SPACE RESEARCH COORDINATION CENTER

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

BY

T. M. DONAHUE

DEPARTMENT OF PHYSICS

SRCC REPORT NO. 11

UNIVERSITY OF PITTSBURGH

PITTSBURGH, PENNSYLVANIA

5 AUGUST 1965

The Space Research Coordination Center, established in May, 1963, coordinates space-oriented research in the various schools, divisions and centers of the University of Pittsburgh. Members of the various faculties of the University may affiliate with the Center by accepting appointments as Staff Members. Some, but by no means all, Staff Members carry out their researches in the Space Research Coordination Center building. The Center's policies are determined by an SRCC Faculty Council.

The Center provides partial support for space-oriented research, particularly for new faculty members; it awards annually a number of postdoctoral fellowships and NASA predoctoral traineeships; it issues periodic reports of space-oriented research and a comprehensive annual report. In concert with the University's Knowledge Availability Systems Center it seeks to assist in the orderly transfer of new space-generated knowledge into industrial application.

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.

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

II

T. M. Donahue

Planetary and Space Science

University of Pittsburgh
Pittsburgh, Pennsylvania

August 5, 1965

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

II

T. M. Donahue

University of Pittsburgh, Pittsburgh, Pennsylvania

(Received)

ABSTRACT

An attempt is made to obtain a set of ion-molecule reaction rates and recombination coefficients consistent with recent mass spectrometric data obtained between 120 and 220 km. It is found that the daytime ionospheric data at 130 km are explicable in terms of the processes

$$\begin{array}{lll}
N_2^+ + O \rightarrow NO^+ + N & \text{at} & 5 \times 10^{-10}\ \text{cm}^3/\text{sec} \\
O^+ + N_2 \rightarrow NO^+ + N & \text{at} & 4 \times 10^{-12}\ \text{cm}^3/\text{sec} \\
N_2^+ + O_2 \rightarrow O_2^+ + N_2 & \text{at} & 2 \times 10^{-10}\ \text{cm}^3/\text{sec} \\
N_2^+ + O \rightarrow O^+ + N_2 & \text{at} & 6 \times 10^{-12}\ \text{cm}^3/\text{sec} \\
O^+ + O_2 \rightarrow O_2^+ + O & \text{at} & 4 \times 10^{-11}\ \text{cm}^3/\text{sec} \\
O_2^+ + N_2 \rightarrow NO^+ + NO & < & 4 \times 10^{-14}\ \text{cm}^3/\text{sec} \\
N^+ + O_2 \rightarrow NO^+ + O & \text{at} & 5 \times 10^{-10}\ \text{cm}^3/\text{sec} \\
 & & \\
e + NO^+ \rightarrow N \quad O & \text{at} & 5.2 \times 10^{-7}\ \text{cm}^3/\text{sec} \\
e + O_2^+ \rightarrow O + O & \text{at} & 1.2 \times 10^{-7}\ \text{cm}^3/\text{sec}
\end{array}$$

all in good agreement with the most recent laboratory data.

To account for the ion densities at higher altitudes it is shown that many rates must have strong temperature dependences. In particular the O^+ removal rates cannot increase with temperature and the N_2^+, O

ion-atom interchange rate must decrease with increasing temperature. The recombination coefficient for NO^+ decreases with electron temperature as $T_e^{-1.4 \pm 0.1}$ for O_2^+ as about T_e^{-1} and for N_2^+ as about $T_e^{-0.2}$.

To account for the nighttime ionosphere with the reaction rates implied by the daytime data is shown to require that there be weak sources of ionization above 180 km and below 140 km with rates of the order of 5-10 ion pairs/cm^3. The data also indicate that O_2^+, NO charge exchange must be very rapid with a rate of the order of 5×10^{-10} cm^3/sec.

1. INTRODUCTION

There now appears to be a consensus among laboratory experimentalists(1,2) that the rate of the charge transfer reaction

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

at 300°K is of the order of 2×10^{-10} cm^3/sec.* This large value which is perhaps surprising on theoretical grounds is nevertheless all but indispensable to account for the very high rate at which N_2^+ disappears in the E region during the daytime. The only other effective channel for removal of N_2^+ is through formation of NO^+ in the ion-atom interchange reaction

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

A very low rate for the charge exchange process would place a very severe requirement on the ion-atom interchange reaction. This is a consequence of the fact that the charge exchange with O

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

cannot be permitted to go very rapidly if the O^+ removal in the reaction

---

*This note is a revised version of a paper which was prepared when it appeared that laboratory measurements were yielding a value of 4×10^{-13} cm^3/sec for this rate coefficient.(3) The earlier paper attempted to show that this measurement was incompatible with ionospheric data unless certain other rate coefficients were extremely large. Copies of that paper in report form are available from the author.

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

is as slow as the value (4×10^{-12} cm^3/sec) on which laboratory measurements have now settled.(3,4) Since the laboratory data are also consistent with the ionospheric requirement that the N_2^+, O charge exchange be slower than 10^{-11} cm^3/sec the recent agreement on the high value for the N_2^+, O_2 charge transfer rate is very gratifying. Also encouraging the observation that the N_2^+, O ion atom interchange rate is very fast.(5)

These and a number of other important ion-molecule reaction rates have recently been measured at room temperature.(1-5) Increasingly reliable values for the room temperature rates for dissociative recombination of N_2^+, O_2^+ and NO^+ are being obtained also.(6,7,8) Using these values at 300°K as a basis it is interesting to determine what sort of temperature dependence for reaction rates would be required for consistency with recently obtained densities of ionic species in the E and F regions.(9) It is the purpose of this note to show that the laboratory reaction rates are consistent with ionospheric conditions in the daytime near 130 km where the gas temperature is not much higher than 300°. It is the further purpose to extend the analysis to higher altitudes and show within broad limits how these rates must vary with temperature to be consistent with ionospheric observations up to 220 km in the daytime. Although it will not be possible to fix on a single unique set of temperature dependences a number of qualitative predictions will be forthcoming. With regard to dissociative recombination rate coefficients rather firm statements about temperature dependence will be possible.

The densities of the ionic species from 130 km to 220 km have also been measured at night.(9) It will be shown that the altitude profiles of these densities cannot be accounted for by simple decay of ionization via ion-molecule and dissociative recombination. In fact the data will be shown to be explicable in terms of weak nocturnal ionization sources in the E region and F region -- in particular ionization by electron impact. The nocturnal conditions also serve to select a narrow range of possibilities out of the broad spectrum of temperature dependences for reaction rates left from the daytime analysis.

An obvious caveat should be entered before any comparison of rates measured in the laboratory and those applicable in the ionosphere is made. This is that the states of the ions and molecules observed may not be the same in the two places. What is taken to be evidence for temperature dependence may be in part evidence for a variation in altitude and time of the relative population of states. It is also necessary to bear in mind the large experimental uncertainties still attach to most of the measurements under discussion. The time has certainly not arrived for a definitive analysis. An observation most seriously lacking, for example, is one that would give a direct measurement of the total rate of ion production as a function of altitude.

2. IONIC CHEMISTRY

Prior to the publication of the latest series of laboratory reaction rate measurements by the group at the National Bureau of Standards(1,3, 5) and the ionospheric mass spectrometer observations at NRL[9] several exhaustive reviews of the chemistry of the ionosphere have been published.(10,11) The basic chemistry is set forth adequately in those papers and will not be discussed here. To systematize somewhat the notation atomic and molecular species, whether ion or neutral will be designated by number, O or O^+ being 1, N_2, 2; O_2, 3; NO, 4; and N, 5.

The ion-molecule reaction rate coefficients will be written (ij,k) where i denotes the ion before collision and k the ion afterward. For the concentration [X] or N(X) the chemical symbol X will be employed and the product of concentrations written X∘Y to distinguish it from the symbol XY for the molecule.

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^+

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

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

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

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

$N_2^+ + NO \rightarrow NO^+ + N_2$ (24,4)

O_2^+:

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

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

N^+:

$N^+ + O_2 \rightarrow O_2^+ + N$ (53,3)

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

The dissociative recombination rate coefficients will be designated α_2 for N_2^+, α_3 for O_2^+ and α_4 for NO^+. The ion production rates by photons and photoelectrons will be written as Q_i.

Since the review by Paulson[12] a large number of new determinations of rate coefficients has been made. In this paper the following values from the laboratory are adopted as guides for selecting rates at 300°K.

$(12,4) = 4 \times 10^{-12}$ cm^3/sec (1,4)
$(13,3) = 4 \times 10^{-11}$ cm^3/sec (13,14)
$(21,1) < 1 \times 10^{-11}$ cm^3/sec (5)
$(21,4) = 2 \times 10^{-10}$ cm^3/sec (5)
$(23,3) = 2 \times 10^{-10}$ cm^3/sec (1,2)
$(23,4) \sim 10^{-14}$ cm^3/sec (15)
$(24,4) = 5 \times 10^{-10}$ cm^3/sec
$(32,4) \sim 10^{-14}$ cm^3/sec (16)
$(34,4)$
$(53,3) = 5 \times 10^{-10}$ cm^3/sec (1)
$(53,4) = 5 \times 10^{-10}$ cm^3/sec (16)
$\alpha_2 = 3 \times 10^{-7}$ cm^3/sec (6)
$\alpha_3 \quad 2 \times 10^{-7}$ cm^3/sec (7)
$\alpha_4 \quad 4\text{-}20 \times 10^{-7}$ cm^3/sec (17)

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 nightime.(9) The results are shown in Table 1 at altitudes of 130, 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 28^+ above 200 km at night is a surprise if it is ionospheric N_2^+ in view of the rapid removal processes which dispose of this ion in the day time.

There are also available now mass spectrometric values for the densities of the neutral species.(17,18,19) These are tabulated in Table 1. On the basis of these densities Zipf(20) has reevaluated the rates of photoionization, 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.

In the absence of significant diffusive flow

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

$$\frac{dN_2^+}{dt} = Q_2 - [(21,4) + (21,1)]\ N_2^+ \circ O + [(23,3) + (23,4)]\ N_2^+ \circ O_2 + (24,4)\ N_2^+ \circ NO + \alpha_2\ N_2^+ \circ Ne \qquad (2)$$

$$\frac{dO_2^+}{dt} = Q_3 + (23,3)\ N_2^+ \cdot O_2 + (13,3)\ O^+ \cdot O_2 - (32,4)\ O_2^+ \cdot N_2 - (34,4)\ O_2^+ \cdot NO - \alpha_3\ O_2^+ \cdot N_e \tag{3}$$

$$\frac{dNO^+}{dt} = (12,4)\ O^+ \cdot N_2 + (21,4)\ N_2^+ \cdot O + (23,4)\ N_2^+ \cdot O_2 + (24,4)\ N_2^+ \cdot NO + (32,4)\ O_2^+ \cdot N_2 + (34,4)\ O_2^+ \cdot NO + (53,4)\ N_2^+ \cdot O_2 - \alpha_4\ NO^+ \cdot N_e \tag{4}$$

One of these relationships may be replaced by

$$Q_i = (\alpha_2\ N_2^+ + \alpha_3\ O_2^+ + \alpha_4\ NO^+)\ N_e \tag{5}$$

3. THE IONOSPHERIC CONDITIONS: DAYTIME

In the steady state insertion of the observed ion and neutral densities and Zipf's ion production rates into Eqs. (1-5) yields the following relationships.

For N_2^+

at 130 km: $2[(21,4) + (21,1)] + [(23,3) + (23,4)] = 12.6 \times 10^{-10}$ (6)

at 140 km: $3.1\ [(21,4) + (21,1)] + [(23,3) + (23,4)] = 11.5 \times 10^{-10}$ (7)

at 160 km: $6[(21,4) + (21,1)] + [(23,3) + (23,4)] + 3 \times 10^{-4}\alpha_2 = 19 \times 10^{-10}$ (8)

at 220 km: $23[(21,4) + (21,1)] + [(23,3) + (23,4)] + 1.2 \times 10^{-2}\ \alpha_2 = 41 \times 10^{-10}$ (9)

For O^+

at 130 km: $28\ (12,4) + 2.8\ (13,3) - (21,1) = 2.2 \times 10^{-10}$ (10)

at 140 km: $32\ (12,4) + 2.9\ (13,3) - (21,1) = 1.6 \times 10^{-10}$ (11)

at 160 km: $66(12,4) + 5.3\ (13,3) - (21,1) = 1.6 \times 10^{-10}$ (12)

at 220 km: $192\ (12,4) + 10\ (13,3) - (21,1) = 1.9 \times 10^{-10}$ (13)

For NO^+

at 130 km: $\alpha_4 = 1.70 \times 10^4 (12,4) + 610(21,4) + 1.26 \times 10^6 (32,14)$
$+ 1.15 \times 10^2 (34,4) + 42\ (53,4)$ (14)

at 140 km: $\alpha_4 = 2.3 \times 10^4 (12,4) + 730\ (21,4) + 3.7 \times 10^5\ (32,4)$ (15)

at 160 km: $\alpha_4 = 1.5 \times 10^4 (12,4) + 240\ (21,4) + 2.8 \times 10^4\ (32,4)$ (16)

at 220 km: $\alpha_4 = 3.6 \times 10^4 (12,4) + 190(21,4) + 1.1 \times 10^3\ (32,4)$ (17)

From $\Sigma Q_i = \Sigma\ \alpha_i\ N_i^+\ N_e$

at 130 km: $\alpha_4 + 1.4\ \alpha_3 = 6.8 \times 10^{-7}$ (18)

at 140 km: $\alpha_4 + 1.1\ \alpha_3 = 5.0 \times 10^{-7}$ (19)

at 160 km: $1.6\ \alpha_4 + \alpha_3 + 0.02\ \alpha_2 = 2.1 \times 10^{-7}$ (20)

at 220 km: $10\ \alpha_4 + 7\ \alpha_3 + \alpha_2 = 7.5 \times 10^{-7}$ (21)

The N_2^+ and O^+ conditions may be combined to eliminate (21,1). The result, neglecting (23,4) compared to (23,3) is

130 km: $(21,4) + 28\ (12,4) = 8.5 \times 10^{-10} - 2.8\ (13,3) - 0.5\ (23,3)$ (22)

140 km: $(21,4) + 32\ (12,4) = 5.3 \times 10^{-10} - 2.9\ (13,3) - 0.32\ (23,3)$ (23)

160 km: $(21,4) + 66\ (12,4) = 4.8 \times 10^{-10} - 5.3\ (13,3) - 0.17\ (23,3) - 5 \times 10^{-5}\ \alpha_2$ (24)

220 km: $(21,4) + 192(12,4) = 3.4 \times 10^{-10} - 10\ (13,3) - 4.3 \times 10^{-2}\ (23,3)$
$- 5.2 \times 10^{-4}\ \alpha_2$ (25)

It is also possible to rewrite the conditions (14-17) on α_4 to read

130 km $\alpha_4 = 5.2 \times 10^{-7} + 1.26 \times 10^6\ (32,4) + 1.15 \times 10^2\ (34,4) + 42\ (5,34)$
$- 1.7 \times 10^3\ (13,3) - 3.05 \times 10^2 (23,3)$ (26)

$$140 \text{ km: } \alpha_4 = 3.9 \times 10^{-7} - 2.1 \times 10^{3}\,(13,3) - 2.3 \times 10^{2}\,(23,3) + 3.7 \times 10^{5}\,(32,4) \quad (27)$$

$$160 \text{ km: } \alpha_4 = 1.15 \times 10^{-7} - 1.34 \times 10^{3}\,(13,3) - 40\,(23,3) \quad (28)$$

$$220 \text{ km: } \alpha_4 + 0.1 \quad _2 = 0.65 \times 10^{-7} - 1.9 \times 10^{3}\,(13,3) \quad (29)$$

expressing the condition that the NO^+ loss rate must equal the sum of the N_2^+ and O^+ formation rates less the principal loss rates for these ions other than NO^+ formation. The values of (21,4) and (21,1) which are permitted at three altitudes 130, 160 and 220 km are plotted as functions of (12,4) in Fig. 1. (13,3) is treated as a parameter and (23,3) is taken to have the value 2×10^{-10} cm^3/sec. From these curves it will be seen that at 130 km it is possible to explain the ionospheric data with the reaction rates obtained in the laboratory except that (21,4) must be of the order of 5×10^{-10} cm^3/sec if all of the other rates have their laboratory values. Considering all of the experimental uncertainties this has to be taken as an excellent accord between ionospheric and laboratory measurements.

The set of rates

$$(21,4) = 5.2 \times 10^{-10} \text{ cm}^3/\text{sec}$$
$$(12,4) = 4 \times 10^{-12} \text{ cm}^3/\text{sec}$$
$$(23,3) = 2 \times 10^{-10} \text{ cm}^3/\text{sec}$$
$$(21,1) = 6 \times 10^{-12} \text{ cm}^3/\text{sec}$$
$$(13,3) = 4 \times 10^{-11} \text{ cm}^3/\text{sec}$$
$$(32,4) = 4 \times 10^{-14} \text{ cm}^3/\text{sec}$$
$$(53,4) = 5 \times 10^{-10} \text{ cm}^3/\text{sec}$$

then determine the recombination coefficients

$$\alpha_4 = 4.6 \times 10^{-7} + 1.15 \times 10^{2}\ (34,4)$$
$$\alpha_3 = 1.6 \times 10^{-7} - 80\ (34,4)$$

at 335°K.

As the altitude and temperature increase it is apparent that the data call for a large variation in some of the reaction rates if the ionospheric measurements are valid and if photons and their secondaries are the only sources of ionization. The upper limits to various rates at 220 km are

$$(13,3) < 3.4 \times 10^{-11}$$
$$(21,4) < 3.4 \times 10^{-10}$$
$$(12,4) < 1.8 \times 10^{-12}$$
$$\alpha_4 < 0.65 \times 10^{-7}$$
$$\alpha_3 < 1.05 \times 10^{-7}$$

All of these are less than the values at 300°. In Fig. 1 the case represented at 220 km is for the limiting case of negligible contribution by α_2 to the N_2^+ loss rate. It is clear that even under such an extreme circumstance ($\alpha_2 < 2 \times 10^{-8}$ cm^3/sec) both (21,4) and (12,4) must decrease considerably from the values at 300°K unless (13,3) has been reduced to less than 10^{-11} cm^3/sec. Even a modest decrease in (13,3) to 3×10^{-11} cm^3/sec would entail a decrease in (21,4) to at most 3×10^{-11} cm^3/sec (accompanied by a decrease in (12,4) to about 5×10^{-14} cm^3/sec) or a decrease in (12,4) to at most 2×10^{-13} cm^3/sec (whereupon (21,4) would be about 3×10^{-12} cm^3/sec). In any case such a high value for O^+ removal by charge exchange with O_2 at 220 km would imply that O^+ replenishment through charge exchange of N_2^+ with O (21,1) must be faster than 10^{-10} cm^3/sec, i.e. that (21,1) must increase rapidly with temperature. This restriction would be even more severe if α_2 were of the order of 10^{-7} cm^3/sec.

To permit (13,3) to be 4×10^{-11} cm^3/sec and (1,24) to be 8×10^{-12} cm^3/sec at 920°K as some laboratory experiments suggest (provided the states of ions and molecules are the same in the laboratory and the ionosphere and the cross sections do not oscillate between 0.25 eV and 1 eV) would mean that conditions (25) and (13) have to read

$$(21,4) = 3.4 \times 10^{-10} - 19 \times 10^{-10} - 5.2 \times 10^{-4}\ \alpha_2 \qquad (30)$$

and

$$(21,1) = 17 \times 10^{-10}\ \text{cm}^3/\text{sec} \qquad (31)$$

It is difficult to believe that the rocket measurements of ion and neutral densities and the calculation of ionization rates could accumulate errors of the order of 600%. It should be recognized that the difficulties confronting acceptance of a rate of O^+ removal as fast as 8×10^{-12} cm^3/sec at 220 km are really a consequence of the fact that O^+ has become the major ion at that altitude. And the low N_2^+ densities which would lead to the absurd condition (30) are confirmed by optical observations of the 3914 Å dayglow.(21)

Thus although the conditions at 140 km and 160 km would tolerate a fairly large range of possible temperature variations, (particularly if factors of two uncertainties in observational parameters are kept in mind) it is difficult to avoid the conclusion that at 220 km and 1000°K (13,3) (12,4) and (21,4) must be considerably less than at 300°. Only (21,1) might be larger. The results are not sensitive to the value of (23,3) at the higher altitudes.

To attempt a quantitative evaluation requires that α_2 be known at 220 km where the electron temperature is probably in excess of 2000°K. The only way to estimate this coefficient is to compute values of α_4 and α_3 at lower altitudes where all rates are insensitive to α_2 and then assume that the temperature dependence set in evidence prevails all the way to 2000°K. From the extrapolated values of α_4 and α_3 the value of α_2 at 220 km is determined from Eq. (21).

According to Eqs. (26-29) α_4 surely decreases rapidly with electron temperature. A specific temperature variation may be determined by assuming some variation of (13,3) with altitude starting at 4×10^{-11} cm^3/sec at 130 km and computing α_4 from (26-29). For four different models in which (13,3) ends up respectively at 3×10^{-11}, 2×10^{-11}, 1×10^{-11} and 0.7×10^{-11} cm^3 sec at 220 km the resulting variation in α_4 and α_3 is shown in Fig. 2. The point plotted at 220 km are really for $\alpha_4 + 0.1\,\alpha_2$. It is evident that α_4 alone tends to follow a power law dependence on T_e somewhere between $T^{-1.3}$ and $T^{-1.6}$. The less rapidly (13,3) is assumed to decrease the more rapidly α_4 decreases with temperature. Only the case in which (13,3) changes from 4×10^{-11} cm^3/ sec at 130 km to 0.7×10^{-11} cm^3/sec produces something close to a smooth power law variation in α_3 as well as α_4. In this case α_4 extrapolates to 0.3×10^{-7} cm^3/sec at 220 km, from which it would follow that α_2 is 2.1×10^{-7} cm^3/sec there and α_3 is 0.33×10^{-7} cm^3/sec. α_2 would vary then as $T^{-.2}$, α_3 as T^{-1} and α_4 as $T^{-1.43}$.

For this kind of variation of (13,3) with altitude the range of permissible values of (21,4), (21,1) and (12,4) can be determined (even at 220 km taking α_2 to be 2.1×10^{-7} cm^3/sec there). The extreme available limits as well as one sample possible variation are shown in Fig. 3 for this case. The results show that both (21,4) and (12,4) decrease rather sharply with increasing temperature. If (21,1) rises with temperature the decrease in (21,4) will be minimized, although it is still at least tenfold, while that of (12,4) is maximized.

Any increase in the rate at which O^+ is converted into O_2^+ at high altitude to conform to a slow decrease or an increase of (13,3) with temperature will result in much more dramatic temperature variations in (12,4), (21,4) and, as already noted, the recombination coefficient α_4. For example if (13,3) were 3 x 10^{-11} cm^3/sec at 220 km $\alpha_4 + 0.1\ \alpha_2$ would be 8 x 10^{-9} cm^3/sec, α_2 would be 9.5 x 10^{-8} cm^3/sec and the possible range of (12,4)(21,4) and (21,1) would be as indicated for this case in Fig. 1. The largest possible value of(12,4)would be 2.1 x 10^{-13} cm^3/sec. Basically the reason for this result is that the production rate of O^+ is so low and its density so high that a high rate of removal by charge transfer to O_2 constrains the auxiliary production of O^+ from N_2^+ (21,1) to be very high and the loss rate in NO^+ production to be low. (It also leads to so much O_2^+ production that the recombination coefficient α_3 for O_2^+ must be high and those for NO^+ and N_2^+ low.) In turn the high rate of N_2^+ loss in N_2^+, O charge transfer leaves no room for a high rate of N_2^+ loss in the N_2^+, O interchange reaction.

To double the ion production rates at 220 km would permit (13,3) to be of the order of 4 x 10^{-11} cm^3/sec, (21,4) of the order of 2 x 10^{-10} cm^3/sec but still would leave (12,4) no higher than 10^{-12} cm^3/sec. Thus values for (12,4) of the order of 8 x 10^{-12} cm^3/sec at 1000° especially combined with values of (13,3) well in excess of 10^{-11} cm^3/sec would pose a very serious dilemma implying as they do that the calculated O^+ production rate is an order of magnitude too low or that O^+ is a minor ion in the F_2 region.

In passing it may be noted that to argue that because the NO^+ density follows the N_2 density above 160 km the reaction between N_2^+ and O cannot be important in forming NO^+(9) is based on several assumptions. For one thing the possibility that the reaction rate coefficients are temperature dependent could mean that this reaction is important in one altitude regime and not in another. For another if

$$NO^+ \cong \frac{(12,4)}{\alpha_4} N_2$$

the NO^+ density will follow N_2 density only under the fortuitous circumstance that (12,4) and α_4 have the same altitude dependence in a region where ion temperature and electron temperature are changing in radically different fashions with altitude.

4. THE IONOSPHERIC CONDITIONS: NIGHT TIME

The ratio of the day to the night densities of ionic species measured in the NRL experiments is displayed in Table 2. Above 200 km a most remarkable result is that which shows the presence of an ion of mass 28 some 2×10^4 seconds after sunset. If this ion is N_2^+ and is atmospheric its persistence can be explained but only on the basis of an influx of N_2^+ either through transport or through ionization. N_2^+ is removed too rapidly by ion molecule reactions and dissociative recombination judging by its low daytime densities to decay by a factor of only 50 in 2×10^4 seconds if these same processes are active at night and Q_2 is zero. This slow decay would demand a decay constant of only 5×10^{-4} sec^{-1} which would require

$$[(21,4) + (21,1)]\, O + [(23,3) + (23,4)]\, O_2 + \alpha_2 N_e = 5 \times 10^{-4} \qquad (32)$$

or

$$[(21,4) + (21,1)] + 3 \times 10^{-2} [(23,3) + (23,4)] + 2 \times 10^{-5} \alpha_2 = 10^{-12} \qquad (33)$$

where, in the daytime at 220 km

$$(21,4) + (21,1) + 4.4 \times 10^{-2}[(23,3) + (23,4)] + 5.2 \times 10^{-4} \alpha_2 = 1.8 \times 10^{-10}$$

a factor of 200 higher than the nocturnal requirements.

What seems to be needed is a production of N_2^+ ions by some mechanism at a rate 2×10^{-2} times the daytime rate, or

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

Comparable ionization rates for O and O_2 are also required to account for the O^+, O_2^+ and NO^+ densities in the F region. If diffusion is neglected the ratio of O^+ to N_2^+ densities in the steady state is given by

$$\frac{O^+}{N_2^+} \doteq \frac{Q_1/Q_2\left\{[(21,4) + (21,1)]\, O + (23,3)\, O_2 + \alpha_2 N_e\right\} + (21,1)\, O}{[(12,4) + (13,3)]\, N_2} \qquad (34)$$

This ratio is observed to increase by a factor of 7 from night to day while N_e changes by a factor of 100. Q_1 and Q_2 are equal during the daytime. If it is assumed that Q_2 is twice as large as Q_1 at night - as it would be for electrons of a few hundred electron volts -- then what is required to explain the diurnal variation in the O^+/N_2^+ ratio is

$$\begin{aligned} &2\,[(21,4) + (21,1)]\, O + (23,3)\, O_2 + (\alpha_2 N_e)_{day} + (21,1)\, O \\ &= 7\,[(21,4) + (21,1)]\, O + (23,3)\, O_2 + (\alpha_2 N_e)_{night} + (21,1)\, O \end{aligned} \qquad (35)$$

or, with $(N_e)_{day} = 100\, (N_e)_{night}$

$$5\,[(21,4) + (21,1)]\, O + (23,3)\, O_2 + 6\,(21,1)\, O = 193\, (\alpha_2 N_e)_{night} \qquad (36)$$

Since N_e is 5×10^3 electrons/cm^3 the requirement becomes

$$\alpha_2 = 5 \times 10^{-6}\,(21,4)\,O + 1.1 \times 10^{-5}\,(21,1)\,O + 5 \times 10^{-6}\,(23,3)\,O_2$$

or

$$\alpha_2 = 3.7 \times 10^{3}\,(21,4) + 8.2 \times 10^{3}\,(21,1) + 1.7 \times 10^{2}\,(23,3) \qquad (37)$$

If the night time temperature at 220 km was of the order of 750° then there are compatible values of α_2, (21,4) and (21,1) in Figs. 2 and 3 satisfying this requirement. For example

$$\alpha_2 = 2.6 \times 10^{-7}\ \text{cm}^3/\text{sec}$$

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

$$(21,1) \cong 1.5 \times 10^{-11}\ \text{cm}^3/\text{sec}$$

$$(23,3) \lesssim 1 \times 10^{-10}\ \text{cm}^3/\text{sec} \quad .$$

at 750°. With such rates it is the decreased electron density coupled with a higher ionization efficiency for N_2 than for O which could account for the high ratio of N_2^+ to O^+ at night.

O_2^+ and NO^+ exhibit an even greater persistence than N_2^+ (and O^+) at 220 km. This may be a consequence of the fact that both NO^+ and O_2^+ feed on O^+ and N_2^+ but decay by dissociative recombination involving the reduced electron densities at night.

$$O_2^+ = \frac{(13,3)\,O^+ \cdot O_2 + (23,3)\,N_2^+ \cdot O_2 + Q_3}{\alpha_3 N_e + (32,4)\,N_2 + (34,4)\,NO} \qquad (38)$$

Since O^+/N_2^+ is of the order of 60 at night the first term in the numerator will dominate the second unless $(13,3) \ll 10^{-1}\,(23,3)$. This term changes by a factor of 360 from night to day while N_e only changes by two orders of magnitude. The increase in (13,3) is by about the same factor as that in α_3. Thus a change in the O_2^+ density by a factor of four is to be expected, provided Q_3 in the day is considerably smaller than the other two production terms. In fact it is less than about 20% of these terms.

Similarly for NO^+

$$NO^+ = \{(12,4)\ O^+ \cdot N_2 + (32,4)\ O_2^+ \cdot N_2 + (21,4)\ N_2^+ \cdot O + (53,4) N^+ \cdot O_2 (34,4) O_2^+ \cdot NO + (24,4) N_2^+ \cdot NO\} / \alpha_4\ N_e \tag{39}$$

A change by a factor of 6 from night to day in the presence of a hundred fold increase in N_e could be a consequence of the dominant role of the first term in the numberator. The O^+ density increases by a factor of 360 while the rate (12,4), according to the temperature variation adopted in Fig. 3, is cut in half going from night to day, leading to a 180 fold increase in the numerator. On the other hand, N_e increases by two orders of magnitude while α_4 is cut down by a factor of 1/5. This gives an increase in NO^+ density by a factor of 9 which is certainly close enough to 6 for the purpose of this paper. Qualitatively the greater amplitude of the NO^+ variation is a consequence of the fact that α_4 is more strongly temperature dependent than α_3.

Hence, without regard to the effect of diffusion in controlling ion densities in this region, the 28^+ peak can be explained as an N_2^+ peak and the other ion densities also accounted for on the same model of reaction rates and their temperature dependence used in the daytime if there is a nocturnal ion source producing something between 5 and 10 ion pairs/cm^3 sec at 220 km. On the basis of 35 eV per ion pair this calls for an energy deposition of only about 3×10^{-10} ergs/cm^3 sec or about 2 x 10^{-3} ergs/cm^2 sec if the lower limit of ionization from this source is at 180 km. This is below the acceptable upper limit according to arguments by Dalgarno.(22) It would result in a 3914Å emission rate of about 1.5 x 10^{-2} photons per cm^3 per sec or about 10^{-1} Rayleighs. To penetrate only to 180 km electrons would need a few hundred electron volts of kinetic energy initially.

In the region around 160 km on the other hand it is possible to account for the nocturnal densities on the basis of a straightforward conversion of O^+ and N_2^+ to O_2^+ and NO^+ and subsequent dissociative recombination. No ionization source is required. In 2 x 10^4 seconds the electron density is reduced from about 1.5 x 10^5 per cm^3 to about 500 per cm^3. From the relationship

$$\frac{1}{N_e} = \frac{1}{N_e(0)} + \alpha t \tag{40}$$

this decay requires an average recombination coefficient

$$\alpha \cong 1 \times 10^{-7} \text{ cm}^3/\text{sec}. \tag{41}$$

This agrees very well with the daytime condition

$$1.6\ \alpha_4 + \alpha_3 = 2.1 \times 10^{-7} \text{ cm}^3/\text{sec} \tag{42}$$

In terms of the behavior of the individual ionic species the decay of O_2^+ follows the law

$$\frac{dO_2^+}{dt} = - [(32,4) + \alpha_3 N_e]\, O_2^+ . \tag{43}$$

If

$$N_e = \frac{N_e(0)}{1 + \alpha N(0)t} \tag{44}$$

the solution of the differential equation for O_2^+ is

$$O_2^+ = \frac{O_2^+(0)\, e^{-(32,4)\, N_2\, t}}{(1 + \alpha\, N_e(0)\, t)^{\alpha_3/\alpha}} \tag{45}$$

In 2×10^4 seconds O_2^+ is down by a factor of 440 from its initial value, so it is required that

$$300^{\alpha_3/\alpha} \exp\, [2 \times 10^{14}\, (32,4)] = 440\ . \tag{46}$$

Hence unless $\alpha_3 << \alpha$ it is required that at 160 km

$$(32,4) < 10^{-14}\ \text{cm}^3/\text{sec}\ . \tag{47}$$

If (32,4) is 10^{-14} cm^3/sec, α_3 is 0.73×10^{-7} cm^3/sec. The upper limit on α_3 is 1.07×10^{-7} cm^3/sec.

For NO^+

$$\alpha = \alpha_3\, \frac{O_2^+}{N_e} + \alpha_4\, \frac{NO^+}{N_e} \tag{48}$$

or

$$\alpha = .16\, \alpha_3 + .84\, \alpha_4 = 10^{-7}\ \text{cm}^3/\text{sec} \tag{49}$$

If α_3 is 1.07×10^{-7} cm^3/sec, α_4 is 1×10^{-7} cm^3/sec. If $\alpha_3 = 0.73 \times 10^{-7}$ cm^3/sec, α_4 is 1.05×10^{-7} cm^3/sec. According to the adopted model the average nighttime values for α_3 and α_4 at this altitude are about 0.8×10^{-7} and 1.4×10^{-7} cm^3/sec.

On the other hand, at lower altitudes the curious fact is that, whereas O_2^+ decays in approximately the same fashion from 160 km to 130 km, the NO^+ density remains high below 140 km and exhibits a peak near 130 km. The day to night ratio of NO^+ densities decreases all the way from 160 km to below 130 km. Although it is possible to argue that this behavior indicates that α_4 increases with increasing temperature the behavior of α_4 in the daytime does not show such a tendency -- quite the contrary. To postulate a source of ionization specific to NO is not satisfactory. For one thing no adequate mechanism seems to exist. The ionization rate required is given by the relationship

$$Q_4 = \alpha_4 N_e^2 = 10 \text{ ion pairs/cm}^3 \text{ sec} \qquad (50)$$

if α_4 is 5×10^{-7} cm^3/sec. Nightglow Lyman α can ionize NO which has a density in this region of the order of 10^7 per cm^3 according to Barth.(23) However, calculation shows that only 3×10^{-2} ions/cm^3 would be produced every second by this source. No meteoric ions can charge exchange with NO at low energy. Furthermore, there is also too much O_2^+ to be accounted for on the basis of simple nocturnal decay by recombination. As Holmes et al have pointed out, in the presence of an electron density greater than 10^3 per cm^3 the O_2^+ density would have decreased to far below the 150 ions/cm^3 observed 6 hours after sunset if α_3 is of the order of 10^{-7} cm^3/sec and all Q_i, except perhaps Q_4, have vanished. For then

$$\frac{d\, O_2^+}{dt} = - \alpha_3\, O_2^+ \cdot N_e \qquad (51)$$

$$\frac{d\, N_e}{dt} = Q_4 - \alpha\, N_e^2 \qquad (52)$$

which give

$$O_2^+ = Q_2^+(0) \exp[- \alpha_3 \int_0^t N_e(t')\, dt'] \qquad (53)$$

and

$$N_e(t) = \frac{2\, N_{el}\, N_{e0}}{N_{e0}(1-e^{-kt}) + 2\, N_{el}\, e^{-kt}} - N_{el} \qquad (54)$$

where

$$N_{el} = \sqrt{Q_4/\alpha} \tag{55}$$

and

$$k = 2\sqrt{Q_4\,\alpha} = 2\,N_{el}\,\alpha\,. \tag{56}$$

These decay laws show that

$$O_2^+ = O_2^+(0)e^{-20} \tag{57}$$

at 2 x 10^4 seconds. Hence it appears necessary to postulate a source of ionization below 140 km which can produce O_2^+ as well as NO^+ ions.

The steady state versions of Eqs. (1-4) at 130 km are,

$$O^+ = \frac{Q_1 + 2.2 \times 10^{10}\, N_2^+\, (21,1)}{1.1 \times 10^{10}[10(12,4) + (13,3)]} \tag{58}$$

$$N_2^+ = \frac{Q_2}{1.2 \times 10^{10}\,(21,4) + 1.1 \times 10^{10}\,(23,3)} \tag{59}$$

$$7 \times 10^5\,\alpha_3 + 1.7 \times 10^{13}(32,4) + 1.5 \times 10^9(34,4) = Q_3 + 1.1 \times 10^{10}\,[(23,3)\,N_2^+ + (13,3)O^+] \tag{60}$$

$$10^{-3}\,\alpha_4 = 5\,(12,4)\,O^+ + (21,4)\,N_2^+ + 0.5\,(53,4)\,N^+ \tag{61}$$

where all clearly trivial terms have been eliminated.

Taking the same set of rate constants that were used for the daytime ionosphere at 130 km these conditions on the Q_1 and the N_2^+ and O^+ densities may be written as

$$0.9\,O^+ = Q_1 + 0.2\,N_2^+ \tag{62}$$

$$[6 + (23,3) \times 10^{10}]\,N_2^+ = Q_2 \tag{63}$$

$$0.9 + 1.5 \times 10^{9}(34,4) = Q_3 + (23,3)\ 10^{10}\ N_2^{+} + 0.4\ O^{+} \tag{64}$$

$$1 = 0.04\ O^{+} + N_2^{+} \tag{65}$$

The N^+ contribution has been neglected but would need to be restored if N^+ is comparable to N_2^+ in density.

If charge transfer between O_2^+ and NO does not make an appreciable contribution to O_2^+ loss and NO^+ gain and the rate of N_2^+ transfer to O_2 is of the order of 10^{-10} cm^3/sec it is difficult to reconcile these conditions with reasonable ratios of primary production rates. They leave no room for Q_3 in (60), that is for any O_2^+ production other than the ion molecule reactions. Considering the uncertainties in the data this discrepancy cannot perhaps be regarded as grave. However, taking the observations at their face value, it would be more comfortable if the O_2^+, NO charge exchange should turn out to have a rate of the order of 5×10^{-10} cm^3/sec at 300°K. In that case the relationships (62-65) would be satisfied by

$$N_2^{+} \cong 1\text{cm}^{-3}$$

$$O^{+} \cong 1\text{cm}^{-3}$$

from (61),

$$Q_1 \cong 0.7\ \text{cm}^{-3}\ \text{sec}^{-1}$$

from (58),

$$Q_2 = 7\ \text{cm}^{-3}\ \text{sec}^{-1}$$

from (59),

and

$$Q_3 \cong 0.3\ \text{cm}^{-3}\ \text{sec}^{-1}$$

from (60).

Where the ratios of the N_2, O and O_2 densities are

10:2.2:1

the corresponding primary ion production rates are

20:2.3:1

indicating twice as great an efficiency for N_2 ionization as that for O_2 and O.

As was the case above 180 km this ionization could be by electrons, this time with kilovolt energies, and the excitation of the nightglow first negative band system would remain below observable limits.

5. CONCLUSIONS

Recent mass spectrometric determinations of the abundance of ionic species in the ionosphere are consistent with laboratory measurements of ion-molecule reaction rates and recombination coefficients at 300°K. As the altitude and temperature increase the observations call for decreasing rate coefficients in all important cases except, perhaps, the rate for N_2^+, O charge transfer. In particular it appears to be necessary that the dissociative recombination coefficient for NO^+ decrease as $T_e^{-1.4 \pm 0.2}$ while that for O_2^+ decrease more slowly. It is probable that the coefficient for N_2^+ decreases very slowly with temperature. The rates for N_2^+, O and O^+, N_2 ion atom interchange and for O^+, O_2 charge transfer all must decrease with temperature to be compatible with the ionospheric data.

The mass spectrometric data for the night-time ionosphere are consistent with the same set of reaction rates with their temperature dependences deduced from the daytime observations. However, this is true only if weak primary ionization sources are present. One of these, perhaps involving electrons of a few hundred electron volts, causes ionization at a rate of 5-10 ion pairs/cm^3 sec above 180 km. The other source, again possibly electronic, would produce about 10 ion pairs/cm^3 sec near 130 km at night. In the latter case it appears likely that the conversion of O_2^+ to NO^+ by charge transfer is a very efficient process.

These conclusions are based on a recalculation of the ionization rates by photons and photo-electrons using recent information concerning the composition of the neutral atmosphere. A direct measurements of this primary rate would be most desirable.

ACKNOWLEDGEMENTS

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

Table 1

Daytime Ionic Densities in cm^{-3}

Altitude km	(1) O^+	(2) N_2^+	(3) O_2^+	(4) NO^+	N^+	Ne
130	8.5×10^2	1.5×10^2	6.2×10^4	4.5×10^4		1.1×10^5
140	8.5×10^3	1.5×10^2	6.2×10^4	4.5×10^4		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
130	7.3×10^2	2.1×10^3	8.5×10^2
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
130	2.2×10^{10}	1.1×10^{11}	1.1×10^{10}	1.6×10^7	335°
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. Q_i are for 30° solar elevation.

Table 2

Nighttime 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
130					1.6×10^2	400	5.2×10^3	9
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

REFERENCES

(1) F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, Planetary Space Sci. 13, (1965), in press.

(2) W. L. Fite, J. A. Rutherford, W. R. Snow, and V. A. J. VanLint, Discussions Faraday Soc. 33, 518 (1963).

(3) F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, Planetary Space Sci. 13, 219 (1965).

(4) G. F. O. Langstroth and J. B. Hasted, Discussions Faraday Soc. 33, 298 (1962).

(5) E. E. Ferguson, F. C. Fehsenfeld, P. D. Goldan, A. L. Schmeltekopf, and H. I. Schiff, Planetary Space Sci. 13, (1965).

(6) M. A. Biondi and W. H. Kasner, Phys. Rev. 137A, 317, 1965.

(7) W. H. Kasner, W. A. Rogers and M. A. Biondi, Phys. Rev. Letters 7, 321, 1961.

(8) M. A. Biondi, Ann. de Geophysique 20, 34, 1964.

(9) J. C. Holmes, C. Y. Johnson and J. M. Young, Space Research V, North Holland Publishing Co., 1965.

(10) M. Nicolet and W. Swider, Planet. Space Sci. 11, 1459, 1963.

(11) Popoff and Whitten

(12) J. F. Paulson, Ann. de Geophysique, 20, 18, 1964.

(13) F. C. Fehsenfeld, P. D. Goldan, A. L. Schmeltekopf, and E. E. Ferguson, Planetary Space Sci. 13, (1965), in press.

(14) J. Sayers and D. Smith, Discussions Faraday Soc. 37, 167 (1964).

(15) A. Falli, A. Giardini-Guidoni, and G. G. Volpi, J. Chem. Phys. 39, 518, 1963.

(16) W. H. Kasner and M. A. Biondi, private communication.

P. D. Goldan, F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, J. Chem. Phys. to be submitted.

(17) A. O. Nier, J. H. Hoffman, C. Y. Johnson and J. C. Holmes, J. Geophys. Res. <u>69</u>, 979, 1964.

(18) A. E. Hedin, C. P. Avery and C. D. Tschetter, J. Geophys. Res. <u>69</u>, 4637, 1964.

(19) E. J. Shaefer and M. H. Nichols, J. Geophys. Res. <u>69</u>, 4649, 1964.

(20) E. Zipf, Private Communication.

(21) E. C. Zipf, J. Geomagnet. Geoelec. Kyoto, (1965) in press.

(22) A. Dalgarno, Annales de Geophysique <u>20</u>, 67, 1964.

(23) C. Barth, Space Research V, North Holland Publishing Co., to be published.

FIGURE CAPTIONS

Fig. 1. Reaction rates for $N_2^+ + O \rightarrow NO^+ + N$ and $N_2^+ + O \rightarrow O^+ + N_2$ plotted against the rate for $O^+ + N_2 \rightarrow NO^+ + N$ for various values of (13,3), the rate of $O^+ + O_2 \rightarrow O_2^+ + O$ expressed in units of 10^{-11} cm^3/sec.

Fig. 2. Required dependence of various reaction rates on gas temperature for the indicated variation of (13,3) with temperature. Self consistent curves are labeled with the same letters.

Fig. 3. Dependence of recombination coefficients on electron temperature for various assumed values of (13,3) at 220 km expressed in units of 10^{-11} cm^3/sec. High temperature point is really $\alpha_4 + 0.1\ \alpha_2$. Power law extrapolations of rate coefficients are also shown.

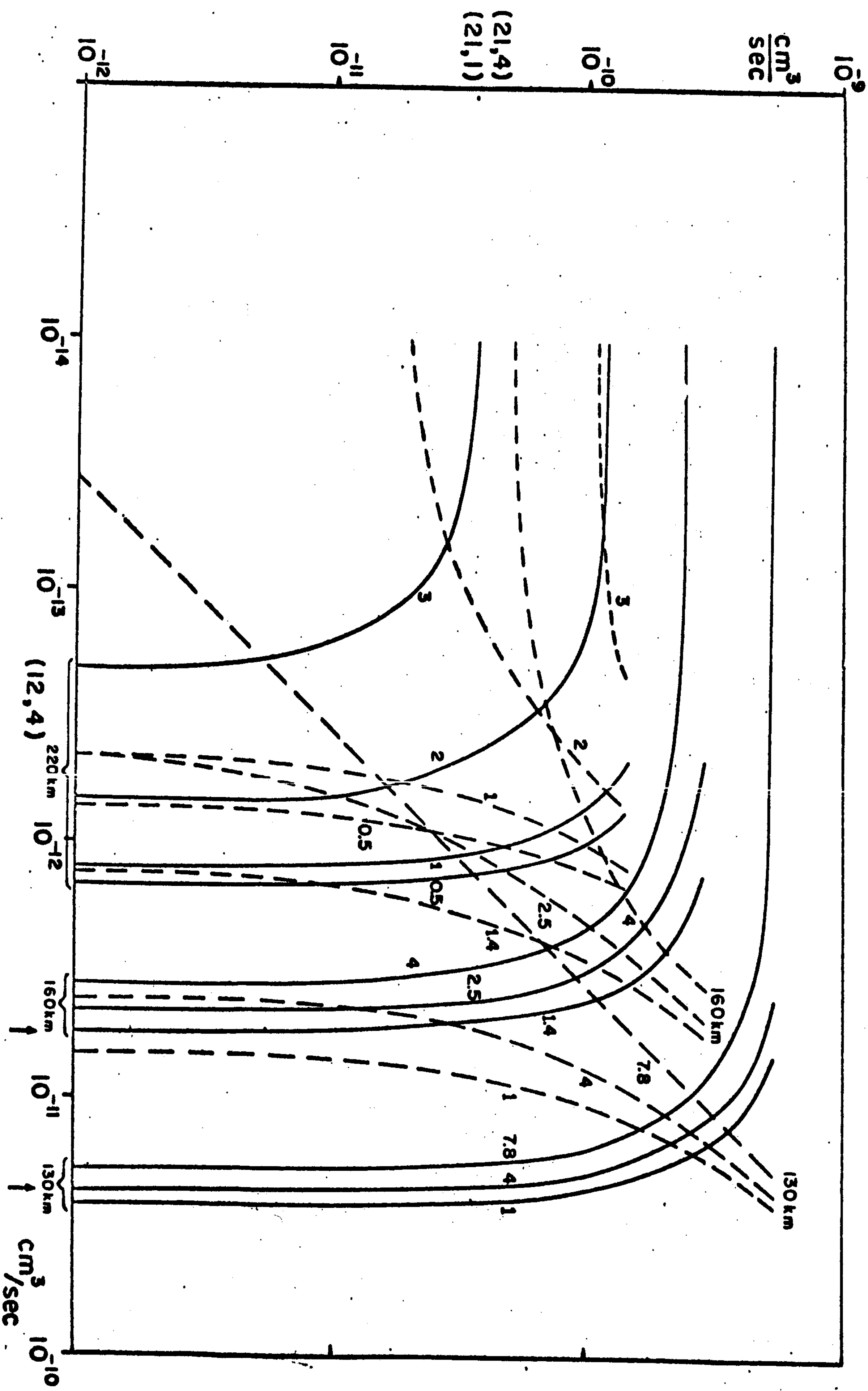

10^{-12}
10^{-11}
(21,1)
(21,4)
10^{-10}
$\frac{cm^3}{sec}$
10^{-9}
10^{-14}
10^{-13}
(12,4)
220 km
10^{-12}
160 km
10^{-11}
130 km
cm^3/sec
10^{-10}
3
3
2
2
1
0.5
1
0.5
2.5
1.4
4
4
2.5
1.4
7.8
4
1
160 km
7.8
4
1
130 km

Figure 1

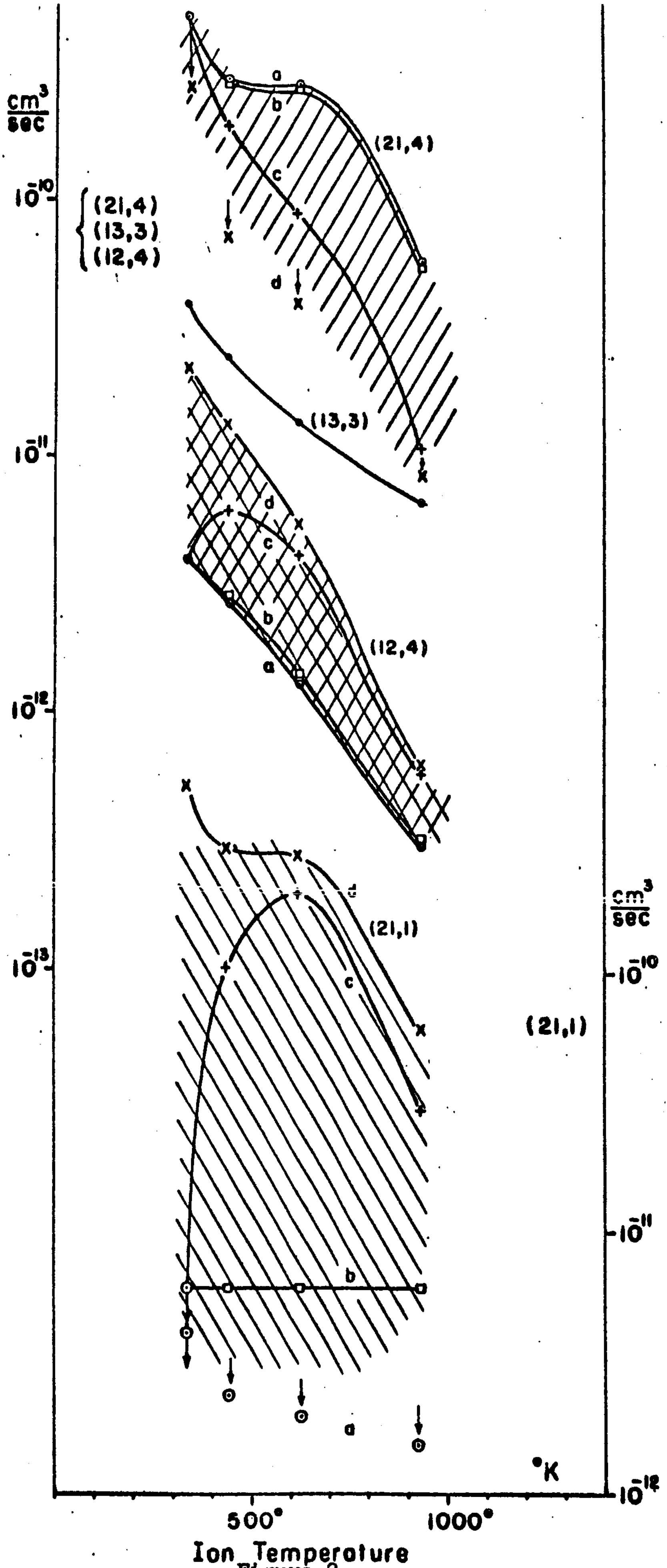
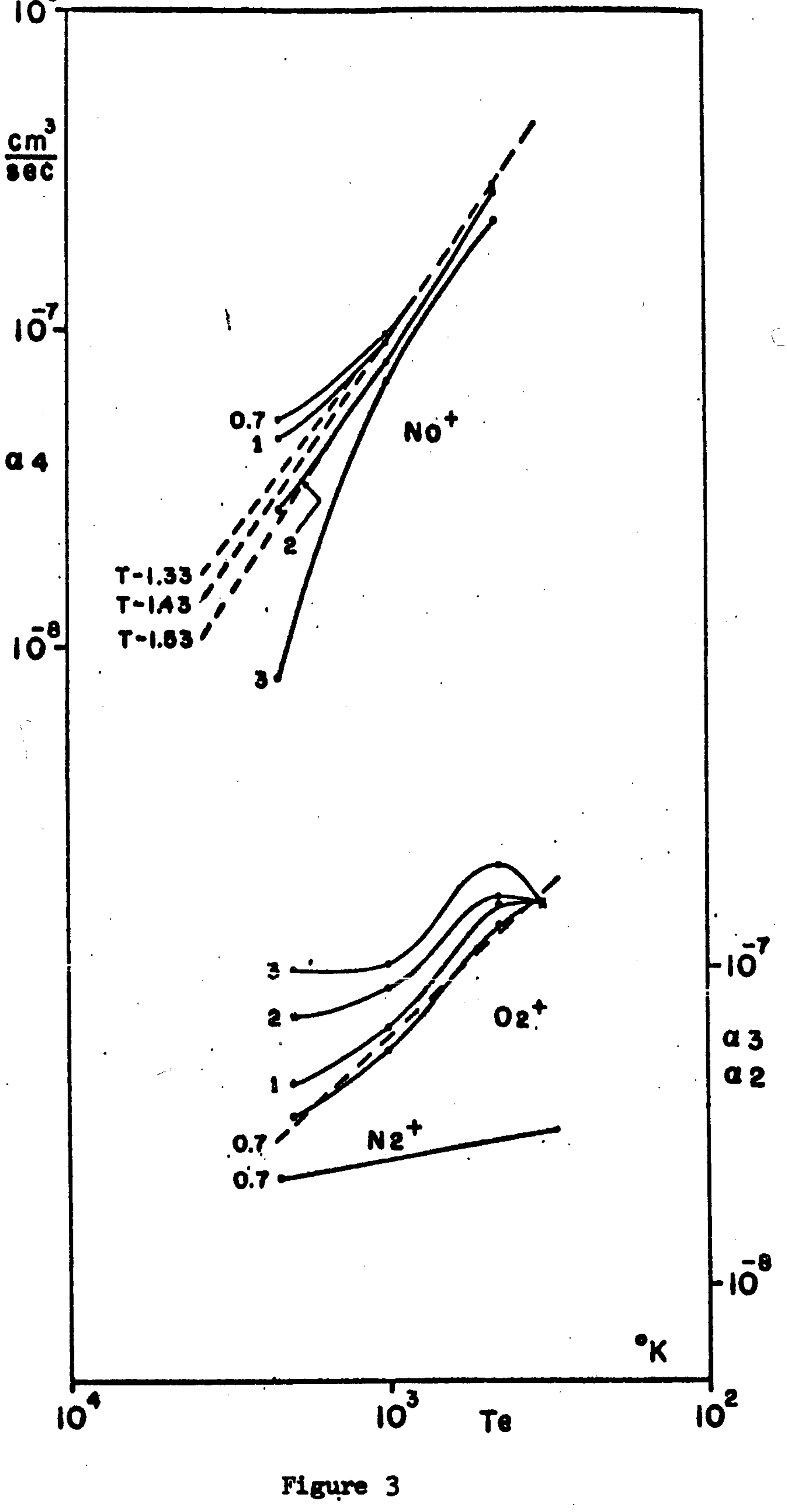

cm^3/sec
10^{-10}
10^{-11}
10^{-12}
10^{-13}
(21,4)
(13,3)
(12,4)
a
b
c
d
(21,4)
(13,3)
d
c
b
a
(12,4)
d
(21,1)
c
b
a
cm^3/sec
10^{-10}
(21,1)
10^{-11}
10^{-12}
°K
500°
1000°
Ion Temperature

Figure 2



10^{-6}
$\frac{cm^3}{sec}$
10^{-7}
$\alpha 4$
10^{-8}
0.7
1
2
3
No$^+$
T-1.33
T-1.43
T-1.53
3
2
1
0.7
0.7
O$_2^+$
N$_2^+$
10^{-7}
$\alpha 3$
$\alpha 2$
10^{-8}
°K
10^4
10^3
Te
10^2

Figure 3