

AD 741702

DNA 2835T

**RDA-TR-017-DNA
September 1971**

THE CHEMISTRY OF NITROGEN OXIDES AND OZONE IN THE DISTURBED D-REGION

**THIS WORK WAS SUPPORTED BY THE DEFENSE NUCLEAR
AGENCY UNDER NWER/SUBTASK DB001-06.**

H. A. Ory and F. R. Gilmore

**HEADQUARTERS
Defense Nuclear Agency
Washington, D.C. 20305**

Contract No. DASA01-71-C-0103

**This effort supported by Defense Nuclear Agency under Contract
Number DASA01-71-C-0103. These results were presented at
the DNA-HANE Symposium, 10-12 August 1971.**

**PREPARING AGENCY
R & D Associates**

**Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151**

**APPROVED FOR PUBLIC RELEASE
DISTRIBUTION UNLIMITED**



Destroy this report when it is no longer needed. Do not return to sender.

DNA 2835T

**RDA-TR-017-DNA
September 1971**

**THE CHEMISTRY OF NITROGEN OXIDES
AND
OZONE IN THE DISTURBED D-REGION**

H. A. Ory and F. R. Gilmore

**HEADQUARTERS
Defense Nuclear Agency
Washington, D.C. 20305**

**PREPARING AGENCY
R & D Associates**

Contract No. DASA01-71-C-0103

**APPROVED FOR PUBLIC RELEASE
DISTRIBUTION UNLIMITED**

THIS PAGE IS INTENTIONALLY LEFT BLANK.

SESSION NO	
POST	WHITE SECTION <input checked="" type="checkbox"/>
NO	DIFF SECTION <input type="checkbox"/>
ARRANGED	<input type="checkbox"/>
CLASSIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
DISC.	AVAIL. and/or SPECIAL
A	

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D		
<i>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</i>		
1. ORIGINATING ACTIVITY (Corporate author) R & D Associates Post Office Box 3580 Santa Monica, California 90403		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
		2b. GROUP
3. REPORT TITLE The Chemistry of Nitrogen Oxides and Ozone in the Disturbed D-region		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Topical Report		
5. AUTHOR(S) (First name, middle initial, last name) H. A. Ory and F. R. Gilmore		
6. REPORT DATE September 1971	7a. TOTAL NO. OF PAGES 42	7b. NO. OF REFS 12
8a. CONTRACT OR GRANT NO. DASA01-71-C-0103	9a. ORIGINATOR'S REPORT NUMBER(S) RDA-TR-017-DNA	
b. PROJECT NO. NWER CODE: XAXD		
c. Task and Subtask: B001	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) DNA-2835T	
d. Work Unit: 06		
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Director Defense Nuclear Agency Washington, D.C. 20305	
13. ABSTRACT <p>Chemical kinetic calculations are presented which describe the chemistry of nitrogen oxides and ozone in D-region air bombarded by an intense pulse of X-rays. Relatively late-time behavior is emphasized; early deionization processes are treated in a summary fashion. Special attention is given to the reactions of excited species, which have not been included previously, but which greatly affect the yields of NO, NO₂, and O₃. Results are given for various altitudes, bombardment intensities, and both day and night conditions. The reactions that mainly control the chemistry are identified, and the effects of the excited species are summarized.</p>		

DD FORM 1 NOV 65 1473

UNCLASSIFIED

Security Classification

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
D-region Ionization effects Radiochemistry X-ray High-altitude radiation effects HANE						

UNCLASSIFIED

Security Classification

ABSTRACT

Chemical kinetic calculations are presented which describe the chemistry of nitrogen oxides and ozone in D-region air bombarded by an intense pulse of X-rays. Relatively late-time behavior is emphasized; early deionization processes are treated in a summary fashion. Special attention is given to the reactions of excited species, which have not been included previously, but which greatly affect the yields of NO, NO₂, and O₃. Results are given for various altitudes, bombardment intensities, and both day and night conditions. The reactions that mainly control the chemistry are identified, and the effects of the excited species are summarized.

TABLE OF CONTENTS

	<u>Page</u>
Abstract -----	iii
1-1. Introduction -----	1
1-2. Initial dissociation, ionization, and excitation by the X-rays -----	1
1-3. Chemical reactions included in the calculations -----	3
1-4. Computational method -----	4
2-1. Results and discussion -----	6
3-1. Conclusions -----	16
References -----	19
Distribution list -----	21

LIST OF ILLUSTRATIONS

<u>Figure</u>	<u>Page</u>
2-1. Concentration variation produced by ionization pulse of 10^{10} ion pairs/cm. ³ at 60 km. during the night -----	7
2-2. Concentration variation produced by ionization pulse of 10^{10} ion pairs/cm. ³ at 60 km. during the day -----	8
2-3. Concentration variation produced by ionization pulse of 8.8×10^{11} ion pairs/cm. ³ at 60 km. during the night -----	9
2-4. Concentration variation produced by ionization pulse of 8.8×10^{11} ion pairs/cm. ³ at 60 km. during the day -----	10
2-5. Concentration variation produced by ionization pulse of 10^{10} ion pairs/cm. ³ at 80 km. during the night -----	11
2-6. Concentration variation produced by ionization pulse of 10^{10} ion pairs/cm. ³ at 80 km. during the day -----	12
2-7. Concentration variation produced by ionization pulse of 10^8 ion pairs/cm. ³ at 100 km. during the night -----	13
2-8. Concentration variation produced by ionization pulse of 10^{10} ion pairs/cm. ³ at 100 km. during the night -----	14
2-9. Concentration variation produced by ionization pulse of 10^{10} ion pairs/cm. ³ at 100 km. during the day -----	15

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1-1.	Initial species produced by X-ray bombardment -----	2
1-2.	Species included in the calculations -----	3
1-3.	Chemical reactions included -----	5
2-1.	Main neutral reactions -----	16

THE CHEMISTRY OF NITROGEN OXIDES AND OZONE IN THE DISTURBED D-REGION

H. A. Ory and F. R. Gilmore, R & D Associates

1-1. INTRODUCTION.

1-1.1 X-rays from a nuclear explosion within or above the D-region are deposited in the D-region, where ionization and dissociation produce species that undergo subsequent reaction and alter the chemical composition of the air. Among the products, NO, NO₂, and O₃ are important because they are efficient infrared emitters, and also because by charge transfer they influence the ionization history. It is difficult to simulate this set of processes at D-region pressures in the laboratory, because of wall effects, so a theoretical treatment is necessary. However, laboratory results from experiments at higher pressures are available to guide the theoretical calculations.

1-1.2 Willis and coworkers (Reference 1) measured the yield of ozone from the radiolysis of air and nitrogen-oxygen mixtures near atmospheric pressure with intense electron pulses. Calculated ozone yields based on their assumed mechanism agreed well with experimental results at high pressures but not at low pressures. Hirsch and Elsner (References 2 and 3) studied the kinetics of charged species produced in air at pressures corresponding to 50-km. altitude using a low-intensity continuous-electron beam. Calculations for similar conditions, based on an extensive set of reactions, were reported by Niles (Reference 4). The calculations agreed with the measurements for short times (< 50 sec.), but the agreement became poorer with longer times. Scheibe (Reference 5) reported calculations for the 40- to 70-km. altitude region following short ionization impulses.

1-1.3 The present calculations were undertaken to incorporate several recently discovered excited-state reactions in the calculations and to extend the results up to the 100-km. altitude.

1-2. INITIAL DISSOCIATION, IONIZATION, AND EXCITATION BY THE X-RAYS.

1-2.1 When a kilovolt X-ray is absorbed by a nitrogen or oxygen molecule, a fast electron is ejected carrying most of the energy, while the balance of the energy goes into excitation of the molecular ion that remains. This excitation is usually so great that one or more Auger electrons immediately are ejected. The multiple-charged molecular ion thus produced is unstable and rapidly dissociates into atomic ions. The photoelectron and Auger electrons rapidly lose their energies by colliding with and exciting, dissociating, or ionizing other molecules. Some of the secondary electrons produced by ionizing collisions also have enough energy to excite, dissociate, or ionize. Species produced by secondary and tertiary processes generally dominate those produced by the initial absorption. This conclusion is supported by the experimental result that the total number of ion pairs produced per unit energy deposited is essentially the same for X-rays and fast electrons and is independent of the incident energy per particle over a wide range.

1-2.2 In order to calculate the subsequent chemistry, one needs not only the number of ion pairs but also their identity and the identity and number of any new neutral species produced. Since the cross sections for ionization of N_2 and O_2 by electron impact are nearly equal, the ion production may be divided between the two species in accordance with the ambient air composition. The division between molecular and atomic ions can be estimated from cross sections for dissociative ionization. The fractional production of the four ions (N_2^+ , O_2^+ , N^+ , and O^+) used in the present calculations are shown in table 1-1.

TABLE 1-1. --Initial species produced by X-ray bombardment

Species	Particles per ion pair
N_2^+	0.75
O_2^+	0.19
N^+	0.04
O^+	0.02
$N_2(A \ ^3\Sigma_u^+)$	0.6
$O_2(a \ ^1\Delta_g)$	2.
$N(^1S)$	0.2
$N(^2D)$	0.3
$O(^3P)$	0.3

1-2.3 The production of neutral species is much less certain. The values used here (table 1-1) have been estimated from published electron-impact cross sections and theoretical considerations; they may be in error by a factor of 2. The value for the N_2 A state includes contributions from the B, C, D, and E states, which rapidly decay radiatively to the A state. The total value for N atoms is much smaller than the number usually assumed in radiolysis calculations (Reference 1). However, the larger number was derived by assuming that isotopic scrambling in bombarded nitrogen and other reactions in mixtures containing nitrogen are caused primarily by nitrogen atoms, while actually reactions by excited nitrogen molecules probably make important contributions.

1-2.4 Several excited species, such as $O(^1D)$ and $O_2(b \ ^1\Sigma_g^+)$, were not treated separately in the calculations, even though they are produced in considerable amounts, because in air they are rapidly quenched by collisions without chemical reaction. Likewise, vibrational excitation was ignored.

1-3. CHEMICAL REACTIONS INCLUDED IN THE CALCULATIONS.

1-3.1 The concentration histories of species in bombarded D-region air can be described reasonably well by using only a moderate number of species and reactions, especially if early deionization is not treated in great detail. A more extensive set of reactions would serve primarily to allow coverage of a wider range of conditions; include details of early deionization; take account of additives, such as H₂O and CO₂; and follow species present in quite small concentrations. Only slightly greater accuracy would be obtained for the important neutral species.

1-3.2 The species included in the calculations are listed in table 1-2. Some of the species that are ignored deserve comment. Inclusion of N₄⁺ would permit faster charge transfer to O₂ and subsequent recombination; however, these reactions are sufficiently fast that increasing their rates would have little effect on later, slower reactions. Therefore N₄⁺ is ignored, since early deionization is not of primary interest. Similar considerations apply to O₄⁺. Likewise, O₂⁻ and other negative ions are neglected. These negative ions would have some effect on the late electron density, especially at the lower altitudes and lower bombardment intensities, but their effect on the neutral species is small.

TABLE 1-2. --Species included in the calculations

Neutral species	Ionic species
N(⁴ S)	e ⁻
N(² D)	N ⁺
O(³ P)	O ⁺
N ₂ (X ¹ Σ _g ⁺)	N ₂ ⁺
N ₂ (A ³ Σ _u ⁺)	NO ⁺
NO	O ₂ ⁺
O ₂ (X ³ Σ _g ⁻)	
O ₂ (a ¹ Δ _g)	
N ₂ O	
NO ₂	
O ₃	

1-3.3 The chemical reactions included in the calculations are listed in table 1-3, along with the assumed rate constants. Actually, certain reactions are included which play only negligible roles in the D-region but which were included to permit calculations also at lower altitudes. Many of the rate constants are widely used and require no special discussion. Photodissociation rates (reactions 11 to 13) vanish at night, and daytime rates as functions of altitude are taken from Shimazaki and Laird (Reference 6). Rate constants for quenching of electronically excited species have usually been measured at room temperature; a temperature variation like $T^{0.5}$ has been assumed here, which is plausible for the fast reactions (negligible activation energy) and probably better than assuming a constant value for the slow ones.

1-3.4 For reaction 19, the products have not been identified but are assumed to be the same as for the ground-state N reaction (Reference 7). For reaction 25, experiments (Reference 8) show that a significant fraction of the products are oxygen atoms; theoretical considerations suggest that essentially all of the O_2 participating will be dissociated. No measurements are available on the excitation of the products of reactions 1 and 2. The excitation indicated for reaction 1 was estimated from N_2 potential curves; preliminary results of a more careful theoretical study (Reference 9) indicate that an even division between the two states would be a better approximation. The products indicated for reaction 2 were deduced by Meira (Reference 10) from measured NO concentrations in the undisturbed D-region. Although a later analysis by Strobel (Reference 11) shows that the fraction of $N(^2D)$ produced is rather uncertain, this reaction is generally unimportant compared to reaction 1 under the conditions of the present study. Several papers included in reference 12 provide a good summary of reaction rates.

1-4. COMPUTATIONAL METHOD.

1-4.1 The simultaneous differential equations for the changes in species concentrations with time were solved numerically step by step, simply by taking the changes over each time step proportional to the derivatives at the beginning of the step. It is well known that to obtain high accuracy by this method extremely short time steps must be used, which makes the method less efficient than more refined methods. However, since even the best-established rate constants are uncertain to 10 or 20 percent, a highly accurate integration is unnecessary; and for moderate accuracy, the simple integration method is relatively efficient. In the present work, the time step was continuously adjusted to allow a 30-percent change per step in the most rapidly varying species. The calculations were checked in some cases by repeating them with time steps limited to a 15-percent change. The results usually agreed to within a few percent. Greater disagreements occurred when species decreased by several orders of magnitude over the integration period. However, for the same situations, similar large uncertainties in the late-time concentrations are produced by smaller uncertainties in the rate

TABLE 1-3. --Chemical reactions included

Reaction	Rate constant*
1. $e^- + N_2^+ = 0.8 N(^4S) + 1.2 N(^2D)$	2.9×10^{-7}
2. $e^- + NO^+ = 0.13 N(^4S) + 0.87 N(^2D) + O$	$1.23 \times 10^{-4}/T$
3. $e^- + O_2^+ = 2 O$	$6.6 \times 10^{-5}/T$
4. $N^+ + O_2 = 0.5 NO^+ + 0.5 O_2^+ + 0.5 N(^4S) + 0.5 O$	5×10^{-10}
5. $O^+ + N_2 = NO^+ + N(^4S)$	1.2×10^{-12}
6. $O^+ + O_2 = O_2^+ + O$	2×10^{-11}
7. $N_2^+ + O = NO^+ + N(^4S)$	1.4×10^{-10}
8. $N_2^+ + NO = NO^+ + N_2$	3.3×10^{-10}
9. $N_2^+ + O_2 = O_2^+ + N_2$	$2.3 \times 10^{-9} \times T^{-0.6}$
10. $O_2^+ + NO = NO^+ + O_2$	7.2×10^{-10}
11. $O_2 + h\nu = 2 O$	Ref. 6
12. $NO_2 + h\nu = NO + O$	Ref. 6
13. $O_3 + h\nu = O_2 + O$	Ref. 6
14. $N(^4S) + O + M = NO + M$	$1.8 \times 10^{-31}/T^{0.5}$
15. $N(^4S) + O_3 = NO + O_2$	5.7×10^{-13}
16. $N(^4S) + O_2 = NO + O$	$2.3 \times 10^{-11} \exp(-3950/T)$
17. $N(^4S) + NO = N_2 + O$	$5.1 \times 10^{-11} \exp(-167/T)$
18. $N(^2D) + O_2 = NO + O$	$3.5 \times 10^{-13} \times T^{0.5}$
19. $N(^2D) + NO = N_2 + O$	$3.5 \times 10^{-12} \times T^{0.5}$
20. $O + NO = NO_2 + h\nu$	$6.4 \times 10^{-17} \times (300/T)^2$
21. $O + NO + M = NO_2 + M$	$4.0 \times 10^{-33} \exp(970/T)$
22. $O + O_2 + M = O_3 + M$	$2.8 \times 10^{-35} \exp(910/T)$
23. $O + NO_2 = O_2 + NO$	$1.7 \times 10^{-11} \exp(-300/T)$
24. $O + O_3 = 2 O_2$	$1.3 \times 10^{-11} \exp(-2120/T)$
25. $N_2(A) + O_2 = N_2(X) + 2 O$	$3 \times 10^{-13} \times T^{0.5}$
26. $N_2(A) + NO = N_2(X) + NO$	$5 \times 10^{-12} \times T^{0.5}$
27. $NO + O_3 = NO_2 + O_2$	$9.5 \times 10^{-13} \exp(-1240/T)$
28. $O_2(a) + O_2 = 2 O_2$	$1 \times 10^{-19} \times T^{0.5}$
29. $O_2(a) + O_3 = 2 O_2 + O$	$1.7 \times 10^{-16} \times T^{0.5}$
30. $N(^4S) + NO_2 = 0.44 N_2O + 0.66 NO + 0.23 N_2 + 0.1 O_2 + 0.7 O$	$6 \times 10^{-12}^{**}$
31. $O + N_2O = 2 NO$	$3.8 \times 10^{-11} \exp(-12100/T)$
32. $O_2(a) = O_2 + h\nu$	2.6×10^{-4}

*Units for two-body reactions are $cm.^3/sec.$, and for three-body reactions $cm.^6/sec.$ Units for reaction 32 are $sec.^{-1}$.

**This value is one-third the published value, but this error does not significantly affect the compositions calculated here, because $N(^4S)$ is primarily removed by reactions 16 and 17 and NO_2 by reactions 12 and 23.

constants for the destruction reactions. Consider, for example, an exponential decay; a 20-percent error in the decay constant causes a factor of 4 error in the concentration after it has decayed 3 orders of magnitude. Hence, the additional inaccuracy introduced by the computational procedure is unimportant.

1-4.2 At various points during the calculations, unrealistic oscillations and very short time steps occurred, when the net production and destruction rates of certain species nearly canceled. These problems were eliminated by using the "steady state" algebraic equations for these species under these conditions.

2-1. RESULTS AND DISCUSSION.

2-1.1 The results of calculations for altitudes of 60 to 100 km., ionization of 10^8 to 10^{12} ion pairs/cm.³, and both day and night conditions, are shown in figures 2-1 through 2-9.

2-1.2 By far, the major factor in the decay of ionization is the dissociative recombination of O_2^+ (reaction 3). Most of the N_2^+ undergoes charge transfer with O_2 (reaction 9). Only a small fraction of the N_2^+ recombines dissociatively (reaction 1); but under more intense bombardment, the relative importance of this reaction would increase. Very little of the O_2^+ charge transfers with NO (reaction 10) because reaction 3 is faster and the concentration of NO does not peak until after much of the O_2^+ has been removed. Dissociative recombination thus produces many more O atoms than N atoms, so that the potential production of O_3 exceeds that of NO in all cases.

2-1.3 The initial production of $N_2(A)$ leads to further increase in the potential production of ozone. Nearly all of the $N_2(A)$ reacts with O_2 to yield two O atoms for each excited N_2 (reaction 25).

2-1.4 The main reactions involved in the production and removal of NO, NO_2 , and O_3 are shown in table 2-1, where the reaction systems controlling these species are denoted.

2-1.5 O_3 . Most of the O atoms participate in the three-body reaction with O_2 to produce O_3 (reaction 22). During the day, photodissociation of ozone leads to the shuffling of O_3 and O, through reactions 13 and 22; and combined with other O and O_3 removal reactions, this depresses the ozone concentrations. Since the ozone formation reaction is three-body, it is relatively less effective with increasing altitude; and the ozone concentration is more depressed. During night conditions, the major removal of ozone occurs through reaction with NO (reaction 27). This reaction tends to proceed until either NO (during night) or O_3 (during day) is removed completely, although at low densities and weak bombardments the reaction is very slow. Some of the $O_2(a)$ removes ozone through reaction 29, but most of the $O_2(a)$ simply quenches physically (reaction 28) or radiatively (reaction 32).

2-1.6 NO. Besides O_3 , $N(^2D)$ and $N(^4S)$ strongly affect the concentration of NO. Nearly all the $N(^2D)$ reacts rapidly with O_2 to produce NO (reaction 18) so that an appreciable concentration is built up very early. Considerably later, $N(^4S)$ reacts with NO and partly removes it (reaction 17); at the higher altitudes, this reaction proceeds before the concentration of O_3 builds up. (Even at 60 km., very

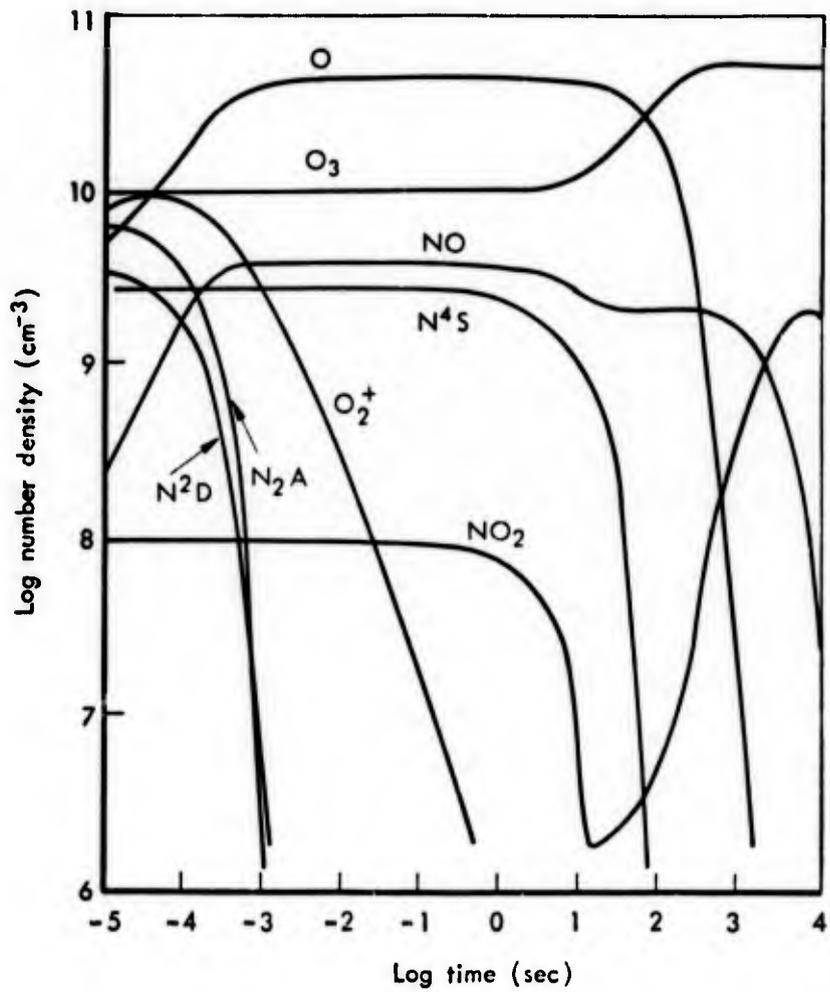


Figure 2-1.--Concentration variation produced by ionization pulse of 10^{10} ion pairs/ cm^3 at 60 km. during the night.

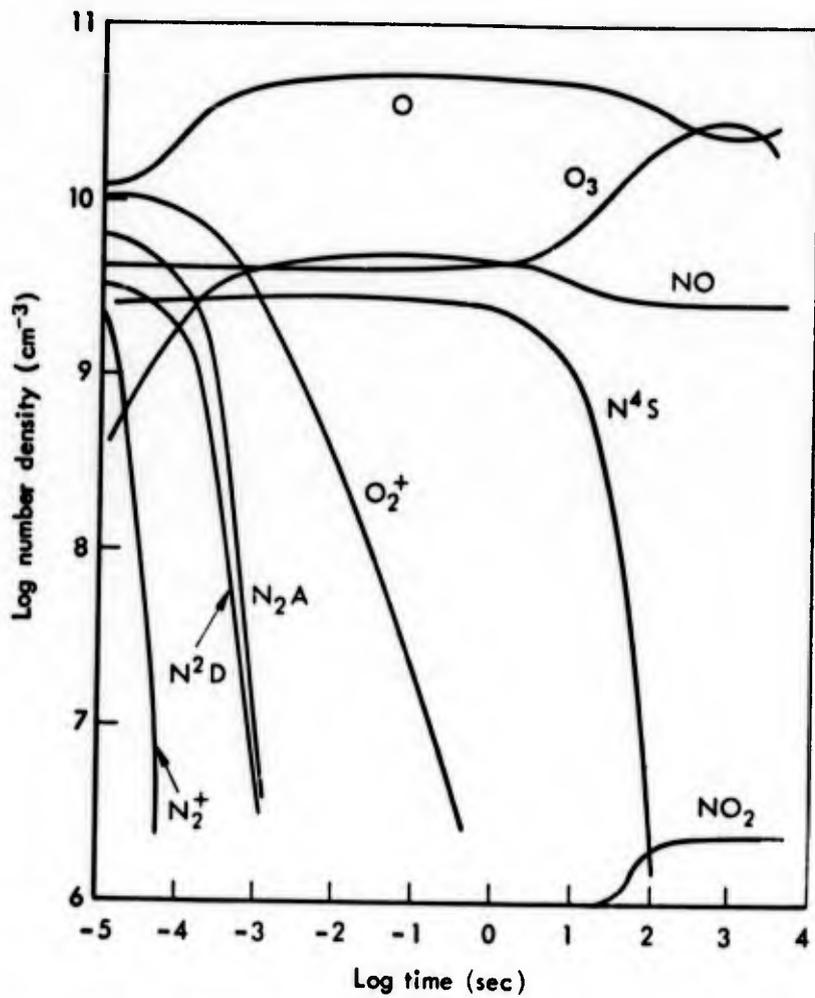


Figure 2-2. --Concentration variation produced by ionization pulse of 10^{10} ion pairs/cm.³ at 60 km. during the day.

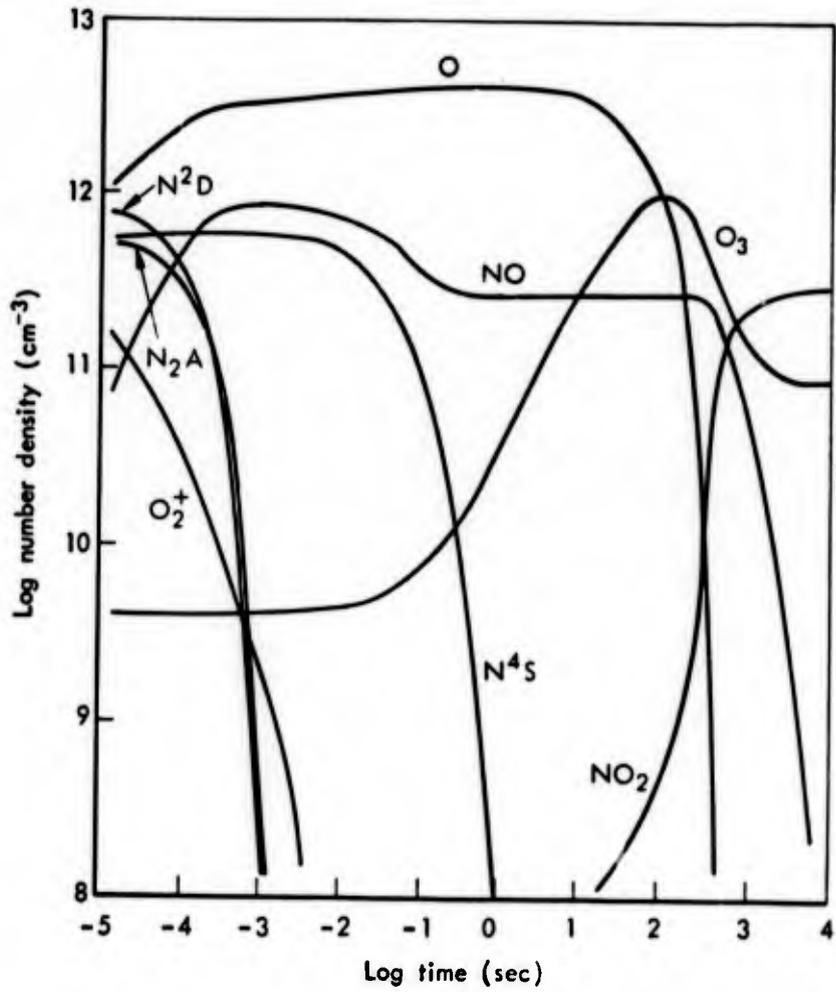


Figure 2-3. --Concentration variation produced by ionization pulse of 8.8×10^{11} ion pairs/cm.³ at 60 km. during the night.

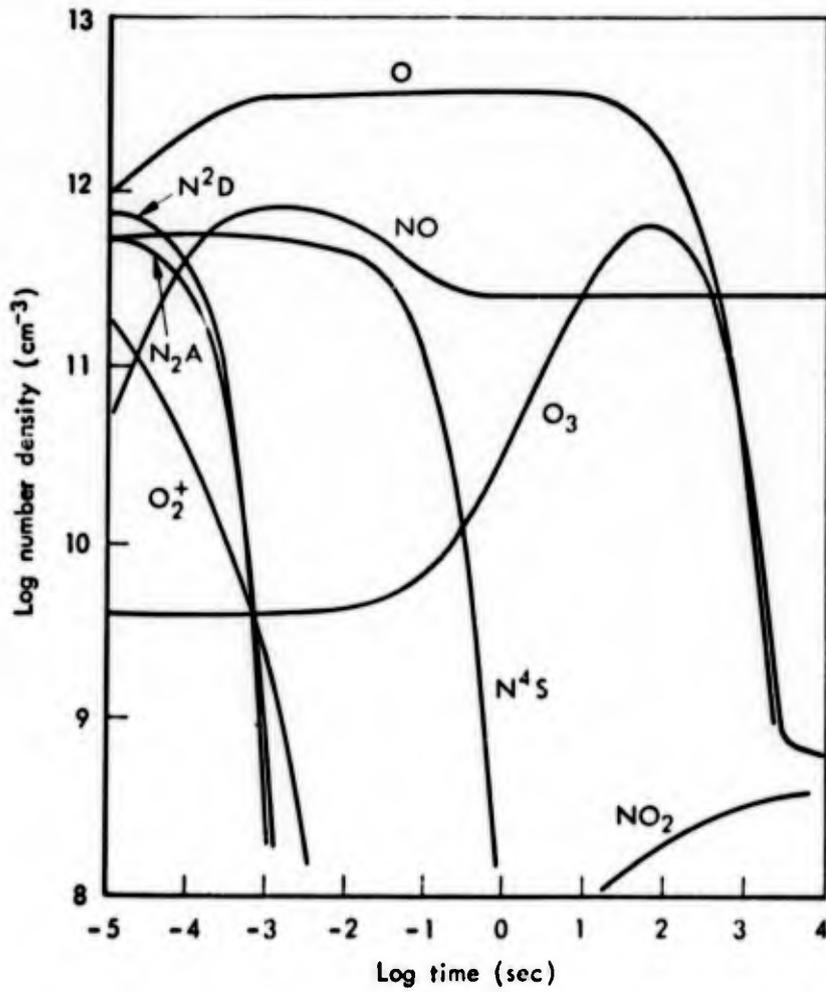


Figure 2-4. --Concentration variation produced by ionization pulse of 8.8×10^{11} ion pairs/cm.³ at 60 km. during the day.

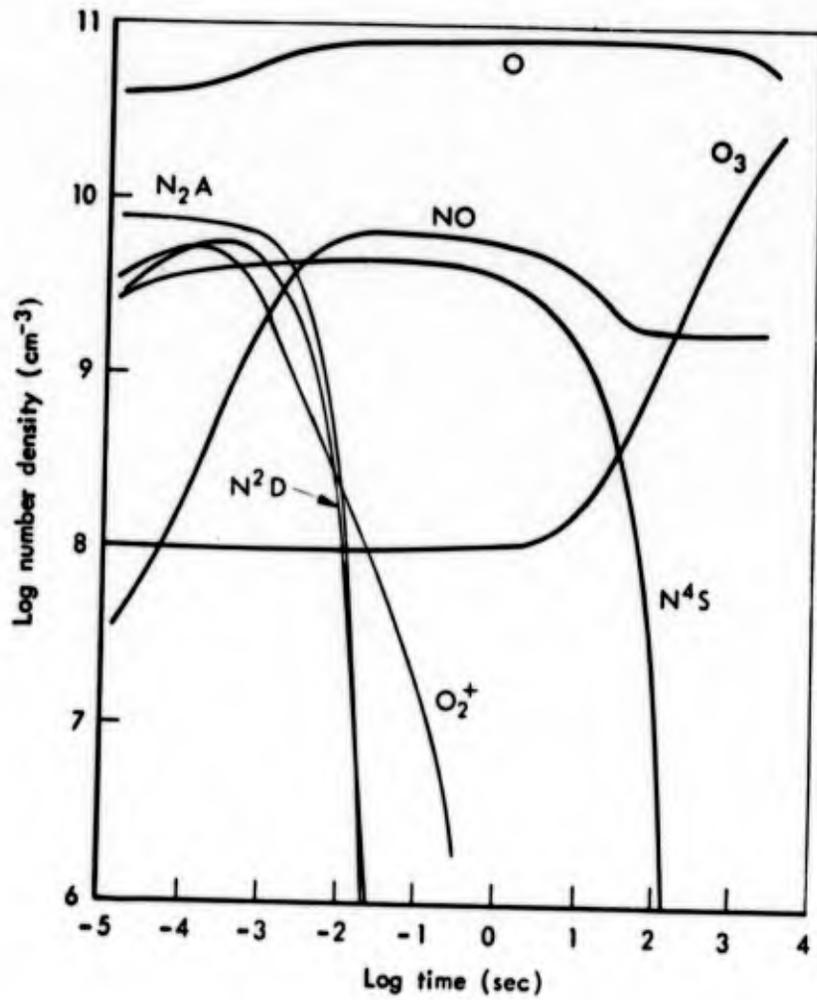


Figure 2-5. --Concentration variation produced by ionization pulse of 10^{10} ion pairs/cm.³ at 80 km. during the night.

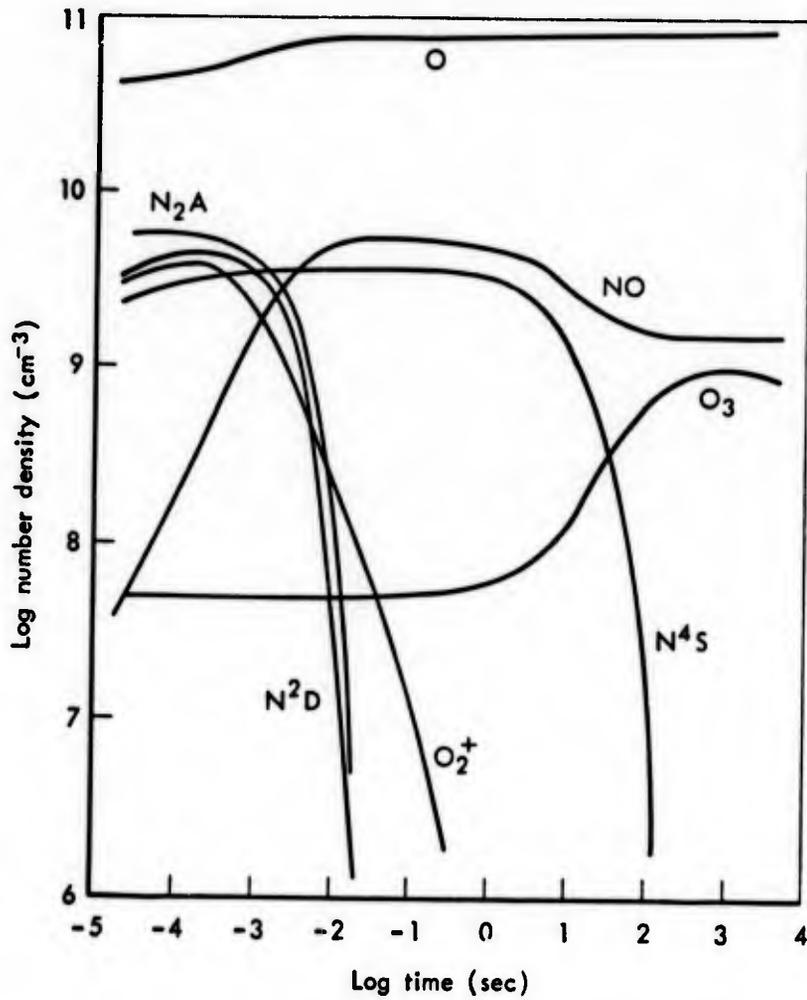


Figure 2-6. --Concentration variation produced by ionization pulse of 10^{10} ion pairs/cm.³ at 80 km. during the day.

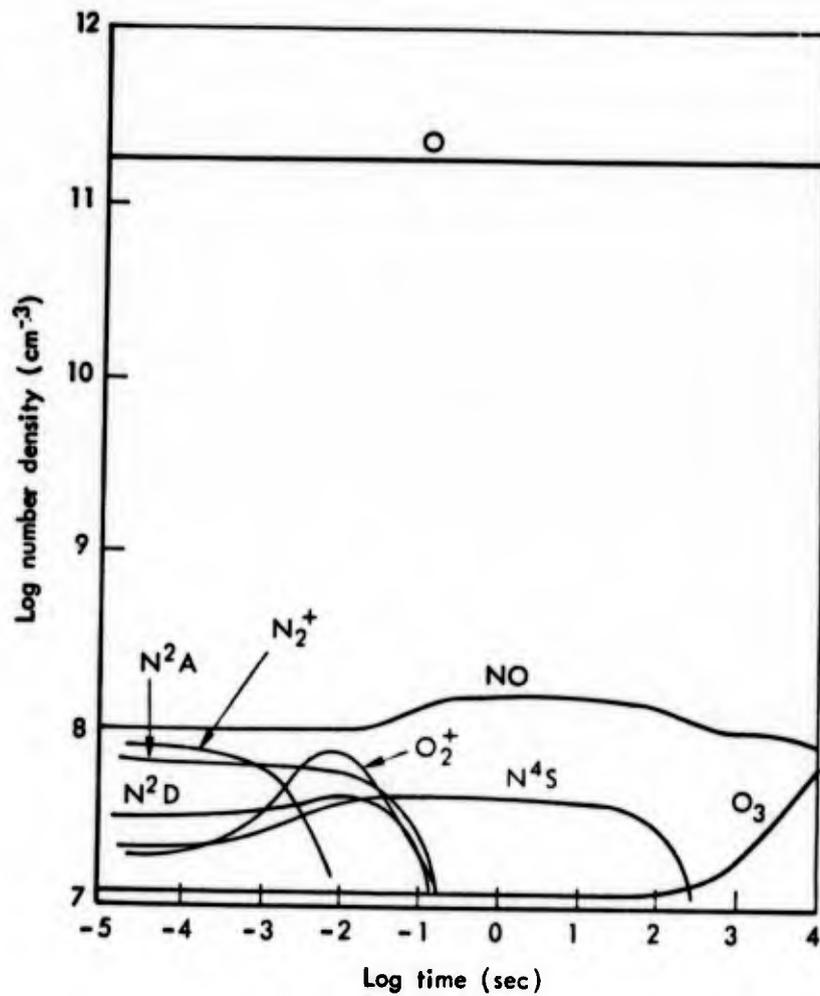


Figure 2-7. --Concentration variation produced by ionization pulse of 10^8 ion pairs/cm.³ at 100 km. during the night.

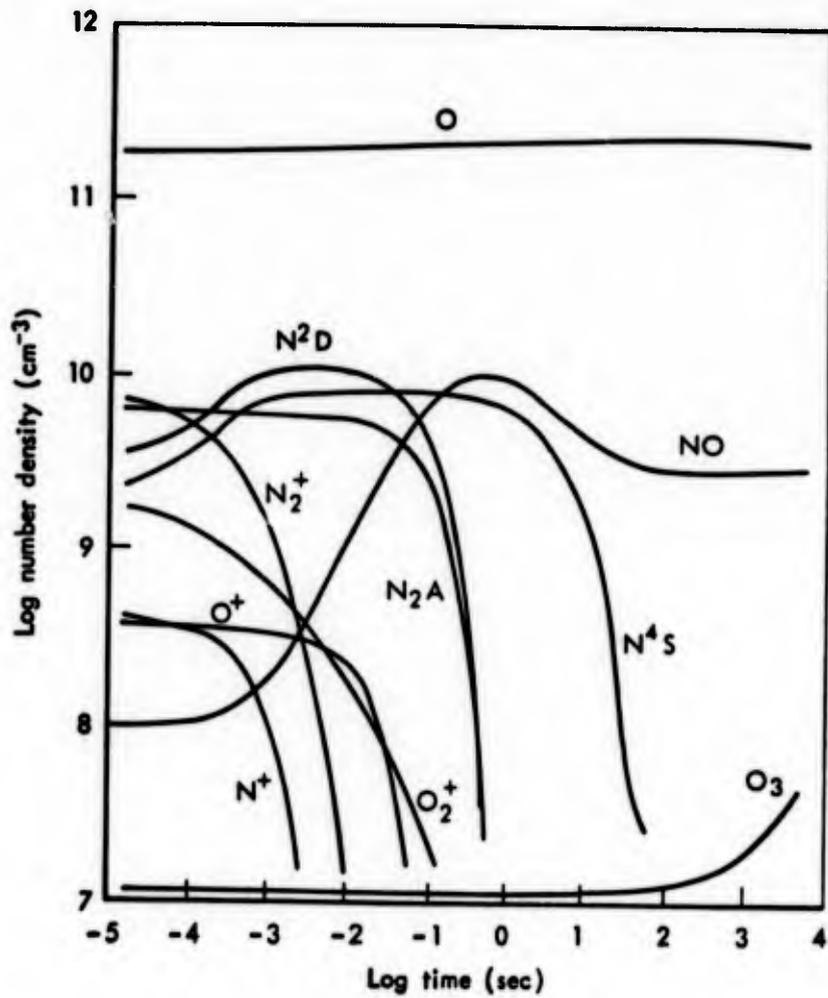


Figure 2-8. --Concentration variation produced by ionization pulse of 10^{10} ion pairs / $cm.^3$ at 100 km. during the night.

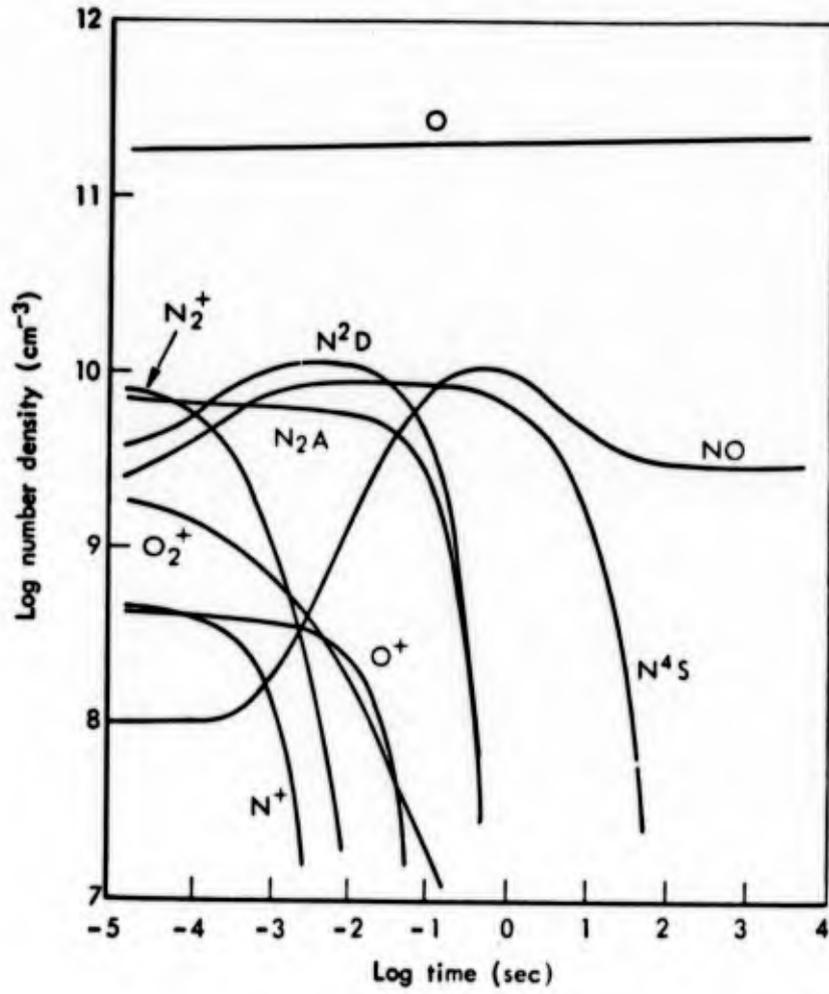


Figure 2-9. --Concentration variation produced by ionization pulse of 10^{10} ion pairs/cm.³ at 100 km. during the day.

derive analytical approximations and establish their accuracy over ranges of altitude, bombardment intensity, and time.

REFERENCES

1. Willis, C., Boyd, A. W., and Young, M. J. Can. J. Chem. **48**, 1515 (1970).
2. Hirsch, M. N. "A Laboratory Study of the Perturbed Upper Atmosphere." R-211-4, DASA No. 2197, The G. C. Dewey Corp., New York, January 1969.
3. Hirsch, M. N. and Eisner, P. N. "Further Laboratory Studies of the Perturbed Upper Atmosphere." R-251, DASA 2536, The Dewey Electronics Corp., New Jersey, September 1970.
4. Niles, F. E. J. Chem. Phys. **52**, 408 (1970).
5. Scheibe, M. "Neutral D-Region Chemistry Following High Level Ionization Impulses." N-15-68-1, Lockheed Missiles and Space Co., Sunnyvale, California. July 1968.
6. Shimazaki, T., and Laird, A. R. J. Geophys. Res. **75**, 3221 (1970).
7. Lin, C. L. and Kaufman, F. "Deactivation and Reaction of $N(^2D)$." DASA Symposium on the Physics and Chemistry of the Upper Atmosphere, J. Chem. Phys., Stanford Research Institute, June 1969; to be published.
8. Meyer, J. A., Setser, D. W., and Stedman, D. H. J. Phys. Chem. **74**, 2238 (1970).
9. Michels, H., Kolker, H., and Peterson, G. "Theoretical Analysis of Dissociative Recombination in N_2 ." DNA High-Altitude Nuclear Effects Symposium, Stanford Research Institute, 10-12 August 1971.
10. Meira, L. G., Jr. J. Geophys. Res. **76**, 202 (1971).
11. Strobel, D. F. J. Geophys. Res. **76**, 2441 (1971).
12. "Proceedings of the Symposium of Laboratory Measurements of Aeronomic Interest." Schiff, H. I. (Ed.) Can. J. Chem. **47**, 1703 *et seq.* (1969).