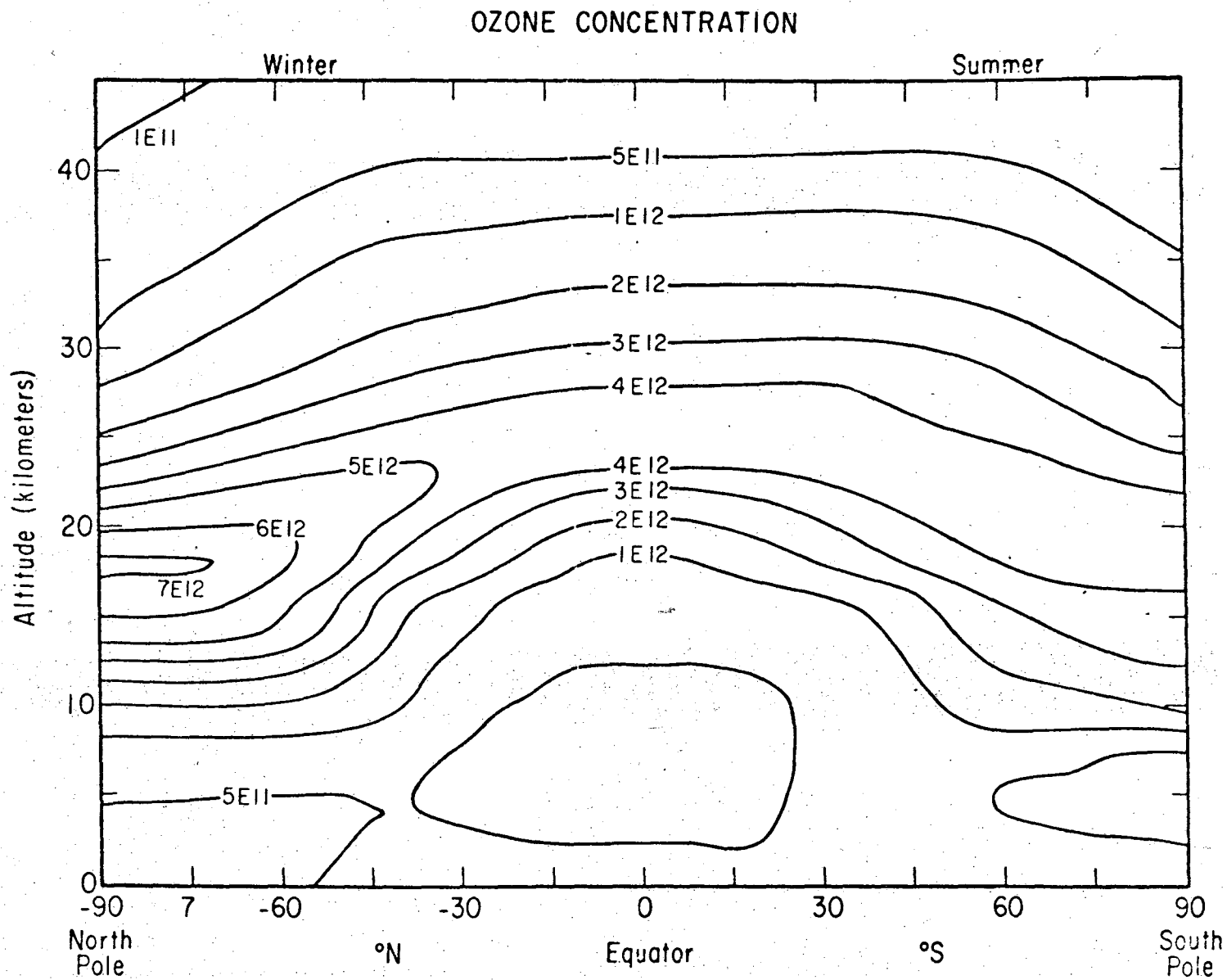


Fig. 2

XBL 7310-5540

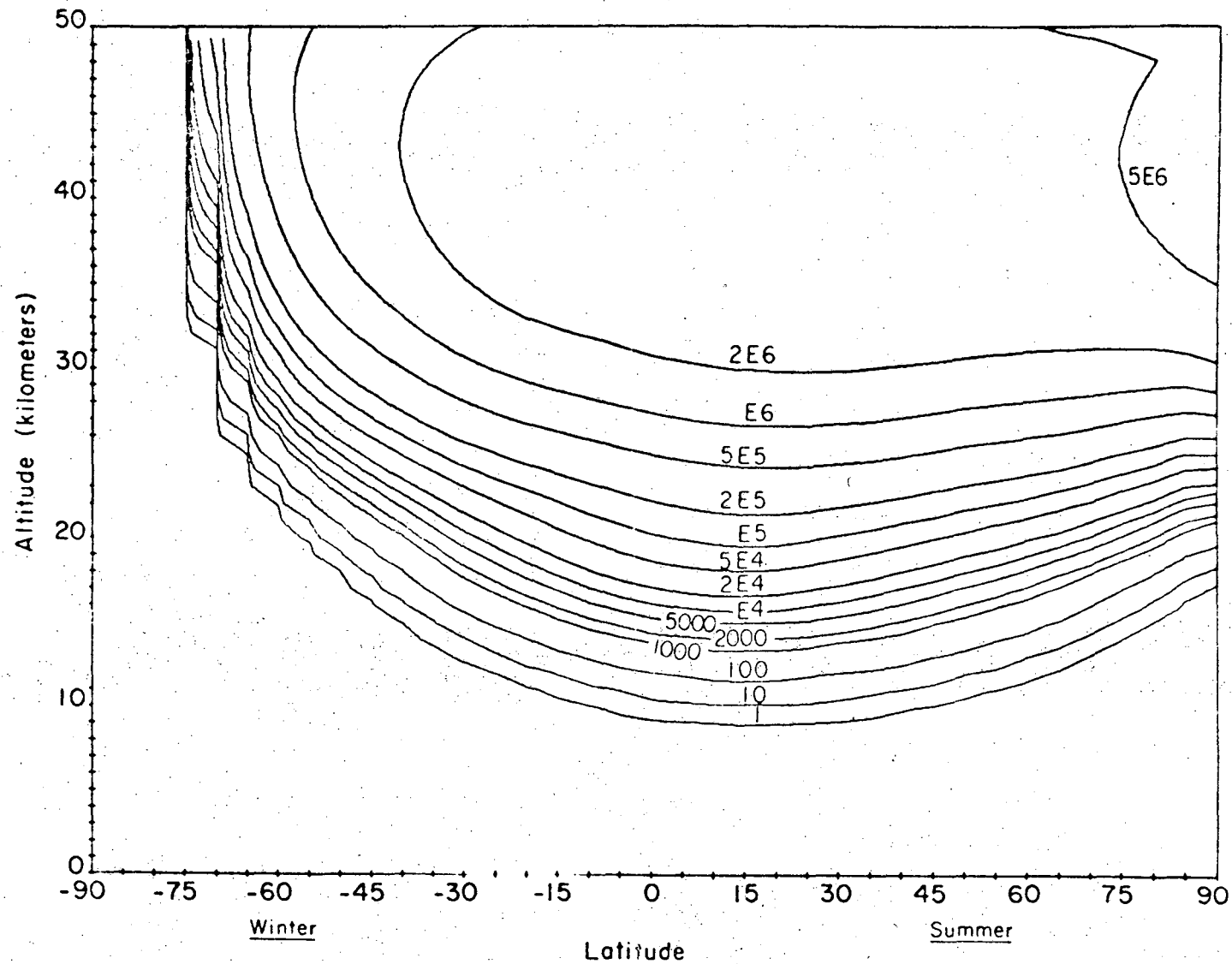
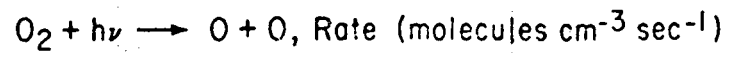


Fig. 3

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

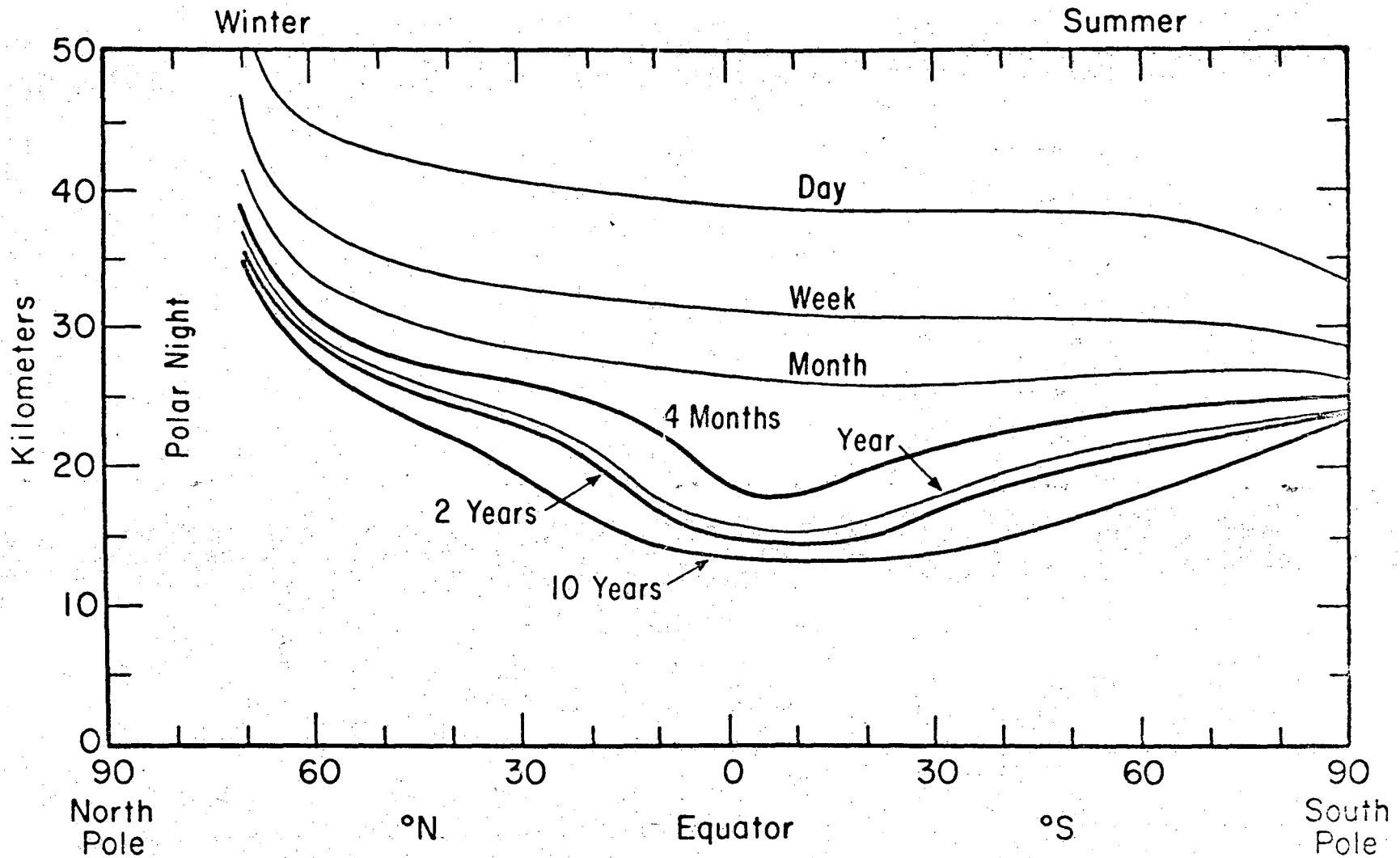


Fig. 4

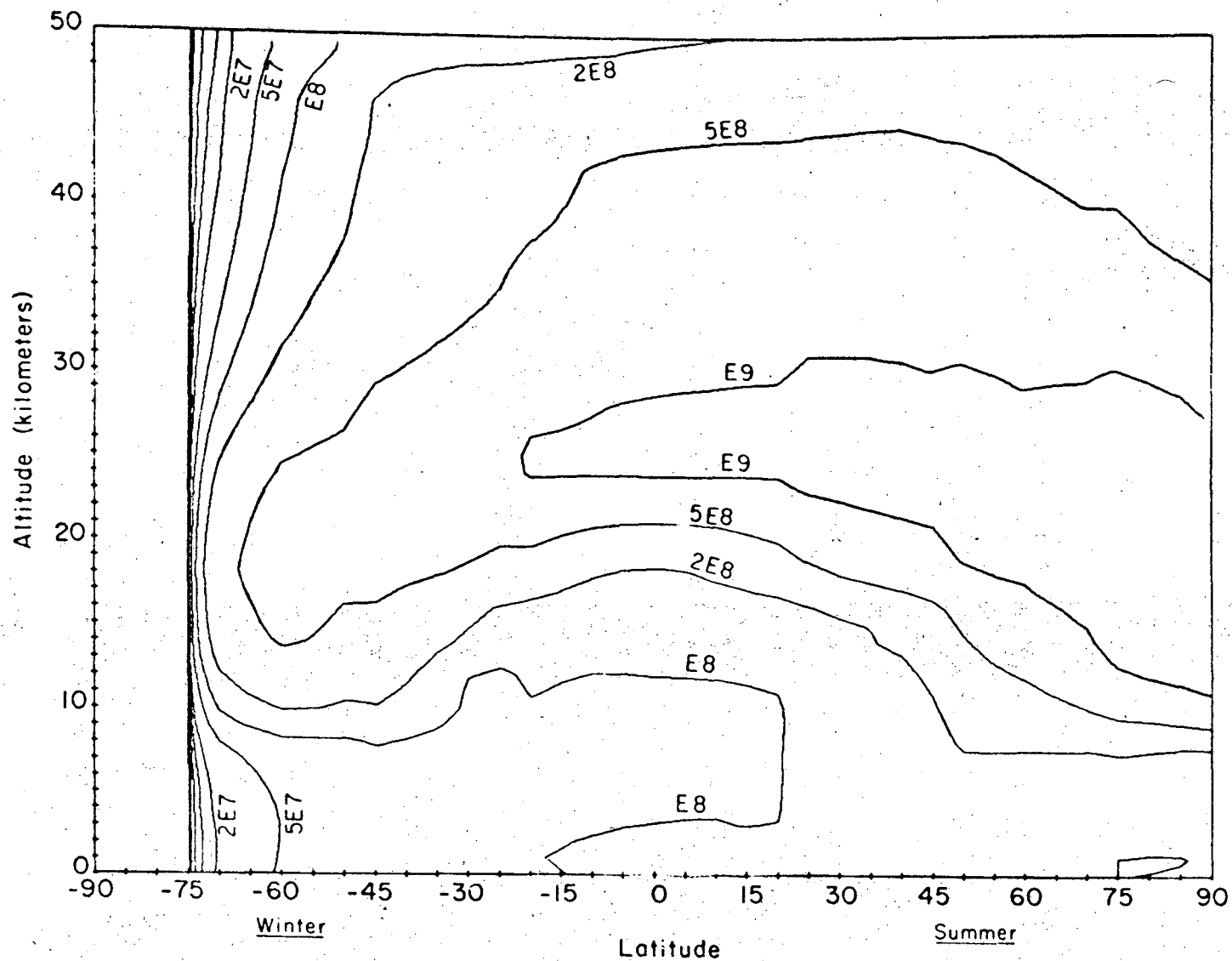
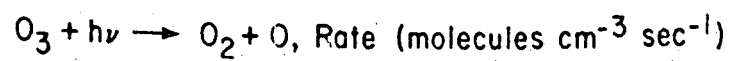


Fig. 5

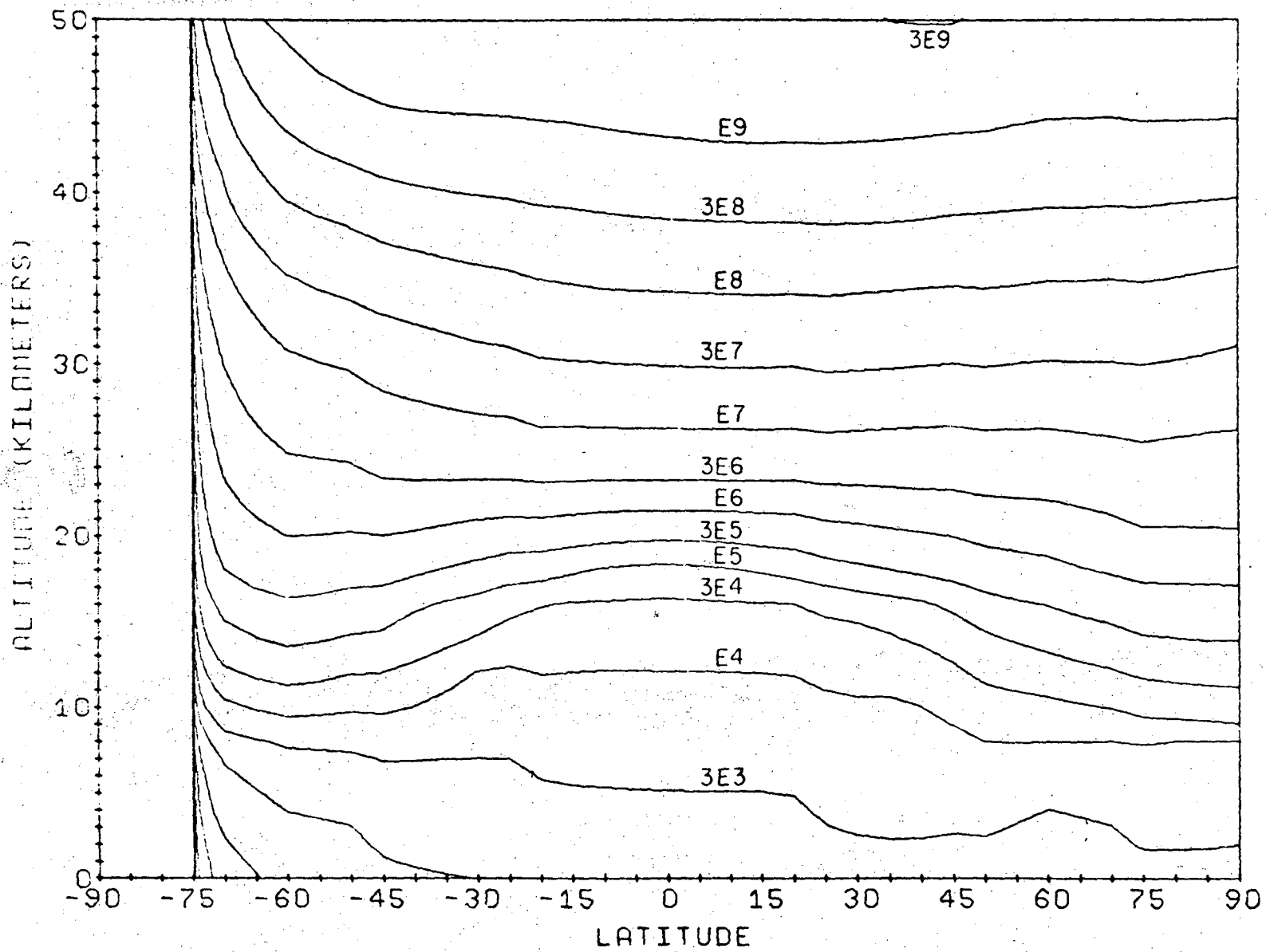
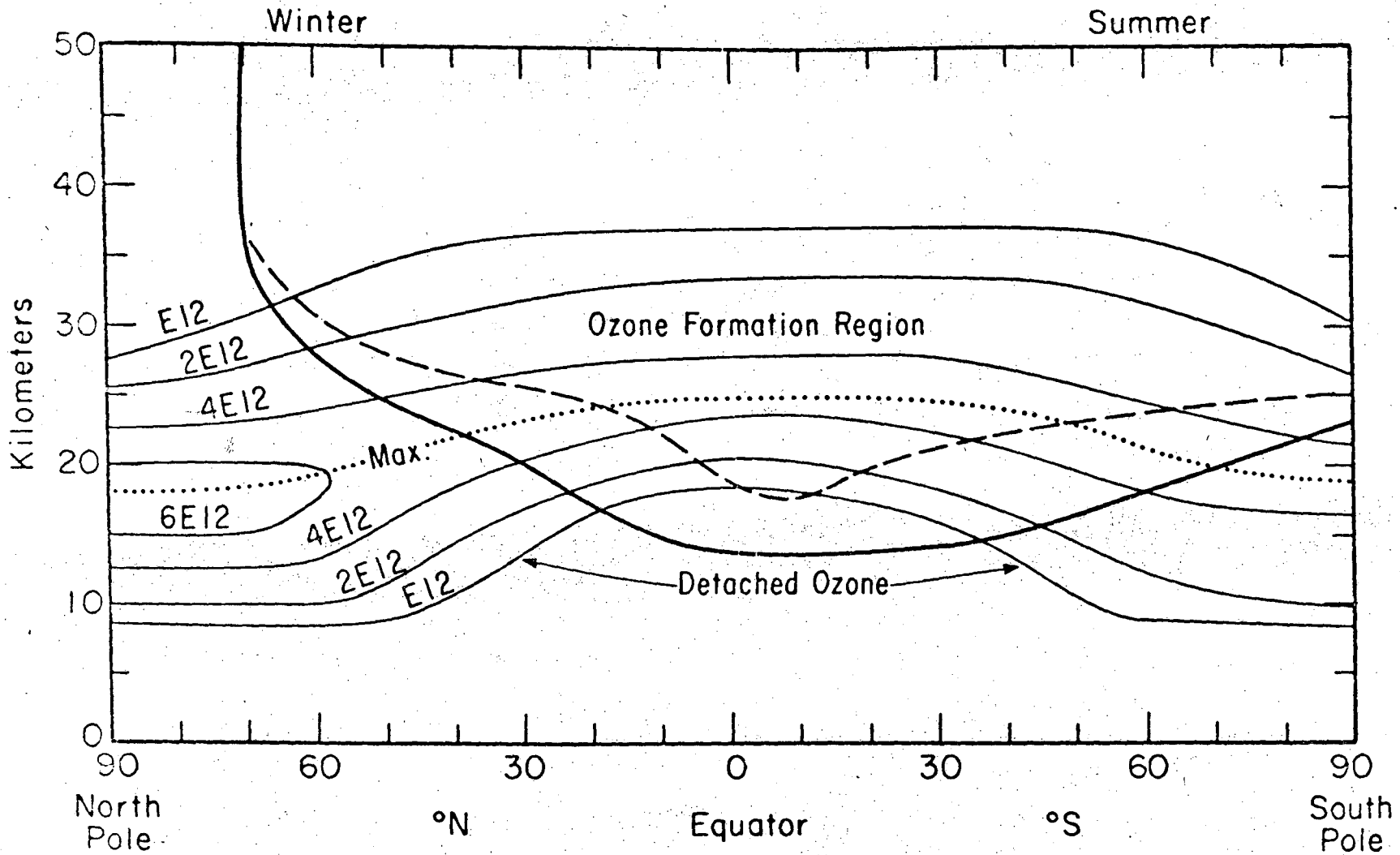


Fig. 6

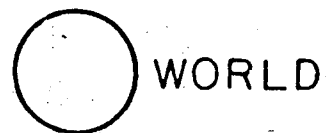
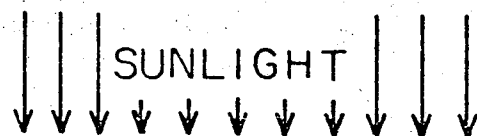
OZONE CONCENTRATION, JANUARY 15, RELATIVE TO OZONE FORMATION REGION, TRANSITION REGION, AND DETACHED OZONE REGION



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Fig. 7

PHOTOCHEMICAL CALCULATIONS
INSTANTANEOUS RATES, MOLECULES $\text{CM}^{-3} \text{SEC}^{-1}$



WAVELENGTH GRID	1 NANOMETER
ELEVATION GRID	1 KILOMETER
LATITUDE GRID	5 DEGREES
LONGITUDE GRID	1 HOUR (15°)

- (1) SPRING - FALL (MARCH 21)
- (2) WINTER - SUMMER (JAN. 15)

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

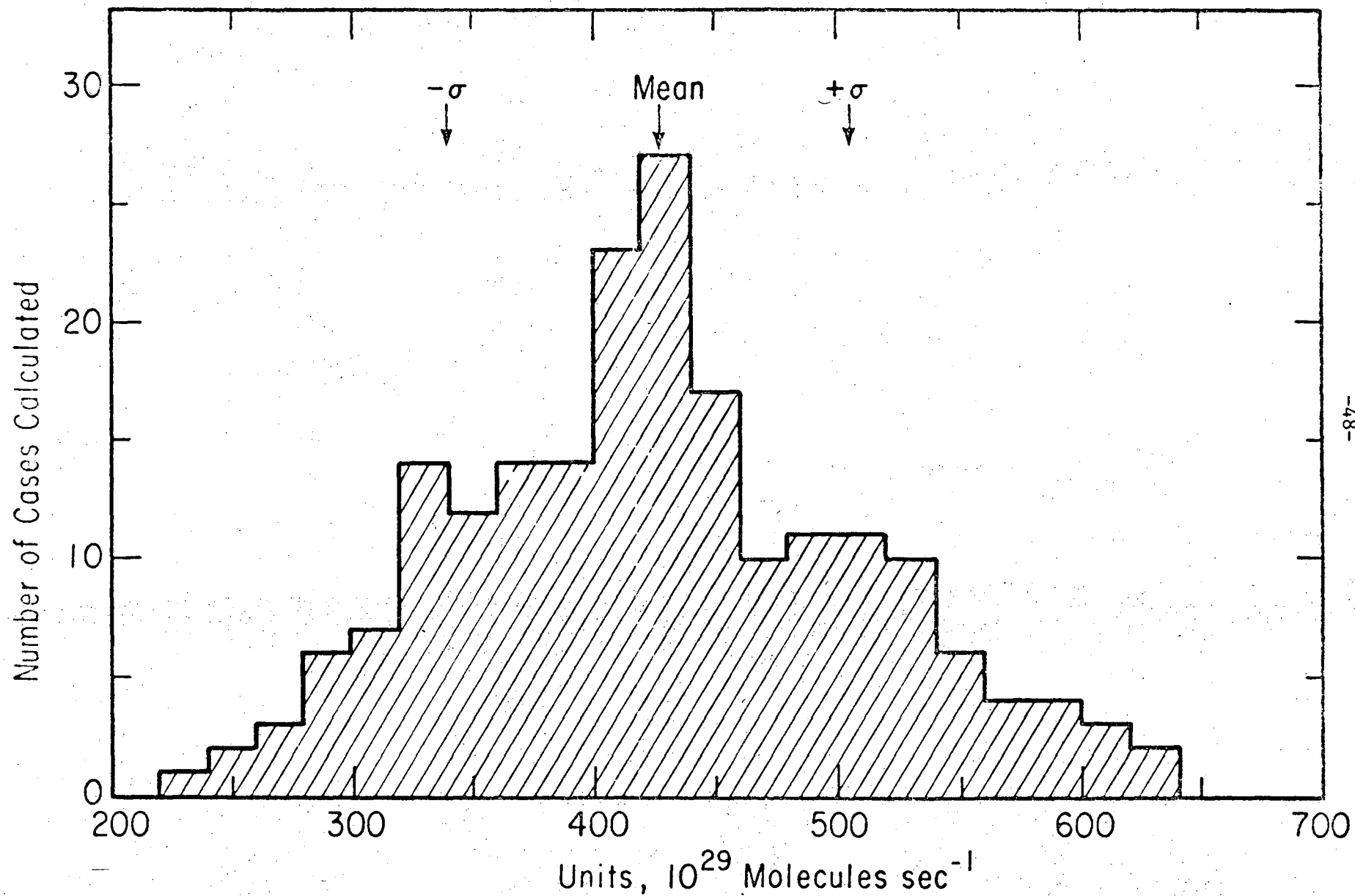
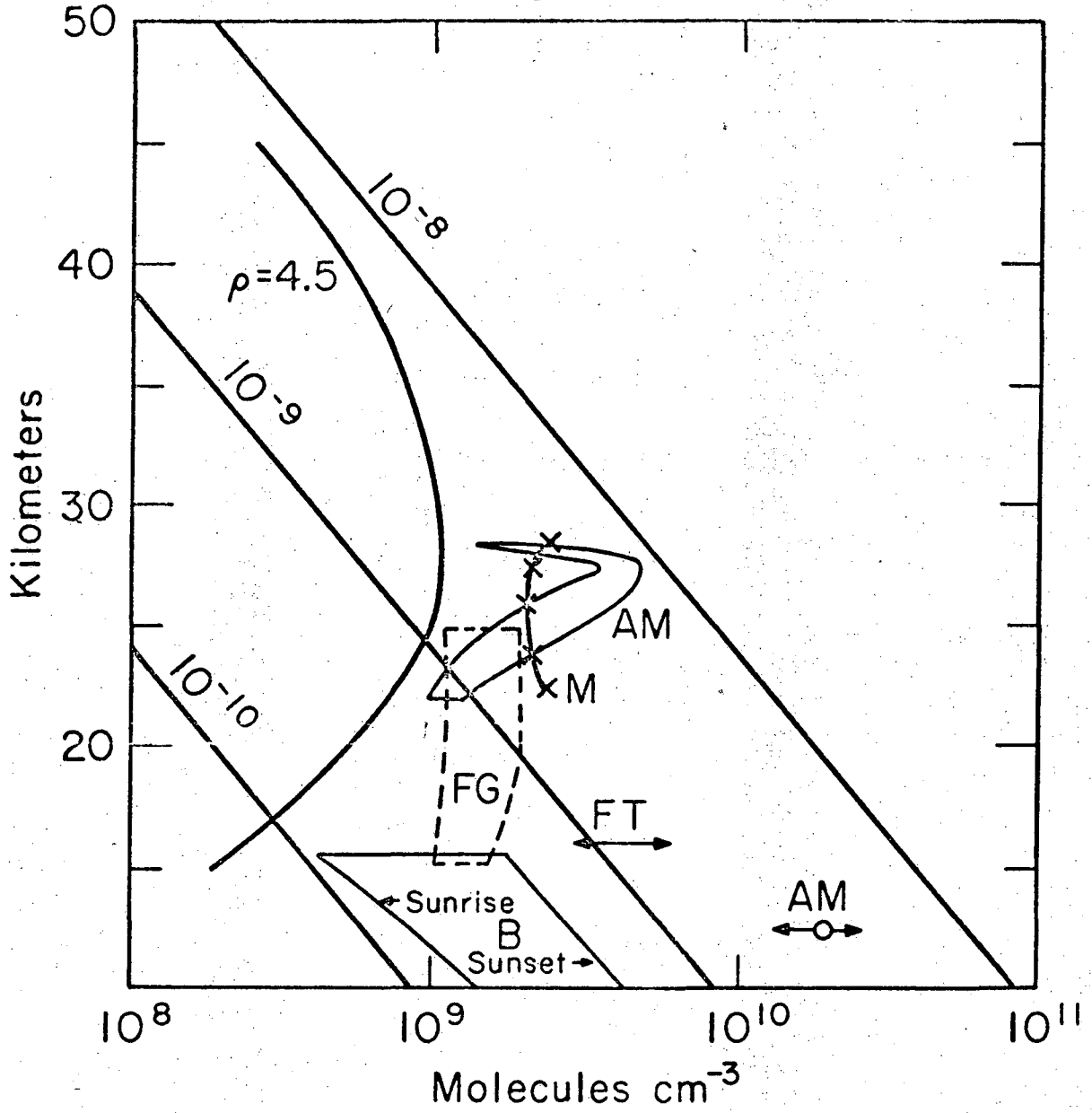


Fig. 9

Nitrogen dioxide



XBL748-3836

Fig. 10

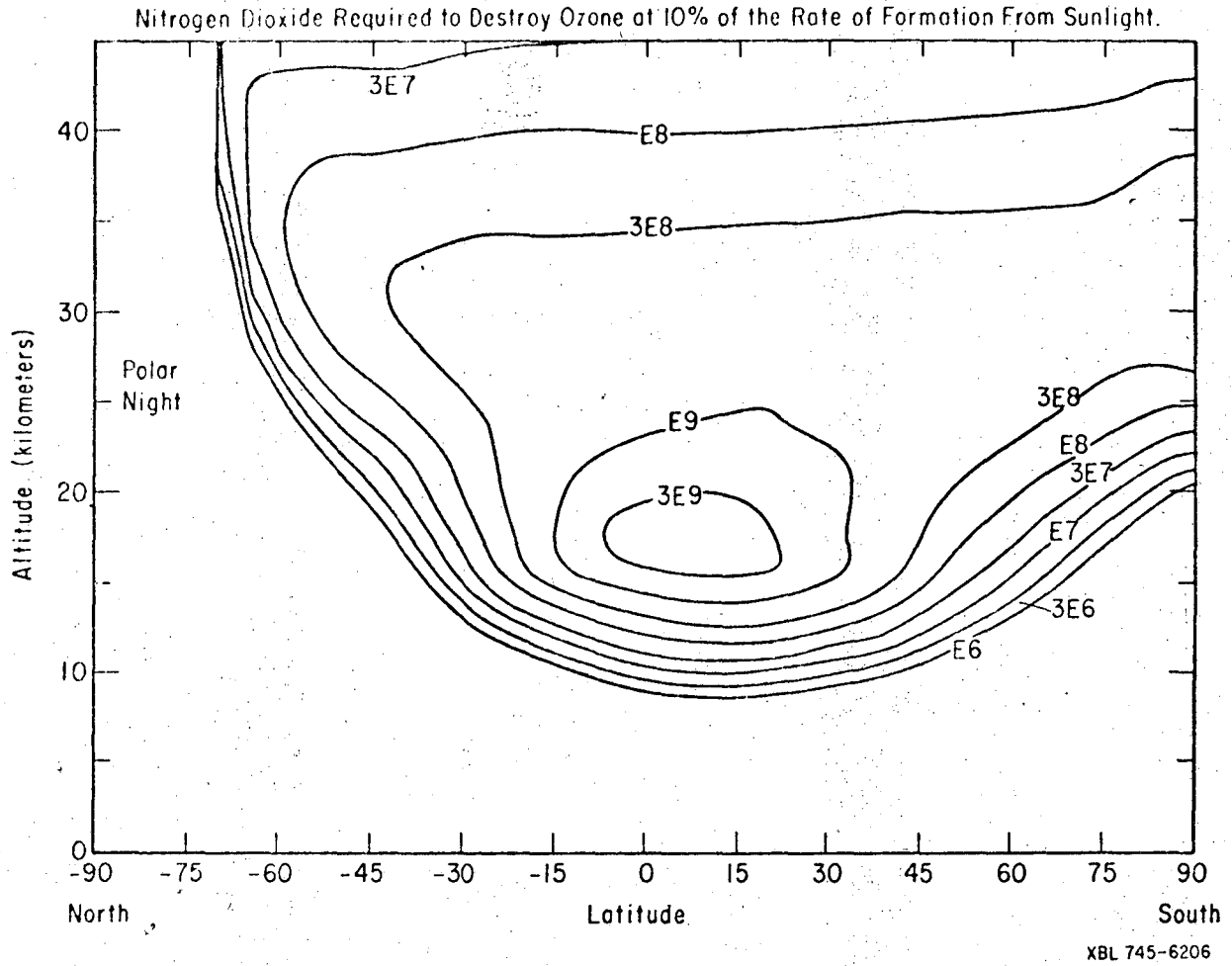
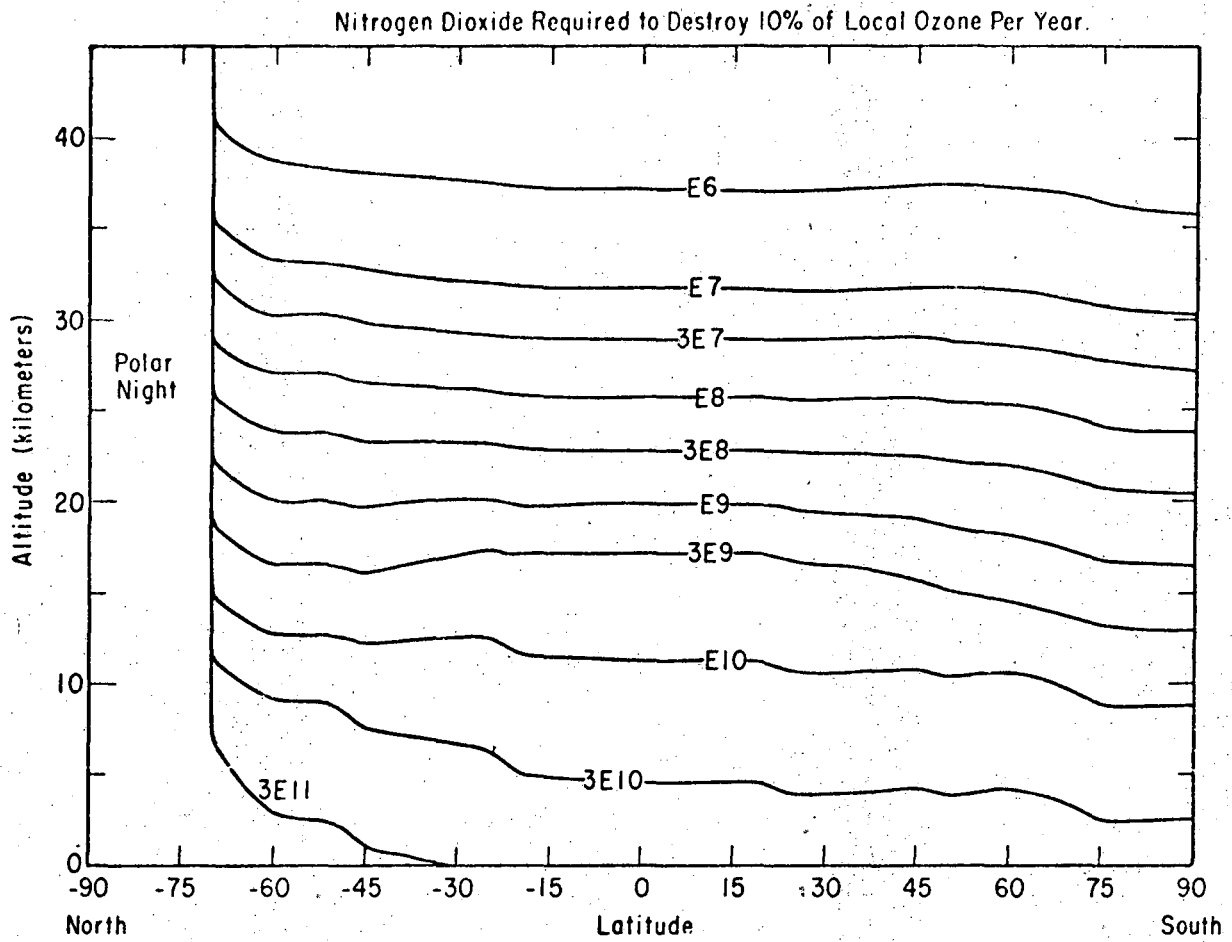
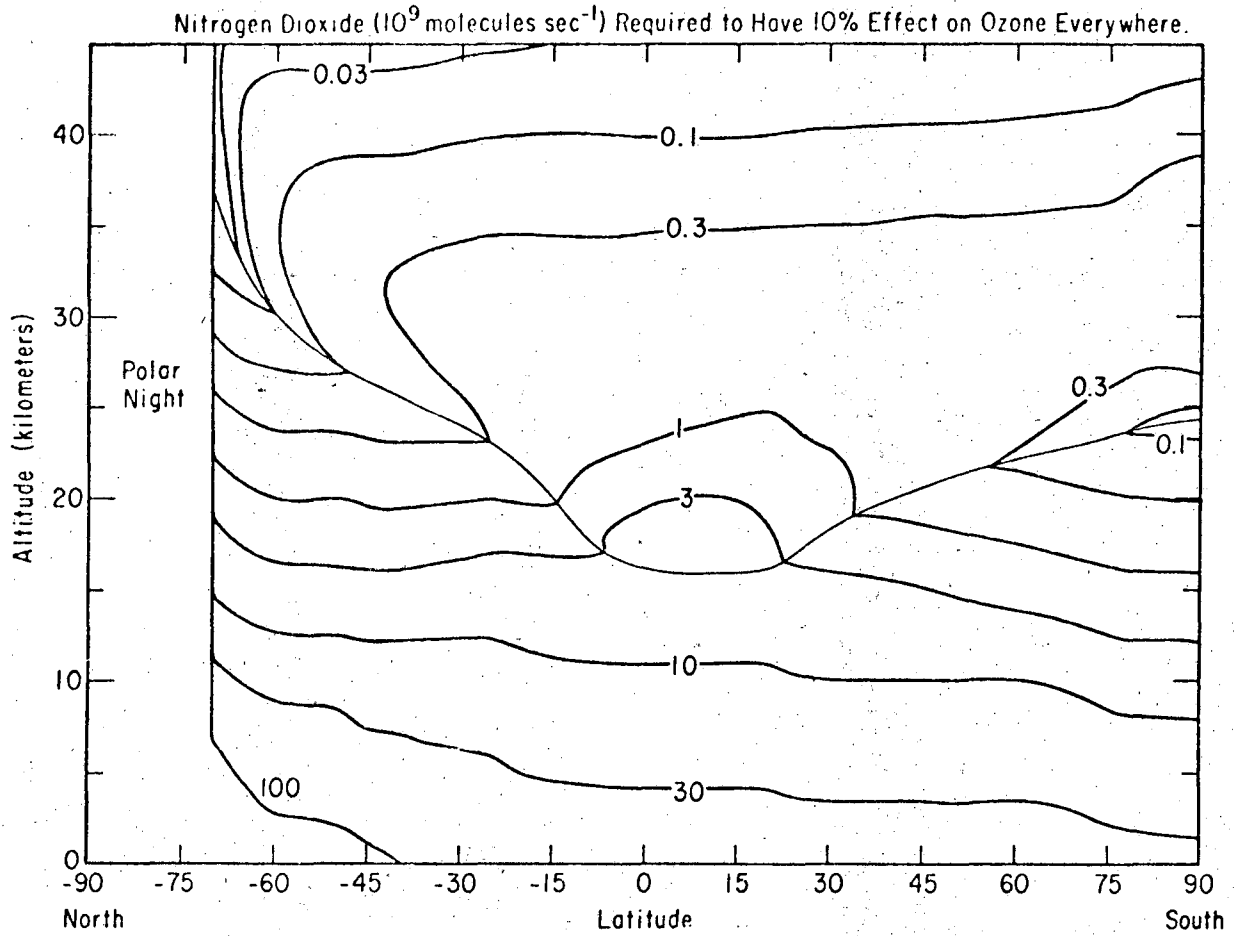


Fig. 11



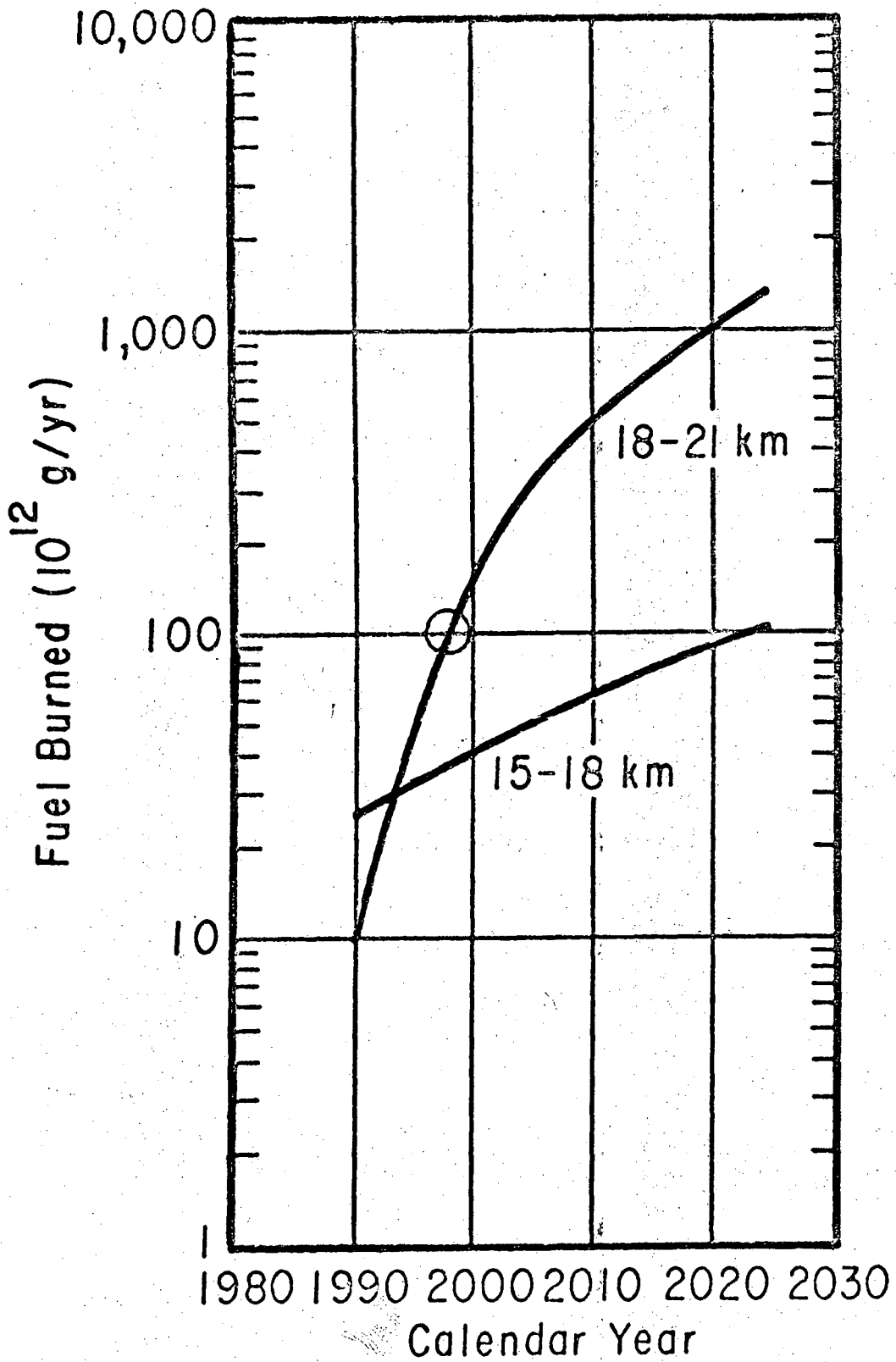
XBL 745-6204

Fig. 12



XBL 745-6205

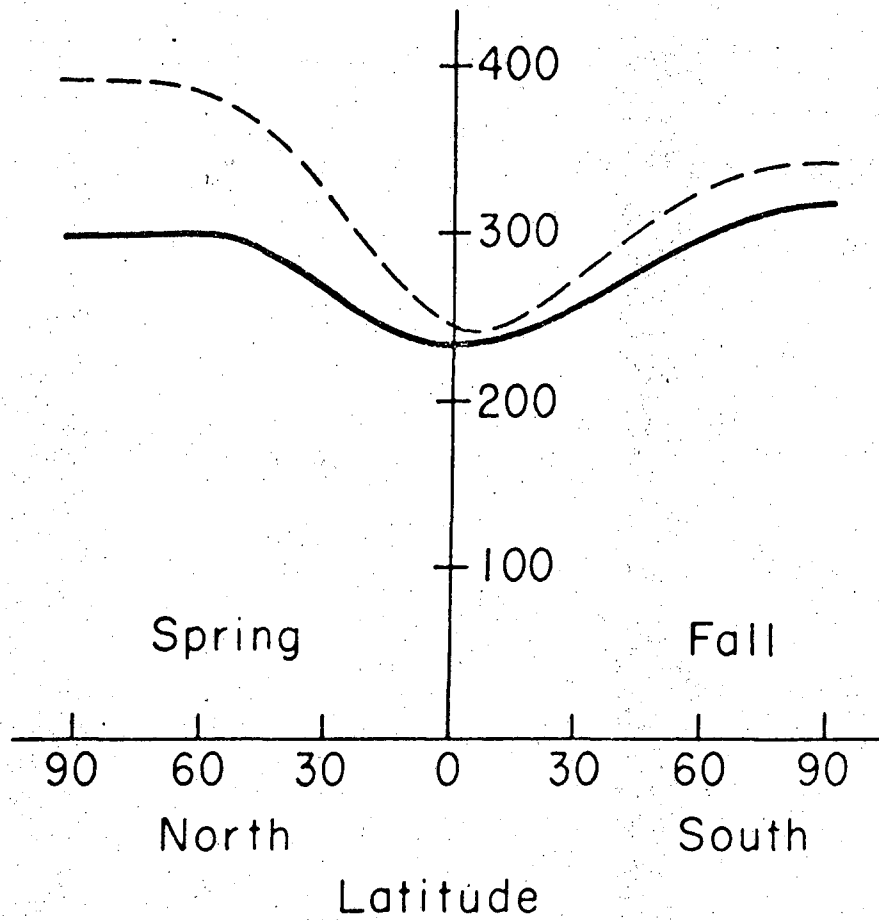
Fig. 13



XBL 748-6986

Fig. 14

TOTAL OZONE DISTRIBUTION (DOBSON UNITS)



--- Natural Ozone
— Perturbed Ozone

Fig. 15

MODULATION AMPLITUDE OF NITRIC OXIDE FORMATION FROM COSMIC RAYS PER YEAR

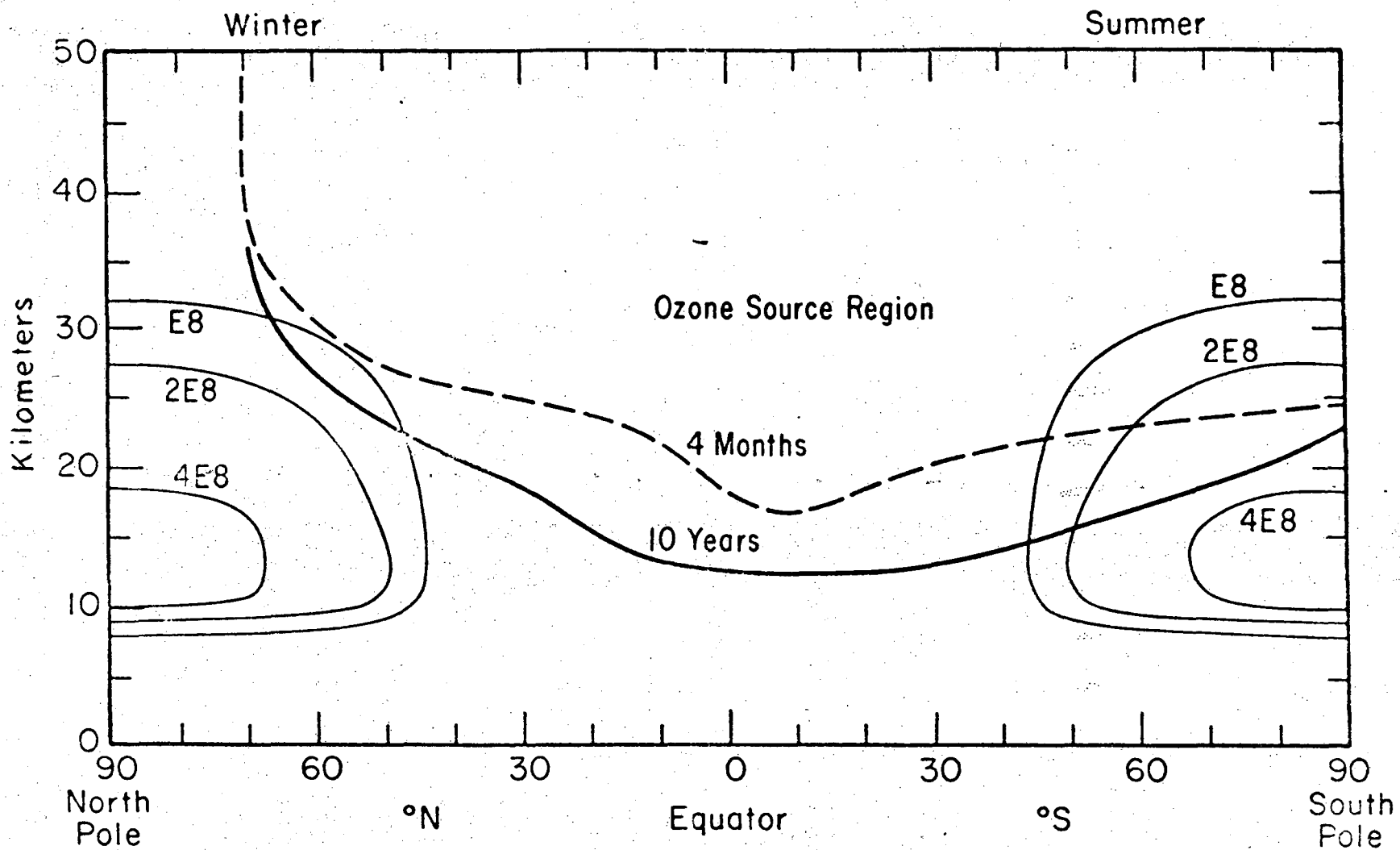


Fig. 16

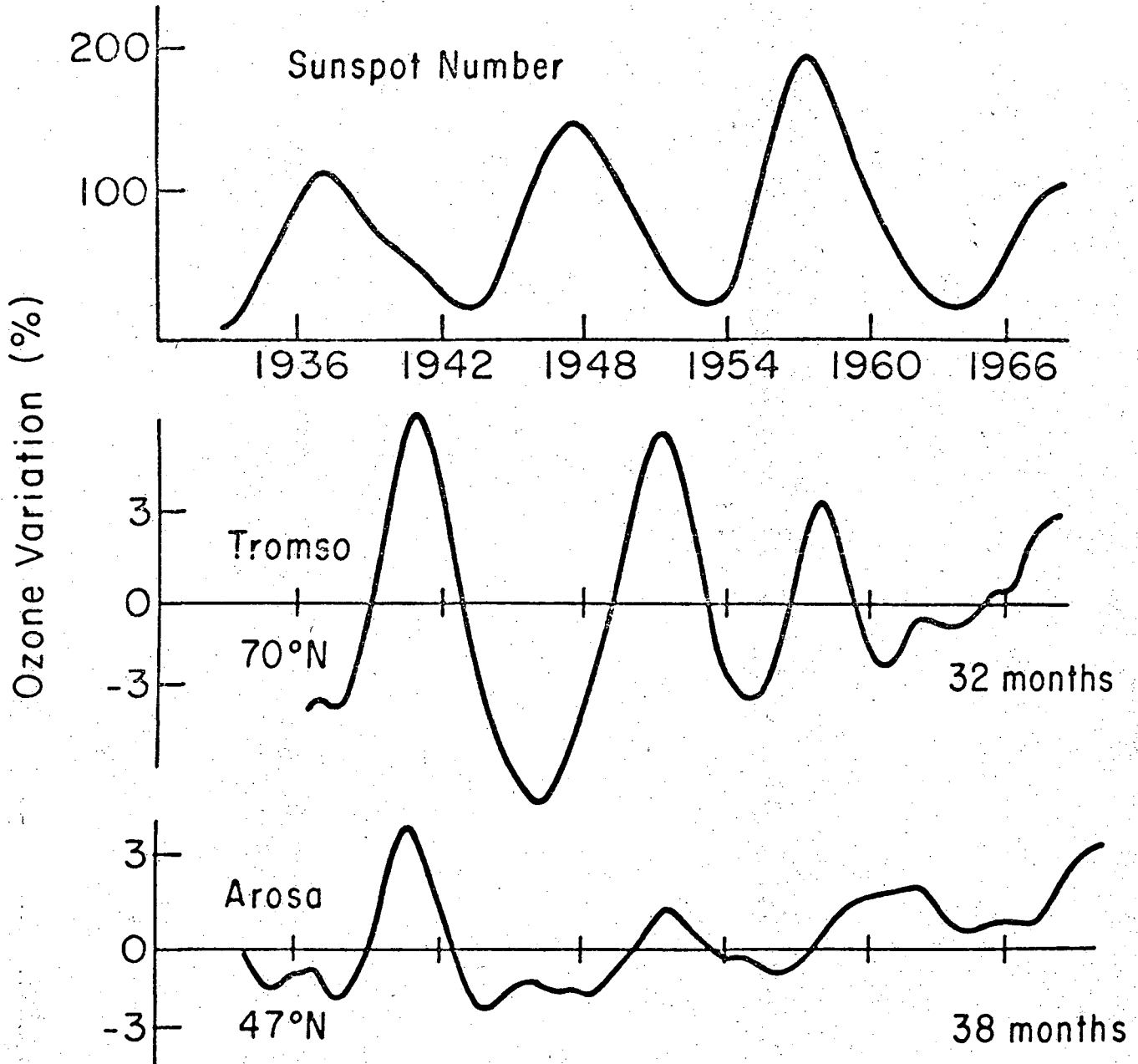
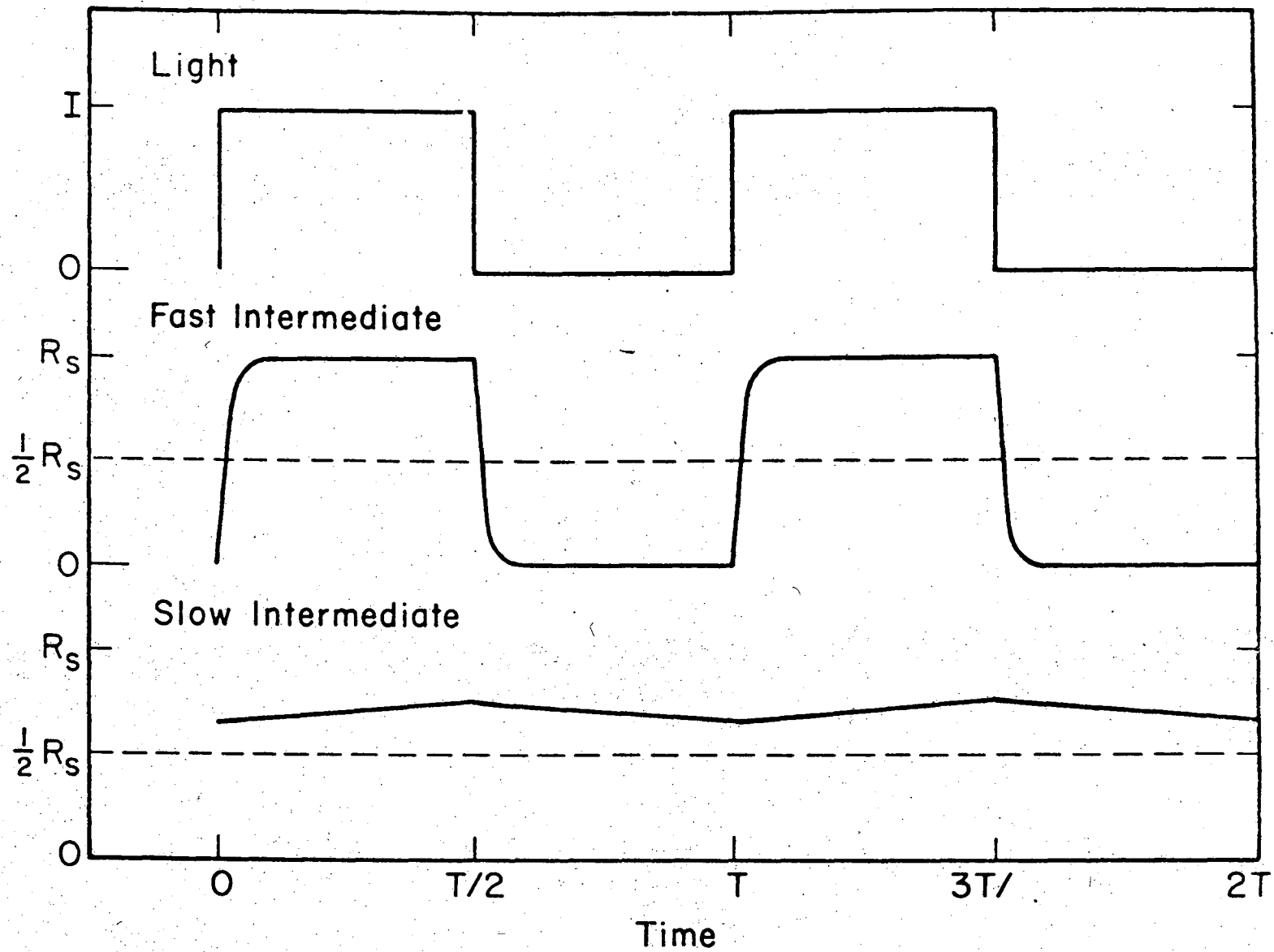


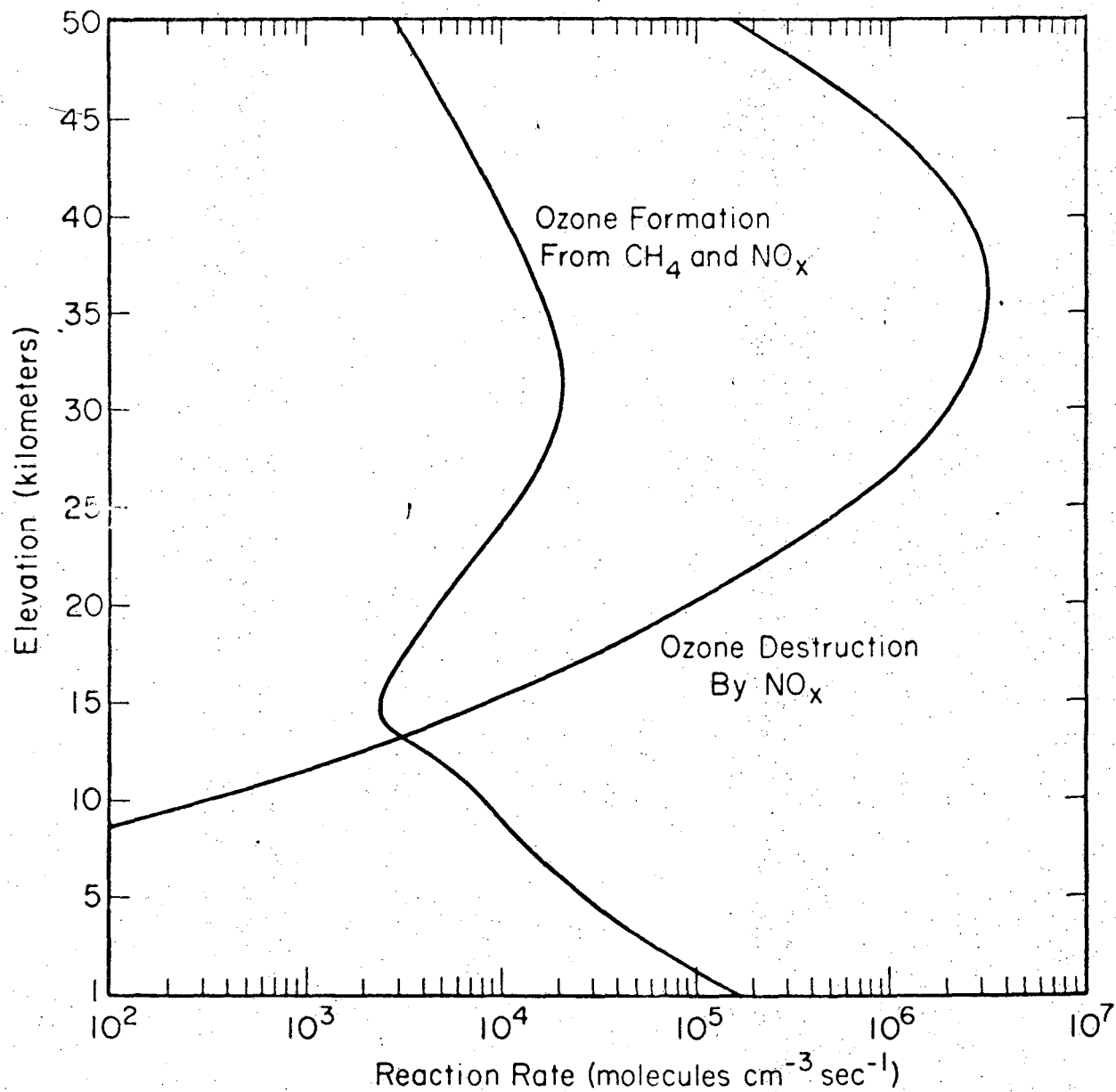
Fig. 17



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Fig. 18

OZONE FORMATION FROM THE SMOG REACTIONS BASED
ON METHANE AND NITROGEN OXIDES
(45° LATITUDE, SPRING)



XBL 747-6687

Fig. 19

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