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LABORATORY CHEMICAL KINETICS AS AN ATMOSPHERIC SCIENCE*

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ABSTRACT

As a demonstration of the predictive power of the science of laboratory chemical kinetics, it is shown that one laboratory reaction (the N_2O_5 catalyzed decomposition of ozone) can be exactly predicted from other laboratory reactions; and it is shown that a non-controversial atmospheric quantity (the vertical profile of singlet delta oxygen molecules) can be predicted quite satisfactorily from chemical rate constants obtained in the laboratory. The chemical and photochemical constants of the pure air substances, O , O_2 , and O_3 , are fairly well known, and these constants predict about twice as much stratospheric ozone in clean air as that observed, implicating some other agent or agents in the natural destruction of ozone. Neither transport to the troposphere nor the water reactions are adequate (by about a factor of 50) to explain the ozone deficit. A natural source of NO_x in the stratosphere is the reaction of nitrous oxide (N_2O) with singlet oxygen, $O(^1D)$, and the source strength has been calculated by three different investigators to lie in the range of 0.25 to 2.5×10^8 molecules $cm^{-2} sec^{-1}$.

* Paper presented at Survey Conference, Climatic Impact Assessment Program (CIAP). U.S. Department of Transportation, Cambridge, Massachusetts, February 15-16, 1972.

The NO_x inventory built up by this natural flux (in the face of all the complexities of atmospheric motions and photochemistry) is sufficient to explain the ozone deficit. The source strength of NO_x from 500 SST is equal to or several times greater than the natural NO_x source strength. If the natural source strength of NO_x , which already exerts the dominant influence on reducing stratospheric ozone to its natural level, is increased artificially by a factor of two or more, it would require a remarkable cancellation of effects if this artificial increase should not exert a major reduction on stratospheric ozone.

Introduction

During the past year, I have presented a series of papers^{1,2,3} on the problem: What are the important variables in stratospheric ozone photochemistry? In particular, I have emphasized, in agreement with Crutzen^{4,5,6}, that the oxides of nitrogen are one of the most important photochemical variables in the stratosphere and that the water reactions are negligible compared to reactions of NO_x (NO , NO_2 , NO_3). Furthermore, commercial fleets of SST would add NO_x to the stratosphere in amounts sufficient to bring about a major reduction of stratospheric ozone. These papers represent calculations based on laboratory studies of chemical kinetics and photochemistry and on a standard model of the stratosphere. In this paper I do not try to reproduce all of the previous calculations. Rather, I examine the questions: What sort of science is photochemistry? What validity might it be expected to have in predicting chemistry in the stratosphere?

In the laboratory of the chemical kineticist and photochemist, quantities are measured such as rate constants, cross sections, and quantum yields. To what extent may these laboratory observations be extrapolated to different environments, such as the stratosphere? This general question has been the guiding principle behind my research in photochemistry and chemical kinetics, and I have three publications^{7,8,9} that reach conclusions on the present status of this question.

The first part of this article gives examples of the transferability of rate constants from one environment to another. The second part of this article uses rate constants measured in the laboratory to identify the important variables in the problem of stratospheric ozone. This identification of important variables applies both to the natural stratosphere and to the stratosphere as it might be perturbed by 500 supersonic transport planes, SST.

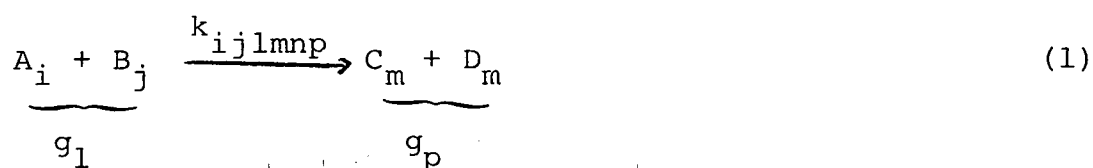
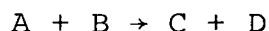
Laboratory Photochemistry and Reaction Kinetics

Apparatus.⁷--In laboratory studies of chemical and photochemical reaction rates, a wide variety of chemical and physical methods are used. The range of quantities sought to be measured is illustrated in Figure 1 by a highly schematic drawing of a crossed molecular beam and of a constant-volume, constant-temperature reaction vessel. In the crossed molecular beam experiment the ideal is to select the internal quantum states of the reactants and to measure the reaction cross sections to produce specific product states as a function of relative velocity. In the bulk reaction flask, the object is to measure the rate of disappearance of all reactants

and the rate of appearance of all products; if there are intermediate species the ideal is to measure their build-up and decay with time.

General Consideration.⁹--The cross sections observed by molecular beam techniques and also by a number of spectroscopic methods are strictly mechanical quantities. Such cross sections can be transferred without limit to other environments. However, for even the simplest chemical reaction there are a vast number of parallel reaction paths in terms of the purely mechanical cross sections; and in general the full lists of such quantities have not yet been evaluated. Although full use should be made of these sharp quantities where they are available, few practical atmospheric problems can be solved completely (at this time) in terms of such data.

Phenomenological rates measured in the laboratory reaction flask are sums over a large number of elementary physical processes. These sums involve the cross sections σ and probability distributions P for every quantum process. If the reactants have an equilibrium distribution over all states (internal as well as translational), then every element of the distribution P is specified by one parameter, the temperature, T . The sum of the strictly mechanical cross sections over the equilibrium distribution of reactants is thus also a single-valued function of the temperature. These words can be compactly expressed by the relations



$$\text{Rate} = [A][B] \sum_i \sum_j \int_g \sigma_{ij}(g) g^{P_i P_j P_g} dg \quad (2)$$

$$= k[A][B]$$

$$k = k(T) \text{ if } P_i, P_j, P_g \text{ are equilibrium distributions.} \quad (3)$$

where square brackets indicate total concentration. This description is readily generalized¹⁰ to reactions of first or third order



$$k' = \text{Rate}/[A] \quad (5)$$



$$k'' = \text{Rate}/[A][B][C] \quad (7)$$

In a large number of readily identified situations, the reactants have a grossly non-equilibrium distribution over internal quantum states, in particular, the vibrational states. In some of these situations there are good grounds to believe that the translational degrees of freedom have an equilibrium distribution and thus a temperature T ; but the vibrational degrees of freedom are strongly non-equilibrium. Figure 2 gives data for the unimolecular decomposition of N_2O_5 . The departure from the dashed line, k_{eq} , is all due to the non-equilibrium distribution of the vibrational degrees of freedom of N_2O_5 . Consider the situation at 0.1 torr. The rate is not particularly fast; the half-time is 700 seconds; and yet the

rate is a factor of 300 slower than the value that would obtain at equilibrium over vibrational states. The reaction is neither first order nor second order, but it displays the complex rate function

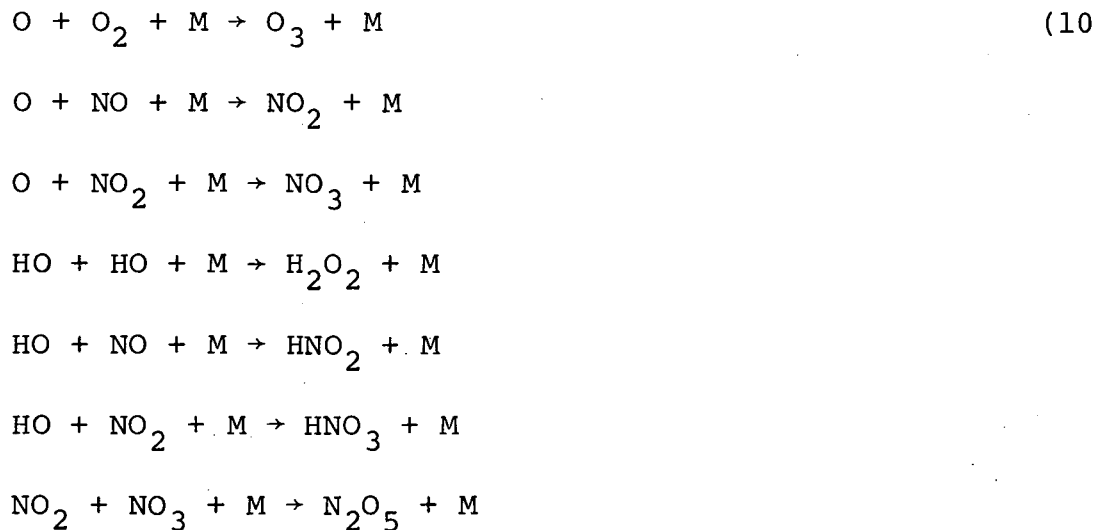
$$k = \sum_i \frac{a_{Mi} c_i [M]}{b_{Mi} [M] + c_i} \quad (8)$$

The reaction cross sections reside in the terms c_i , and the non-equilibrium distribution function is

$$P_i = a_{Mi} [M] / (b_{Mi} [M] + c_i) \quad (9)$$

In this instance the distribution function depends reproducibly on three macroscopic variables: T , identity of gas M , and $[M]$, the concentration of gas. Thus the non-equilibrium rate "constant" can be characterized and reproduced by statement of the three variables: T , M , $[M]$.

This phenomenon of reproducible, non-equilibrium distribution, with its effect of non-integral, variable reaction order, occurs for a large number of atmospheric reactions, for example:



Under stratospheric conditions, the first two reactions are very nearly third order, but the last two are in the middle of the complex "fall off" region. These variable, non-integral rate constants may be transferred from one environment to another if one gives proper recognition to all three macroscopic variables: T, M, [M].

Reaction products are generally formed initially in a non-equilibrium distribution, for example,



The product HO has a remarkably different reactivity toward ozone depending on its vibrational state. In the ninth vibrational state of the hydroxyl radical the reaction is very fast¹¹



$$k = 7.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

In the ground vibrational state of the hydroxyl radical, the reaction is vanishingly slow¹²



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

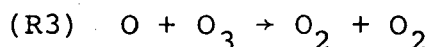
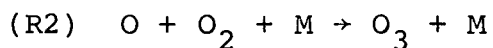
If we knew the rate constant as a function of vibrational state of HO, these constants could be transferred reliably from the laboratory to another environment. However, in the new environment we require large amounts of additional information about the distribution of HO over its vibrational states under the actual conditions. In principle, this problem could be solved in terms of the distribution

of HO over its vibrational states in the reaction of H with O₃ and in terms of the rate constants for deactivation of HO by all major atmospheric species. In the absence of such detailed data, these rates must be regarded as non-transferrable from one set of conditions to another, and the reaction must be studied under "realistic conditions".

Reactions measured in the laboratory are subject to another kind of complexity. The thermal decomposition of ozone⁸ follows the balanced chemical equation



However, the reaction occurs as a sequence of three elementary chemical reactions



The general definition of the rate is based on Eq. 14

$$R = -\frac{1}{2} \frac{d[\text{O}_3]}{dt} = \frac{1}{3} \frac{d[\text{O}_2]}{dt} \quad (16)$$

and the rate expression derived from (15) is

$$R = \frac{k_1 k_3 [\text{O}_3]^2 [\text{M}]}{k_2 [\text{M}] [\text{O}_2] + k_3 [\text{O}_3]} \quad (17)$$

Empirical rates based on (14) are of no value in transferring data from one environment to another. The quantities suitable for prediction of new situations are the elementary chemical rate constants: $k_1(T, M, [M])$, $k_2(T, M, [M])$, and $k_3(T)$.

This section can be summarized by a quotation from the preface of reference 8.

"Now that chemical kinetics is approaching a certain level of maturity, with some of the field passing from frontline research to established applied science, its quantitative data should be tabulated in handbooks. Decisions must be made as to what to tabulate; suggestions have included: Empirical rate constants with defined order and regardless of mechanism, parameters of the Arrhenius equation or parameters of activated-complex theory, nothing but molecular transition probabilities or cross sections for identified changes of quantum states. The position taken in this review is that we should tabulate individual rate constants for elementary chemical reactions. I oppose basing handbooks on the other proposals listed above for the following reasons: Empirical rate data for an unanalyzed complex reaction are analogous to empirical thermodynamic data for an impure unanalyzed substance; the data may be useful for the case in hand but of no general interest. The bare reporting of parameters of the Arrhenius equation or activated-complex theory equation conceals the source of the numbers, the probable error, the relationship to other investigations. In tables of data of this sort one entry may represent an average of several hundred observed points as obtained by a dozen different investigators over a wide temperature range, and another entry may be a wild guess by an amateur in the field or the

unsupported prediction of a crude theory. A refusal to tabulate any kinetic data except fundamental, quantum-state transitions is analogous to a refusal to tabulate any thermodynamic data until they are obtained by statistical mechanics from molecular parameters".

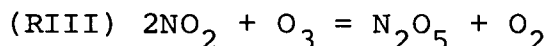
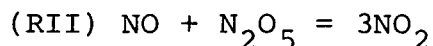
Prediction of a laboratory result.⁷ --The decomposition of ozone is strongly catalyzed by dinitrogen pentoxide, N_2O_5 . Experimental data are given in Figure 3. Over a wide range of conditions the observed¹³ reaction rate is given by

$$\frac{-d[O_3]}{dt} = k_{IV}[N_2O_5]^{2/3} [O_3]^{2/3} \quad (18)$$

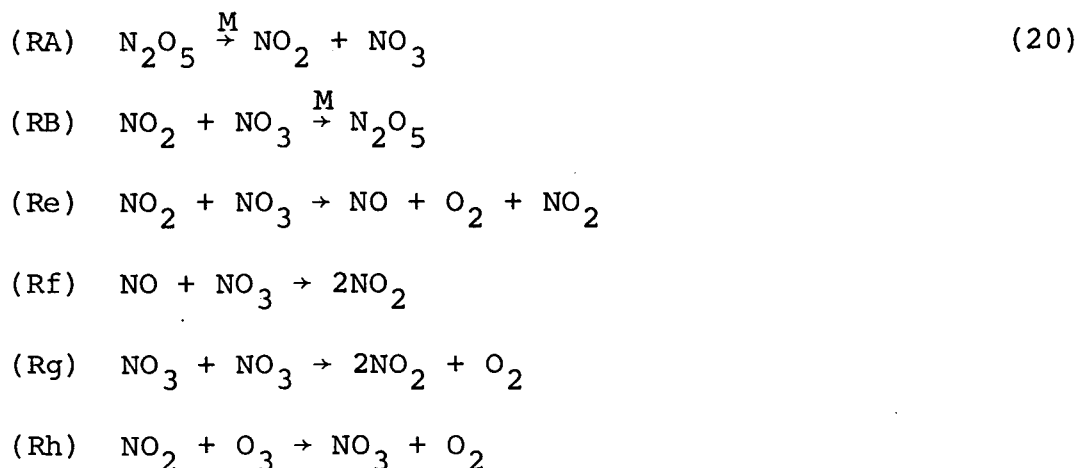
The rate is precisely two-thirds order in N_2O_5 and two-thirds order in ozone. The overall order is thus 4/3.

The points entered in Figure 3 are based on the observed rates of this magnificently strange, four-thirds order reaction. The lines are not based on these observed points. The lines are predicted on the basis of other laboratory studies.

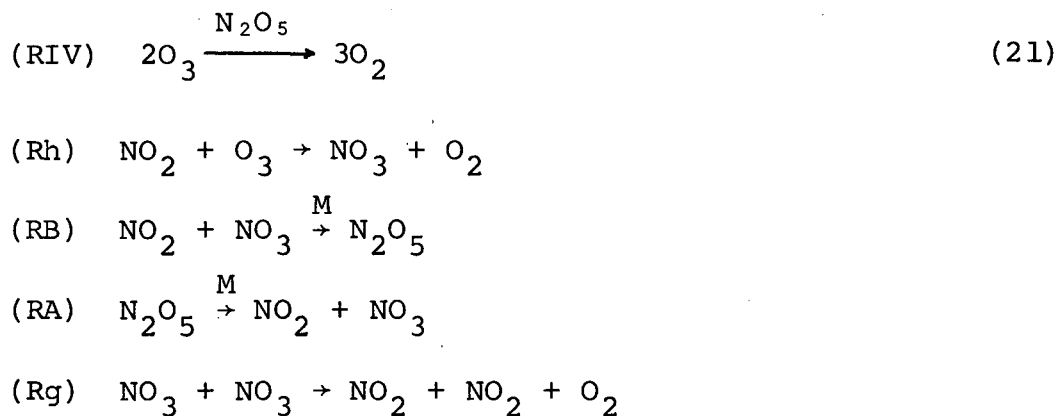
There are three other complex reactions involving N_2O_5 .



These three reactions represent different special cases of the effect of six elementary chemical reactions.



By studying these three laboratory reactions under a wide range of reactant pressure, total pressure, and temperature, the 6 elementary reactions were separately evaluated and tabulated. The N_2O_5 catalyzed decomposition of ozone depends on the four elementary reactions



The rate equation derived exactly from this mechanism is

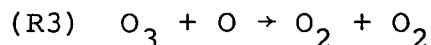
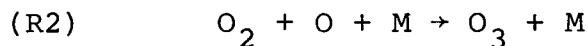
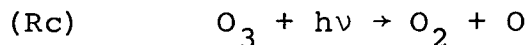
$$R_{\text{IV}} = \frac{1}{2} (k_A k_h / k_B)^{2/3} (2k_g)^{1/3} [\text{N}_2\text{O}_5]^{2/3} [\text{O}_3]^{2/3} \quad (22)$$

Thus the strange 4/3 order is predicted. The rate constants for A, B, g, and h as derived from the complex reactions I, II, and III were used to calculate the lines in Figure 3, and there is excellent agreement between calculated and observed rate.

In conclusion to this section: The rate of one laboratory reaction can be accurately predicted from the rates of other laboratory reactions.

Laboratory Kinetics Applied to the Atmosphere

Prediction of an atmospheric result. --In a stratosphere of pure air, the formation and natural balancing of ozone is given by the Chapman reactions^{14,8,1-6}



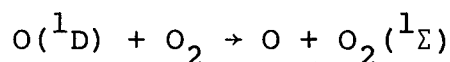
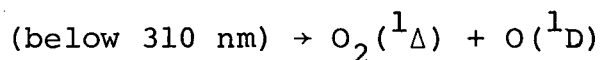
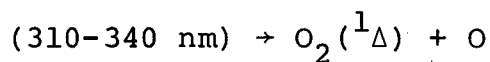
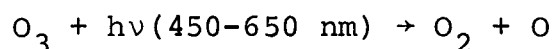
The photochemical steady state set up by these reactions gives

$$\frac{[O_3]_{ss}}{[O_2]} = \left(\frac{J_a k_2 [M]}{J_c k_3} \right)^{1/2} \quad (24)$$

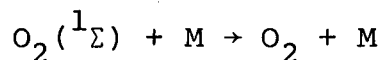
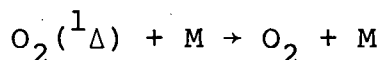
where J is a photochemical and k is a chemical rate constant. "Odd oxygen" (O and O_3) is formed by R_a and destroyed by R_3 . The processes, R_c and R_2 , interconvert O and O_3 , but do not increase or decrease them. The net effect of R_c and R_2 is to convert solar energy to heat in the stratosphere, which is the source of the temperature inversion and great stability of the stratosphere against vertical mixing. The steady-state concentration of ozone depends on the ratio of J_a to J_c and on the ratio of $k_2 [M]$ to k_3 .

There are many other reactions that involve excited electronic states of oxygen atoms and molecules. This field has been reviewed recently by Wayne¹⁵ and it continues to be an active field of current research. In addition to the Chapman reactions we must consider¹⁶ (where O and O₂ represent the stable species and a fuller statement of excited species is ¹Δ_g and ¹Σ_g⁺):

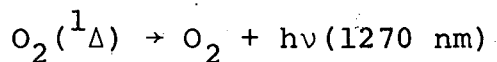
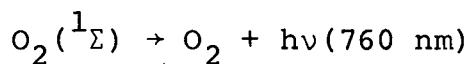
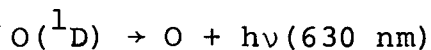
(i) Formation of excited species (25)



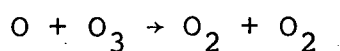
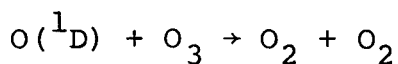
(ii) Deactivation of excited species (26)

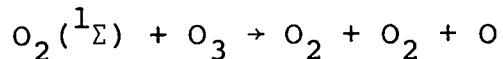
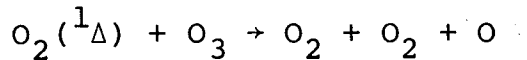


(iii) Light emission by excited species (27)



(iv) Reaction with ozone (28)





Under stratospheric conditions the deactivation processes (ii) predominate over the ozone destruction processes (iv), and loss of odd oxygen to electronically excited species is very small (a few percent) compared to the loss by the Chapman reactions.

The formation and quenching of $O_2(^1\Delta)$ lead to a fairly large concentration of this species in the stratosphere. It signals its presence by the airglow radiation at 1.27 μm . The rate constants for reactions (25)-(28) have been measured in the laboratory and reviewed by Wayne.¹⁵ The vertical profile of $O_2(^1\Delta)$ was deduced from a rocket sounding, and the result as quoted by Wayne¹⁵ is plotted in Figure 4. Wayne emphasized that the calculated curve in Figure 4 involves no adjustable parameters; it is exclusively based on rate constants as measured in the laboratory and the ozone vertical profile as measured by a rocket sounding. The observed $O_2(^1\Delta)$ is based on the radiation intensity at 1.27 μm as observed in another rocket sounding of the upper atmosphere. The agreement between calculated and observed curves is quite satisfactory.

The conclusion to this section: for a non-controversial quantity such as the $O_2(^1\Delta)$ air-glow, rate constants as measured in the laboratory are capable of predicting a concentration profile in the upper atmosphere.

Pure air rate constants.--Before considering the effect of trace components in the stratosphere, it is important to get straight the effect of the major component, namely oxygen. In pure

air, the ozone steady state depends on the ratio of k_2 and k_3 , Equations (23) and (24). The status of laboratory studies of reactions 1, 2, and 3 (Equations 23 and 15) will be reviewed in detail.

During the years 1966 and 1967, I spent all of my available time for research in preparing a book for the National Bureau of Standards (NSRDS-NBS-20) giving a critical review of all published data on the reaction rates of O, O_2 , and O_3 .⁸ All available kinetic data published in English, German, and French since 1900 were reviewed. Tabulated rate constants were recomputed into common units. Data that appeared only as points on a graph were read off the graph and combined with other data. These reactions were extensively studied in the 1920's and early 1930's, and again after about 1955. Some of the early work showed very poor precision, and these data could be associated with reaction vessels containing surfaces that catalyze the decomposition of ozone. Some of the early work showed good precision for a given series of runs but very poor reproducibility from one series to another; these data could often be shown to involve oxides of nitrogen in the ozone. Studies of the photolysis of ozone by ultraviolet light was shown by the original authors to involve ozone destruction by free radicals based on water. Studies before 1964 of k_3 in fast flow systems with oxygen atoms produced by an electric discharge are known to be invalidated by the presence of large amounts of $O_2(^1\Delta)$ in the gas stream, which also decompose ozone, Equation (28). Studies shown to involve catalysis by surfaces, water, or the oxides of nitrogen were rejected in toto.

After this screening of all available data, there remained a large quantity of apparently valid data. A consistency test for the validity of the data was to compare the ratio of k_1 and k_2 as determined strictly from kinetics with the equilibrium constant obtained from thermodynamic data in the JANAF tables¹⁷

$$\frac{k_1 \text{ (kinetic)}}{k_2 \text{ (kinetic)}} \text{ compared with } K_1 \text{ (thermo.)} \quad (29)$$

This comparison is reproduced in Figure 5. It can be seen that k_1/k_2 is in excellent agreement with the thermodynamic equilibrium constant. By virtue of this test, the constant for reaction 2 may be obtained more reliably from

$$k_2 = k_1/K_1 \quad (30)$$

than from direct observation in certain regions of pressure and temperature. Likewise the value of k_1 can be extended by adding to it the values of

$$k_1 = K_1 k_2 \quad (31)$$

The observed values of k_2 are given as points in Figure 6. Observations have been made at temperatures typical of the stratosphere. The best estimate of the rate constant k_2 is based on the extended data for k_1 reflected through the equilibrium constant, Equation (30); the line in Figure 6 was evaluated in this way. It can be seen that this rate constant is still uncertain by perhaps $\pm 50\%$. Care must be taken to consider the correct M-gas, since k_2 depends on T,

identity of M, and concentration of M, Equation (10). The data in Figure 6 are based on equivalent ozone as M-gas, and air is about 0.4 as effective as ozone in this respect. Several laboratory studies were carried out with argon as M gas, which is 0.25 as effective as ozone.

All data points regarded as valid in 1968 were listed in Tables in NBS-20. The purpose of this listing was to permit easy extension of that study as new data on these reactions are obtained. New data can be added to the fifty years of experience embodied in NBS-20, and the revised best estimate based on new plus old data is easily obtained. Such a treatment²⁰ was carried out by Krezenski, Simonaitis, and Heicklen (1971). They measured the rate of reaction 3 from room temperature down to 196°K, whereas the lowest temperature previously investigated was 273°K. Figure 7 shows all data included in NBS-20, the new low-temperature points, and the curve previously used in stratospheric calculations.^{1,2} As this example illustrates, a "most recent" study should be added to the basic background of 50 years of experience, not used to displace the full body of previously established data.

In the early 1950's Benson and Axworthy¹⁸ re-evaluated the experimental data of Glissman and Schumacher.¹⁹ The temperature range of these data are indicated by the bar in Figure 7. This temperature range is very narrow compared to the full range now available. All of Benson and Axworthy's points were included in this study, and thus their study is superseded by NBS-20.

In summary, the full body of laboratory data in Figures 6 and 7 probably give the ratio $(k_2/k_3)^{1/2}$ with an accuracy of ± 50 per cent under stratospheric conditions.

Photolysis rates.--The rate of photolysis of oxygen is written as $J_a[O_2]$, and the rate of photolysis of ozone is written as $J_c[O_3]$. The parameters J_a and J_c are not rate constants; rather they depend on the summation over wavelength of light absorption cross section σ , quantum yield ϕ , and local light intensity I . The local light intensity depends on the intensity of incoming solar radiation and on all species that absorb that radiation above the point in question. Both ozone and oxygen absorb below 242 nm, and thus the light intensity depends on the optical path L of both O_2

and O_3 between the sun and the region of interest. If x represents O_3 and z represents O_2 , the functional dependence of the photolysis factors is

$$J_a = \sum_{\Delta\lambda} \sigma_z(\lambda, T, P) \phi_z(\lambda) I(I_{O\lambda}, L_x, L_z) \quad (32)$$

$$J_c = \sum_{\Delta\lambda} \sigma_x(\lambda) \phi_x(\lambda) I(I_{O\lambda}, L_x, L_z)$$

In the stratosphere oxygen absorbs radiation between 190 and 242 nm in the Herzberg continuum, a highly "forbidden" transition. This absorption is enhanced by the perturbation of molecular collisions, and thus the cross section for absorption by oxygen is a weak function of pressure P and temperature T .

Both old and recent data on the cross sections σ and solar intensities I_o have been reviewed by Ackerman.²¹ Before Ackerman's review was published, the solar intensities I_o were most conveniently obtained from a review by Brinkman et.al.²², and the cross sections were obtainable from several journal articles.^{23,24}

The calculations reported in my two reports^{1,2} in the summer of 1971 were based on references 22-24. Recently I have made calculations with the data as summarized by Ackerman.²¹ For the case of pure, dry air, the photolysis parameters given by Ackerman predict 15 percent less ozone (total vertical column, steady-state calculation) than is predicted by the constants based on references 22-24.

Calculation of the absolute concentration of ozone in pure air.--In the stratosphere, the steady-state concentration of ozone is given by Equation 24. The laboratory quantities needed are k_2/k_3 , which are available^{8,20} at temperatures between 200 and 1000°K, and J_a/J_c , which can be calculated from photochemical data.^{21,22-24} From pressure and temperature as a function of elevation, the chemical kinetic ratio $k_2[M]/k_3$ can be calculated in a straightforward way. The calculation of the photochemical ratio J_a/J_c poses certain problems. The earth rotates every 24 hours and the seasons undergo the annual cycles. As is well known from the theory of photochemical rotating sectors²⁵, there is a difference between a given light intensity half the time and half the light intensity all the time. If the period (light on and light off) is long compared to the time for a substance to reach the steady state, then the calculation should be done in terms of full light intensity, which is on for half the time. If the period (light on and light off) is short compared to the lifetime of a substance, then the calculation should be done in terms of half light intensity for all the time. The active ultraviolet radiation is so rapidly attenuated as one moves down from 50 kilometers to 15 kilometers in the stratosphere that there is a profound gradient^{26,1} of half-times for ozone to reach the steady state: about a day at 45 km, about two weeks at 35 km, about 3 months at 25 km, and several years at 15 km. In terms of photochemical sector theory, it is appropriate at and below 40 km to use the average intensity for all times. In my calculations¹⁻³, I have averaged the solar intensity for each nanometer of wave length

over every 5 degrees of solar angle for the 24 hour day. In this way, I have evaluated steady-state ozone profiles between the equator and 75° latitude at the solar equinox.

Recently Randhawa (1971) published two ozone profiles²⁷ obtained from rocket soundings at Panama, 9° North, November 1970. These profiles are replotted in Figure 8, where some fine structure of the original data is lost. The calculated curves^{1,2} for pure air at the equator and at 30° latitude are also given in Figure 8; these calculated curves follow directly from the two ratios discussed above and vary as $(k_2[M]/k_3)^{1/2} (J_a/J_c)^{1/2}$. The curves calculated on the basis of pure air indicate far more ozone than is observed.

The calculated curves in Figure 8 are drawn with a heavy line above 27 kilometers and a light line below that elevation. This distinguishes between the region where the photochemical half-time for ozone is less than 3 months (above 27 km) and greater than 3 months (below 27 km). Vertical eddy diffusion and transport (equatorial to polar) may modify a vertical profile in times longer than three months, but probably such modification is small for times less than three months in the lower temperate and tropical regions considered in Figure 8. The calculated curve, based on pure air, is far greater than the observed profiles at all elevations, including the high elevations where photochemical reactions are fast.

Conclusion: In the stratosphere ozone is destroyed by some process other than pure air reactions. In tropical regions above 25 kilometers (the ozone factory of the world) there is an ozone

deficit of a factor between 2 and 3. Something else is very active in destroying ozone in the natural stratosphere (compare reference 4).

Other loss processes.--Various proposals have been made to explain this stratospheric ozone deficit: (1) Loss of ozone by eddy diffusion to the troposphere; (2) loss of ozone to the troposphere by the spring polar overturn; (3) catalytic destruction of ozone by free radicals based on water, the HO_x system; and (4) catalytic destruction of ozone by the oxides of nitrogen, the NO_x system.

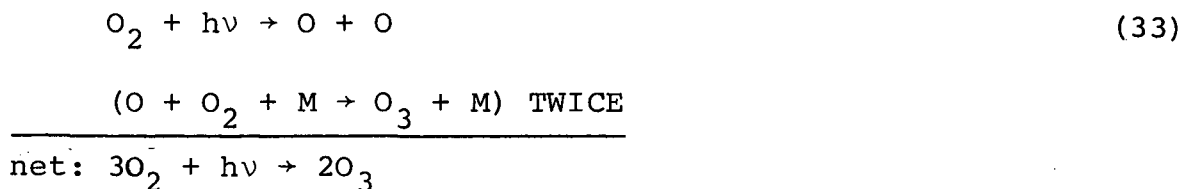
Loss of ozone from the stratosphere by air motions.--It has been suggested by London²⁸ that the "ozone deficit" is an artifact of the steady-state calculation. In a large scale computation considering day and night variation and global circulation, he found little or no ozone deficit for a model simulating the month of January. On the other hand, I find an ozone deficit of a factor of almost three in the tropics and a factor of about $1\frac{3}{4}$ on a global basis. The difference between my results and those of London probably lies more in the rate constants than in the atmospheric models. In a list circulated in April 1971, London gave as his rate constants: $k_2 = 5.5 \times 10^{-34} (300/T)^{2.6}$, $k_3 = 1.86 \times 10^{-11} \exp(-2130/T)$. The values I used^{1,2} were: $k_2 = 2.4 \times 10^{-35} \exp(1080/T)$ and $k_3 = 1.33 \times 10^{-11} \exp(-2120/T)$. The significant quantity is the ratio, k_2/k_3 . For three representative stratospheric temperatures, these ratios are related as follows:

	220°K	237°K	260°K
(k_2/k_3) Johnston	2.7	2.3	2.0
(k_2/k_3) London			

To be sure, there is uncertainty as to the values of these rate constants, especially k_2 , at low temperatures in air. However, the difference between London and Johnston as to a small or large "ozone deficit" seems to depend more on the values used for rate constants than on the difference between steady-state calculations and calculations including global circulation.

It is agreed that air motions are dominant in controlling the distribution of stratospheric ozone at low elevations at all latitudes and at all elevations at very high latitudes. The transport of ozone from 30 to 20 km or from 30° to 70° latitude at 30 km does not remove ozone from the stratosphere, but it merely displaces it from one part of the stratosphere to another. The purpose of this section is to examine the magnitude of processes that transport ozone from the stratosphere to the troposphere.

Consider a volume element of fixed coordinates in the stratosphere, for example, a cubic meter. For a short interval of time (say, a few minutes) the change of ozone in this volume may be factored into three vectors, each one of which has multiple components. These three vectors are: (A) The gross rate of formation of ozone from the photolysis of oxygen. This photochemical reaction is brought about by two processes:



The rate of this reaction can be calculated from the local intensity of sunlight and the concentration of oxygen. If one takes the ozone concentration to be the observed average value appropriate

for the given elevation, latitude, and season, then one can calculate the local intensity of sunlight as a function of wave length and evaluate the rate vector A. This calculation is very straightforward, and it makes no assumption about photochemical steady state or the magnitude of the other rate vectors B and C. (B) Chemical destruction of ozone. Odd oxygen is destroyed by three families of reactions O_x (O_3 , O_2 , O), NO_x (NO, NO_2), and HO_x (H, HO, HOO). These reactions are discussed in some detail later. These chemical reactions are driven by photochemically produced reactive species, O, HO, etc. (C) Net transport of ozone by air motions. Eddy diffusion or a wind component could bring ozone into any of the six faces of the cubic volume element. The air brought in has itself been subject to photochemical and chemical reactions in a nearby region of space, and in general its ozone concentration will not be greatly different from that in the reference volume element. If winds come in through some faces of the cube, it goes out through other faces, transporting with it the ozone concentration currently in the volume element. Depending on the instantaneous gradients of the mole fraction of ozone, these air motions will remove more, or less, or no ozone from the reference volume element. The net difference between transport in and transport out of the volume element is the vector C.

Three cases of these three rate vectors, A, B, C, are given in Figure 9. Case I illustrates the situation where there is a net transport of ozone out of the reference volume element, by virtue of the directions of the winds and the gradients. In this case the photochemical formation rate A is larger than the chemical destruction rate B. Case II represents a photochemical "steady state".

(Chemists reserve the word "equilibrium" for the situation where the balancing forward and reverse processes are the exact reverse; the photochemical process A and the chemical reactions B are not exact mirror images; and chemists call such a balance a "steady-state". Meteorologists usually refer to this as photochemical "equilibrium". Of course, either name is satisfactory so long as it is clearly defined.) In this photochemical steady state, the rate of formation of ozone from photolysis of oxygen is exactly balanced by the various chemical reactions that destroy odd oxygen. This situation can come about if the absolute value of the rates, A or B, is very much larger than the net transport processes C. Also, it can happen if the transport of ozone into the volume element is equal to the transport out, that is, zero gradients in the direction of the wind, etc. Case III represents a net transport of ozone into the volume element. Air transport and photochemistry add ozone; chemical reactions destroy it.

For the cases I, II, and III the combination of photochemistry, chemistry, and transport gives a steady state; the concentration of ozone in the volume element is not changing with time. On the other hand, cases IV, V, and VI in Figure 9 parallel cases I, II, and III except that the gain processes exceed the loss processes. Thus the concentration of ozone increases with time. There are, of course, processes VII, VIII, and IX, not shown in Figure 9, where the loss processes exceed the gain processes, and the concentration of ozone in the volume element would be decreasing.

Consider a smoothed, average, actual distribution of ozone over latitude and elevation at the fall equinox. At each nm of

wavelength between 190 and 400 nm, consider the solar intensity averaged over a 5° angular grid for the 24 hour day. With an elevation grid of one kilometer and a latitude grid of 15° , the integral of the gross rate of formation of ozone, vector A, over the stratosphere from 15 to 45 kilometers in the northern hemisphere is 8×10^{10} tons of ozone per year (the solar flux for the year is approximated as that for the solar equinox). This calculation, of course, involves no assumption about a photochemical steady state.

When ozone is transported from one part of the stratosphere to another, that does not represent ozone destruction or removal from the stratosphere. To estimate the loss of ozone from the stratosphere to the troposphere, one must integrate the vector C over the boundary between the stratosphere and troposphere. Vertical eddy diffusion brings large amounts of ozone from the photochemically active region above 25 kilometers down into the photochemically sluggish region between 15 and 20 kilometers. Further vertical eddy diffusion brings ozone down into the troposphere. Paetzold²⁹ has calculated the average loss from this process to be about 10^{11} molecules $O_3 \text{ cm}^{-2} \text{ sec}^{-1}$. Such a loss integrated over the northern hemisphere is 7×10^8 tons per year. Horizontal transport and diffusion move large amounts of ozone from tropical toward polar regions. Further horizontal transport and subsidences during the winter months build up a thick column of ozone in polar regions, which is broken up and scattered into the troposphere^{30a} in the "spring overturn". It is assumed that this loss is equal to the difference in the spring maximum and late full summer minimum^{30b} integrated over all latitudes. Such a loss of ozone to the troposphere is 4×10^8 tons per year for the northern

hemisphere.³ Junge^{31a} made a similar calculation, finding the difference of total ozone in the northern hemisphere between spring maximum and fall minimum to be 3.5×10^8 metric tons per year. Ascribing all of this difference to the ozone loss at the "spring overturn" is probably accurate within a factor of two. The sum of these two effects gives 1.1×10^9 tons per year as an estimate of the loss of ozone to the troposphere as a result of air motions. This is regarded as the integral of rate C over the boundary of the stratosphere.

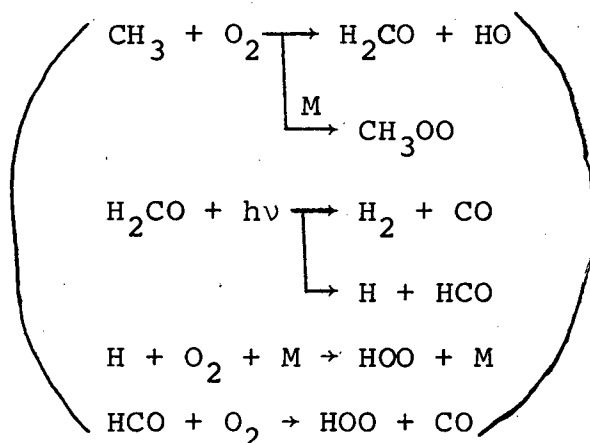
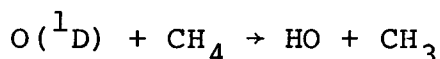
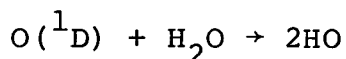
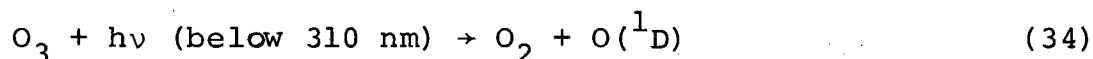
For the entire stratosphere of the northern hemisphere, the integral of rate A, the gross rate of formation of ozone from sunlight, is 8×10^{10} tons per year. The integrated losses due to transport at the boundaries, rate C, is 1.1×10^9 tons per year, or between 1 and 2 per cent of the total of rate A. The total ozone inventory of the stratosphere is very nearly in a steady-state from a long-term, year-to-year basis. Thus the difference in the gross rate of formation of ozone, A, and the transport of ozone from the stratosphere, C, must be ascribed to chemical destruction by the reaction systems O_x , HO_x , and NO_x . These chemical destruction rates, over the entire stratosphere and entire year, must account for 98 to 99 per cent of the balancing of ozone production. Thus the long-term global ozone balance is approximately given by A = 100%, C = -2%, and B = -98%.

At $45^\circ N$ at the fall solar equinox, the instantaneous (one day average) rate of A integrated over the vertical column is 90×10^{-11} molecules $cm^{-2} sec^{-1}$, and loss to the troposphere by eddy diffusion (according to Paetzold²⁹) is 1×10^{-11} .

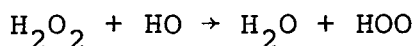
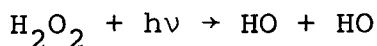
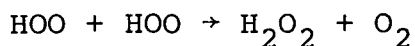
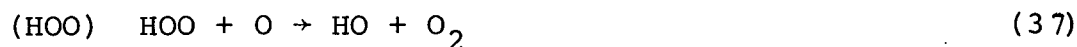
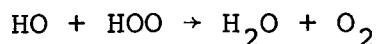
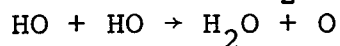
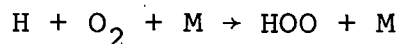
These considerations bring out that the ozone deficit as illustrated by Figure 8 cannot be explained in terms of mechanical transport.

Conclusion: Although atmospheric motions are dominant in determining the vertical distribution of ozone in the lower stratosphere and in determining the world-wide distribution at high latitudes, mechanical transport of ozone from the stratosphere to the troposphere balances out less than 2 per cent of the gross rate of ozone formation. Therefore, at least 98 per cent of natural ozone destruction is brought about by processes in the stratosphere, probably photochemical reactions.

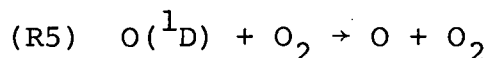
Loss of ozone by water reactions.--The free radicals based on water are indicated by the symbol HO_x (H, HO, HOO). These free radicals are formed from singlet D oxygen atoms, which are produced by the photolysis of ozone below 310 nm.



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



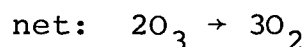
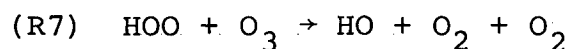
The rate constants for these reactions are given in references 32-35, 5, 12, and in other references cited there. There has been a great deal of activity in this field during the immediate past, and some of the recent estimates have varied rather widely, for example, the ratio of rate constants k_4/k_5 for the reactions



has been reported as 10.7 (ref. 33a, 1971), 4.2 (ref. 33b, 1971),

and 0.12 (ref. 33c, 1970). In the stratosphere, the important quantity is the ratio of rate constant of $O(^1D)$ with water and with air, since this determines the fraction of $O(^1D)$ that goes to form two hydroxyl radicals. It appears that this important ratio is not yet satisfactorily known, although this situation will probably be corrected very soon, in view of current active interest.

The reaction of $O(^1D)$ with water to form hydroxyl radicals was discovered³⁶ by McGrath and Norrish in 1960. They then speculated that the chain decomposition of wet ozone by ultraviolet light was brought about by the reactions



Kaufman³⁷ (1964) attempted to measure the first of these reactions, but it was not observed to occur. He was able to set a limit on its rate

$$k_6 < 5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

Many unsuccessful attempts have been made to measure the rates of these reactions. Recently Langley and McGrath¹² have looked for this reaction in a situation where it would produce a big effect if it was present. They showed that reaction 6 is 5000 times slower than the limit set by Kaufman, that is

$$k_6 < 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \quad (42)$$

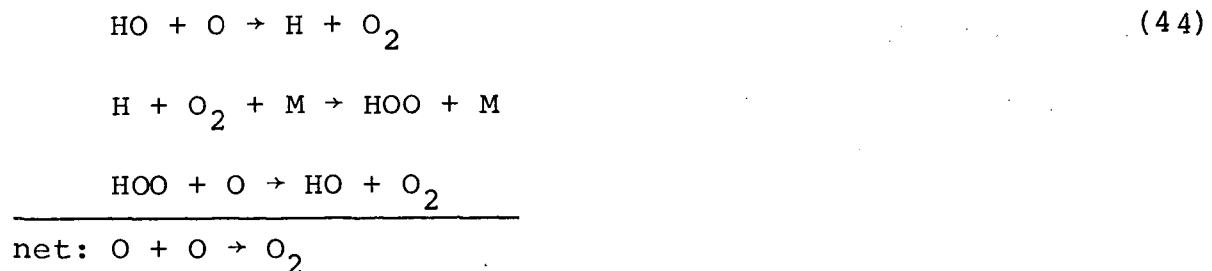
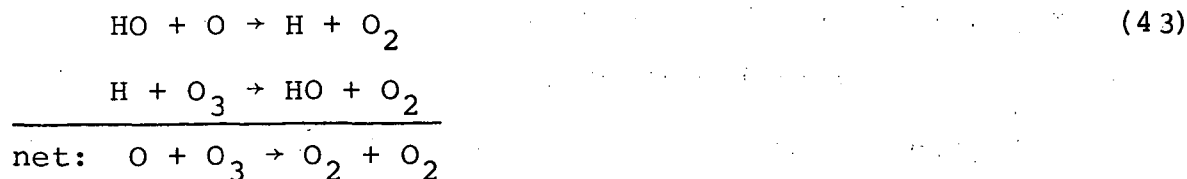
With this very low limit, the thermal chain reaction based on HO and HOO is ruled out as an important process in the stratosphere.

Hunt^{38,39} pointed out the need to consider loss processes for ozone other than those based on pure air, and he adopted McGrath and Norrish's hypothetical³⁶ reaction chain for model calculations. He replaced Kaufman's inequality³⁷, $k_6 < 5 \times 10^{-13}$, by an equality

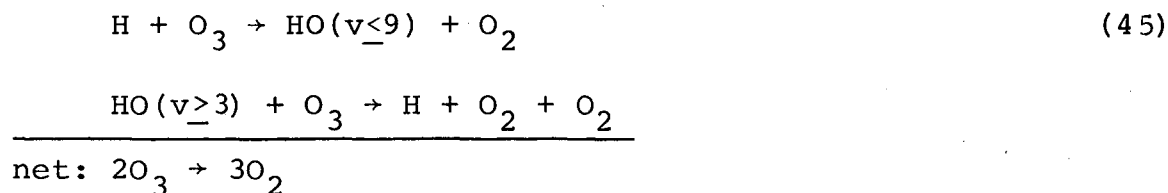
$$k_6 = 5 \times 10^{-13}$$

Hunt said: "A rather arbitrary assignment of 10^{-14} was made for the value of k_7 , but the reaction must be rather slow as the rate has not been measured yet...The ozone profile was...sensitive to the value of k_7 ...varying k_7 from 10^{-13} to 10^{-15} changed the total O_3 amount from 0.1 to 0.35 cm. STP". Thus by adjusting the rate constant of this hypothetical reaction, one can calculate any desired reduction of the total ozone column. In his article, Hunt³⁹ made model calculations in which he demonstrated that water reactions would be sufficient to explain the ozone deficit if the rate constants were as big as $k_6 = 5 \times 10^{-13}$ and $k_7 = 10^{-14}$. The demonstration by Langley and McGrath¹² that k_6 is less than 10^{-16} shows that these water reactions are not sufficient to explain the ozone deficit. There is no longer any justification for using these hypothetical reactions in stratospheric photochemical models.

In terms of known chemical reactions, there are several catalytic cycles involving the HO_x system, but they are very minor in effect below 45 km. Examples⁸ of such cycles are



At high pressures (laboratory conditions) of water and ozone, an energy chain involving vibrationally excited hydroxyl radicals may occur¹²



Recently two key rate constants in the HO_x system have been found to be much larger than previously supposed



may be as much as 10 times faster than the deactivation of O(¹D) by air^{33a}, whereas previous estimates indicated these rate constants to be about the same size. The reaction



has been directly observed for the first time⁴⁰, and its rate constant is 20 times larger than Kaufman's estimate.³⁵ This large rate constant, 2×10^{-10} , for an HO_x termination step has the effect of

reducing the calculated HO_x below previous estimates. Also it is so much larger than the rate constants for $2\text{HOO} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ and $2\text{HO} \rightarrow \text{H}_2\text{O} + \text{O}$ that one is not able to use Nicolet's ingenious method³² of calculating the sum of HO and HOO. However, the large increases^{of} these two rate constants over their previously presumed values tend to offset each other, and the total HO + HOO is probably not greatly different from Nicolet's 1970 estimate.

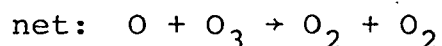
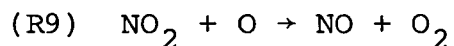
In the summer of 1970, the reactions R6 and R7 were believed⁴¹ to occur with large rate constants, and these reactions were the primary basis of the "water model" of stratospheric ozone. At that time the rate constants for deactivation of $\text{O}(^1\text{D})$ by air and for the reaction of $\text{O}(^1\text{D})$ with water were not known; the rate constant for $\text{HO} + \text{HOO}$ was presumed to be 20 times lower than it has now been found to be. Recall, however, a quotation⁴¹ from the SCEP report (page 69): "Both carbon monoxide and nitrogen in its various oxide forms can also play a role in stratospheric photochemistry, but despite greater uncertainties in the reaction rates of CO and NO_x than for water vapor, these contaminants would be much less significant than the added water vapor and may be neglected". Laboratory chemical kinetics is a predictive atmospheric science only if one sticks to known reactions with measured and re-measured and thoroughly verified rate constants. The use of rate constants of hypothetical reactions as adjustable parameters must be excluded. We have an example, Hunt (1966) through SCEP (1970), where the hypothetical water reactions were promoted from arbitrary artificial models³⁹ to where they were believed and used as a basis to dismiss reactions of the oxides of nitrogen.⁴¹

The other water reactions, Equations (43) and (44), can account for about one per cent of the gross destruction rate of ozone, which is about the same as the effect of the reaction $O(^1D) + O_3 \rightarrow 2O_2$. The full family of water reactions is not sufficient to account for the ozone deficit demonstrated by Figure 8.

Conclusions: Not only are the HO_x reactions inadequate to explain the ozone deficit in the stratosphere, these reactions are negligible in the ozone budget.

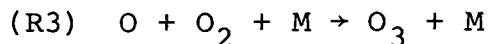
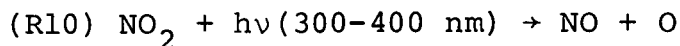
Loss of ozone by catalytic reactions with the oxides of nitrogen.--

Anyone who has worked extensively with ozone in the laboratory is aware that oxides of nitrogen in very small amounts greatly reduce the yield of an ozonizer and increase the decomposition rate of ozone in any experiment. At room temperature and with relatively high concentrations of ozone, the dominant process is the thermal catalytic reaction already discussed at length⁷, Equations (18)-(22). Under conditions of the stratosphere (low temperature, low mole fraction of ozone, and powerful ultraviolet radiation field), the dominant process whereby NO_x (NO , NO_2 , NO_3) destroys ozone is the simple catalytic cycle



Both ozone and oxygen atoms are destroyed, but nitric oxide and nitrogen dioxide are not destroyed. The cycle can be repeated indefinitely, limited by the rate of the second step. This

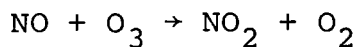
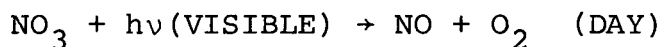
catalytic cycle occurs in competition with another, "do nothing" cycle



net: no reaction

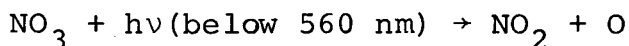
Thus reaction (R9) is the rate determining step in the catalytic cycle.

In the lower stratosphere the steady-state concentration of oxygen atoms is very low and reactions involving it become slow. Another catalytic cycle becomes very important in the lowest stratosphere



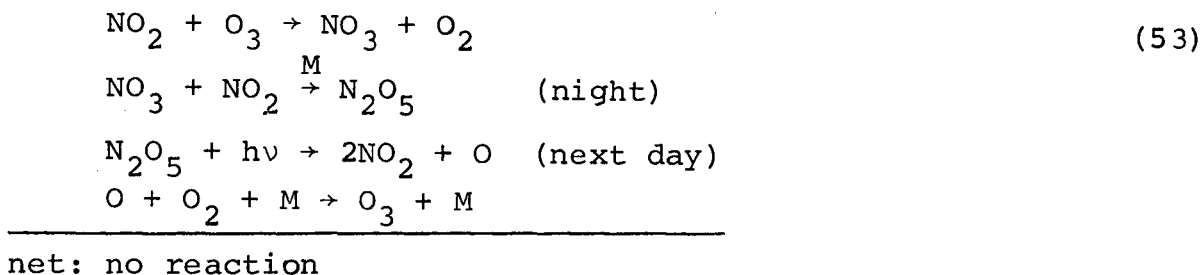
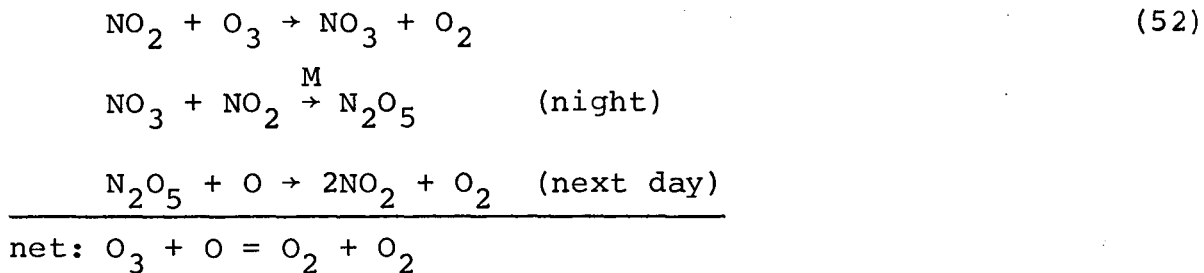
net: $2\text{O}_3 + h\nu(\text{VISIBLE}) \rightarrow 3\text{O}_2$

This reaction is driven by visible light, which is abundant at low elevations (unlike the radiation required to produce oxygen atoms). This catalytic cycle, too, may involve a non-catalytic competing reaction

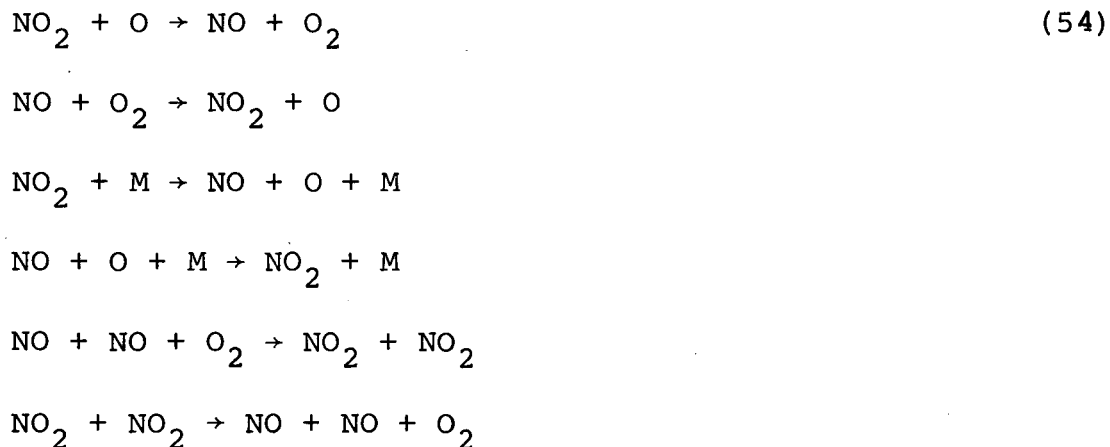


net: no reaction

At night NO_3 adds to NO_2 to form N_2O_5 . The next day N_2O_5 is destroyed by both oxygen atoms and by photolysis, one of which destroys ozone and the other is neutral

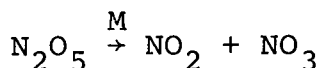
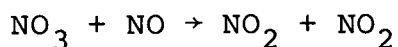
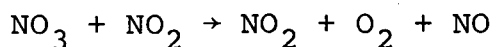
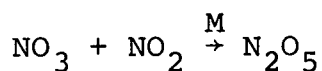


The rate constants for the following reactions

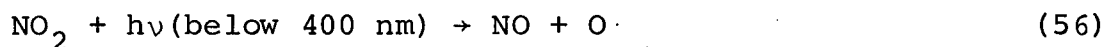


have been critically evaluated and summarized ^{by} Baulch and coworkers at Leeds University.⁴² This volume should be used in the same way as that of reference 8; new data should be added to this critical compilation; and the status of each reaction should be based on the sum of new data and old.

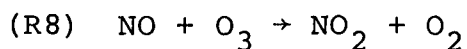
The following reactions



have been critically reviewed and tabulated in reference 7. The primary photochemical processes in the photolysis of nitrogen dioxide have been reviewed in detail by Leighton⁴³



The reaction of nitric oxide with ozone has been studied over a range of temperature in three cases⁴⁴



An interesting feature about this reaction is that a fraction (depending on pressure) of the product NO_2 molecules emit chemiluminescent light, which can be used as a sensitive analytical method for either NO or O_3 . The values of the rate constants in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ as found by three investigators are:

$$1.33 \times 10^{-12} \exp(-2.5/RT) \quad \text{ref. 44a}$$

$$0.95 \times 10^{-12} \exp(-2.46/RT) \quad \text{ref. 44b}$$

$$1.97 \times 10^{-12} \exp(-2.55/RT) \quad \text{ref. 44c}$$

These three investigations cover a wide range of reactant pressure and temperature, 198-345°K, and they agree quite satisfactorily with each other and with values observed at room temperature.^{44d}

The rates of photolysis of NO_3 and N_2O_5 and the rates of reaction of oxygen atoms with N_2O_5 are not known. Whether the reaction $\text{NO}_2 + \text{O}_3$ during the day leads to ozone destruction or not depends respectively on whether NO_3 is dissociated as $\text{NO} + \text{O}_2$ or $\text{NO}_2 + \text{O}$. During the night the reaction $\text{NO}_2 + \text{O}_3$ leads to N_2O_5 , and whether this leads to ozone destruction or not depends on the relative rates (during the next day) of the reactions



In summary, the rate constants for the key NO_x catalytic cycle ($\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$, $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$) are fairly well known, but some of the reactions of the secondary cycle initiated by $\text{NO}_2 + \text{O}_3$ have not yet been adequately determined in the laboratory.

Apparently there are no measurements of the oxides of nitrogen in the stratosphere. The concentration of nitric oxide at 70 km has been observed to be about 50 parts per billion⁴⁵ (ppb, parts in 10^9). Nitrogen dioxide has been demonstrated to be present in the lower stratosphere by infrared absorption^{46,47}, but quantitative data were not obtained. In the troposphere⁴⁸ the oxides of nitrogen are about one to four ppb, soil bacteria are the principal source, and rainfall is the principal mechanism for removal of NO_x in the form of nitric acid or dissolved nitrates. With a ground source and upper tropospheric sink (dissolved nitrates), the gradient of

NO_x is a decrease with increasing elevation in the troposphere. The boundary value of NO_x at the tropopause must be about one ppb.⁴⁸ The boundary value at the stratopause must be about 50 ppb.⁴⁵ The direction of the diffusion flux is downward throughout the stratosphere, and its mole fraction surely lies within the range of one to 50 ppb. These general considerations suggest that we arbitrarily assume the natural stratosphere to contain 10 ppb and 100 ppb for model calculations of the effect of NO_x on the ozone profile.

One of the observed ozone curves in Figure 8 is reproduced and given in Figure 10. The ozone profile calculated for uniform backgrounds of NO_x at 10 ppb and at 100 ppb are also given in Figure 10. It is immediately obvious that uniform distributions of NO_x between 10 and 100 ppb are sufficient to account for the ozone deficit shown by Figure 8. Crutzen⁴ and Johnston^{1,2} have shown that non-uniform distributions of NO_x averaging respectively 12 and 6.6 ppb account very well for the actual ozone profile in the upper, photochemically active stratosphere.

Conclusion: The oxides of nitrogen (NO and NO_2) at an average mole fraction of about 10^{-8} in the stratosphere are sufficient to account for the ozone deficit shown by Figure 8.

Nitric acid.--From its infrared absorption spectrum, nitric acid has been observed in the lower stratosphere.^{47,49} It is formed⁵⁰ by the bimolecular association

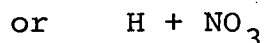


which is in its transition region between third order and second order kinetics. (The rate constant is not second order and it is

not third order, but it is variable between these limits.) This rate constant under stratospheric conditions is uncertain by a factor of three or so. Nitric acid is both formed and destroyed by hydroxyl radicals

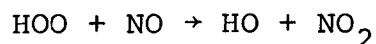
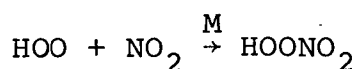
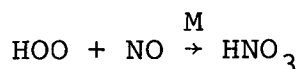
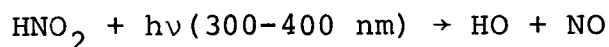


The rate constant for this reaction is known. Nitric acid is photolyzed by ultraviolet radiation



Wayne⁵¹ has suggested that the primary product may be a hydrogen atom, instead of the hydroxyl radical, at short wavelengths, but this suggestion has not yet been tested. Nitric acid vapor has an extremely large light-absorption cross section (about 10^{-17} cm^2) around 200 nm. The quantum yield as a function of wavelength is not known, and thus the rate of photolysis is not known. However, if the quantum yield is close to unity below 250 nm then we can make semi-quantitative statements about the balance between HNO_3 and NO_2 in the stratosphere: (1) The steady state between HNO_3 and NO_2 favors HNO_3 in the lowest stratosphere and favors NO_2 above about 30 km. (2) The rate of attaining the steady state is slow (years) in the lowest stratosphere and relatively fast ^(months) above about 30 km. There is a great need to establish the values of the rate constants in this system.

A number of other reactions in the mixed HO_x, NO_x system have been discussed, but the rate constants have not been measured, such as



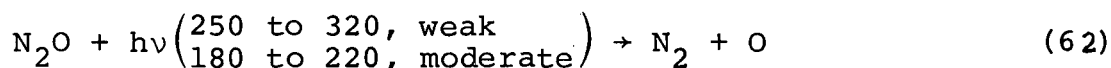
Sources of NO_x

Sources of natural NO_x.--Up to this point it has been argued that the ozone deficit is a real problem, that atmospheric motions, excited neutral oxygen, O₂ (¹Δ), O₂ (¹Σ), and O(¹D), and the HO_x reactions are insufficient to account for the ozone deficit, and that the NO_x reactions are sufficient to explain the ozone deficit if the natural NO_x background is the order of magnitude of 10⁻⁸ mole fraction. Now the natural sources of NO_x in the stratosphere are considered.

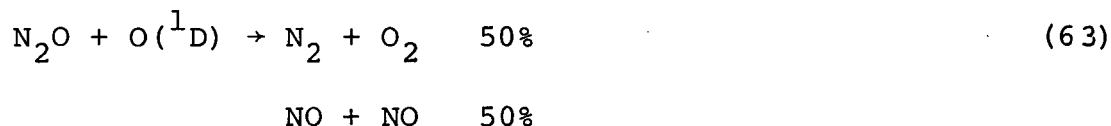
If there were no sources or sinks of NO_x in the stratosphere, then the flux and background concentration of NO_x could be calculated by means of the eddy diffusion equation from the boundary values of 50 ppb at the stratopause and about 1 ppb at the tropopause. Such a background is given by one of the curves in Figure 11.

terms of this model
 In \wedge the average NO_x background (that is, the total column of stratospheric NO_x divided by the total column of all stratospheric gases) is 2.3 ppb, and this is the minimum value, consistent with the boundary conditions. The flux for this model is 0.015×10^8 molecules $\text{cm}^{-2} \text{sec}^{-1}$ if the diffusion constant K_z is $10^3 \text{ cm}^2 \text{sec}^{-1}$, and it is 0.15×10^8 if K_z is 10^4 , presumably the range to be expected in the stratosphere.^{31b}

There is a recently-recognized natural source of NO_x inside the stratosphere: Crutzen⁵, McElroy⁵¹, Nicolet.⁵² Bacteria in the soil and perhaps in surface ocean waters produce a small amount of nitrous oxide N_2O as a part of the nitrogen cycle. Nitrous oxide resembles carbon dioxide in many respects. It is virtually inert in the troposphere, and it has a natural background value of 0.25 parts per million, ppm. It diffuses up into the stratosphere where it is photolyzed



and where it reacts with singlet oxygen atoms⁵³



The flux of NO into the stratosphere from this source, according to Crutzen, is between 0.29×10^8 molecules cm^{-2} ($K_z = 10^3$, $k_5 = 8 \times 10^{-11}$) and 1.5×10^8 ($K_z = 10^4$, $k_5 = 4 \times 10^{-11}$). These sources produce a steady-state of NO_x in the troposphere as given by Figure 11. These quantities of NO_x are large enough to cut the clean-air ozone in half and to account for the ozone deficit.

Figure 11 also gives a curve, Johnston.^{1,2} This estimate of the NO_x background was deduced as a result of a systematic exploration of the effect of NO_x on the steady-state ozone profile. Since the HO_x reactions were shown to contribute only one or two percent to ozone destruction, these reactions were omitted. The steady-state calculations were made with a narrow grid of elevation (every kilometer from 15 to 50), a narrow grid of solar radiation (every nm from 190 to 400 nm), a narrow grid of solar angles (every 5 degrees averaged over 24 hours), a standard pressure and temperature model for the stratosphere, and the standard time was the solar equinox. The rate constants used were based on known reactions with rate constants established in the laboratory. There were no adjustable parameters. Thus the method could be used to explore the effect of one unknown parameter, namely the NO_x background. Although a uniform NO_x background is a highly improbable distribution, model calculations were made for a wide range of uniform distributions with mole fractions of NO_x varying from 10^{-11} to 10^{-6} . A large number of calculations were made with non-uniform distributions of NO_x , where the distributions were selected with an eye to a 50 ppb boundary value at the stratopause, to a one ppb boundary value at the tropopause, to a natural source (such as N_2O) in the body of the stratosphere, and to a natural sink (HNO_3) in the lowest stratosphere. Ozone profiles (calculated on an absolute basis) were compared with observed profiles⁵⁴ with respect to shape in the upper half of the stratosphere, the total vertical column, and the elevation of the maximum ozone concentration. The selected background distribution is compared with Crutzen's distributions

and the diffusion model in Figure 11. Crutzen included HNO_3 in his inventory of NO_x and I excluded it. This different method of Bookkeeping accounts for the large difference between us in the lower stratosphere. In other respects the agreement between Crutzen and ^{Johnston} \wedge as to the natural background is rather good, although they were derived in considerably different ways. (This background was used in the Science article² and in the UCRL report¹ to demonstrate that the extent of vertical spread of artificial NO_x in the stratosphere is itself an important variable in this problem: For a given stratospheric load of NO_x added to this natural background, the reduction in ozone, steady state calculation, varied between 3 per cent and 50 per cent, depending on the thickness of spread of the artificial NO_x .)

A calculation of the diffusion of N_2O into the stratosphere and its degree of conversion to NO there has also been made by Nicolet⁵² and by McElroy.⁵¹ Their results and Crutzen's are:

Range of calculated NO_x flux in units of molecules $\text{cm}^{-2} \text{sec}^{-1} \times 10^8$	Author	Ref.
0.29 to 1.5	Crutzen	5
1.5 \pm 1.0	Nicolet	52
0.25 to 0.65	McElroy	51

McElroy compared the limited data on the observed N_2O profile in the stratosphere with the prediction made by different values of the vertical diffusion coefficient K_z . He obtained his best agreement of calculated and observed N_2O profile in the stratosphere with $K_z = 10^3$, for which the associated value of the flux of NO in

the stratosphere is the low extreme, 0.25×10^8 molecules $\text{cm}^{-2} \text{sec}^{-1}$. The elevation of maximum rate of NO formation was 24 kilometers.

Conclusions: (1) The reaction of nitrous oxide with singlet oxygen atoms is the most important known source of NO_x in the natural stratosphere. (2) This source strength is adequate to build up a steady state of NO_x in the stratosphere high enough to account for the observed ozone deficit. (3) Three different investigators obtained comparable estimates for the NO_x source strength.

Comparison of the chemical mechanisms for ozone balance.--For the two models of an NO_x background shown in Figure 11 (diffusion model and Johnston's model in the Science article²) and for a model for stratospheric water, the relative effects of NO_x , O_x , and HO_x on the integrated column rate of ozone destruction is given in Table 1. It can be seen that in the present natural stratosphere, NO_x is the dominant agent for ozone control. It is more than 50 times as important as the water reactions.¹²

Artificial source of NO_x from the SST.--The exhaust gases of the SST contain some NO_x . Various estimates of this quantity have covered a fairly wide range. A definite way to define the quantity is in units of grams of NO from the exhaust per kilogram of fuel burned. In these units the SCEP report⁴¹ gave 42 grams NO per kilogram of fuel. I used the figure^{1,2} of 14.8 grams of NO per kilogram of fuel. A number of calculations have been made based on a fleet of 500 SST or Concordes⁵⁵, but of course the number of craft is another independent variable. Recent measurements reported by McAdams⁵⁶ show that the SST would have emitted between 20 and 30 grams of NO per kilogram of fuel, which is 5 or 10 times greater than a number of estimates made in the spring of 1971.

Table 1. Column contributions to gross rate of formation of ozone for different models of background oxides of nitrogen. (Units 10^{11} molecules cm^{-2} sec^{-1})

Process	ozone rate	
	model 1	model 2
O_2 photolysis	+91	+108
NO_x	-64	-88
O_x	-26	-19
HO_x	-1.4	-1.4

model 1. 1 ppb at 15 km, 50 ppb at 45 km, logarithmic interpolation (similar to diffusion model of Figure 10).

model 2. Item 27, Table 1, reference 2.

regularly
 If 500 SST flew ^{regularly} in the stratosphere 7 hours per day, there would eventually develop a new steady-state distribution of NO_x in the stratosphere. The new artificial flux of NO would spread horizontally and vertically to a varying degree. The final NO_x inventory of the stratosphere would depend on numerous complex atmospheric motions and many photochemical reactions. A large problem would be the nitric acid reservoir and vertical distribution. This complex superposition of atmospheric motions and photochemistry constitutes an extremely difficult problem, which eventually should be worked out.

On the other hand, it is not necessary to work out this extremely complex problem to get an estimate of the size of the problem itself. 500 SST each burning 66 tons of fuel per hour, each flying 7 hours per day in the stratosphere, and each emitting 15 grams of NO per kilogram of fuel would constitute a world-wide average flux of NO of 1.5×10^8 molecules $\text{cm}^{-2} \text{sec}^{-1}$ (If the number of planes, fuel per hour, hours per day, or NO in g/kg are other than the values given above, this figure can be scaled up or down accordingly). This artificial flux is equal to Nicolet's estimate of the natural NO_x flux (although he indicated uncertainty by a plus or minus 67%). This flux of 1.5×10^8 is equal to Crutzen's estimate of the maximum natural value and it is over 5 times greater than his low estimate of 0.29×10^8 molecules $\text{cm}^{-2} \text{sec}^{-1}$. The world-wide average SST flux of NO into the stratosphere is 2.3 times greater than McElroy's maximum estimate of the natural NO flux, and it is 6 times his low estimate.

To be sure, the NO_x from the SST encounters all the complexities of stratospheric dynamics and photochemistry, but the natural NO produced from N_2O around 24 kilometers is also subject to these complexities of stratospheric dynamics and photochemistry. The present NO_x flux (subject to all the stratospheric complexities) builds up to such a point that it seems to be the agent that reduces the otherwise pure air ozone column by about a factor of two on a world wide basis. If the artificial flux is equal to or up to six times larger than the natural flux, then as a first approximation one can expect stratospheric NO_x to increase by a factor between two and seven. If one measure of NO_x (the natural flux) has reduced the natural worldwide ozone by about a factor of two, then two to seven measures of NO_x (the natural plus the artificial flux) threatens to reduce the ozone shield by another very large amount, a 25 to 50 percent reduction on a world wide basis appears to be the size of the threat.

The NO_x flux from the natural N_2O mechanism as estimated by Crutzen and ^xby McElroy is indicated by a bar graph in Figure 12, where high and low estimates are given. The expected fluxes of NO_x from 500 Concorde⁵⁵ and from 500 SST are also given on this figure. It can be easily visualized from Figure 12 that the projected artificial source of NO_x from the SST is equal to or greater than the natural source of NO_x . It is difficult to conceive a model that would lead one to expect the artificial NO_x to behave quite differently from the natural NO_x .

Conclusions: It is easier to get a grasp on the magnitude of the threat to the ozone shield from artificial NO_x if one compares natural and artificial source strengths of NO_x , instead of trying to compare the stratospheric inventory of NO_x before and after SST flights. In terms of relative source strengths, it appears that 500 SST will inject NO_x into the stratosphere at a rate equal to or several times greater than the natural source strength. Since the natural NO_x already exerts the dominant role in controlling the stratospheric ozone inventory, such an increase in source strength will probably bring about a large reduction in the world's ozone shield.

Discussion

In previous reports^{1,2}, I have presented evidence that the oxides of nitrogen, which previously had been neglected, are an important variable in stratospheric photochemistry, and it may not "be neglected."⁴¹ The evidence that NO_x is an important variable took the form of several different model calculations; there was no attempt to solve the complete problem of all the stratosphere. One calculation (Tables 5 and 6 of reference 1) was based exclusively on chemistry; it showed that for the stratospheric range of temperature and pressure, and for the amount of NO_x that the SCEP report⁴¹ said would be added to the stratosphere, the rate of destruction of stratospheric ozone by NO_x (NO , NO_2) was faster than the rate of ozone destruction by O_x (O , O_2 , O_3) for 95% of range of independent variables, and the reaction rates were fast

enough to be significant for 90 per cent of the range of these variables. Another line of calculations involved about an equal blend of chemistry and atmospheric structure; it was shown¹:

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

This report specifically illustrates that laboratory chemical kinetics can supply accurate predictions, both in the laboratory and in the atmosphere. However, one must follow strict rules to do so. One must adhere to measured and verified rate constants. One must never use unknown rate constants as adjustable parameters in atmospheric calculations.

In previous reports¹⁻⁶ available rate constants were used to calculate the direction of change of stratospheric ozone upon addition of NO_x . A wide range of NO_x distributions were considered, and in all cases additional NO_x resulted in a decrease in stratospheric ozone. These calculations of the relative effect of increased NO_x are fairly insensitive to the absolute value of the pertinent rate constants. In this report an absolute value of the ozone concentration in pure air is calculated, and it is concluded that "something else" besides neutral oxygen species is dominant in reducing stratospheric ozone (compare similar conclusions in reference 4). This calculation depends on the absolute value of two rate constants and is thus sensitive to the accuracy of these quantities. If the ratio k_2/k_3 in conditions of the upper half of the stratosphere should turn out (after further, refined laboratory measurement) to be four-fold or more less than the value used here, then the "ozone deficit" argument would be largely eliminated, that is, NO_x would not now be dominant in the stratospheric ozone balance. Even so, the effect of large artificial additions of NO_x is subject to the considerations of the previous reports^{1,2,6}; large increases of NO and NO_2 as such would have a large effect on ozone, but large increases as HNO_3 would have a smaller effect.

In this problem, laboratory chemical kinetics serves in a role analogous to a grand jury: on the basis of current knowledge NO_x is an important variable in the stratosphere, it must be "brought to trial", it may not "be neglected". A grand jury does not attempt to prove guilt or innocence; it merely certifies whether a case should be tried. The CIAP program should serve the role of "trial

by jury" on this issue. Knowledge must be developed as to the concentration and distribution of NO_x in the stratosphere, as it is now and as it would be after full operation of the SST.

Acknowledgement

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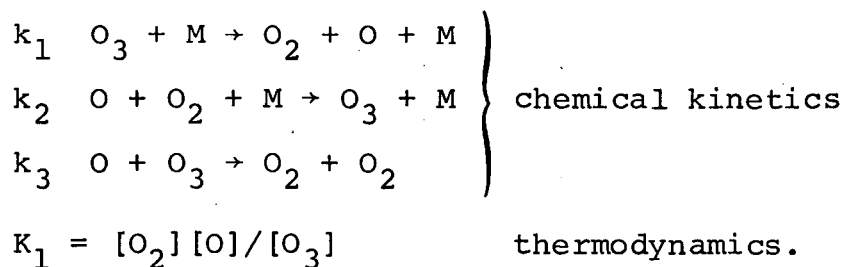
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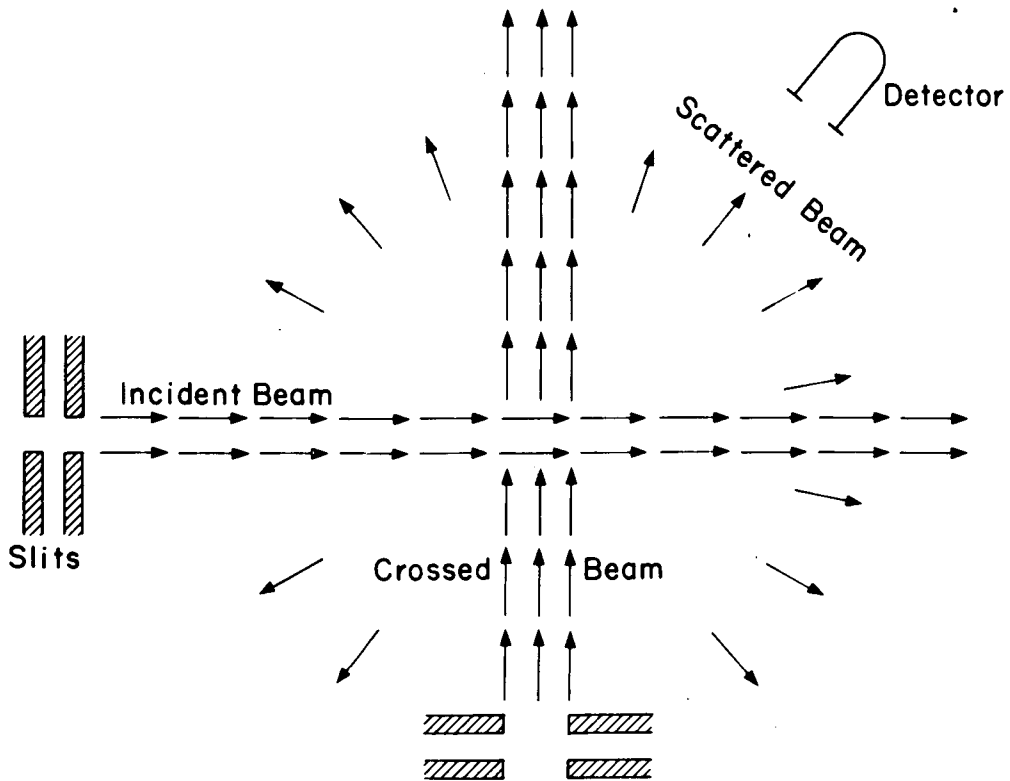
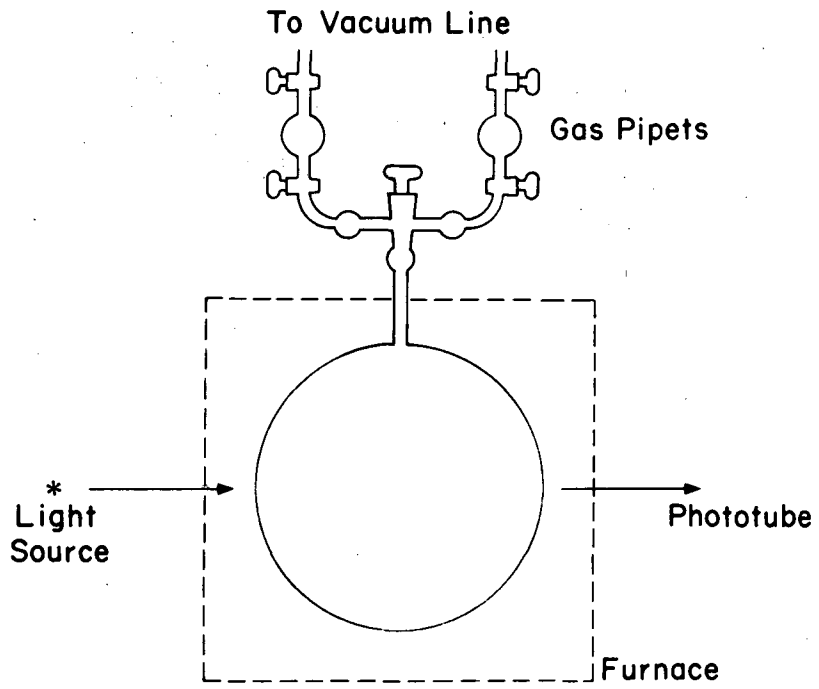
Titles to Figures

- Figure 1. Schematic diagram of a crossed molecular-beam apparatus and a constant-volume reaction flask, illustrating the range of quantities observed in gas-phase reaction kinetics.
- Figure 2. Experimental data for the unimolecular decomposition of nitrogen pentoxide, N_2O_5 , showing the large effect of the non-equilibrium distribution of N_2O_5 over its vibrational states when reaction occurs.
- Figure 3. Experimental data and calculated lines for the N_2O_5 catalyzed decomposition of ozone. The prediction of the rate of one laboratory reaction from laboratory measurements made on other reactions. Note the unusual rate law: $k[N_2O_5]^{2/3}[O_3]^{2/3}$.
- Figure 4. The observed vertical profile of $O_2(^1\Delta_g)$ and the profile calculated on the basis of photochemical constants observed in the laboratory.
- Figure 5. Consistency test for quality of data. The ratio of rate constants k_1/k_2 as observed in the laboratory and analyzed by NSRDS-NBS-20 compared to the equilibrium constant K_1 , obtained from JANAF thermochemical tables



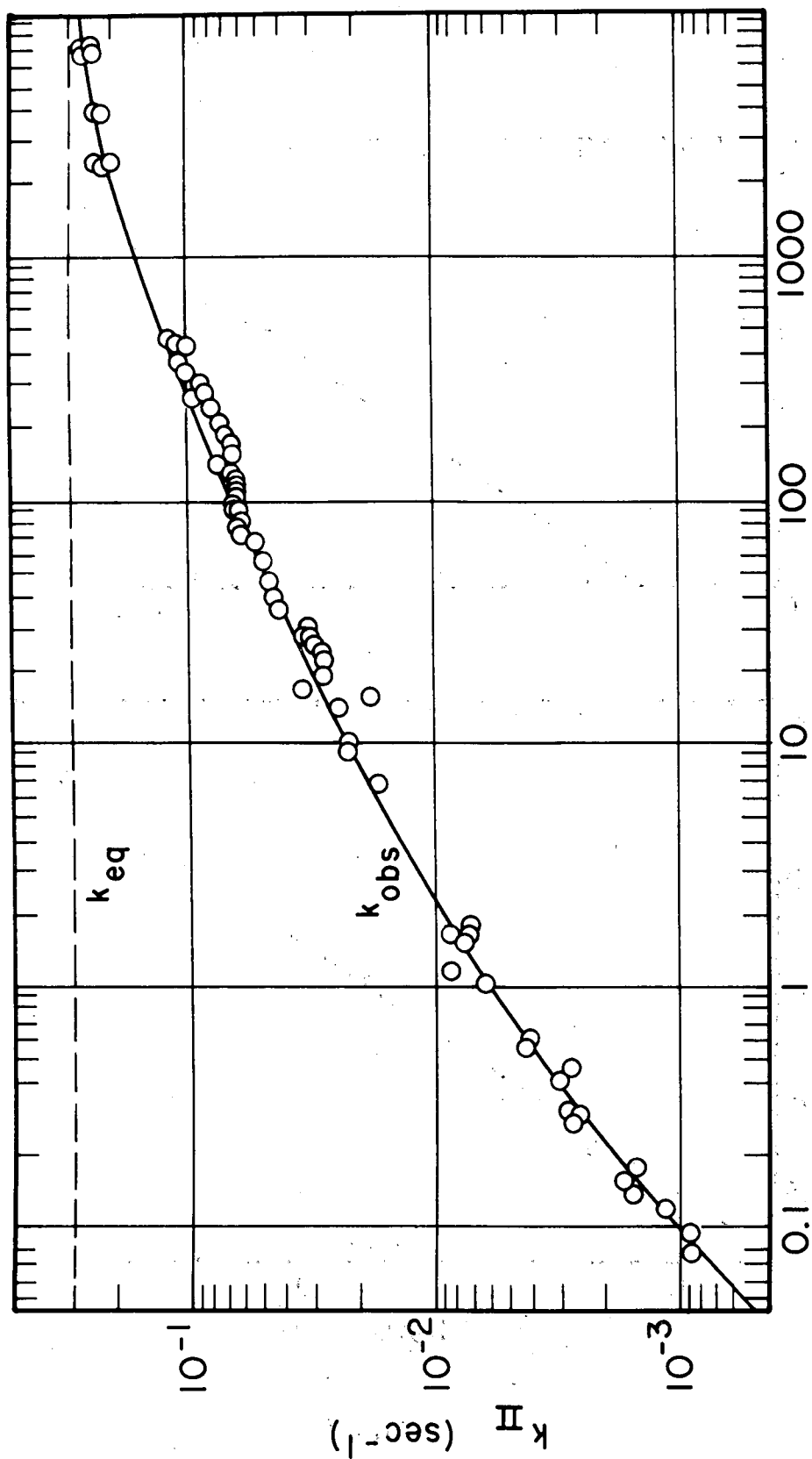
- Figure 6. Points, the observed values of k_2 ; line, k_2 calculated from $k_2 = k_1/K_1$ (Data points from NBS-20, reference 8).
- Figure 7. The collective data for k_3 (1906-1966) as reviewed in NBS-20, 0; data recently observed²⁰ at low temperatures, ●; the line used by references 1 and 2.
- Figure 8. Ozone profiles observed at Panama (9°N) and ozone profiles calculated from a model of pure dry air. The difference between the observed and calculated (pure air) curve is referred to as the "ozone deficit".
- Figure 9. Rate vectors in the ozone balance: A. Gross rate of formation of ozone from photolysis of oxygen; B. rate of destruction of odd oxygen (ozone) by chemical reactions; C. net rate of transfer of ozone by air motions. Cases I, II, III, local steady-state considering photochemistry, chemistry, and air transport. Cases IV, V, VI, unbalanced A, B, C leading to net increase in local ozone concentration.
- Figure 10. An ozone profile observed at Panama (9°N) and ozone profiles calculated for the equator with uniform NO_x mole fractions of 10 ppb and 100 ppb. NO_x is sufficient to account for the ozone deficit.
- Figure 11. Natural background of NO_x as deduced from various models and methods. Crutzen's models derived from the reaction of N_2O and $\text{O}(^1\text{D})$ in the stratosphere. Diffusion model based on boundary values of 50 ppb NO_x at stratopause and one ppb at tropopause. Johnston's model is entry 5, Table 17, reference 1 or entry 27, Table 1, reference 2.

Figure 12. Relative source strengths of NO_x in the stratosphere, including the natural source $[\text{N}_2\text{O} + \text{O}(^1\text{D})]$ as calculated by references 5 and 51 and the world-wide average source strength from 500 SST according to different estimations.



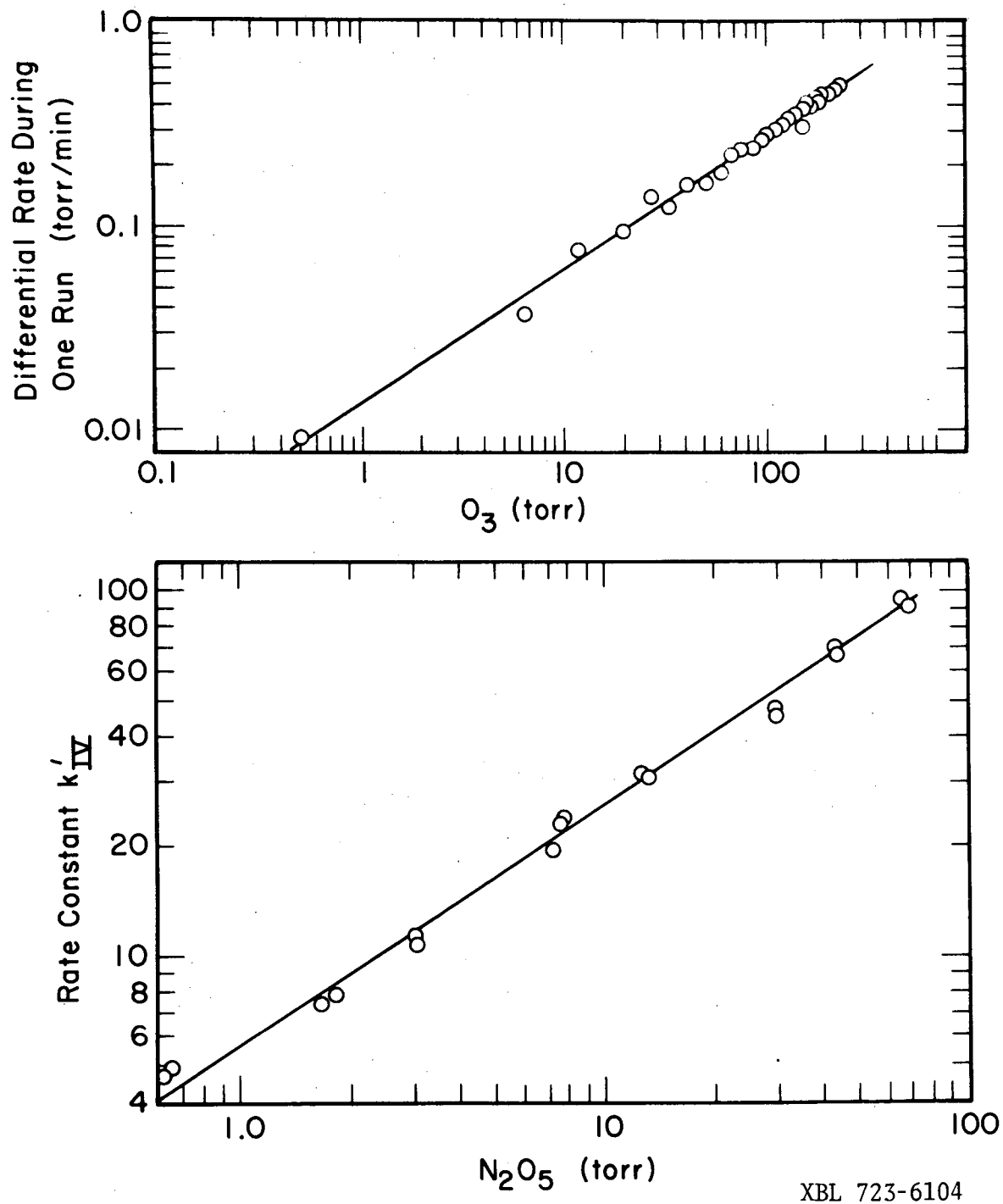
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Fig. 1.



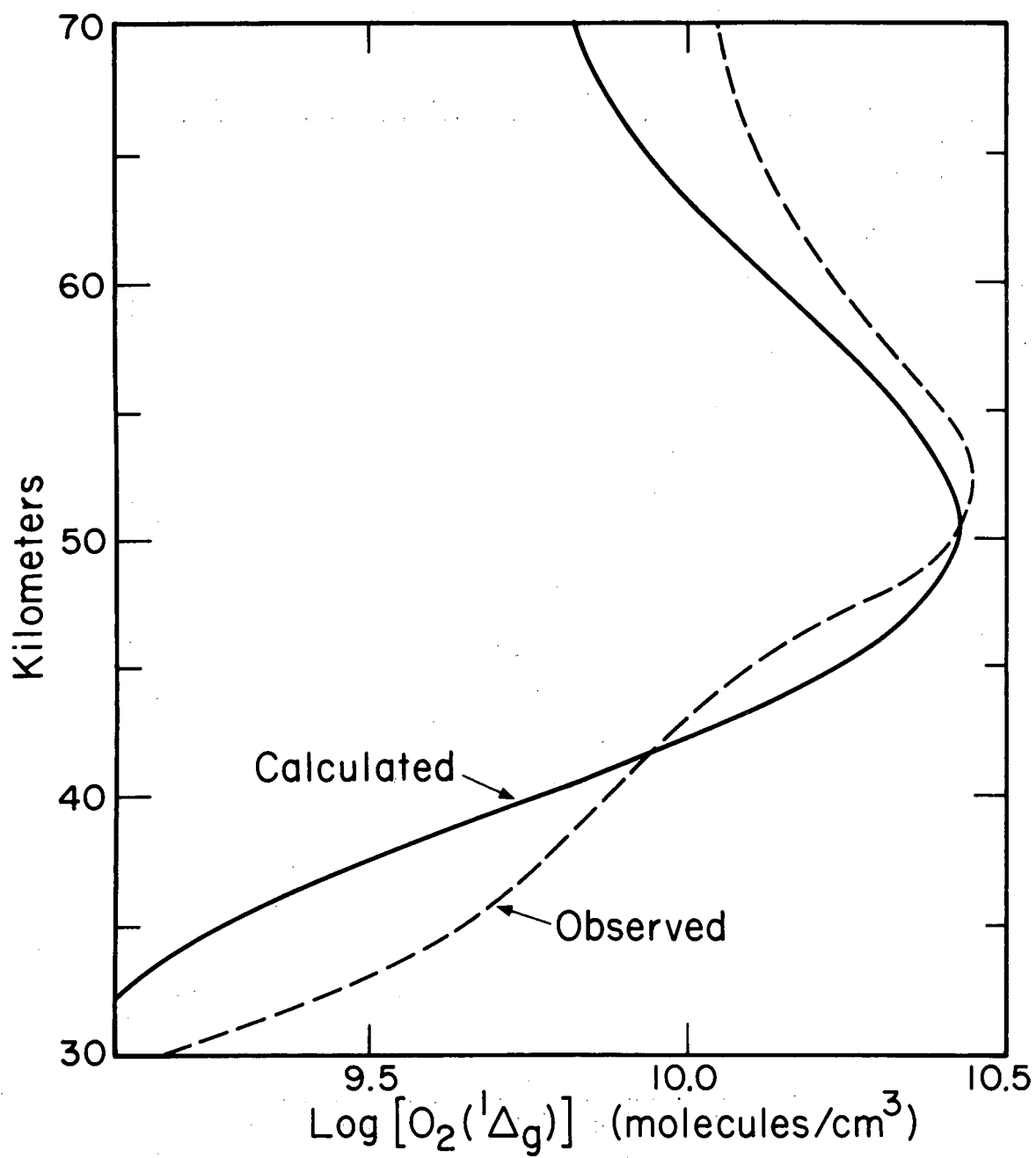
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Fig. 2.



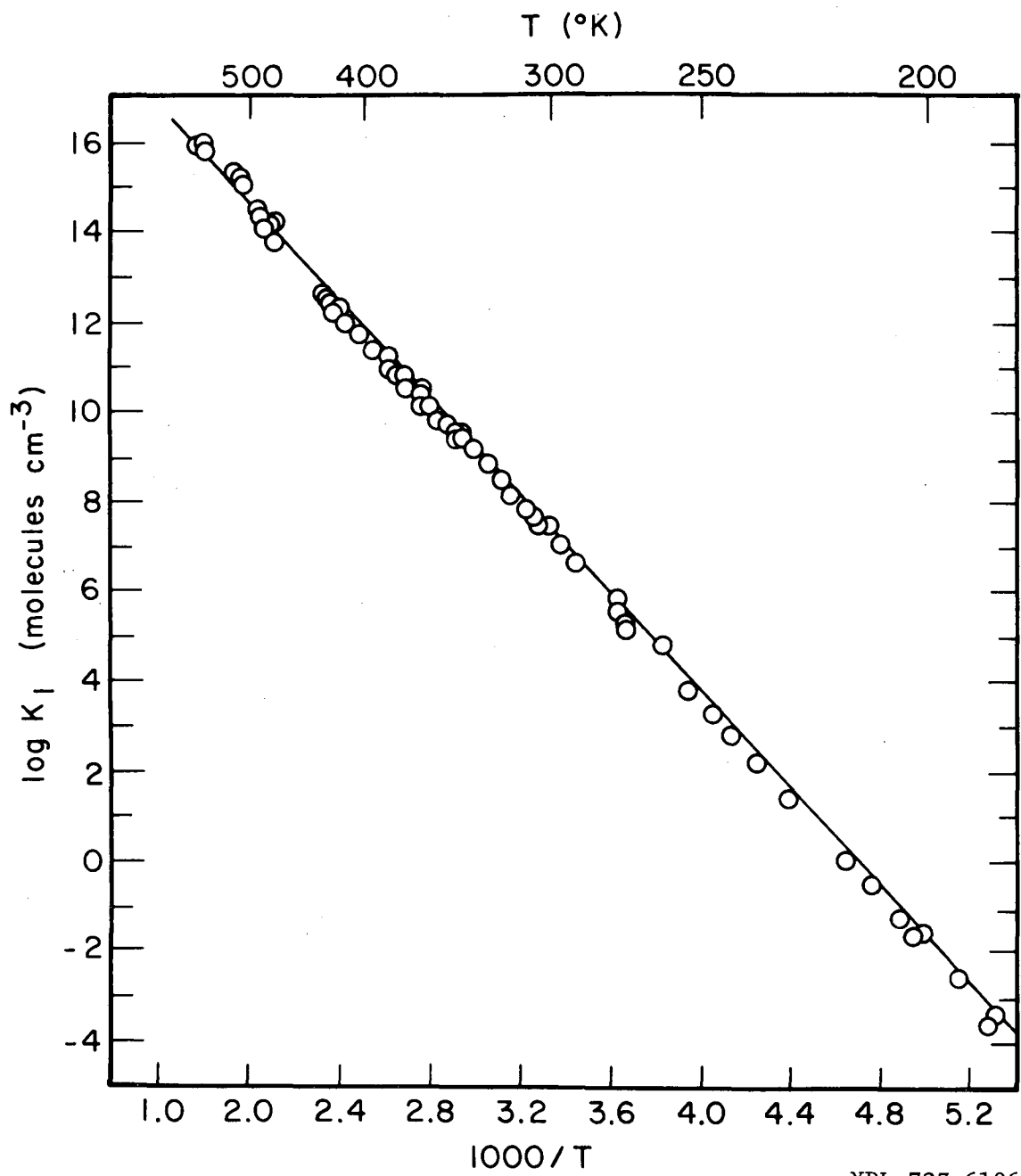
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Fig. 3.



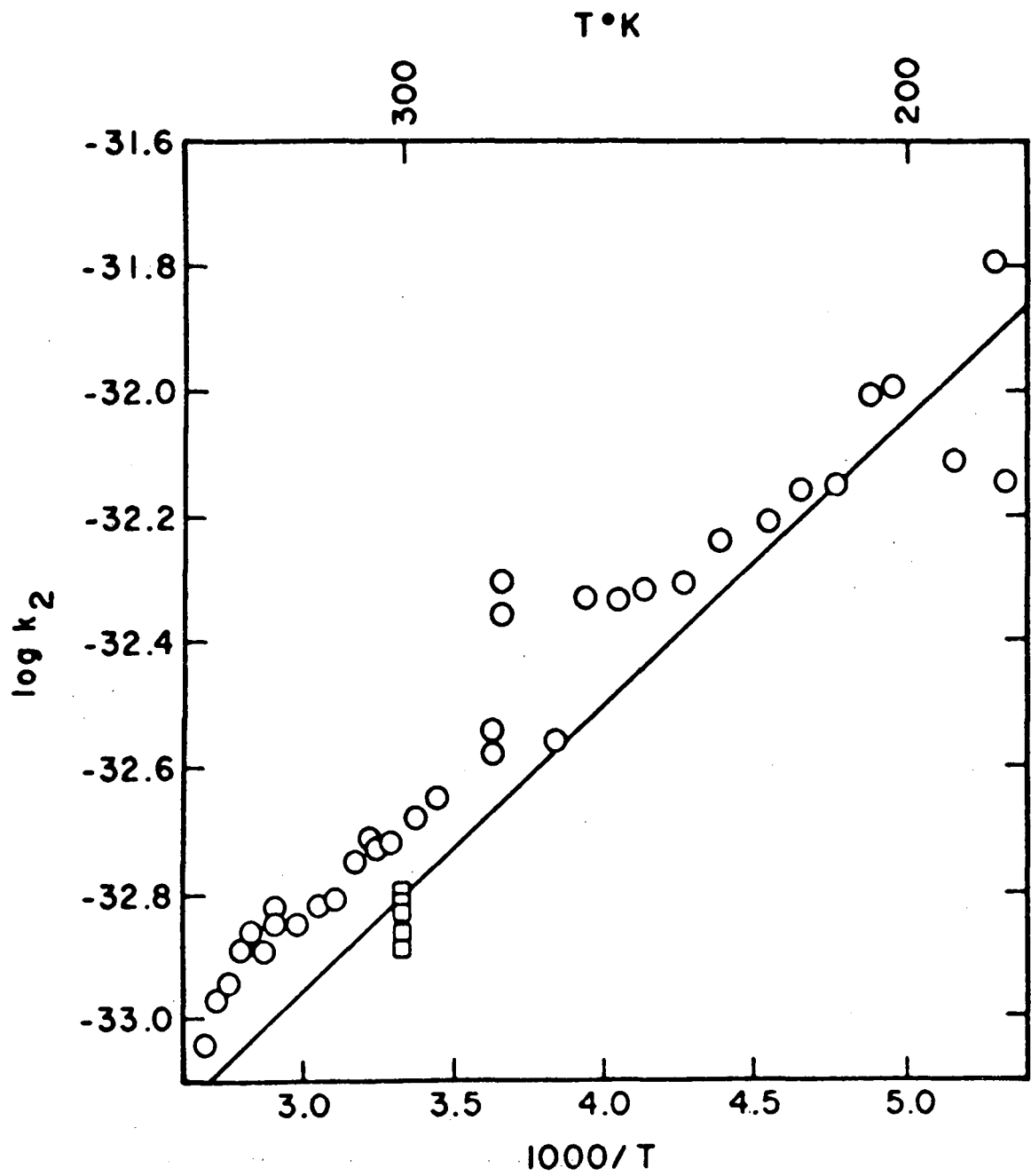
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Fig. 4.



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Fig. 5.



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Fig. 6.

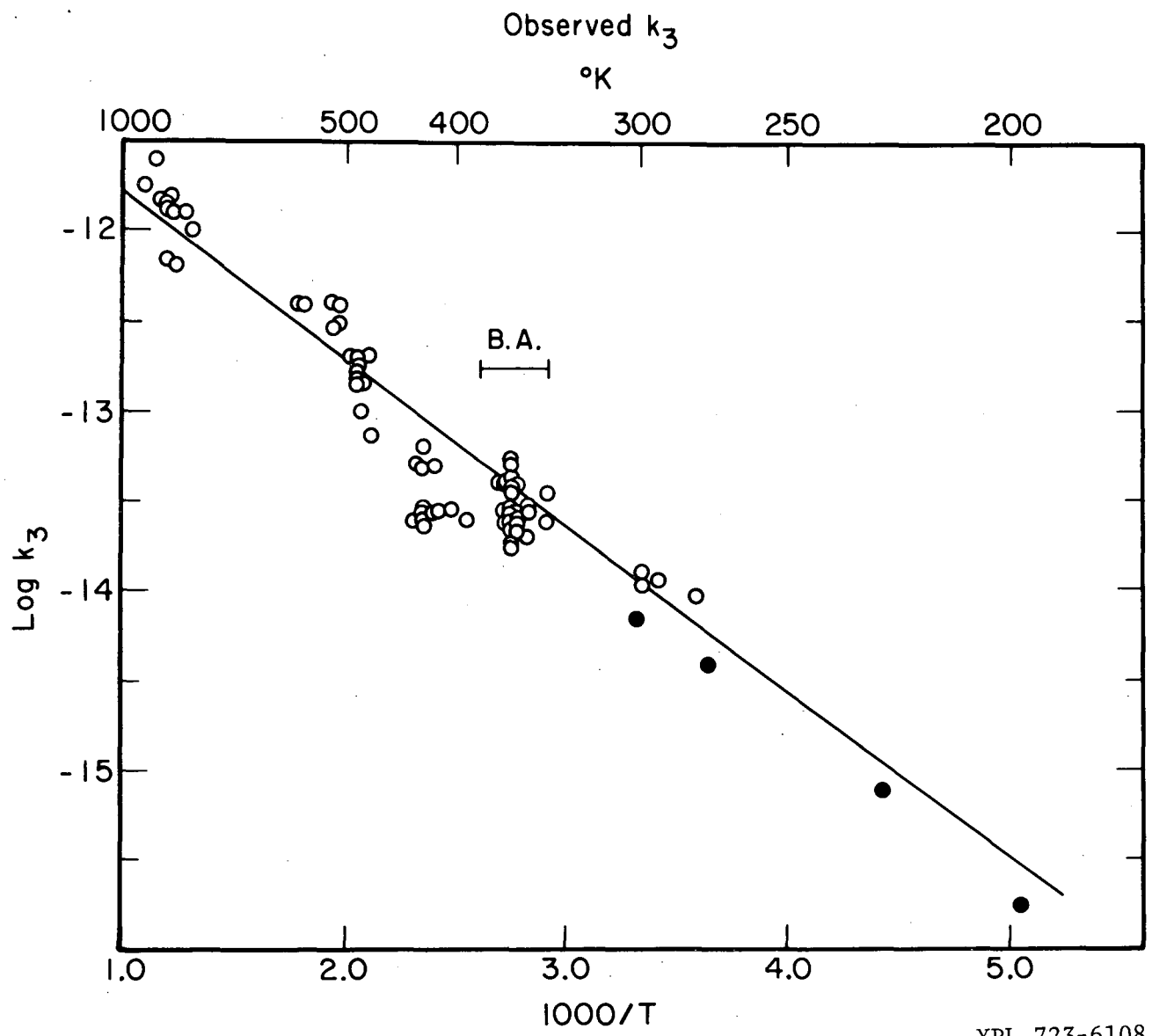
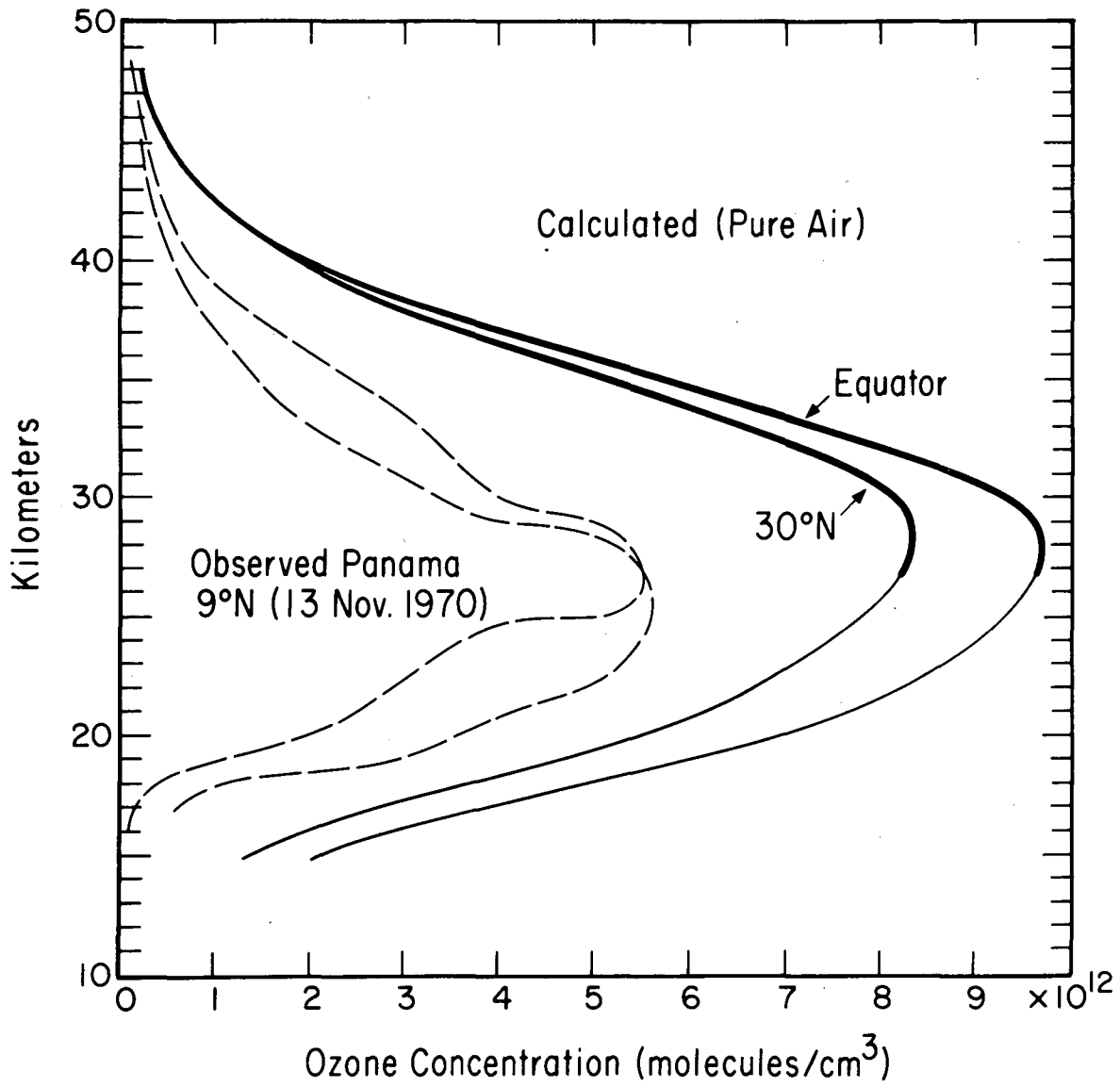
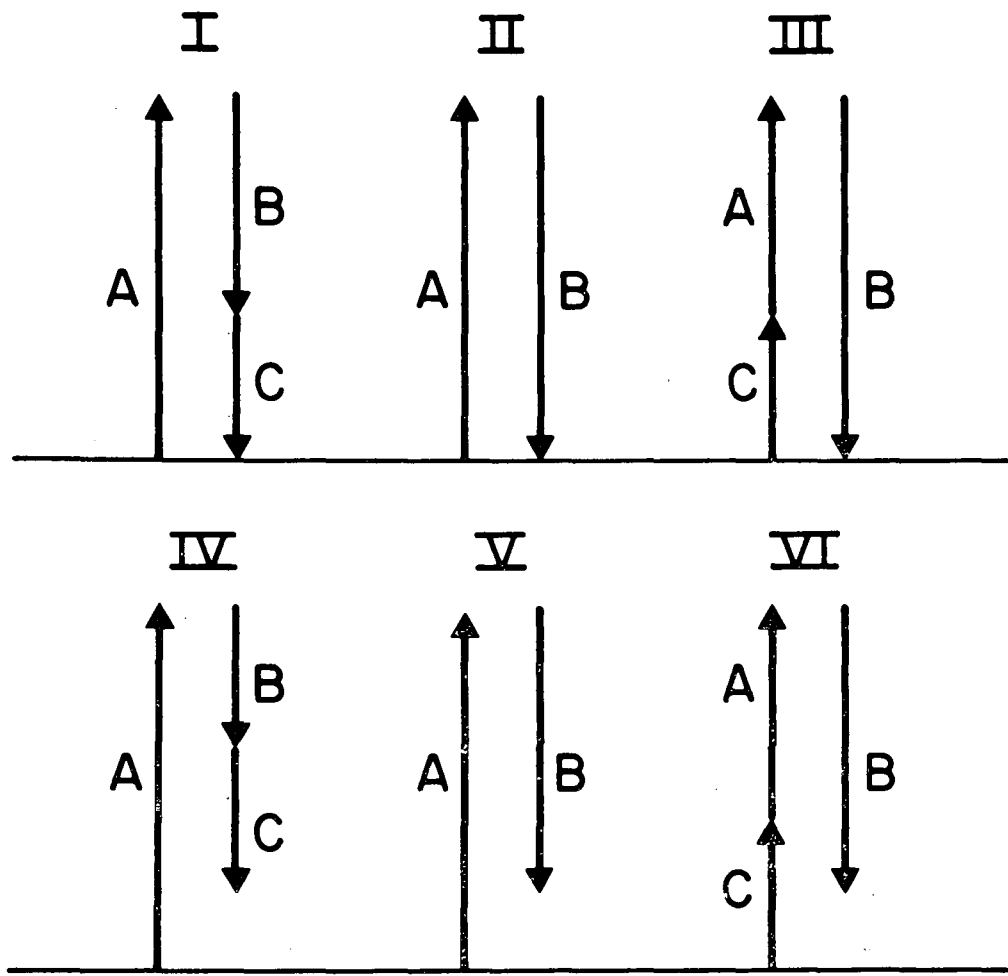


Fig. 7.



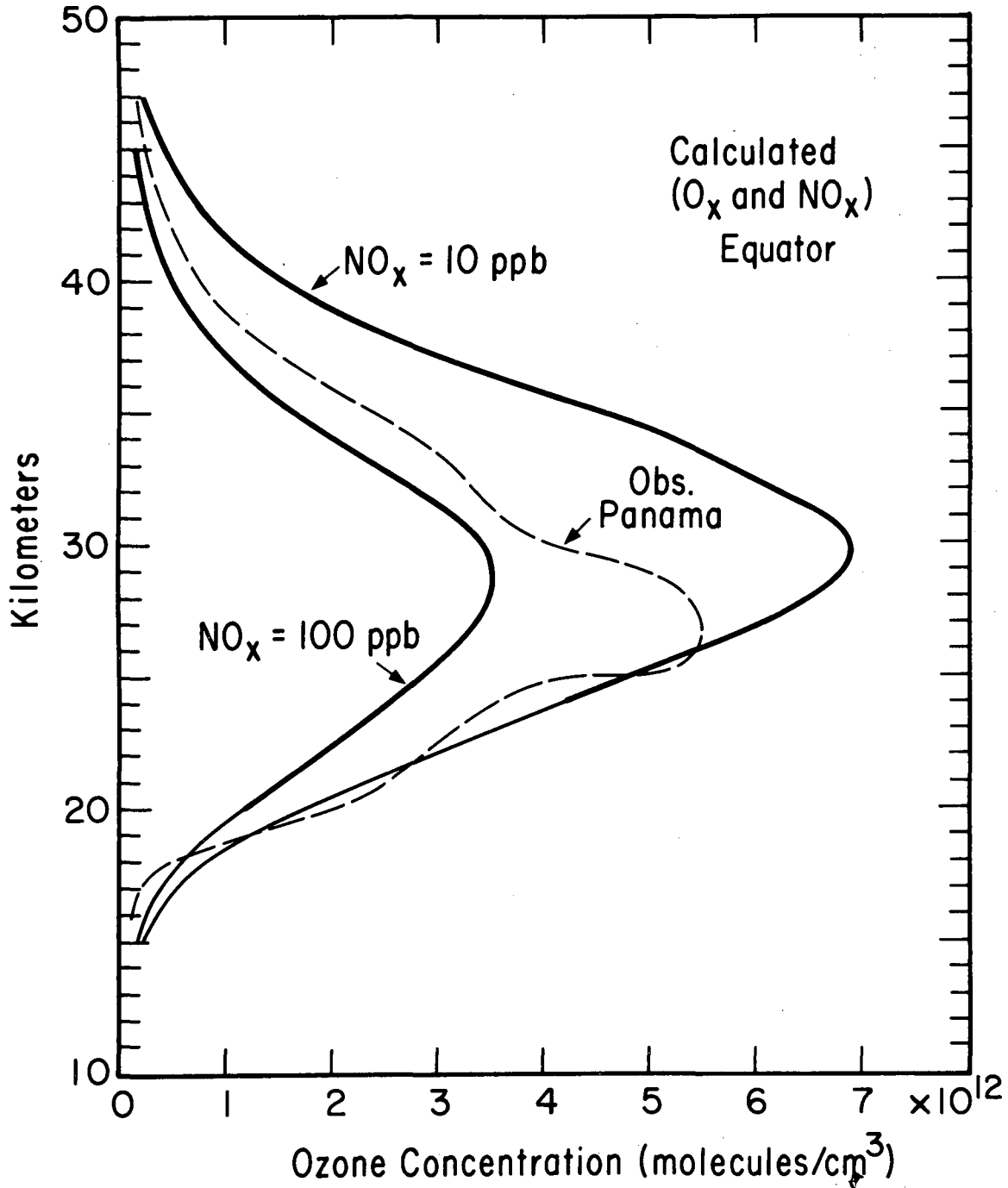
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Fig. 8.



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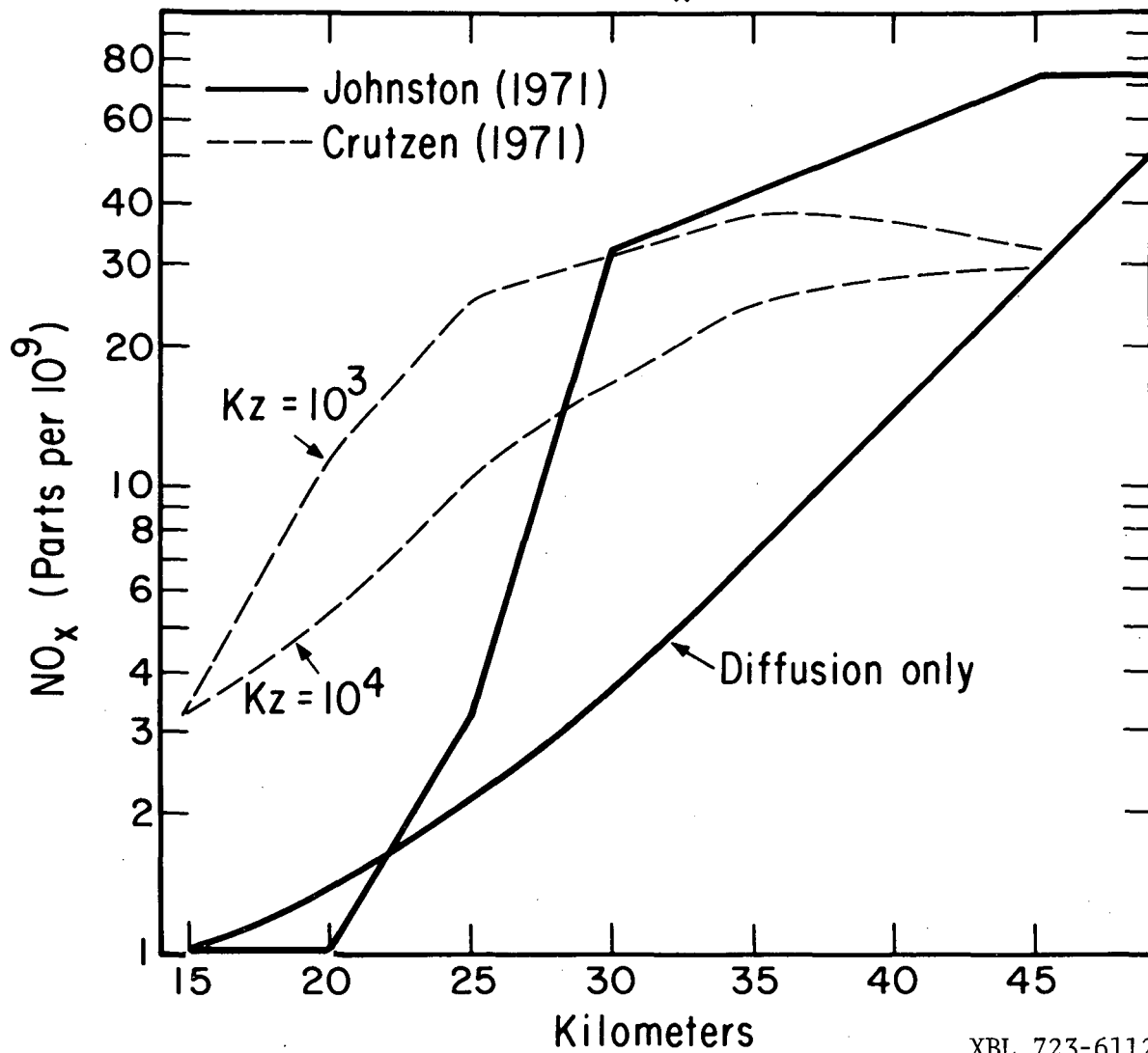
Fig. 9.



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Fig. 10.

ESTIMATES OF NO_x BACKGROUND



XBL 723-6112

Fig. 11.

Stratospheric NO_x Source Strength Worldwide Average

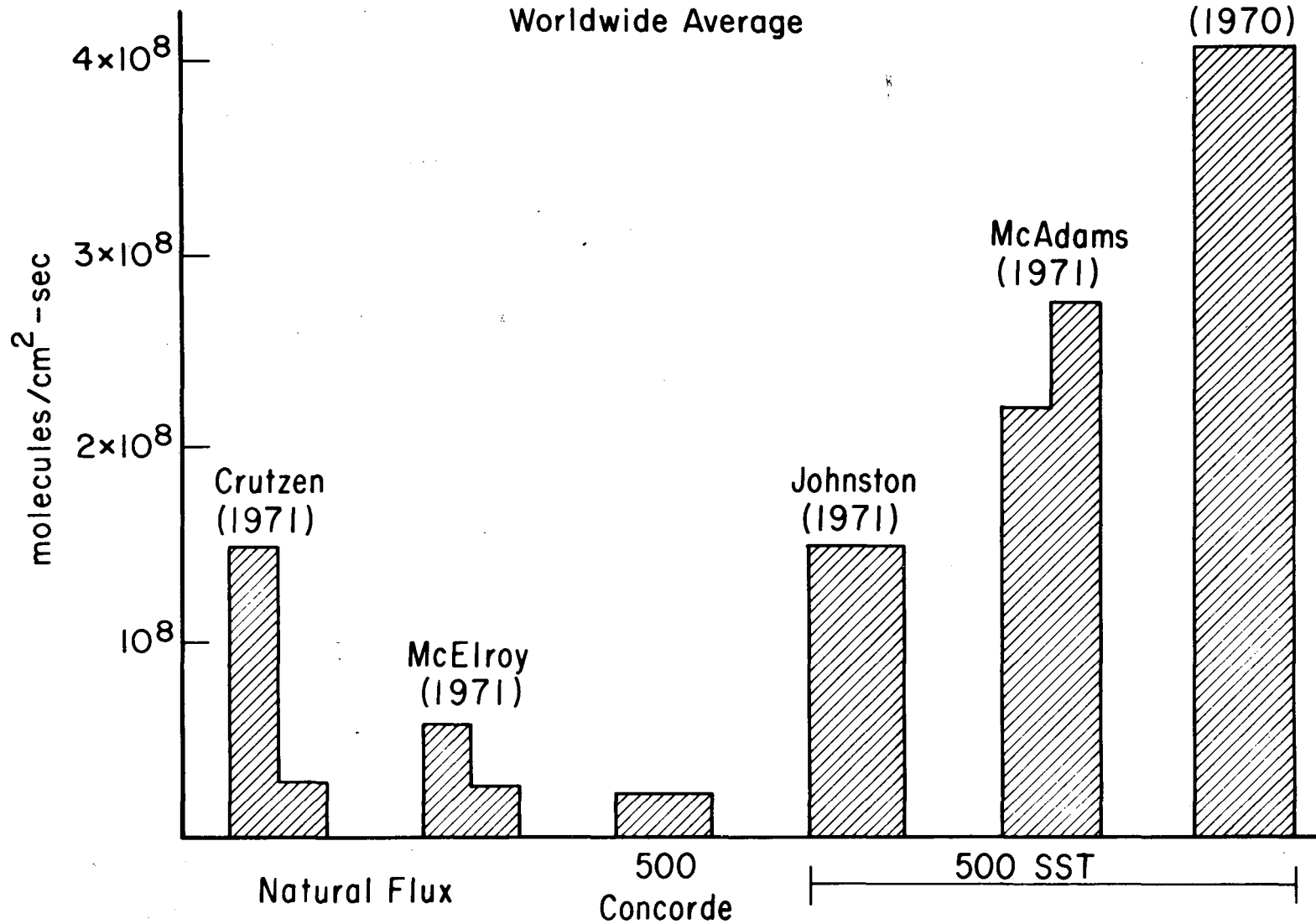


Fig. 12.

XBL 723-6113

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