THE UNIVERSITY OF MICHIGAN

COLLEGE OF ENGINEERING DEPARTMENT OF AEROSPACE ENGINEERING HIGH ALTITUDE ENGINEERING LABORATORY

Scientific Report

Distributions and Lifetimes of N and NO Between 100 and 280 Km

S. N. GHOSH

| GPO PRICE \$ | • | | · | . · · · · · · · · · · · · · · · · · · · | |
|---------------------|-------------|--------------------|--|---|---------------------------------------|
| CFSTI PRICE(S) \$ | | N67-31 | .506 | (THRU) | e Antonio References Antonio |
| Hard copy (HC) 3,00 | CULITY FORM | ACCESSION (PAGES) | 618 | (code) /3 (category) | |
| Microfiche (MF)65 | | (NASA CR OR TMX OR | AD NUMBER) | | |
| 1053 July 85 | | | 18 8 18 19 19 19 19 19 19 19 19 19 19 19 19 19 | | |

Under contract with:

National Aeronautics and Space Administration Contract No. NASr-54(05) Washington, D. C.

Administered through:

March 1967

OFFICE OF RESEARCH ADMINISTRATION - ANN ARBOR

THE UNIVERSITY OF MICHIGAN

COLLEGE OF ENGINEERING Department of Aerospace Engineering High Altitude Engineering Laboratory

Scientific Report

DISTRIBUTIONS AND LIFETIMES OF N AND NO BETWEEN 100 AND 280 Km

S. N. Ghosh

ORA Project 05627

under contract with:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION CONTRACT NO. NASr-54(05) WASHINGTON, D.C.

administered through:

OFFICE OF RESEARCH ADMINISTRATION ANN ARBOR

March 1967

TABLE OF CONTENTS

•

ļ

| LIST OF TABLES | v |
|--|-----|
| LIST OF FIGURES | vii |
| ABSTRACT | ix |
| 1. INTRODUCTION | l |
| 2. COMPUTATION OF N AND NO DISTRIBUTIONS AND LIFETIMES | 3 |
| 3. CONCLUSIONS | 11 |
| REFERENCES | 15 |

MECEDING PAGE BLANK NOT FILMED.

LIST OF TABLES

| Table | | Page |
|-------|--|------|
| 1. | Reactions Leading to N-Atom Production and Their Rate Co- efficient | 4 |
| 2. | Reactions Leading to N-Atom Loss and Their Rate Coefficients | 5 |
| 3. | Reactions Leading to NO Production and Their Rate Coefficients | 6 |
| 4. | Reactions Leading to NO Loss and Their Rate Coefficients | 7 |
| 5. | Altitude Distributions of Ions | 8 |
| 6. | Lifetimes of N and NO | 10 |

PRECEDING PAGE BLANK NOT FILMED.

- - -

}

LIST OF FIGURES

| Figure | | Page |
|--------|---|------|
| l. | Variations of assumed ion densities with altitude. Solid curves are obtained from rocket-borne experiments. The broken curves are extrapolated (see Table 5). | 18 |
| 2. | Production rates of N atoms by various reactions for rate co- efficients at laboratory temperature (300°K) assumed constant for the whole altitude range. | 19 |
| 3. | Variation of x with altitude for rate coefficients at lab- oratory temperature $(300^{\circ}K)$ assumed constant for the whole altitude range. To obtain loss rate of N atoms, multiply x by [N]. | 20 |
| 4. | Variation of x' with altitude for reactions involving 2 nitro- gen atoms. To obtain loss rate multiply x' by $[N]^2$. Loss rates by three-body reactions are very small compared with those for two-body reactions. | 21 |
| 5. | Production rates of N atoms by various reactions for rate co- efficients varying with temperature. | 22 |
| 6. | Variation of x with altitude for two-body reactions having rate coefficients varying with temperature. Loss rate = $x[N]$. NO(1) and NO(4) represent NO density obtained from Curves (1) and (4) of Fig. 9, respectively. | 23 |
| 7. | Production rates of NO molecules by various reactions with rate coefficients varying with temperature. | 24 |
| 8. | Variation of x with altitude for various reactions having rate coefficients varying with temperature. To obtain loss rate of NO molecules, multiply x by [NO]. | 25 |
| 9. | Computed altitude distributions of N and NO. For comparison, the distributions of O, O_2 and N_2 obtained from CIRA 1965 are also shown. | 26 |
| | | |

ABSTRACT

The distribution of N atoms between the altitude range 100 and 280 km has been computed from reactions between constituent particles of the atmosphere and assuming their rate coefficients at laboratory temperature $(300^{\circ}K)$ to be constant for the whole altitude range. It is also calculated for rate coefficients varying with temperature. It has been found that the latter distribution, which is considerably different from the former, gives a reasonably good profile. Since in many cases, reactions involving loss of N-atoms lead to the production of NO molecules, the altitude distribution of NO molecules is also calculated. The computed N and NO distributions compare favorably with certain rocket experiments and laboratory data. From the loss processes, the lifetimes of N and NO are computed.

PRECEDING PAGE BLAUK MOT FILMED.

1. INTRODUCTION

Distributions of ions and neutral particles with altitude have been obtained by rocket-borne mass spectrometers and are computed from reaction rates of upper atmospheric constituents-ions, electrons, and neutral particles. The reaction rates are obtained from laboratory experiments or from theoretical computations. For obtaining the distribution of minor constituents of the atmosphere like N and NO, mass spectrometers may introduce uncertainties due to "wall effect" or dissociation of molecules by accelerated electrons. Again, to determine rates of reactions experimentally for thermal and nearly thermal ions, difficulties are experienced. In theoretical work too, techniques for calculating cross-sections of reactions involving atmospheric particles are yet to be evolved possibly by semiclassical treatments, and methods for calculating cross sections at thermal energies should be devised. Also in many cases, temperature variations of rate coefficients, which may be altered by a factor of several orders by the ambient temperature range at different layers of the upper atmosphere, are not available. However, the altitude distributions of atmospheric ion and neutral particle densities computed with the available collisional data may cross check those obtained by rocket-borne experiments or from rate coefficients determined in the laboratory. Also from the loss processes, the life times of atmospheric particles can be computed.

In this report the altitude distribution of N-atom density between 100 and 280 km is calculated. Since in many cases, reactions involving loss of N atoms are related to the production of NO molecules, its altitude distribution is also calculated. The lifetimes of these particles are also computed.

2. COMPUTATION OF N AND NO DISTRIBUTIONS AND LIFETIMES

For computing N-atom distribution, the following scheme has been adopted:

First, to postulate from geophysical observations and laboratory data, conceivable collisional reactions involving N atoms in the atmosphere.

Second, to determine the relative importance of these reactions and for a particular reaction its importance at different layers of the atmosphere, after closely examining the rate coefficients of these reactions as determined by different investigators. A distribution is then obtained by equating the production and loss rates.

The reactions leading to the production of N atoms and their observed rate coefficients obtained by different authors are given in Table 1. The coefficients which are used for the computation are given in the last column. The loss processes and their rate coefficients are given in Table 2.

The reactions which produce NO molecules and those by which they are consumed are given in Tables 3 and 4.

0, O_2 , and N_2 profiles and the temperature distribution of the atmosphere are obtained from CIRA, 1965. For calculating N-atom distribution, a profile of NO is needed which is initially taken for 100-120 km from the Handbook of Geophysics (1960) and for the altitude range 120-280 km from Nawrocki and Papa (1963). After obtaining the NO distribution from reactions given in Tables 3 and 4, the N-atom distribution is recalculated.

The ion distributions (Fig. 1) used for computations are given in Table 5. The electron density is assumed to be the sum of the ion densities.

TABLE 1

| | Observed Rate Coefficient | Rate Coefficien (cm3 pa | t Used For Computation rticle ⁻¹ sec ⁻¹) |
|---|---|-------------------------------------|--|
| Reaction | (cm ³ particle ⁻¹ sec ⁻¹) | Coefficient at 300°K | Coefficient Varying With Temperature |
| n2+e→N+N | 1-2x10-7 (Gibbons, 1961) by mass spectrometric technique | 3x10-7 | * |
| | 3x10 ⁻⁷ (Biondi, 1963) for thermal (300°K) electron | | |
| | 7x10 ⁻⁷ (Nawrocki, <u>et al</u> ., 1963) | | |
| N0 ⁺ +e→N+0 | 3.5x10 ⁻⁷ (Whitten, <u>et al</u> ., 1965) at 300°K | 3.5x10-7 | Varies as T ⁻¹ from 2x10 ⁻⁸ at 2000°K to 6x10-7 at 208°K |
| | ∠10-7 (Sugden, 1%1) at flame temperature | | |
| 0 ⁺ +N ₂ →NO ⁺ +N | <pre>3x10⁻¹² (Fehsenfeld, et al., 1965b) 2x10⁻¹² (Danilov, 1966) 1.4x10⁻¹¹ (Dickison, et al., 1960) 4.7x10⁻¹² (Langstroth, et al., 1962) 2.2x10⁻¹¹ (Galli, et al., 1963) 6.75x10⁻¹² (Talrose, et al., 1962)</pre> | 2x10 ⁻¹² | 4.2x10 ⁻¹² exp(-470/RT) (E = 0.47 Kcal) Adjusted to 2x10 ⁻¹² at 300°K, E is the activa- tion energy. |
| n ⁺ +0≁n0 ⁺ +n | 2.5x10 ⁻¹⁰ (Ferguson, <u>et al</u> ., 1965) | 2.5x10 ⁻¹⁰ | l.0x10 ⁻⁷ exp(-3560/RT) (E = 3.56 Kcal) Adjusted to 2.5x10 ⁻¹⁰ at 300°K |
| N++0 ⁵ +0 ⁵ +N | 5x10 ⁻¹⁰ (Fehsenfeld, <u>et al</u> ., 1965) 1x10 ⁻⁹ (Goldan, <u>et al</u> ., 1966) | 1x10 ⁻⁹ | 1x10 ⁻⁹ |
| N ⁺ +NO≁NO ⁺ +N | 8x10 ⁻¹⁰ (Goldan, <u>et al</u> ., 1966) at 300°K | 8x10-10 | * |
| 0 ⁺ +NO≁O2+N | 2.4x10 ⁻¹¹ (Goldan, <u>et al</u> ., 1966) | 2.4x10-11 | * |
| N ₂ +hν→N ₂ (a ¹ πg) | Cross-section, Q = 6x10 ⁻²³ cm ² (Ditchburn, <u>et al</u> ., 1959) | $Q = 1 \times 10^{-21} \text{cm}^2$ | $Q = 1 \times 10^{-21} \text{cm}^2$ |
| →N+N | 10 -21 cm ² (Watanabe, et al., 1953) | | ** |

REACTIONS LEADING TO N-ATOM PRODUCTION AND THEIR RATE COEFFICIENTS

After computing the N-atom production rates for rate coefficients at 300°K, it was found that for reactions marked (), the contributions are small and hence for varying temperature these reactions are not considered.

**Most of the absorption occurs in the (8,0) band at 1226A (Nicolet, 1960). For this wavelength, the absorption cross section of 0_2 is 4×10^{-19} cm² (Watanabe, 1958) and $N(h\nu)_{\infty} = 1.5 \times 10^9$ photons/cm² sec (Gast, et al., 1965).

Rate Coefficient Used For Computation (cm3 particle⁻¹ sec⁻¹) Observed Rate Coefficient Reaction (cm³ particle⁻¹ sec⁻¹) Coefficient Varying Coefficient **at 300°**K With Temperature 2x10⁻¹⁰ at 300°K (Goldan, et 2x10-10 $2.9 \times 10^{-9} \exp(-1590/\text{RT})$ 03+N+N0++0 al., 1966) (E = 1.59 Keal)Adjusted to 2x10-10 at 300°K 1x10-11 < 10-11 4x10⁻⁹ exp(-3560/RT) N⁺₂+N+N₂+N⁺ (E = 3.56 Kcal)Adjusted to 1x10-11 at 300°K 7.4x10-33 cm⁶ particle-2 sec-1 7.4x10-33 cm⁶ N+N+M→N2+M *.** particle-2 (200-450°K)(Herron, et al., 1958) sec-1 1.7x10⁻³² at 300°K (Harteck, et al., 1958) 1.5x10-32 cm6 particle-2 sec-1 5x10-33 cm6 N+O+M→NO+M (at 300°K) (Kaplan, et al., particle-2 sec⁻¹ 1958) 5x10-33 (Byron, 1959) 1.7x10-16 m-1/2 < 10⁻¹⁴ (Nawrocki, et al., 1963) 1x10⁻¹⁷ N+N+No+hv Adjusted to 1x10-17 **a**t 300°K 1.7x10-16 T-1/2 < 10⁻¹⁴ (Nawrocki, et al., 1963) 1x10-17 N+O+NO+hv Adjusted to 1x10-17 at 300°K 1x10⁻¹⁷ (Young, et al., 1963) 1x10-16 $3.3 \times 10^{-12} \exp(-3100/T)$ $3.3 \times 10^{-12} \exp(-3100/T)$ N+02+N0+0 (Kistiakowsky, 1957) 1x10-16 at 300°K (Harteck, et al., 1957) 2.6x10-11 $1.5 \times 10^{-12} \text{m}^{1/2}$ N+NO→N2+O 8x10-11 at 300°K (Kistiakowsky, 1958) 1-3x10⁻¹³ at 300°K (Harteck, et al., 1957) 1.5x10⁻¹² T^{1/2} (Nicolet, 1965a)

REACTIONS LEADING TO N-ATOM LOSS AND THEIR RATE COEFFICIENTS

TABLE 2

After computing the N-atom production rates for rate coefficients at 300°K, it was found that for reactions marked (), the contributions are small and hence for varying temperature these reactions are not considered.

**n(M) is assumed to be equal to $n(0_2)+0.6n(N_2)$ (Young, et al., 1962).

| | REACTIONS LEADING TO NO PRODUCTION AND TH | EIR RATE COEFFICIENTS |
|---|---|--|
| Reaction | Observed Rate Coefficient (cm ⁵ particle ⁻¹ sec ⁻¹) | Rate Coefficient Used For Computation $(cm^{5} particle^{-1} sec^{-1})$ |
| v+0+N+N | lxl0 ⁻¹⁷ (Young, et al., 1965) | 1.7x10-16 $T^{-1/2}$ Adjusted to 1x10 ⁻¹⁷ at 500°K |
| W+ON+W+O+N | 1.5x10-32 cm ⁶ particle ⁻² sec ⁻¹ at 300°K (Kaplan, <u>et al</u> ., 1958) | ** |
| | 5x10-33 (Byron, 1959) | |
| 0+01+20+N | <pre>2xl0⁻¹³ T^{-1/2} exp(-300/T) (Ntcolet, 1965a) 1xl0⁻¹⁶ at 300°K (Harteck, et al., 1957) 3.3xl0⁻¹² exp(-3100/T) (Kistiakowsky, et al., 1957)</pre> | 3.3xl0 ⁻¹² exp(-3100/T) |
| 0+002∻N0+02 | 3.5x10 ⁻¹² at 300°K (Ford, et al., 1957b) | * |
| 2NO N+N0 ₂ +N ₂ 0+0 N ₂ +02 | $\sum_{3\times10^{-1}^{4}}^{4} at 300^{6} K (Harteck, et al., 1957)$ | * |
| n±+0≥+n0 | <pre>lxl0⁻¹3, E = 7 Kcal (Whitten, et al., 1965) lxl0⁻¹³ by afterglow technique (Fehsenfeld, et al., 1965a) < l0⁻¹⁴ (Harteck, et al., 1961) < 2.1xl0⁻¹³ (Galli, et al., 1963)</pre> | * |
| 02+N2+N0++N0 | 7.5x10-11 T ^{1/2} exp(-6000/RT) (Nicolet, 1965b) < 2x10 ⁻¹³ (Galli, <u>et al</u> ., 1963) | 7.5xl0 ⁻¹¹ T ^{1/2} exp(-6000/RT) |
| *N ₂ O and NO ₂ molecules ar **These react1 are small. | do not affect appreciably the NO concentration e not considered. ons are not considered as their contributions | and hence reactions involving these for 300°K or for varying temperatures |

ļ

TABLE 3

| | KEACTIONS LEADING TO NO LOSS AND THEIR | RATE COEFFICIENTS |
|---|--|--|
| Reaction | Observed Rate Coefficient (cm ³ particle ⁻¹ sec ⁻¹) | Rate Coefficient Used for Computation (cm3 particle ⁻¹ sec ⁻¹) |
| 0+ ² N≁ON+N | 1.5x10 ⁻¹² T ^{1/2} (Nicolet, 1965a) | 1.5x10-12 T1/2 |
| | 8x10 ⁻¹¹ at 300°K (Kistiakowsky, 1958) | |
| N0+03+N02+02 | 5xl0 ⁻¹⁴ at 300°K (Ford, <u>et al</u> ., 1957a) 1.7xl0 ⁻¹⁴ at 300°K (Johnston, <u>et al</u> ., 1951) | * |
| M+ ^Z ON≁M+ON+O | 5.2xl0 ⁻³² cm ⁶ particle ⁻² sec ⁻¹ at 300°K (Ford, <u>et al</u> ., 1957b) | * |
| v4t20N+001+0 | 2.5xl0 ⁻¹⁷ for average quanta of 5500A (Kaufman, 1958) | 4.3x10-16 T-1/2 * |
| NO+hv(l216A) ≁NO ⁺ +e | Cross-section Q = 2x10 ⁻¹⁸ cm ² (Watanabe, 1959) | Q = 2x10 ⁻¹⁸ cm ² |
| NO+h√(1900A) →N+O | q = 2x10-1 9 cm ² | $q = 2 x lo^{-19} cm^2$ |
| 0 ⁺ +N0+N0 ⁺ +0 +0 ² +N | 2.4xl0 ⁻¹¹ at 300°K (Goldan, <u>et al</u> ., 1966) | 4.6x10 ⁻⁸ exp(-4500/RT) (E = 4.5 Kcal) Adjusted to 2.4x10 ⁻¹¹ at 300°K |
| 02+N0+N0 ⁺ +02 | 8 xlo^{-l0} a t 300°K (Goldan, <u>et al</u> ., 1966) | 1.5xlo ⁻⁶ exp(-4500/RT) (E = 4.5 Kcel) Adficted to 8v10-10 at z00°v |
| *These reactio are small. | ns are not considered as their contributions i | for 300°K or for varying temperatures |

. 7

TABLE 4

TABLE 5

ALTITUDE DISTRIBUTIONS OF IONS

| Ion | Altitude Range (km) | | |
|---|--|--|--|
| 0+ | 100-200 (Whitten, <u>et al</u> ., 1964) 200-250 (Johnson, 1966) 260-280* | | |
| 02 | 100-240 (Whitten, <u>et al</u> ., 1964) 240-280** | | |
| N_2^+ | 100-220 (Whitten, <u>et al</u> ., 1964) 220-280** | | |
| N + | 130 (Ghosh, <u>et</u> <u>al</u> ., 1964) 140-220 (Johnson, 1966) 220-280** | | |
| NO+ | 100-200 (Whitten, <u>et al</u> ., 1964) 200-240 (Johnson, 1966) 240-280** | | |
| *For the altitude range 260-280 km, 0 ⁺ and electron | | | |
| distributions (Cormier, 1965) are assumed same. | | | |
| **Extrapolated to follow the trend given in Fig. 3 | | | |
| (Ghosh, <u>et al</u> ., 1964). | | | |

Assuming rate coefficients for various reactions at 300°K given in column 3 of Tables 1 and 2, the production and loss rates of N for the altitude range 100-280 km are computed and are given in Figs. 2-4.* The corresponding rates for rate coefficients varying with temperature given in the last columns of the above tables, are computed and are illustrated in Figs. 4-6. A comparison of Figs. 2-4 with Figs. 4-6 shows that the production and loss rates of N atoms are significantly altered if the temperature variation of rate coefficients, which may sometimes be altered by several orders in the above altitude range, are considered.

*For calculating N-atom production by predissociation using the formula

$$2n(N_2)_{z}QN(h\nu)_{z}$$

(the factor 2 accounts for the production of two neutral atoms), it has been assumed that above altitude z, photons are absorbed mainly by O_2 , so that the photon flux of frequency v at an altitude z for overhead sun is given by

$$N(h\nu)_{Z} = N(h\nu)_{\infty} \exp(-\tau)$$

where

$$\tau(z) = \int_{z}^{\infty} \sigma_{02} n(0_2)_2 \exp(-z'/H_{02,z}) dz'$$

 $N(h\nu)_{\infty}$ = number of photons of frequency ν outside the earth's atmosphere = 1.5x10⁹ photons/cm² sec for 1226A (Gast, <u>et al.</u>, 1965)

$$H_{0_{2,Z}}$$
 = scale height of 0_2 molecules at an altitude z

Q = cross-section for absorption of 1226A by $N_{\rm 2}$ molecules = $1 \times 10^{-21} \ {\rm cm}^2$

 σ_{0_2} = cross-section for absorption of 1226A by 0₂ molecules = 4×10^{-19} cm² (Watanabe, 1958)

 $n(N_2)_{\tau}$ = concentration of N₂ molecules at altitude z

 $n(0_2)_z$ = concentration of 0_2 molecules at altitude z.

Again, for calculating the production and loss rates from neutralneutral or ion-neutral particle reactions, the usual formula, namely, the rate is equal to the product of rate coefficient and concentrations of the reacting particles, is used. The calculated rates of production and loss of NO molecules for rate coefficients varying with temperature are shown in Figs. 7 and 8.

After calculating the loss rates of N atoms, it is found that the lifetime of N atoms for the altitude range 100-280 km varies between 5.7×10^4 and 1.3×10^3 sec (Table 6 and Figs. 4 and 6).

The N-atom distribution is calculated by equating the production and loss rates (Fig. 9). In a similar manner for 100-280 km the distribution of NO (Fig. 9), for which the lifetime varies between 3.6×10^2 and 58 sec (Table 6 and Fig. 8), is calculated.

TABLE 6

| Altitude | Lifetime of NO | Lifetime of N |
|-------------|---------------------|---------------------|
| (km) | (sec) | <u>(sec)</u> |
| 100 | 3.6x10 ² | 5.7x104 |
| 110 | 2.9x10 ² | 1.9x10 ⁴ |
| 120 | 2.5x10 ² | 5.7x10 ³ |
| 130 | 1.8x10 ² | 2.1x10 ³ |
| 140 | 1.2x10 ² | 1.3x10 ³ |
| 150 | 9.1x10 ¹ | 1.6x10 ³ |
| 16 0 | 7.4xlOl | 2.2x10 ³ |
| 170 | 6.7xl0 ^l | 2.7x103 |
| 18 0 | 6.3x10 ¹ | 3.3x10 ³ |
| 19 0 | 5.9x10 ¹ | 4.0x103 |
| 200 | 5.8x10 ¹ | 4.8x10 ³ |
| 220 | 7.3x101 | 7.1x10 ³ |
| 24 0 | 1.0x10 ² | 1.0x10 ⁴ |
| 25 0 | 1.1x10 ² | 1.7x10 ⁴ |
| 26 0 | 1.2x10 ² | 2.2x10 ⁴ |
| 28 0 | 1.0x10 ² | 3.9x10 ⁴ |

LIFETIMES OF N AND NO

3. CONCLUSIONS

1. After analyzing various reactions leading to the production and loss of N and NO, it may be concluded that the predissociation of N₂ molecules does not contribute significantly to the production of N atoms. In the higher region, they are produced mainly by the ion-atom interchange reaction

$$0^+ + N_{2} \rightarrow N0^+ + N$$

and in the lower region, jointly with the reaction

$$NO^+ + e \rightarrow N + O$$
.

N atoms are lost by the following reactions

$$O_2^+ + N \rightarrow NO^+ + O$$
 and $N + NO \rightarrow N_2 + O$.

The computed N distribution shows that the first reaction is important at the upper and the latter at the lower region.

The accuracy of calculated N and NO distributions is limited mainly by the values of rate coefficients of reactions (the coefficients are now believed to be accurate by orders but not by factors) and their temperature variations.

For the major portion of 100-280 km altitude range, the NO production and loss rates are given, respectively, by

$$O_2^+ + N_2 \rightarrow K_1 NO^+ + NO$$

and

$$O_2^+ + NO \rightarrow K_2 NO^+ + O_2$$
.

At equilibrium

 $k_1 n(O_2^+) n(N_2) = k_2 n(O_2^+) n(N_0)$ $n(N_0) = \frac{k_1}{k_2} n(N_2)$

Therefore n(NO) distribution follows (N_2) profile and is independent of N-atom distribution (see Fig. 9).

2. From the rocket-borne mass spectrometric measurements of neutral constituents in the altitude range 100-200 km, Hedin and Nier (1965) concluded that the concentration of N atoms is about 1% of N₂. Again the mass spectrometric data obtained by Schaefer constantly show a small increase of N over laboratory calibrations. Also, from the analysis of peak heights for N and N₂ between 100 and 200 km, it is found that atomic nitrogen does not occur more than 3% of N₂ (Mirtov, 1964). The computed N distribution shows that at the upper region of the above altitude range N is about 1-3% of N₂. In the lower region the percentage is much smaller. Therefore, for accurate determination of N-atom concentration by a rocket-borne mass spectrometer, it should be measured above 200 km where its concentration becomes relatively larger.

3. By observing absorption of solar radiations in a rocket-borne spectrograph with pointing control, Jursa, <u>et al.</u> (1959), obtained the upper limit of NO molecules as 10^{15} molecules cm⁻² above the altitude range 63-87 km. Again, Barth (1964) obtained a NO column density of 1.5×10^{13} molecules cm⁻² above 125 km. This agrees with the value obtained from the computed curve which gives about 3×10^{13} molecules cm⁻² column⁻¹ above this altitude.

4. NI(5200A, ${}^{2}D^{-4}S$) line is observed in twilight and night airglows and appears with an intensity less than 5R at night and lOR at twilight (Silverman, <u>et al.</u>, 1965). Assuming that this line is emitted at 90-100 km and that the lifetime of the N(${}^{2}D$) atom is about 26 hours (Hunten, <u>et al.</u>, 1966), the concentration of N atoms at twilight can be obtained from the rate of production and quenching of the N(${}^{2}D$) atoms, namely

$$n(N)Bn(h\nu) = n(N^2D)[A+n(M)\gamma]$$

where

Therefore, the emission rate of 5200A line is given by

$$\mathbf{r} = \mathbf{n}(\mathbf{N}^2 \mathbf{D})\mathbf{A} = \frac{\mathbf{n}(\mathbf{N})\mathbf{B}\mathbf{n}(\mathbf{h}_V)}{\mathbf{A} + \mathbf{n}(\mathbf{M})\gamma}\mathbf{A}$$

Substituting B in terms of A and $n(h\nu)$ from Planck's formula,* we obtain

$$n(N) = \frac{r(A+n(M)\gamma)}{A^2 D} \exp(h\nu/kT) ,$$

where

D = dilution factor = 5.41×10^{-6} , and k = Boltzmann constant.

No precise information regarding the quenching cross-section involving metastable atoms is available. According to Laidler (1954) the coefficient of quenching reactions involving nonmetastable atoms is of the order of $10^{-12} \text{ cm}^3/\text{particle}$ sec. The coefficient for the metastable $N(^2\text{D})$ atoms by N₂ and O₂ is assumed to be one order smaller than the above value, that is, $\gamma = 10^{-13} \text{ cm}^3/\text{particle}$ sec. Assuming the sun's temperature T = 6000°K and the mean altitude of emission of 5200A line at twilight to be 90 km, we obtain $n(N) = 3 \times 10^7 \text{ cm}^{-3}$. The computed N-atom distribution shows that at 100 km the concentration is $1 \times 10^8 \text{ cm}^{-3}$.

^{*}In the visible region the number of photons calculated from Planck's blackbody formula for T = 6000°K agrees with the observed value.

REFERENCES

- Barth, C. A., J. Geophys. Res. <u>69</u>, 3301 (1964); Space Research <u>5</u>, 767 (1965), North-Holland Publishing Company, Amsterdam.
- Biondi, M. A., Advances in Electronics and Electron Physics, Academic Press, 18, 152 (1963).

Byron, S. R., J. Chem. Phys. 30, 1380 (1959).

- Cormier, R. J., J. C. Ulwick, J. A. Klobuchar, W. Pfister, and T. J. Keneshea, Handbook of Geophysics and Space Environments, 1965, p. 12-8.
- Danilov, A. D., Cospar Seventh International Space Science Symposium, Vienna, May, 1966, Abstract of Papers.

Dickison, P.H.G. and J. Sayers, Proc. Phys. Soc. London, 76, 137 (1960).

- Ditchburn, R. W., J.E.S. Bradley, C. G. Cannon, and G. Munday, Rocket Exploration of the Upper Atmosphere, Ed. R.L.F. Boyd and J. J. Seaton, Pergamon Press, p. 313, 1954.
- Fehsenfeld, F. C., A. L. Schmeltekopf, and E. E. Ferguson, Planet. Space Sci. <u>13</u>, 219 (1965a).
- Fehsenfeld, F. C., A. L. Schmeltekopf, and E. E. Ferguson, Planet. Space Sci. 13, 919 (1965b).
- Ferguson, E. E., F. C. Fehsenfeld, P. D. Goldan, A. L. Schmeltekopf, and H. I. Schiff, Planet. Space Sci. 13, 823 (1965).
- Ford, H. W., G. J. Doyle, and N. Endow, J. Chem. Phys. 26, 1337 (1957a).

Ford, H. W. and N. Endow, J. Chem. Phys. 27, 1156 (1957b).

- Galli, A., A. Giardini-Guidoni, and G. G. Volpi, J. Chem. Phys. <u>39</u>, 518 (1963).
- Gast, P. R., A. S. Jursa, J. Castelli, S. Basu, and J. Aarons, Handbook of Geophysics and Space Environments, 1965, p. 16-14.

Ghosh, S. N., K. D. Sharma, and A. Sharma, Ind. J. Phys. <u>38</u>, 106 (1964).

Gibbons, J. J., Abstracts of D.A.S.A. Reaction Rate Conference, 1961, Boulder, Colorado, Nat. Bur. Std. (U.S.).

- Goldan, P. D., A. L. Schmeltekopf, F. C. Feshenfeld, H. I. Schiff, and E. E. Ferguson, J. Chem. Phys. <u>44</u>, 4095 (1966).
- Handbook of Geophysics, Air Force Cambridge Research Laboratories, Ed. S. L. Valley, 1960.
- Harteck, P. and S. Dondes, J. Chem. Phys. 27, 546 (1957).
- Harteck, P., R. R. Reeves, and G. Manella, J. Chem. Phys. 29, 608 (1958).
- Harteck, P. and R. R. Reeves, Chemical Reactions in the Lower and Upper Atmosphere, Interscience, 1961, p. 233.
- Harteck, P. and R. R. Reeves, Chemical Reactions in the Lower and Upper Atmosphere, Interscience, 1961, pp. 231, 234.
- Hedin, A. E. and A. O. Nier, J. Geophys. Res. 70, 1273 (1965).
- Herron, J. T., J. L. Franklin, P. Bradt, and V. H. Dibeler, J. Chem. Phys. <u>30</u>, 879 (1959); <u>29</u>, 230 (1958).
- Hunten, D. M. and M. B. McElroy, Rev. Geophys. 4, 303 (1966).
- Johnson, C. W., J. Geophys. Res. <u>71</u>, 330 (1966).
- Johnston, H. S. and H. J. Crosby, J. Chem. Phys. 19, 799 (1951).
- Jursa, A. S., Y. Tanaka, and F. LeBlanc, Planet. Space Sci. 1, 161 (1959).
- Kaplan, J. and C. A. Barth, Proc. Nat. Acad. Sci. <u>44</u>, 105 (1958).
- Kaufman, F., Proc. Roy. Soc. A. 247, 123 (1958).
- Kistiakowsky, G. B. and G. G. Volpi, J. Chem. Phys. 27, 1141 (1957).
- Kistiakowsky, G. B. and G. G. Volpi, J. Chem. Phys. <u>28</u>, 665 (1958).
- Laidler, K. J., Chemical Kinetics of Excited States, Oxford University Press, 1954, p. 159.
- Mirtov, B. A., Gaseous Composition of the Atmosphere and Its Analysis, NASA (1964), p. 133.
- Mitra, A. P., Advances in Upper Atmosphere Research, MacMillan Company, 1963, p. 57.

- Nawrocki, P. J. and R. Papa, Atompsheric Processes, Prentice-Hall, Inc., 1963, pp. 3-27.
- Nawrocki, P. J. and R. Papa, Atmospheric Processes, Prentice-Hall, Inc., 1963, pp. 3-46 (Coeff. is assumed to be same for similar reactions).
- Nicolet, M., Physics and Medicine of the Atmosphere and Space, Ed. Benson, O. O. Jr., and H. Strughold, John Wiley, 1960.

Nicolet, M., J. Geophys. Res. 70, 679 (1965a).

Nicolet, M., J. Geophys. Res. 70, 691 (1965b).

Schaefer, E. J., Private Communication.

- Silverman, S. M., G. J. Hermandez, A. L. Carrigan, and T. P. Markham, Handbook of Geophysics and Space Environments, 1965, p. 13-3.
- Sugden, T. M., Chemical Reactions in the Lower and Upper Atmosphere, Interscience, 1961, p. 330.
- Talrose, V. L., M. I. Markin, and I. K. Larin, Disc. Faraday Soc. 33, 257 (1962).
- Watanabe, K., M. Zelikoff, and E.C.Y. Inn, Geophysical Research Paper No. 21, June 1953.
- Watanabe, K., J. Chem. Phys. 22, 1564 (1954).
- Watanabe, K., Advances in Geophysics 5, 153 (1958), Academic Press.
- Whitten, R. C. and I. G. Poppoff, J. Atmos. Sci. 21, 117 (1964).
- Whitten, R. C. and I. G. Poppoff, Physics of the Lower Ionosphere, Prentice-Hall, 1965. See Fig. 4., 1, p. 77.
- Whitten, R. C. and I. G. Poppoff, Physics of the Lower Ionosphere, Prentice-Hall, 1965, p. 103.
- Whitten, R. C. and I. G. Poppoff, Physics of the Lower Ionosphere, Prentice-Hall, 1965, p. 122.
- Young, C. and E. S. Epstein, J. Atmos. Sci. 19, 435 (1962).
- Young, R. A. and R. L. Sharpless, J. Chem. Phys. 39, 1071 (1963).
- Young, R. A., J. Chem. Phys. 34, 1295 (1961).











rate of N atoms, multiply x by [N].







Fig. 5. Production rates of N-atoms by various reactions for rate coefficients varying with temperature.



ļ

Fig. 6. Variation of x with altitude for two-body reactions having rate co-efficients varying with temperature. Loss rate = x [N]. NO(1) and NO(4) represent NO density obtained from Curves (1) and (4) of Fig. 9, respectively.



Fig. 7. Production rates of NO molecules by various reactions with rate co-efficients varying with temperature.



Fig. 8. Variation of x with altitude for various reactions having rate coefficients varying with temperature. To obtain loss rate of NO molecules, multiply x by [NO].



Fig. 9. Computed altitude distributions of N and NO. For comparison, the distributions of O, O₂ and N₂ obtained from CIRA 1965 are also shown.
(1) Assumed NO distribution; (2) N distribution for (1) for constant rate coefficient; (3) N distribution for (1) for rate coefficient varying with temp.;
(4) calculated NO distribution for (3) for rate coefficient varying with temp.;
(5) N distribution calculated from (4); (6) N₂ distribution from CIRA 1965;
(7) O distribution from CIRA 1965; (8) O₂ distribution from CIRA 1965.