NsG-416

SPACE RESEARCH COORDINATION CENTER

FACILITY FORM 602

N65-27951
(ACCESSION NUMBER)

(THRU)

39
(PAGES)

1
(CODE)

CR 63763
(NASA CR OR TMX OR AD NUMBER)

06
(CATEGORY)

IONOSPHERIC REACTION RATES IN THE LIGHT OF RECENT MEASUREMENTS IN THE IONOSPHERE AND THE LABORATORY

BY

T. M. DONAHUE

DEPARTMENT OF PHYSICS

GPO PRICE $ ______

OTS PRICE(S) $ ______

Hard copy (HC) 2.00

Microfiche (MF) .50

SRCC REPORT NO. 5

UNIVERSITY OF PITTSBURGH

PITTSBURGH, PENNSYLVANIA

27 MAY 1965

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The Center is supported by a Research Grant (NsG-416) from the National Aeronautics and Space Administration, strongly supplemented by grants from The A. W. Mellon Educational and Charitable Trust, the Maurice Falk Medical Fund, the Richard King Mellon Foundation and the Sarah Mellon Scaife Foundation. Much of the work described in SRCC reports is financed by other grants, made to individual faculty members.

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T. M. Donahue

Planetary and Space Science

University of Pittsburgh
Pittsburgh, Pennsylvania

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T. M. Donahue

University of Pittsburgh, Pittsburgh, Pennsylvania

(Received)

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ABSTRACT

An attempt is made to obtain sets of ion-molecule reaction rates and recombination coefficients consistent with recent mass spectrometric ion data between 120 and 220 km. It is found that recently measured rates of 3×10^{-12} cm^3/sec for formation of NO^+ from $O^+ + N_2$ and 4×10^{-13} cm^3/sec for charge exchange in $N_2^+ + O_2$ require that the rate of formation of NO^+ in the $N_2 + O$ reaction be larger than 5×10^{-10} cm^3/sec at 300°. Daytime conditions are susceptible to explanation with a wide range of possible rates. The observations require that the dissociative recombination coefficient for NO^+ decrease from 5×10^{-7} cm^3/sec at 300° as $T^{-3/2}$ and for O_2^+ decrease from 3.5×10^{-7} cm^3/sec as $T^{-2/3}$. The nighttime ionosphere can be explained with the same recombination coefficients. The nocturnal NO^+ maximum in the E region then requires an ionization of N_2 at the rate of 6-10 ion pairs/cm^3 sec. N_2^+, O_2 charge exchange reaction must be slow and the N_2^+ O ion atom interchange reaction rapid unless NO^+ production from N_2^+, O_2 and O_2^+, NO reactions is efficient. A source of ionization is also required above 180 km to explain the appearance of N_2^+ at night.

Author

1. INTRODUCTION

A recent measurement(1) of the rate of the charge transfer reaction

$$N_2^+ + O_2 \rightarrow O_2^+ + N_2$$

at thermal energy has given the surprisingly low value of 4×10^{-13} cm^3/sec. This is almost three orders of magnitude less than a value of 2×10^{-10} cm^3/sec measured previously in an afterglow experiment(2) and it seriously reduces the effectiveness of a mechanism considered very important for the removal of N_2^+ ions in the ionosphere. This is particularly troubling in that during the same series of experiments(1) and by a very similar technique the rate for the ion atom interchange reaction

$$O^+ + N_2 \rightarrow NO^+ + N$$

was found to be only 3×10^{-12} cm^3/sec, again the smallest value measured to this time. Such a low rate of removal of O^+ by this reaction would severely limit the permitted rate at which O^+ ions are created in the charge exchange

$$N_2^+ + O \rightarrow O^+ + N_2$$

These measurements in combination leave very few avenues open for draining away N_2^+. It is the purpose of this note to point out that if the measured rates apply to the states in which O^+ and N_2^+ are found in the E region they are consistent with the most recent ionospheric data only if the rate for the ion-atom interchange

$$N_2^+ + O \rightarrow NO^+ + N$$

is of the order of 5×10^{10} cm^3/sec. Since it has been questioned whether this reaction is exothermic this is a severe requirement and certainly demands a measurement of the rate for this very interesting reaction.

The densities of the principal ionic constituents of the upper E and lower F regions have recently been obtained mass spectrometrically in the daytime and in the nighttime(3). The results are shown in Table 1 at altitudes of 120, 140, 160 and 220 km. Because the sum of the ion densities was less than the electron densities up to about 160 km where O^+ began to be the dominant ionic species the measured values of molecular ions were arbitrarily multiplied by a factor of 1.75 in the table. This was done to render the calculation self-consistent and has no qualitative effect on the principal deductions in this paper.

The salient features of the observations are the low values of N_2^+ densities in the daytime and the near equality of O_2^+ and NO^+ densities at all altitudes. O^+ becomes predominant above 180 km. At night the persistence of NO^+ at low altitude is striking. Only NO^+ and O_2^+ are observed below 200 km. While the density of O_2^+ is low and virtually independent of altitude up to 190 km, the NO^+ density is very high near 125 km, decreases to a minimum at 170 km, then rises again. The O^+ density increases sharply above 200 km along with the NO^+ and O_2^+ densities so that by 200 km, O^+, NO^+ and O_2^+ are equal in abundance. The appearance of a measurable quantity of N_2^+ above 200 km at night is a surprise in view of the rapid removal processes which dispose of this ion in the day time.

Table 1

Daytime Ionic Densities in cm^{-3}

Altitude km	(1) O^+	(2) N_2^+	(3) O_2^+	(4) NO^+	N^+	Ne
120	2×10^2	5.0×10	6.2×10^4	3.5×10^4		10^5
140	4×10^3	4.5×10^2	6.25×10^4	5.7×10^4		1.3×10^5
160	3.3×10^4	1.13×10^3	6.1×10^4	10^5	2×10^2	2×10^5
220	4×10^5	1.7×10^3	1.2×10^4	1.7×10^4	2×10^3	4×10^5

Ionization Rates in ion pairs/cm^3 sec

Altitude km	Q_1	Q_2	Q_3
120	4.6×10^2	1.6×10^3	8.6×10^2
140	8.9×10^2	2.0×10^3	7.1×10^2
160	7.7×10^2	1.5×10^3	3.0×10^2
220	2.5×10^2	2.3×10^2	2.6×10

Neutral Densities in particles/cm^3

Altitude km	(1) O	(2) N_2	(3) O_2	(4) NO	T °K
120	4×10^{10}	$3. \times 10^{11}$	4×10^{10}	1.6×10^7	310°
140	1.2×10^{10}	4.3×10^{10}	3.9×10^9		440°
160	4.2×10^9	9.3×10^9	7×10^8		620°
220	7.5×10^8	6.1×10^8	3.3×10^7		937°

Table 1. Ionospheric and Atmospheric Data in the Daytime. Measured densities for diatomic ions have been multiplied by a factor of 1.75. The ion densities at 120 km represent an extrapolation of some 10 km. Q_i are for 30° solar elevation.

There are also available now mass spectrometric values for the densities of the neutral species(4,5,6). These are tabulated in Table 1. On the basis of these densities Zipf(7) has reevaluated the rates of photoionication, taking into account also the ionization by energetic photoelectrons. His results for the ionization rates for the solar zenith angle which existed at the time of the observations are also shown in the table.

The problem to which this paper is addressed is really the consistency of these particular sets of observations with laboratory reaction rate measurements. The main conclusions hold, however, for most of the observed profiles of ionic abundance in the E and F_1 regions. The comparison of ionospheric reaction rates with measured laboratory rates, however, is subject always to the reservation that the states of the ions and molecules involved may not be the same. Hence, inconsistency cannot be taken to imply inescapably that experimental errors exist in one or another set of measurements.

2. IONIC CHEMISTRY

Nicolet and Swider(8) recently have reviewed the chemistry of the ion and electron reactions involved. Since here the concern is with the region above 120 km the list of reactions of importance is reduced in length compared to theirs. In particular those reactions which involve NO and N as neutral species turn out to be of negligible importance in the day. To systematize somewhat the notation for reaction rates the atomic or molecular species will be denoted by numbers, O being 1; N_2, 2; O_2, 3; NO, 4 and N, 7. The ion-molecule reaction rate coefficients will be written (i j, k) where i is the ion before collision and k the ion afterward.

The following are the reactions which transform

O^+:

$O^+ + N_2 \rightarrow NO^+ + N$, (12,4)

$O^+ + O_2 \rightarrow O_2^+ + O$, (13,3)

N_2^+:

$N_2^+ + O \rightarrow NO^+ + N$, (21,4)

$N_2^+ + O \rightarrow O^+ + N_2$, (21,1)

$N_2^+ + O_2 \rightarrow NO^+ + NO$, (23,4)

$N_2^+ + O_2 \rightarrow N_2 + O_2^+$, (23,3)

O_2^+: $O_2^+ + N_2 \rightarrow NO^+ + NO$, (32,4)

$O_2^+ + NO \rightarrow NO^+ + O_2$, (34,4)

N^+:

$N^+ + O_2 \rightarrow NO^+ + O$ (53,4)

The dissociative recombination rates will be designated α_2 for N_2^+, α_3 for O_2^+ and α_4 for NO^+. The ionization rates by photons and photoelectrons similarly will be written as Q_1.

The situation with regard to slow ion molecule collisions has been reviewed recently by Paulson(9). References to the original researches may be had in that review with a few exceptions to which references will be specifically given here.

The measured rates for the various reactions which have been reported are the following

(12,4) 27×10^{-12} cm^3/sec (10)

22×10^{-12} cm^3/sec (11)

6.7×10^{-12} cm^3/sec

4.7×10^{-12} cm^3/sec

3×10^{-12} cm^3/sec (1)

(13,3)	$< 5 \times 10^{-11}$ cm^3/sec	
	1.6×10^{-11} cm^3/sec	
	0.2×10^{-11} cm^3/sec	
(21,4)	-------	
(21,1)	-------	
(23,3)	2×10^{-10} cm^3/sec	(2)
	4×10^{-13} cm^3/sec	(1)
(23,4)	$< 2 \times 10^{-13}$ cm^3/sec	
	$< 2 \times 10^{-13}$ cm^3/sec	
(32,4)	$< 4 \times 10^{-14}$ cm^3/sec	
	$< 2 \times 10^{-13}$ cm^3/sec	
(53,4)	5×10^{-10} cm^3/sec	
	$\sim 10^{-10}$ cm^3/sec	
α_2	3×10^{-7} cm^3/sec	(12)
α_3	2×10^{-7} cm^3/sec	(13,14)
α_4	$4\text{-}20 \times 10^{-7}$ cm^3/sec	(15)

The great spread in the reported rates for (12,4) and (23,3) presents a most perplexing problem. Neither α_3 nor α_4 has been determined precisely even at 300° K and of course the dependence of these rates on electron and ion temperature and on the states of the reactants is almost entirely unknown. Finally the rates for the key processes (21,4) and (21,1) are not yet measured. Although it has been argued(8) that the state of NO^+ produced in the reactions (21,4) and (23,4) is the excited $^3\Pi$ electronic state and these reactions are endothermic, the situation is not completely clear. For one thing the energy of the $^3\Pi$ state is not well known. While there is plausibility in the argument that this is the final state or, if not, that an electronic transition is involved in the reaction and the cross section should be low, the theory of rearrangement collisions of this sort cannot be said to exist. Thus it would not appear to be safe to reject (21,4) out of hand at this time, distasteful though a high cross section for it may be to some.

In the absence of significant diffusive flow

$$\frac{dO^+}{dt} = \left\{Q_1 + (21,1)\, N_2^+ \cdot O\right\} - \left\{(12,4) O^+ \cdot N_2 + (13,3)\, O^+ \cdot O_2\right\} \qquad (1)$$

$$\frac{dN_2^+}{dt} = Q_2 - \Big\{\big[(21,4) + (21,1)\big]\; N_2^+ \cdot O + \big[(23,3) + (23,4)\big] \qquad (2)$$

$$N_2^+ \cdot O_2 + \alpha_2\, N_2^+ \cdot N_e \Big\}$$

$$\frac{dO_2^+}{dt} = \left\{Q_3 + (23,3)\, N_2^+ \cdot O_2\right\} - \left\{(32,4)\, O_2^+ \cdot N_2 + \alpha_3\, O_2^+ \cdot \mathrm{Ne}\right\} \qquad (3)$$

$$\frac{dNO^+}{dt} = \Big\{(12,4)\, O^+ \cdot N_2 + (21,4)\, N_2^+ \cdot O + (32,4)\, O_2^+ \cdot N_2 + (23,4) \qquad (4)$$

$$N_2^+ \cdot O_2 + (53,4)\, N^+ \cdot O_2\Big\} - \alpha_4\, NO^+ \cdot N_e$$

$$Q_1 + Q_2 + Q_3 = \alpha_2\, N_2^+ \cdot N_e + \alpha_3\, O_2^+ \cdot N_e + \alpha_4\, NO^+ \cdot N_e \qquad (5)$$

For the concentration $[X]$ the chemical symbol X is employed and the product of two concentrations is written $X \cdot Y$ to distinguish it from the symbol for the molecule XY.

3. THE IONOSPHERIC CONDITIONS: DAYTIME

In the daytime steady state from the data in Table 1 the important terms in these equations at 120 km, 140 km and 160 km are as follows.

At 120 km

$$O^+: \quad 7.5\,(12,4) + (13,3) - 0.25\,(21,1) = 6 \times 10^{-11} \tag{6}$$

$$N_2^+: \quad (21,4) + (21,1) + (23,3) = 8 \times 10^{-10} \tag{7}$$

$$O_2^+: \quad \alpha_3 = 1.85 \times 10^{-7} + 1.3 \times 10^3 (13,3) + 3.2 \times 10^2\,(23,3) - 3 \times 10^6\,(32,4) \tag{8}$$

$$NO^+: \quad \alpha_4 = 1.7 \times 10^4\,(12,4) + 5.5 \times 10^6\,(32,4) + 5.7 \times 10^2 (21,4) \tag{9}$$

$$\alpha_4 + 1.75\,\alpha_3 = 11.5 \times 10^{-7} \tag{10}$$

140 km

$$O^+: \quad 9.1\,(12,4) + (13,3) - 0.3\,(21,1) = 5.9 \times 10^{-11} \tag{11}$$

$$N_2^+: \quad 2.5\,\left[(21,4) + (21,1)\right] + (23,3) = 12.5 \times 10^{-10} \tag{12}$$

$$O_2^+: \quad \alpha_3 = 1.2 \times 10^{-7} + 2.4 \times 10^3\,(13,3) + 2.7 \times 10^2\,(23,3) - 3.4 \times 10^5\,(32,4) \tag{13}$$

$$NO^+: \quad \alpha_4 = 2.35 \times 10^4\,(12,4) + 3.6 \times 10^5\,(32,4) + 7.3 \times 10^2 (21,4) \tag{14}$$

$$\alpha_4 + 1.1\,\alpha_3 = 6.6 \times 10^{-7} \tag{15}$$

160 km

$$O^+: \quad 10\ (12,4) + (13,3) - 0.15\ (21,1) = 2.6 \times 10^{-11} \tag{16}$$

$$N_2^+: \quad 4.5\ \left[(21,4) + (21,1\right] + (2.3,3) = 17.5 \times 10^{10} \tag{17}$$

$$O_2^+: \quad \alpha_3 = 3.3 \times 10^{-8} + 2.9 \times 10^3\ (13,3) + 10^2 \times (23,3) - 5.4 \times 10^4\ (32,4) \tag{18}$$

$$NO^+: \quad \alpha_4 = 1.75 \times 10^4\ (12,4) + 3.2 \times 10^4\ (32,4) + 2.5 \times 10^2\ (21,4) \tag{19}$$

$$1.55\ \alpha_4 + \alpha_3 + 0.18\ \alpha_2 = 2.65 \times 10^{-7} \tag{20}$$

It turns out that the term in α_2 for N_2^+ may be neglected at all three altitudes compared to the production term and also that the terms in (23,4) and (53,4) are both small. Still there are only 4 independent relationships for the 6 coefficients (12,4), (13,3) (21,4), (21,1), (23,3) and (32,4) and α_3 and α_4.

If there were no production terms at night the differential equations (1-4) would supply the 4 missing equations. Unfortunately, except perhaps near 160 km, it is not at all clear that a simple decay of ionization describes the nocturnal situation. At this altitude, furthermore, the electron temperature changes considerably from day to night. The recombination coefficients may be quite different for the two sets of conditions.

Under these circumstances it is practically necessary to begin by assuming, where experiments are until now more or less in agreement, that those coefficients have their measured values. Thus (13,3) can be taken to be 5×10^{-11} cm^3/sec - the most favorable condition for a small value of (12,4). An upper limit, in fact, may be put on the rate at which O^+ is changed into O_2^+ in (18) by the upper limit (20) sets on α_3- 2×10^{-7} cm^3/sec. This limit for (13.3) is 6×10^{-11} cm^2/sec.

3.1 120 km

Then at 120 km the O^+ and N_2^+ equations may be combined to eliminate (21,1) and give

$$30(12,4) + 4(13,3) + [(21,4) + (22,3)] = 10.4 \times 10^{-10}.$$

With $$(13,3) = 5 \times 10^{-11} \text{ cm}^3/\text{sec}$$

this becomes

$$(12,4) = 2.8 \times 10^{-11} - 3.3 \times 10^{-12} [(21,4) + (23,3)]$$

and (12,4) may be 3×10^{-12} only if

$$(21,4) + (23,3) = 7.5 \times 10^{-10} \text{ cm}^3/\text{sec}.$$

Then, from (7)

$$(21,1) = 5 \times 10^{-11} \text{ cm}^3/\text{sec}.$$

Thus to require that (23,3) be as small as 4×10^{-13} calls for a very large value, 7.5×10^{-10} cm^3/sec, for (21,4). On the other hand if (23,3) were 2×10^{-10} cm^3/sec (21,4) would still need to be 5.5×10^{-10} cm^3/sec.

From (9) the rates

$$(12,4) = 3 \times 10^{-12} \text{ cm}^3/\text{sec}$$

$$(21,4) = 7.5 \times 10^{-10} \text{ cm}^3/\text{sec}$$

mean that the recombination coefficient for NO^+ must be given by

$$\alpha_4 = 4.8 \times 10^{-7} + 5.5 \times 10^{6} \; (32,4)$$

It will be shown, from a study of the night time decay of O_2^+ that (32,4) probably is only of the order of 10^{-14} cm^3/sec. Thus, we set

$$(32,4) = 10^{-14} \text{ cm}^3/\text{sec}$$

and

$$\alpha_4 = 5.3 \times 10^{-7} \text{ cm}^3/\text{sec}$$

This implies from (10),

$$\alpha_3 = 3.6 \times 10^{-7} \text{ cm}^3/\text{sec}.$$

On the other hand, with

$$(12,4) = 3 \times 10^{-12} \text{ cm}^3/\text{sec}$$

$$(23,3) = 2 \times 10^{-10} \text{ cm}^3/\text{sec}$$

$$(21,4) = 5.5 \times 10^{-10} \text{ cm}^3/\text{sec}$$

the condition on α_4 becomes

$$\alpha_4 = 4.2 \times 10^{-7} \text{ cm}^3/\text{sec}$$

and

$$\alpha_3 = 4.1 \times 10^{-7} \text{ cm}^3/\text{sec}.$$

To require both (23,3) and (21,4) to be small would mean that

$$(12,4) \cong 30 \times 10^{-12} \text{ cm}^3/\text{sec}$$

$$(21,1) \cong 8 \times 10^{-10} \text{ cm}^3/\text{sec}$$

$$\alpha_4 \cong 5.8 \times 10^{-7} \text{ cm}^3/\text{sec}$$

$$\alpha_3 \cong 3.3 \times 10^{-7} \text{ cm}^3/\text{sec}$$

3.2 140 km

Following the same argument at 140 km it turns out that

$$96(12,4) + 8.3(13,3) + 2.5(21,4) + (23,3) = 17.4 \times 10^{-10}$$

With

$$(13,3) = 5 \times 10^{-11} \text{ cm}^3/\text{sec}$$

it follows that

$$(12,4) = 14 \times 10^{-12} - 2.6 \times 10^{-2}(21,4) - 10^{-2}(23,3).$$

If

$$(12,4) = 3 \times 10^{-12} \text{ cm}^3/\text{sec}$$

$$2.6(21,4) + (23,3) = 11 \times 10^{-10}$$

Again the small value

$$(23,3) = 4 \times 10^{-13} \text{ cm}^3/\text{sec}$$

is possible only if (21,4) is large:

$$(21,4) = 4.4 \times 10^{-10} \text{ cm}^3/\text{sec}$$
$$(21,1) = 6 \times 10^{-11} \text{ cm}^3/\text{sec}$$

Then $\alpha_4 = 3.9 \times 10^{-7} + 3.6 \times 10^{5}(32,4)$

which gives

$$\alpha_4 = 3.9 \times 10^{-7} \text{ cm}^3/\text{sec}$$

$$\alpha_3 = 2.4 \times 10^{-7} \text{ cm}^3/\text{sec}$$

with

$$(32,4) = 10^{-14} \text{ cm}^3/\text{sec}.$$

Even if

$$(23,3) = 2 \times 10^{-10} \text{ cm}^3/\text{sec}$$

the small value of (12,4) requires

$$(21,4) = 3.5 \times 10^{-10} \text{ cm}^3/\text{sec}$$

and

$$\alpha_4 = 3.2 \times 10^{-7} \text{ cm}^3/\text{sec}$$

$$\alpha_3 = 3.1 \times 10\text{-}7 \text{ cm}^3/\text{sec}$$

On the other hand, if (23,3) is small then (21,4) can also be small if

$$(21,1) \cong 5 \times 10^{-10} \text{ cm}^3/\text{sec}$$

$$(12,4) = 15.5 \times 10^{-12} \text{ cm}^3/\text{sec}$$

$$\alpha_4 = 3.6 \times 10^{-7} \text{ cm}^3/\text{sec}$$

$$\alpha_3 = 2.7 \times 10^{-7} \text{ cm}^3/\text{sec}$$

3.3 160 km

At 160 km

$$(12,4) + 10^{-1}\,(13,3) + 1.55 \times 10^{-2}\,(21,4) + (3.5 \times 10^{-3})(23,3) = 7.4 \times 10^{-12}$$

Here (13,3) cannot be as large as 5×10^{-11} cm^3/sec if (12,4) is to reach 3×10^{-12} cm^3/sec. If it is assumed that

$$(13,3) = 3 \times 10^{-11} \text{ cm}^3/\text{sec}$$

and

$$(12,4) = 3 \times 10^{-12} \text{ cm}^3/\text{sec}$$

then

$$(21,4) + 2.2 \times 10^{-1}\,(23,3) = 9.2 \times 10^{-11}$$

With

$$(23,3) = 4 \times 10^{-13} \text{ cm}^3/\text{sec}$$

$$(21,4) = 9.2 \times 10^{-11} \text{ cm}^3/\text{sec}$$

$$(21,1) = 3 \times 10^{-10} \text{ cm}^3/\text{sec}$$

and $\alpha_4 = 0.75 \times 10^{-7}$ cm^3/sec

while $\alpha_3 = 1.5 \times 10^{-7}$ cm^3/sec

On the other hand if

$$(23,3) = 2 \times 10^{-10} \text{ cm}^3/\text{sec}$$

it follows that

$$(21,4) = 4.8 \times 10^{-11} \text{ cm}^3/\text{sec}$$

and

$$\alpha_4 = .63 \times 10^{-7} \text{ cm}^3/\text{sec}$$

$$\alpha_3 = 1.7 \times 10^{-7} \text{ cm}^3/\text{sec}$$

Here, if both (21,4) and (23,3) are small it is required that

$$(21,1) \cong 3.9 \times 10^{-10} \text{ cm}^3/\text{sec}$$

$$(12,4) = 4.4 \times 10^{-12} \text{ cm}^3/\text{sec}$$

$$\alpha_4 = 1. \times 10^{-7} \text{ cm}^3/\text{sec}$$

$$\alpha_3 = 1.1 \times 10^{-7} \text{ cm}^3/\text{sec}$$

These results are summarized in Table 2. Also included in that table is a set of conditions which must prevail if (23,3) is 2 x 10^{-10} cm^3/sec and (21,4) is small. In that case it is assumed that

$$(13,3) = 3 \times 10^{-11} \text{ cm}^3/\text{sec}$$

at all levels. The other rates follow from the relationships

at 120 km

$$(12,4) = 3.1 \times 10^{-11} - 3.3 \times 10^{-2} \left[(21,4) + (23,3)\right]$$

at 140 km

$$(12,4) = 15.5 \times 10^{-12} - 2.6 \times 10^{-2} (21,4) - 10^{-2} (23,3)$$

Table 2

Reaction Rate Coefficients at Various Altitudes

120 km $T_e = 280°$)				
(12,4)	3×10^{-12}		24×10^{-12}	30×10^{-12}
(21,1)	5×10^{-11}		6×10^{-10}	8×10^{-10}
(23,3)	4×10^{-13}	2×10^{-10}	2×10^{-10}	4×10^{-13}
(21,4)	7.5×10^{-10}	5.5×10^{-10}	$< 10^{-11}$	$< 10^{-11}$
$\alpha_4 =$	5.3×10^{-7}	4.2×10^{-7}	4.7×10^{-7}	5.8×10^{-7}
$\alpha_3 =$	3.6×10^{-7}	4.1×10^{-7}	3.9×10^{-7}	3.3×10^{-7}
140 km $T_e = 420°$				
(12,4)	3×10^{-12}		13.5×10^{-12}	15.5×10^{-12}
(21,1)	6×10^{-11}		4.2×10^{-10}	5×10^{-10}
(23,3)	4×10^{-13}	2×10^{-10}	2×10^{-10}	4×10^{-13}
(21,4)	4.4×10^{-10}	3.5×10^{-10}	$< 10^{-11}$	$< 10^{-11}$
$\alpha_4 =$	3.9×10^{-7}	3.2×10^{-7}	3.2	3.6
$\alpha_3 =$	2.4×10^{-7}	3.1×10^{-7}	3.1	2.7
160 km $T_e = 1000°$				
(12,4)	3×10^{-12}		3.7×10^{-12}	4.4×10^{-12}
(21,1)	3×10^{-10}		3.5×10^{-10}	3.9×10^{-10}
(23,3)	4×10^{-13}	2×10^{-10}	2×10^{-10}	4×10^{-13}
(21,4)	$.9 \times 10^{-10}$	4.8×10^{-11}	$< 10^{-11}$	$< 10^{-11}$
$\alpha_4 =$	0.75×10^{-7}	$.63 \times 10^{-7}$	0.65×10^{-7}	1×10^{-7}
$\alpha_3 =$	1.5×10^{-7}	1.7×10^{-7}	1.65×10^{-7}	1.1×10^{-7}
α_4	$T_e^{-1.54}$	$T_e^{-1.49}$	$T_e^{-1.55}$	$T_e^{-1.39}$
α_3	$T_e^{-0.68}$	$T_e^{-0.69}$	$T_e^{-0.68}$	$T_e^{-0.86}$

Table 2 (Cont.)

220 km $T_e = 2200°$

$\alpha_4 =$	$.22 \times 10^{-7}$	$.19 \times 10^{-7}$	$.19 \times 10^{-7}$	$.33 \times 10^{-7}$
$\alpha_3 =$	$.88$	1.0	$.97$	0.55
α_2	$.2 \times 10^{-7}$	<0	<0	1.4×10^{-7}

$$\left\{\begin{array}{l|l} (12,4) + 6.2 \times 10^{-3}\,(21,4) = 10^{-12} & 1.7 \times 10^{-12} \\ (21,4) + (21,1) + 3.5 \times 10^{-2}\,(23,3) = 2.8 \times 10^{-10} & 1.8 \times 10^{-10} \\ (12,4) + 5 \times 10^{-2}\,(13,3) - 6.4 \times 10^{-3}\,(21,1) = 2.3 \times 10^{-12} & \end{array}\right.$$

$$\text{or}\left\{\begin{array}{l|l} (12,4) - 6.2 \times 10^{-3}\,(21,1) = -0.7 \times 10^{-12} & +\,0.7 \times 10^{-12} \\ (12,4) - 6.4 \times 10^{-3}\,(21,1) = 2.3 \times 10^{-12} - 5 \times 10^{-2}\,(13,3) & \end{array}\right.$$

$(1.3,3) =$	6×10^{-11}	3×10^{-11}
$(12,4) =$	10^{-12} (upper limit)	1.7×10^{-12}
$(21,1) =$	2.7×10^{-10} (upper limit)	1.6×10^{-10}
$(21,4) <$	10^{-11}	$< 10^{-11}$

at 160 km

$$(12,4) = 4.4 \times 10^{-12} - 1.55 \times 10^{-2} (21,4) - 3.5 \times 10^{-3} (23,3)$$

At low altitude--below 150 km--the very small value of 3×10^{-12} cm^3/sec for removal of O^+ by the formation of NO^+ tolerates only a slow rate of production of O^+ in the N_2^+, O charge exchange (21,1). The loss of this mode of transforming N_2^+ means that for adequately efficient N_2^+ removal the rate (21,4) for NO^+ formation must be large whether (23,3) is fast or not. If it should develop that this ion atom interchange reaction of N_2^+ and O is slower than 10^{-10} cm^3/sec, then neither of the low rates, the one for O^+, N_2 formation of NO^+ (12,4) nor the one for N_2^+, O_2 charge exchange (23,3) could be tolerated at temperatures below 500°K. For the pair (23,3) and (21,4) both to be slow (21,1) and (12,4) must both be extremely fast. The most satisfactory combination seems to be the second column of the table with (12,4) small and both (23,3) and (21,4) large or the third with (12,4), (23,3) and (21,1) large but (21,4) small. The NO^+ and O_2^+ recombination rates are all more or less compatible within experimental uncertainty with the laboratory values, although α_3 is somewhat high and α_4 somewhat low, especially in the second column at 120 km.

In every case there is strong evidence that (21,4) decreases rapidly with increasing temperature. So must (12,4) if it is large at the lower altitudes. (21,1) also appears to decrease somewhat with temperature. This is associated with the very rapidly increasing O^+ density especially above 150 km in a region where the N_2^+ density is also increasing. O^+ removal by (12,4) faster at 4.4×10^{-12} cm^3/sec at 160 km cannot be permitted even if all of the N_2^+ production is converted into O^+ by the charge exchange process (21,1). Because the

N_2^+ density is increasing more rapidly than the NO^+ density the value of (21,4) must be reduced if it is effective at all.

Furthermore the reduced overall ionization rate in a region of maximum NO^+ and O_2^+ concentration, where the electron density is rising because of the increasing importance of O^+, requires a rapidly decreasing recombination coefficient, particularly for NO^+. The deduced dependence of α_3 and α_4 on electron temperature ($T_e \cong 1000°$ at 160 km) is shown in Table 2 for the various cases. In all but the last column it is very nearly $T_e^{-3/2}$ for NO^+ and $T_e^{-2/3}$ for O_2^+.

To extend this analysis to 220 km is straightforward provided that assumption of negligible redistribution of ions by diffusion is valid. The conditions there are, for

$$O^+: \quad (12,4) + 5.1 \times 10^{-2}\,(13,3) - 6.4 \times 10^{-3}\,(21,1) = 2.3 \times 10^{-12}$$

$$N_2^+: \quad (21,4) + (21,1) + 3.5 \times 10^{-2}\,(23,3) + 8 \times 10^{-4}\,\alpha_2 = 2.9 \times 10^{-10}$$

$$NO^+: \quad \alpha_4 = 1.95 \times 10^{4}\,(12,4) + 1.25 \times 10^{2}\,(21,4)$$

$$1.4\,\alpha_4 + \alpha_3 + 0.14\,\alpha_2 = 1.2 \times 10^{-7}$$

Here the possible importance of α_2 dictates the following approach. The values of α_4 and α_3 at 2200° electron temperature are calculated for the temperature dependences in Table 2 and the value of α_2 deduced from the overall recombination rate condition. These values are also shown in Table 2. In the first three cases α_2 would appear to be no larger than $\alpha(NO^+)$ at 220 km suggesting a $T^{-3/2}$ dependence for it also. The conditions on the ion-molecule reaction coefficients are indistinguishably different for the first three columns. They are written out in the table. Upper limits for (12.4) in the first three cases are 10^{-12} cm^3/sec, for (21,1) 2.7 x 10^{-10} cm^3/sec and for (21,4), 10^{-11} cm^3/sec at a gas temperature of 1000°. The upper limit on (12,4) is set by the NO^+ equation and the value of α_4. The limits are only slightly different in the last column which belongs to the case of very large (12,4) and very small (23,3) and (21,4) at low temperature.

The strong temperature dependence of (12,4) and (21,4) are thus confirmed. In the last two columns the rate (12,4) decreases with temperature according to

$$(12,4) = \begin{cases} 8.3 \times 10^{-11} \exp - 6 \quad \times 10^{-3}\, T \\ 11 \times 10^{-11} \exp - 6.1 \times 10^{-3}\, T \; . \end{cases}$$

3.5 Highly Speculative Alternatives

In view of some laboratory experiments (2) which indicate a very high efficiency for conversion of N_2^+ to N_4^+ even at low pressures it might be worthwhile to examine what sort of (two body like) rate would be required for

$$N_2^+ + N_2 \rightarrow N_4^+$$

if it were to be the principal mode of N_2^+ removal. At 120 km, where conditions are most favorable, setting the ionization rate of N_2 equal to the loss rate of N_2^+ by N_4^+ formation demands a reaction rate of 2.5×10^{-10} cm^3/sec, or a cross section of 10^{-14} cm^2. Since the highest cross section measured so far is only 10^{-17} cm^2 this requirement appears to be excessive. (14) Furthermore, since it would then be the case that

$$Q_2 = \alpha(N_4^+) \cdot Ne$$

and $\alpha(N_4^+)$ appears to be about 2×10^{-6} cm^3/sec, (14) the density of N_4^+ would be in excess of 10^4 ions per cm^3. It is interesting that ions of mass 56 have been reported at 105 km (16) where their density was estimated at 1.2×10^4 per cm^3. But until their presence is detected at higher altitudes this mechanism does not seem to be too hopeful.

Another rather remote possibility is that a large fraction of the nitrogen ionization by hard photons in the 120 km region is going into dissociative photo-ionization and the N^+ ions are being rapidly converted to NO^+, O^+ or O_2^+. The measured photo-ionization cross sections do not support this hypothesis however. (17)

This exercise is only illustrative. It certainly cannot pretend to select an approved set of reaction rates for the ionosphere. However, it does insist on the impossibility of reconciling the values.

$$(12,4) = 3 \times 10^{-12} \text{ cm}^3/\text{sec}$$
$$(23,3) = 4 \times 10^{-13} \text{ cm}^3/\text{sec}$$

in the presence of these ionospheric data unless both (21,1) and (21,4) are very large. In fact in the region around 120 km it seems difficult to reconcile them even in this case. On the other hand a larger value of (12,4) permits the accomodation of a large range of possibilities for these other rates.

4. IONOSPHERIC CONDITIONS: NIGHT TIME

The ratio of the day to the night densities of ionic species measured in the NRL experiments(3) is displayed in Table 3. At 200 km the most remarkable phenomenon is the small decrease which the N_2^+ density has suffered in the course of 2 x 10^4 seconds in the face of the very fast rate at which it disappears in the daytime. With $Q_2 = 0$, Equation (2) gives the decay rate of N_2^+. If

$$e^{\gamma t} = 50$$

at

$$t = 2 \times 10^4$$

then

$$\gamma = 5 \times 10^{-4} \text{ sec}^{-1}$$

This would mean

$$[(21,4) + (21,1)]\, O + [(23,3) + (23,4)]\, O_2 + \alpha_2 N_e = 5 \times 10^{-4}$$

Table 3

Nightime Ionic Densities and Ratio of Day to Night Densities in cm^3

Altitude km	(1) O^+	Ratio	(2) N_2^+	Ratio	(3) O_2^+	Ratio	(4) NO^+	Ratio
120					1.6×10^2	440	4.5×10^3	5
140					1.4×10^2	440	4×10^3	14
160		1.5×10^3		45	1.4×10^2	440	8×10^2	115
220	1.8×10^3	360	35	50	2.7×10^3	4.1	3×10^3	5.9

or

$$[(21,4) + (21,1)] + 3 \times 10^{-2} [(23,3) + (23,4)] + 2 \times 10^{-5} \alpha_2 = 10^{12}$$

Thus all the conditions

$$[(21,4) + (21,1)] < 10^{-12}$$

$$[(23,3) + (24,4)] < 3 \times 10^{-11}$$

$$\alpha_2 < 5 \times 10^{-8} \text{ cm}^3/\text{sec}$$

would need to be satisfied if $Q_2 = 0$. Since the temperature at night is only about 700° and α_2 is 3×10^{-7} at 300° and since, at 220 km,

$$[(21,4) + (21.1)] + 3.5 \times 10^{-2} (23,3) + 8 \times 10^{-4} \alpha_2 = 2.9 \times 10^{-10}$$

these conditions do not appear to be possible. It is difficult to avoid the conclusion that, if the observations are correct, a source of ionization for N_2 must exist above 200 km at night. In fact what is needed is a rate 1/50 times the daytime rate or

$$Q_2(\text{Night}) = 6 \text{ ion pairs/cm}^3 \text{ sec.}$$

In such a case, however, it is necessary to account for the much larger decrement in O^+ concentration. The N_2^+ density (again neglecting diffusion) is given from (2) in the steady state by

$$N_2^+ = Q_2 / \left\{ [(21,4 + (21,1)] O + [23,3] O_2 + \alpha_2 N_e \right\} \qquad (21)$$

and the O^+ density from (1) by

$$O^+ = [Q_1 + (21,1) N_2^+ \cdot O] / \left\{ [(12,4) + (13,3)] N_2 \right\} \qquad (22)$$

Thus

$$O^+/N_2^+ = [\ (Q_1/N_2^+) + (21,1)O] \Big/ \Big\{[(12,4) + (13,3)\ ]N_2\Big\} \qquad (23)$$

Making use of (21)it appears that the O^+/N_2^+ ratio is proportional to the ratio of the ionization rates.

$$\frac{O^+}{N_2^+} = a \frac{Q_1}{Q_2} \ (b + \alpha_2 N_e) + C \qquad (24)$$

Thus the O^+/N_2^+ ratio should be the same day and night if Q_1 and Q_2 change in the same way except for the factor

$$b + \alpha_2 N_e = \Big\{[(21,4) + (21,1)\ ]O + (23,3)O_2\Big\} + \alpha_2 N_e \qquad (25)$$

The observation that the ratio actually changes by a factor of 7 from night to day while N_e changes by a factor of 100 indicates that, if indeed Q_1 and Q_2 are essentially equal day and night and do not vanish at night, the term αN_e must produce most of the change in the O^+/N_2 ratio. For this to be the case it is necessary that

$$a(b + 100\ \alpha_2 N_e) + c = 7\ \Big\{a(b + \alpha_2 N_e) + c\Big\} \qquad (26)$$

or

$$\alpha_2 N_e \cong 6 \times 10^{-2}\ (b + \frac{c}{a})$$

Since $c = \dfrac{(21,1)\ O}{[(12,4) + (1,33)\ ]\ N_2}$

and $a = \dfrac{1}{[(12,4) + (1,33)\ ]\ N_2}$

this means that

$$\alpha N_e \cong 6 \times 10^{-2} \left[[(21,4) + (21,1)]\,O + (23,3)O_2 + (21,1)O \right] \quad (27)$$

or with $Ne = 5 \times 10^3$ electrons/cm^3

$$\alpha_2 = 6 \times 10^3 \,(21,4) + 1.2 \times 10^4 (21,1) + 2 \times 10^2 \,(23,3)$$

Hence if $\alpha_2 \cong 3 \times 10^{-7}$, the following conditions would permit α_2 Ne to effect a change of 7 in the O^+/N_2^+ ratio even if Q_1/Q_2 is the same night and day

$$(21,4) \leqslant 5 \times 10^{-11}$$

$$(21,1) \leqslant 2.5 \times 10^{-11}$$

$$(23,3) \leqslant 1.5 \times 10^{-9}$$

These conditions are a little severe considering the daytime N_2^+ removal requirements. Since the cross section for production of N_2^+ (17,18,19) by electrons is larger than that of O (20) by a factor of about 2 a combination of effects involving the ratio of Q_2 to Q_1 and the relative increase in N_2^+ density at night because of the reduced electron density available for dissociative recombination would serve to explain the night time N_2^+ and O^+ density near 220 km.

As for NO^+ and O_2^+ at these altitudes their persistence compared to O^+ and N_2^+ reflects the fact that both NO^+ and O_2^+ feed on O^+ and N_2^+ and decay primarily by dissociative recombination. Thus

$$O_2^+ = \frac{(13,3)O^+ \cdot O_2 + (23,3)N_2^+ \cdot O_2 + Q_3}{\alpha_3 N_e + (32,4)N_2 + (34,4)NO} \quad (28)$$

If (13,3) is of the order of 3×10^{-11} the first term in the numerator dominates the second even at night and even if (23,3) is as large as 2×10^{-10}. This term changes by a factor of 360 from night to day but N_e changes by a factor of 100. Thus a change in O_2^+ by a factor of 4 is easy to account for, provided Q_3 is considerably less than the first two terms in the denominator in the day. This it surely is, since Q_3 is of the order of 50 ion pairs per cm^3 per second, while the first term is about 250 per cm^3 per second.

Similarly for NO^+

$$NO^+ = \frac{(12,4)O^+N_2 + (32,4)O_2^+N_2 + (21,4)N_2^+O + (53,4)N^+O_2 + (34,4)O_2^+ \cdot NO}{\alpha_4 N_e} \qquad (29)$$

A change by a factor of 6 from night to day in the presence of a 100 fold increase in N_e is a consequence of the dominant role of the first term in the numerator, the ion atom interchange of O^+ and N_2. Since O^+ varies by a factor of 3.6 times as large as N_e the same sort of diurnal variation should occur in NO^+ as in O_2^+.

Of course the electron temperature changes diurnally by a very large factor also at 220 km. According to Table 2 the decrease in α_4 from night to day (700° to 2200°) is larger than that of α_3 by a factor of about 2. This could account for the difference in the amplitude of the diurnal variation of O_2^+ and NO^+.

Thus the results appear to demand a source of ionization producing about 6 to 8 ion pairs/cm^3 in the 220 km region at night. At the rate of 35 eV per ion pair this calls for a deposition of only 2 to 3×10^{-10} ergs/cm^3 sec at these altitudes or about 10^{-3} ergs/cm^2 sec.

This is below the limits set by Dalgarno(21). It would produce only about 1.5×10^{-2} photons of 3914Å per cm^3 per sec or 5×10^{-2} Rayleighs if all of the radiation were produced above 220 km. In fact the shape of the O_2^+ and NO^+ peaks suggests that the ionization may extend as low as 180 km. In this case the estimates of radiation and energy flux go up by a factor of two. Fortunately this can be tolerated also. To penetrate only to 180 km the electrons would need to be quite low in energy initially - only a few hundred volts at most.

In the region around 160 km it appears to be possible to account for the behavior at night on the basis of a straightforward conversion of O^+ and N_2^+ to O_2^+ and NO^+ and subsequent dissociative recombination. No source of ionization is required. The O^+ density decays with a time constant of less than 10 seconds. In a time of the order of 2×10^4 seconds the electron density is reduced from about 1.5×10^5 to about 500 (perhaps 750). This gives, from

$$\frac{1}{n_e} = \frac{1}{n_{e0}} + \alpha t \qquad (30)$$

an overall recombination coefficient

$$\alpha = 1 \times 10^{-7} \ cm^3/sec$$

in excellent agreement (despite the reduction in electron temperature) with the daytime condition

$$1.55\ \alpha_4 + \alpha_3 = 2.65 \times 10^{-7} \ cm^3/sec$$

which worked out to an average recombination coefficient of 1.15×10^{-7} cm^3/sec in the illustrative example above.

In terms of the diatomic ions separately the situation is that O_2^+ decreases by a factor of 440 in 2×10^4 seconds. Since

$$\frac{dO_2^+}{dt} = - \left[(32,4)\ N_2 + \alpha_3\ N_e\right]\ O_2^+ \qquad (31)$$

if it is assumed that

$$N_e = \frac{N_{e0}}{1 + \alpha\ N_{e0}\ t}$$

the O_2^+ density is

$$O_2^+ = \frac{O_2^+(0)\ e^{-(32,4)N_2 t}}{(1 + \alpha\ N_{e0} t)^{\alpha_3/\alpha}} \qquad (32)$$

At 2×10^4 seconds the requirement is that

$$440 = 300^{\alpha_3/\alpha} \quad \exp[2 \times 10^{14}\ (32,4)\ ]$$

Hence, unless $\alpha_3 << \alpha$ the condition on (32,4) which was mentioned earlier is obtained, namely

$$(32,4) < 10^{-14}\ cm^3/sec$$

If $(32,4) = 10^{-14}$ cm^3/sec, $\alpha_3 = 0.73 \times 10^{-7}$ cm^3/sec. The upper limit to α_3 is 1.07×10^{-7} cm^3/sec.

For NO^+

$$\alpha = \alpha_3\ \frac{O_2^+}{N_e} + \alpha_4\ \frac{NO^+}{N_e} \qquad (33)$$

or $$\alpha = .16\alpha_3 + .84\,\alpha_4$$

If α_3 is 1.07 x 10^{-7} cm^3/sec then α_4 is 1 x 10^{-7} cm^3/sec.

On the other hand at lower altitudes the curious fact is that, whereas O_2^+ has decayed in approximately the same fashion from 160 km to 140 km, the NO^+ density remains high below 140 km and exhibits a peak near 130 km. The day to night ratio for NO^+ is only 15 near 140 km in contrast with 115 at 160 km and 450 for O_2^+. Although it is possible to argue that this behavior indicates that α_4 increases with increasing temperature(3) the behavior of α_4 in the daytime does not indicate such a tendency - quite the contrary. To postulate a source of ionization specific to NO meets a double difficulty. For one thing there is no adequate mechanism. The ionization rate required at 120 km is

$$Q_4 = \alpha_4\, N_e^{\,2} = 10 \text{ ion pairs/cm}^3 \text{ sec}$$

According to Barth(22), the density of NO near 120 km is about 2 x 10^7 per cm^3. Calculation of the rate at which nitric oxide at this density is ionized by the nightglow Lyman α shows that only about 3 x 10^{-2} NO^+ ions per cm^3 per sec should be produced. None of the meteoric ions so far detected have ionization potential great enough to charge exchange with NO. Finally, as Holmes et al(3) have pointed out, in the presence of an electron density greater than 10^3 per cm^3 the O_2^+ density would have decreased far below the observed 150 ions per cm^3 observed 6 hours after sunset if α_3 is greater than 10^{-7} cm^3/sec and Q_1, Q_2 and Q_3 are all zero. With only Q_4 non vanishing

$$\frac{dO_2^+}{dt} = \alpha_3\, O_2^+\, N_e \qquad (34)$$

$$\frac{dN_e}{dt} = Q_4 - \alpha N_e^2 \qquad (35)$$

$$N_e = \frac{2N_{e1}\ N_{e0}}{N_{e0}(1-e^{-kt}) + 2\ N_{e1}\ e^{-kt}} - N_{e1} \qquad (36)$$

where

$$N_{e1} = \sqrt{Q/\alpha}$$

and

$$k = 2\sqrt{Q_4\alpha} = 2\ N_{e1}\alpha$$

The O_2^+ density is given from (34) by

$$O_2^+ = O_{20}^+ \exp[-\alpha_3 \int_0^t N_e(t')dt'] \qquad (37)$$

from which and (36) it turns out that O_2^+/O_{20}^+ would be less than e^{-20} at 2×10^4 seconds.

Thus, unless α_4 and α_3 increase with T_e it is necessary to assume a nocturnal source of ionization in the E region which can produce O_2^+ ions as well as NO^+ ions. At 130 km the conditions (1)-(4) may be written for

$$NO^+: \quad 2 \times 10^{-10} = 4.5(12,4)\ O^+ + (21,4)\ N_2^+ \qquad (38)$$

$$O_2^+: \quad 3 = 3O^+ + 10^{11}(23,3)\ N_2^+ + 10Q_3 \qquad (39)$$

$$N_2^+: \quad N_2^+ = Q_2\ (175/2700) \qquad (40)$$

$$O^+: \quad O^+ = [Q_1 + 2\text{x}10^{10}(21,1)N_2^+] \,/\, 9\text{x}10^{10}[(12,4)+(13,3)] \qquad (41)$$

where it has been assumed that, as in the daytime,

$$\alpha_4 = 4 \times 10^{-7} \text{ cm}^3/\text{sec}$$
$$\alpha_3 = 3 \times 10^{-7} \text{ cm}^3/\text{sec}$$
$$(32,4) = 10^{-14} \text{ cm}^3/\text{sec}$$

In contrast to daytime conditions the ion atom interchange of O_2^+ with N_2 (32,4) competes with dissociative recombination in reducing the O_2^+ concentration. This only accounts for a factor of two reduction in O_2^+ compared to NO^+. Another factor of 40 is needed. It can only be obtained by a reduction in the importance of Q_3 at night relative to the daytime and an alteration in the O^+ to N_2^+ ratio.

Clearly, from (39), a large value for (23,3) is difficult to tolerate for it would require a low N_2^+ density in order not to overproduce O_2^+. But then the NO^+ would need to be produced from O^+ with a large value for (12,4). There is an absolute upper limit of O^+ density of 1 per cm^3 per sec set by (39). These conditions are not in fact compatible, for (38) and (39) may be combined to read, on the one hand,

$$2\times10^{-10} - 1.5(12,4) = [4.5\times10^{10}(23,3)(12,4) - 0.3(21,4)]\, O^+ - Q_3(21,4)$$

and on the other hand

$$2(23,3) - 0.3(21,4) = [4.5\times10^{10}(23,3)(12,4) - 0.3(21,4)]\, O^+ - Q_3(21,4)$$

Since $(12,4) < 3 \times 10^{-11}$ the first condition says that

$$(21,4) > 1.5 \times 10^{-10} + 0.5\,(23,3) \qquad \text{if } (12,4) = 3 \times 10^{-11}$$
$$(21,4) > 2 \times 10^{-10} + 5 \times 10^{-2}\,(23,3) \quad \text{if } (12,4) = 3 \times 10^{-12}$$

In the second condition it follows that

$$\text{if } (23,3) > 0.15\,(21,4)$$

then

$$(23,3)(12,4) > 0.15\ (21,4)(12,4) > 6.7 \times 10^{-12}\ (21,4)$$

or $$(12,4) > 5 \times 10^{-11}\ \mathrm{cm}^3/\mathrm{sec}$$

which is twice as large as any measured value. To account for the nocturnal bulge of NO^+ relative to O_2^+ it is necessary to take (21,4) greater than 2×10^{-10} cm^3/sec and (23,3) less than 3×10^{-11} cm^3/sec. In the daytime these values are consistent with those in Column 1 of Table 2. If, in fact

$$(12,4) = 3 \times 10^{-12}\ \mathrm{cm}^3/\mathrm{sec}$$
$$(21,1) = 5 \times 10^{-11}\ \mathrm{cm}^3/\mathrm{sec}$$
$$(23,3) = 4 \times 10^{-13}\ \mathrm{cm}^3/\mathrm{sec}$$
$$(21,4) = 5 \times 10^{-10}\ \mathrm{cm}^3/\mathrm{sec}$$

following Table 2 then the nocturnal E region can be accounted for from (38) if

$$N_2^+ = 0.4\ \mathrm{ions}/\mathrm{cm}^3$$

which implies from (40)

$$Q_2 = 6\ \text{ion pairs}/\mathrm{cm}^3\ \mathrm{sec}$$

and any combination of

$$O^+ + 3.3\,Q_3 = 1\ \mathrm{ion}\ /\mathrm{cm}^3$$

If it is desirable that Q_1 and Q_3 be comparable in magnitude then (41) may be used in the form

$$O^+ = \frac{Q_1}{3} + .13$$

to give, say

$$O^+ = 0.25$$

$$Q_3 = 0.23$$

$$Q_1 = 0.36$$

Thus the ionization rates would be in the ratio $Q_2/Q_1/Q_3 = 26/1.6/1$ where the densities are in the ratio $N_2|O|O_2 = 9/2/1$ implying an ionization efficiency for N_2 about 3 times that for the oxygen species.

However, a decision in favor of the rate coefficients in the first column of Table 2 is not to be made as readily as this. There is at 140 km and below a possibility that (32,4) is larger than 10^{-14} cm^3/sec. Since this O_2^+ N_2 reaction converts O_2^+ into NO^+ it is clearly of potential great importance at night if its rate is of the order of 5×10^{-14} cm^3/sec for it changes O_2^+ to NO^+ then at the rate of 45×10^{-4} per second compared to a loss of 9×10^{-4} per second by recombination. Similarly the reaction of charge exchange

$$O_2^+ + NO \rightarrow NO^+ + O_2$$

would convert O_2^+ to NO^+ at a rate of 50×10^{-4} per second if its rate coefficient (34,4) were 5×10^{-10} cm^3/sec.

On the other hand these values for (34,4) and (32,4) would change the values of α_4 and α_3 in the daytime to 7.3×10^{-7} cm^3/sec and 2.4×10^{-7} cm^3/sec and the night time conditions (28) and (29) at 130 km would become

$$15 = 3O^+ + 10^{11}\,(23,3)\,N_2^+ + 10\,Q_3 \qquad (42)$$

$$3 \times 10^{-10} = 4.5\,(12,4)\,O^+ + (21,4)\,N_2^+ \qquad (43)$$

Now it is possible, as can be seen from combining (42) and (43), that

$$(23,3) \; > \; 0.5\,(21,4)$$

if

$$(12,4) \; > \; 13 \times 10^{-12}\ \mathrm{cm}^3/\mathrm{sec}$$

and

$$(21,4) \geq 2.3 \times 10^{-10} + 0.5\,(23,3) \quad \text{if } (12,4)=3 \times 10^{-12}\ \mathrm{cm}^3/\mathrm{sec}$$

$$(21,4) \geq 2\,(23,3) \quad \text{if } (12,4)=13 \times 10^{-12}\mathrm{cm}^3/\mathrm{sec}$$

$$(21,4) \leq 3.7 \times 10^{-10} + 4.5\,(23,3) - 4.5 \times 10^{-10}\,Q_3 \quad \text{if } (12,4)=30 \times 10^{-12}\mathrm{cm}^3/\mathrm{sec}$$

Since $(12,4) < 20 \times 10^{-12}$ cm^3/sec in the daytime some of the possibilities are ruled out, but the conversion of O_2^+ to NO^+ by O_2^+, N_2 and O_2^+, NO reactions now permits high values of (23,3) without requiring the O^+ density to be very low. This in turn permits low values of (12,4) to make an adequate contribution to the NO^+ production. For example (43) can be satisfied with

$$(21,4) = 5 \times 10^{-10}\ \mathrm{cm}^3/\mathrm{sec}$$

$N_2^+ = 0.6$ ions cm/^{3}

and from (40) $\quad Q_2 = 10$ per cm^3 per sec

This value of (21,4) from the daytime requirements implies

$$(23,3) \cong 2 \times 10^{-10}\ \mathrm{cm}^3/\mathrm{sec}$$

$$(21,1) \cong 5 \times 10^{-11}\ \mathrm{cm}^3/\mathrm{sec}$$

$$(12,4) \cong 3 \times 10^{-12}\ \mathrm{cm}^3/\mathrm{sec}$$

Such a value of (12,4) requires that O^+ must be less than 1 per cm^3 in (43). Now the O_2^+ equation (42) can be satisfied, for example, if

$$Q_3 = 0.5$$

$$O^+ = 0.7$$

$$(23,3) = 1.4 \times 10^{-10}\ \mathrm{cm}^3/\mathrm{sec}$$

Such O^+ and N_2^+ densities, from (41), require that

$$Q_1 = 1.2 \text{ per } \mathrm{cm}^3 \text{ per second}$$

The ratio of the ionization rates for N_2, O and O_2 is in this case 20/2.4/1 which implies about twice as high ionization efficiency for N_2 as for O_2 and O.

It is also possible to accommodate a small value for (21,4) if O^+ is large enough. Thus

$$(21,4) < 10^{-11}\ \mathrm{cm}^3/\mathrm{sec}$$

$$(23,3) = 2 \times 10^{-10}\ \mathrm{cm}^3/\mathrm{sec}$$

$$(12,4) = 15 \times 10^{-12}\ \mathrm{cm}^3/\mathrm{sec}$$

$$(21,1) = 5 \times 10^{-10}\ \mathrm{cm}^3/\mathrm{sec}$$

means that

$$O^+ = 4 \text{ per } \mathrm{cm}^3$$

$$N_2^+ \cong .1 \text{ per } \mathrm{cm}^3$$

$$Q_3 = .2 \text{ per } \mathrm{cm}^3 \text{ per sec}$$

and

$$Q_2 = 1.5 \text{ per } \mathrm{cm}^3 \text{ per sec}$$

$$Q_1 = 15 \text{ per } \mathrm{cm}^3 \text{ per sec}$$

Such a state of affairs sets rather peculiar conditions on Q_1, Q_2 and Q_3 and does not appear to be realistic.

5. CONCLUSIONS

The measurements of Holmes, Johnson and Young of ionospheric ion densities in the daytime are consistent with 3×10^{-12} cm^3/sec for the ion atom interchange of O^+ and N_2 if the ion atom interchange of N_2^+ and O is very rapid. A small rate for the charge exchange of N_2^+ and O_2 implies a rate for N_2^+, O ion atom interchange larger than 5×10^{-10} cm^3/sec at 300°K. They are consistent with a low rate for ion atom interchange of N_2^+ and O only if the rate (12,4) for the O^+, N_2 reaction is 24×10^{-12} cm^3/sec or higher. They also imply that the ion atom interchange reaction rates decrease rapidly with temperature. The dissociative recombination coefficients required are 5×10^{-7} cm^3/sec for NO^+ at room temperature and 3.5×10^{-7} cm^3/sec for O_2^+ with respectively a $T_e^{-3/2}$ and a $T_e^{-2/3}$ temperature dependence.

At night the NO^+ maximum and high O_2^+ density in the E region can be explained on the basis of a local source of ionization. If production of NO^+ by N_2^+, O_2 ion atom interchange and O_2^+, NO charge exchange is inefficient, the high ratio of NO^+ to O_2^+ at night demands that the N_2^+, O ion atom interchange have a rate greater than 2×10^{-10} cm^3/sec and the production of O_2^+ by charge exchange from N_2^+ occur with a rate less than 15 per cent of the N^+, O rate. On the other hand both of these rates can be large, consistent with daytime possibilities, if NO^+ formation from N_2^+ - O_2 and O_2^+ - NO, occurs with rates of 5×10^{-14} cm^3/sec and 5×10^{-10} cm^3/sec. The ionization rates are between 5 and 10 per cm^3 per second in a region some 30 km wide and hence need not produce excessive nightglow N_2^+ radiation

Similarly above 180 km ionization by slow electrons with a rate of 5-10 ion pairs/cm^3 sec appears to be needed.

Clearly good measurements of the rates for NO^+ formation in

$$N_2^+ + O \rightarrow NO^+ + N$$

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

$$O_2^+ + NO \rightarrow NO^+ + O_2$$

and also

$$N_2^+ + O \rightarrow N_2 + O^+$$

are necessary in order to select among the possible sets of conditions outlined here.

ACKNOWLEDGEMENTS

This work was supported by the National Aeronautics and Space Administration under Contract NASr-179. The author acknowledges with pleasure the help and information he has received from his colleagues M. A. Biondi, W. L. Fite and E. Zipf.

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