JOURNAL OF MASS SPECTROMETRY, VOL. 32, 1273–1278 (1997)

SPECIAL FEATURE: HISTORICAL

First printed in the *Journal of Geophysical Research*, Vol. 12, No. 17, pp. 4323–4329 (1965).
Reprinted with permission from the American Geophysical Union.

Positive Ion–Neutral Reactions in the Ionosphere

E. E. Ferguson, F. C. Fehsenfeld, P. D. Goldan and A. L. Schmeltekopf
Central Radio Propagation Laboratory, National Bureau of Standards, Boulder, Colorado

Abstract: Daytime positive ion densities calculated using recently measured laboratory ion-neutral reaction rate constants are compared with the NRL rocket results between 120 and 220 km. The calculated O^+ and $N_2{}^+$ densities are found to be in good agreement with the ionospheric observations. The main $N_2{}^+$ loss process in this region is the reaction

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

This reaction is also the major source of NO^+ at 140 km. The charge-transfer reaction

$$O_2{}^+ + NO \rightarrow NO^+ + O_2$$

appears to be a significant source of NO^+ at 120 km and indeed may be the major source. The reaction

$$O_2{}^+ + N \rightarrow NO^+ + O$$

will be significant at 120 km if the ratio of atomic to molecular nitrogen is as large as 10^{-4}. The fast $O_2{}^+$ loss in reaction with NO at 120 km at night requires a local ionization source greater than 1 $O_2{}^+$ ion/cc sec to maintain the observed $O_2{}^+$ concentration. © 1965 American Geophysical Union.

INTRODUCTION

A rapid increase in understanding of ionospheric chemical positive-ion processes has occurred in the past few years, largely owing to direct atmospheric observations of positive ion densities [Holmes *et al.* 1965], solar UV fluxes [Hinteregger *et al.* 1965], neutral densities [Hinteregger *et al.* 1965; and Nier *et al.* 1964], and rocket dayglow observations [Zipf, 1965]. In addition, laboratory measurements on a number of important ionospheric reactions have recently become available. It is the purpose of this paper to discuss the application of some recent laboratory measurements to ionospheric physics.

A similar analysis has recently been presented by Donahue [1965]. Donahue concludes his paper by pointing out the importance of the following reactions which produce NO^+ (numbered by order of appearance in Table 1):

5. $N_2{}^+ + O \rightarrow NO^+ + N$
9. $O_2{}^+ + N_2 \rightarrow NO^+ + NO$
10. $O_2{}^+ + NO \rightarrow NO^+ + O_2$

Laboratory information has now been obtained on all these reactions, as well as on

11. $O_2{}^+ + N \rightarrow NO^+ + O$

since the analysis by Donahue [1965] was written. In addition, ambiguities in laboratory results for the reactions

2. $O^+ + O_2 \rightarrow O_2{}^+ + O$
4. $N_2{}^+ + O_2 \rightarrow O_2{}^+ + N_2$

have now been resolved.

The detailed analysis of Nicolet [1965] was similarly handicapped by lack of relevant reaction rate data. Nicolet did not use reaction 5 for NO^+ production, for example, and this is an important NO^+ production mechanism for the daytime NO^+ ion density around 120–140 km, exceeding the production by

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

LABORATORY REACTION RATE DATA

Table 1 summarizes thermal energy laboratory reaction rate data relevant to the ionospheric positive-ion distribution. Not all thermal laboratory measurements that have been reported in the literature are included in Table 1, but the selection has not been arbitrary. The different experimental results given in Table 1 are discussed in the references thereto. Most of the reactions have not been measured except in this laboratory. A summary of laboratory reaction rate knowledge to 1963 has been given by Paulson [1964].

CCC 1076–5174/97/121273–06 $17.50

Received 4 June 1965

Table 1. Ion-neutral laboratory reaction rate constants. The O^+ and N^+ reactants are ground state in the measurements made in this laboratory. The $N_2{}^+$ is ground electronic state and largely ground vibrational state (>50%). The $O_2{}^+$ is believed to be ground electronic state, but the vibrational distribution has not been determined

	Reaction	Rate constant (300 K) $cm^3\ s^{-1}$	Reference
1.	$O^+ + N_2 \rightarrow NO^+ + N$	$3(\pm 1) \times 10^{-12}$	a
		$4.7(\pm 0.5) \times 10^{-12}$	b
2.	$O^+ + O_2 \leftrightarrow O_2{}^+ + O$	$4(\pm 1) \times 10^{-11}$	c
		$1.64(\pm 0.05) \times 10^{-11}$	d
3.	$O^+ + NO \rightarrow NO^+ + N$	$2.4(\pm 1) \times 10^{-11}$	e
4.	$N_2{}^+ + O_2 \rightarrow O_2{}^+ + N_2$	$1.0(\pm 0.5) \times 10^{-10}$	f*
		$\sim 2 \times 10^{-10}$	g
5.	$N_2{}^+ + O \rightarrow NO^+ + N$	$2.5(\pm 1) \times 10^{-10}$	h
6.	$N_2{}^+ + O \rightarrow O^+ + N_2$	$<10^{-11}$	h
7.	$N_2{}^+ + NO \rightarrow NO^+ + N_2$	5×10^{-10}	e
8.	$N_2{}^+ + O_2 \rightarrow NO^+ + NO$	$<2 \times 10^{-13}$	i
9.	$O_2{}^+ + N_2 \rightarrow NO^+ + NO$	$<10^{-15}$	j
		$<2 \times 10^{-13}$	i
10.	$O_2{}^+ + NO \rightarrow NO^+ + O_2$	8×10^{-10}	e
11.	$O_2{}^+ + N \rightarrow NO^+ + O$	$1.8(\pm 0.5) \times 10^{-10}$	e
12.	$N^+ + O_2 \rightarrow NO^+ + O$	$\sim 5 \times 10^{-10}$	g
		$\leqslant 5 \times 10^{-10}$	a, f
13.	$N^+ + O_2 \rightarrow O_2{}^+ + N$	$0.5\text{–}1 \times 10^{-9}$	f
14.	$N^+ + NO \rightarrow NO^+ + N$	$8(\pm 1) \times 10^{-10}$	e

* This value is a correction to an erroneous value reported in reference a.

[a] F. C. Fehsenfeld, A. L. Schmeltekopf and E. E. Ferguson, Planetary Space Sci., **13**, 219 (1965).

[b] G. F. O. Langstroth and J. B. Hasted, *Discussions Faraday Soc.*, **33**, 298 (1962).

[c] F. C. Fehsenfeld, P. D. Goldan, A. L. Schmeltekopf and E. E. Ferguson, *Planetary Space Sci.*, **13**, 579 (1965).

[d] J. Sayers and D. Smith, *Discussions Faraday Soc.*, **37**, 1567 (1964).

[e] P. D. Goldan, F. C. Fehsenfeld, A. L. Schmeltekopf and E. E. Ferguson, *J. Chem. Phys.*, submitted.

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

[g] W. L. Fite, J. A. Rutherford, W. R. Snow and V. A. J. VanLint, *Discussions Faraday Soc.*, **33**, 518, 1963.

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

[i] A. Galli, A. Giardini-Guidoni and G. G. Volpi, *J. Chem. Phys.*, **39**, 518 (1963).

[j] Unpublished result, this laboratory.

IONOSPHERIC O^+ LOSS

Considering the O^+ loss reactions 1 and 2, it is our opinion that the rates at 300 K are very well known for geophysical purposes, and not uncertain by factors as large as 2 or 3. The situation is now certainly better than was estimated by Nicolet [1965], who took $k_1 = k_2 = 10^{-12\pm 1}$ $cm^3\ s^{-1}$. Temperature dependence are largely unknown for all the reactions listed in Table 1; a program to acquire such information is being undertaken in this laboratory.

The loss rate for O^+ in the daytime equilibrium ionosphere seems to be in very satisfactory agreement with the rate which is predicted using the laboratory rate constants. For example, the rate constants adopted by Norton *et al.* [1963] are $k_1 = 1 \times 10^{-12}$ and $k_2 = 5 \times 10^{-11}$ $cm^3\ s^{-1}$ for the daytime equilibrium E and F_2 regions. Hinteregger *et al.* [1965] have deduced that in the daytime F_2 region ($\sim$250 km and $\sim$750 K) $k_1 + 0.12k_2 \sim 3 \times 10^{-12}$ $cm^3\ s^{-1}$, somewhat less than the laboratory 300 K combination of $k_1 + 0.12k_2 = 8(\pm 2) \times 10^{-12}$ $cm^3\ s^{-1}$.

Following the analysis of Donahue [1965], in which he compares ion densities predicted from different rate constant combinations with NRL rocket results [Holmes *et al.* 1965], the O^+ density is computed in the following manner. Donahue adopts the neutral atmosphere composition measured by Nier *et al.* [1964] and ionization rates computed by Zipf [1965], which include secondary ionization produced by photoelectrons. The same procedure is followed here, and these data are shown in Table 2. For the day time steady state, in the absence of significant diffusive flow, the O^+ concentration is determined by [Donahue, 1965]

$$Q(O^+) + k_6[N_2{}^+][O] = \{k_1[N_2] + k_2[O_2]\}[O^+]$$

where Q is the photoionization source, and the k's are the rate constants for the like numbered reactions in Table 1. At 120 to 220 km altitude, $k_6[N_2{}^+][O] \leqslant 0.05Q_1$, so that photo production of O^+ dominates charge-transfer production from $N_2{}^+$, and we hereafter neglect the latter. Using the first listed rate constant from Table 1 at 120 km, where the ionospheric temperature is close to the laboratory temperature, we find

Table 2

Altitude km	n_e	Densities, particles/cm^3 O	N_2	O_2	NO	T, deg K
120	10^5	4×10^{10}	3×10^{11}	4×10^{10}	$\sim 10^7$	280
140	1.3×10^5	1.1×10^{10}	4×10^{10}	4.4×10^9		420
160	2×10^5	4.5×10^9	1×10^{10}	9.5×10^8		600
220	4×10^5	5×10^8	3.3×10^8	1.7×10^7		1000

Altitude km	Ionization rates, ion pairs/cm^3 s Q(O)	$Q(N_2)$	$Q(O_2)$
120	5×10^2	2.5×10^3	1.1×10^3
140	1.1×10^3	2.5×10^3	8.5×10^2
160	9×10^2	1.8×10^3	3.7×10^2
220	3×10^2	2.5×10^2	25

Table 3

Altitude, km	O^+ loss, s^{-1}, contribution due to $N_2(k_1 = 3 \times 10^{-12})$	$O_2(k_2 = 4 \times 10^{-11})$	O^+ concentration, cm^{-3} Calculated	Observed*	T, deg K
120	0.90	1.600	2.0×10^2	1.5×10^2	280
140	0.12	0.180	3.7×10^3	4×10^3	420
160	0.03	0.038	1.3×10^4	3.3×10^4	600
220	9.9×10^{-4}	6.5×10^{-4}	1.8×10^5	4×10^5	1000

* Rocket-borne ion spectrometer [Holmes et al. 1965].

$[O^+] = 2.0 \times 10^2$ cm^{-3}, comparing well with the value $[O^+] = 1.5 \times 10^2$, which is the NRL result (extrapolated downward ~10 km by Donahue [1965]. Table 3 gives results for several altitudes. The agreement between calculated and observed values is remarkably good. At 120 and 140 km, where the ionospheric temperature is not greatly different from the laboratory temperature, the agreement within ~30% must indeed be partly fortuitous. At the higher temperatures, the calculated values are too low, but agreement is still within a factor of 3. This might be used as an argument in favor of allowing the rate constants to decrease approximately as T^{-1}; however, we do not feel that disagreement of this magnitude is necessarily significant with respect to rate constants, in view of the uncertainties in all the data involved. In the case of reaction 2, an approximate T^{-1} dependence is suggested by the laboratory results of Court and Batey as reported by Sayers and Smith [1964] in the 210 to 452 K temperature range. A T^{-1} dependence of the rate constants of reactions 1 and 2 also brings the laboratory results into almost precise agreement with those of Hinteregger *et al.* [1965]. However, unpublished results obtained from monoenergetic ion beam experiments (R. F. Stebbings, private communication, 1965; C. F. Giese, private communication, 1965) down to energies of only a few electron volts show that the rate constant for reaction 1 definitely increases from 1 to 10 eV. There is a similar indication that the rate constant for reaction 2 also increases in this range (Stebbings, private communication, 1965). It seems most likely that this trend continues down into the thermal range, and that an increase in temperature will increase the rates of (1) and (2) in the thermal range. This matter will remain uncertain until further laboratory investigations of the temperature dependence in the thermal range are carried out.

The laboratory rate constants are considered to be in good agreement with ionospheric data, considering the uncertainties involved in the comparison. An extreme temperature dependence for the rate constants does not seem permissible from purely ionospheric considerations, and in particular neither of the rates is likely to increase drastically with increasing temperature. This seems to preclude invoking solely an activation energy as the explanation for the relative inefficiency of either reaction 1 or 2. Reaction 1, for example, only occurs once in about every 300 or so collisions. To explain this as due largely to an activation energy would imply an exponential increase of rate constant with temperature, which is unacceptable in the ionosphere. The same argument applies to reaction 2.

IONOSPHERIC N_2^+ LOSS

A significant check of ion-neutral reaction rates is also possible for N_2^+ ion concentration. The steady-state equation in this case is [Donahue, 1965]

$$Q(N_2^+ = \{(k_5 + k_6)[O] + (k_4 + k_8)[O_2] + \alpha(N_2^+)n_e[N_2^+]$$

Accepting the 300 K laboratory value for the N_2^+ dissociative recombination coefficient [Kasner and Bionid, 1965], $\alpha(N_2^+) = 3 \times 10^{-7}$ cm^3 s^{-1}, and neglecting its temperature dependence and using the rate constants from Table 1, we obtain the results in Table 4. Since $k_6 \ll k_5$, $k_8 \ll k_4$, the processes corresponding to reactions 6 and 8 are neglected.

Table 4

Altitude km	N_2^+ loss, s^{-1}, by reaction with O	O_2	electrons	N_2^+ concentration, cm^{-3} Calculated	Observed*†	Observed‡	T, deg K
120	10.00	4.01	0.03	1.7×10^2	50	65	280
140	2.80	0.4	0.04	7.5×10^2	450	500	420
160	1.10	0.1	0.06	1.4×10^3	1.1×10^3	1.7×10^3	600
220	0.12	0.002	0.12	1.0×10^3	1.7×10^3	2.2×10^3	1000

* Rocket-borne ion spectrometer [Holmes *et al.* 1965].
† Multiplied by 1.75 to make observed ion densities consistent with observed electron densities, following Donahue [1965].
‡ Rocket dayglow [Zipf, 1965].

The agreement is again remarkably good, better than a factor of 2, except at 120 km. This point represents an uncertain extrapolation of the N_2^+ data of almost 20 km, in a region where it is changing rapidly, and is therefore not considered significant. The chemical loss of N_2^+ dominates the dissociative recombination loss below 220 km. The observed ion densities in the 140 to 160 km range are therefore a significant check on ion-neutral reaction rates. The 220 km data could be fit by adjusting $\alpha(N_2^+)$ for 1000 K to a significantly lower value than the laboratory rate measured at 300 K at 140 and 160 km, the loss of N_2^+ by reaction with O is more important than with O_2. This has not been widely recognized; only Norton *et al.* [1963], among the earlier ionospheric model builders, appear to have recognized this from ionospheric considerations alone.

The rates appear to be in reasonable agreement again. This, of course, is not a sensitive test for the N_2^+ charge transfer with molecular oxygen, because of its minor role in N_2^+ loss in this altitude range. No marked temperature effect on the $N_2^+ + O$ ion-atom interchange reaction, at least over the limited 400 to 600 K temperature range, appears to be called for.

Support for a large rate constant for reaction of N_2^+ with O is also given from rocket observations of the N_2^+ 3914 A resonant scattered dayglow. Zipf [1965], for example, finds that total N_2^+ loss is consistent with O_2 loss $k_4 = 2 \times 10^{-10}$ cm^3 s^{-1} and loss with atomic oxygen $k_5 + k_6 = 5 \times 10^{-11}$ cm^3 s^{-1}. Decreasing k_4 somewhat will raise Zipf's $k_5 + k_6 \approx k_5$, giving slightly better agreement with the laboratory 300 K rate. The Norton *et al.* model, when updated with recent ionospheric positive ion [Holmes *et al.* 1965] and neutral data [Nier *et al.* 1964], leads to $k_5 \approx 7 \times 10^{-11}$ cm^3 s^{-1} and brackets k_5 to lie between 3 and 30×10^{-11} cm^3 s^{-1} [Fehsenfeld *et al.* 1965].

IONOSPHERIC O_2^+ and NO^+ CONCENTRATIONS

The O_2^+ steady-state concentration is not a sensitive test of ion-neutral reaction rates. The production is largely due to photoionization below 140 km and is largely due to reaction 2 above 160 km. The destruction is almost entirely due to dissociative recombination. However, at 120 km the charge transfer of O_2^+ with NO contributes 40% of the O_2^+ loss if we accept Barth's NO concentration of about 1.6×10^7 cm^{-3} at this height. At lower heights, where the NO concentration goes up to about 6×10^7 cm^{-3} and the electron density is lower, this process will presumably dominate O_2^+ loss. The possibility exists that reaction 11, the ion-atom interchange of O_2^+ with N, may contribute to O_2^+ loss. At 120 km, for example, an atomic nitrogen concentration of 10^8 cm^{-3} (and N/N_2 ratio of 3×10^{-4}) would compete about equally with dissociative electron recombination. The O_2^+ concentration can be deduced with rates from Table 1 using $\alpha(O_2^+)$ values consistent with laboratory data, about 2×10^{-7} cm^3 s^{-1} at 300 K. The altitude distribution of O_2^+ is best reconciled with an $\alpha(O_2^+)$ that decreases with increasing temperature.

The significance of the NO^+ concentration is somewhat similar to that for O_2^+ in that its loss is due almost entirely to dissociative recombination. The dissociative recombination coefficient in this case is so poorly known from laboratory measurements that a great latitude for NO^+ production must be allowed. The production is to a large extent a consequence of ion-neutral reactions, and at least some tentative conclusions can be drawn. The steady-state NO^+ equation is

$$\begin{aligned}\alpha[NO^+]n_e[NO^+] = {} & k_1[O^+][N_2] + k_3[O^+][NO] \\ & + k_5[N_2^+][O] + k_7[N_2^+][NO] \\ & + k_8[N_2^+][O_2] \\ & + k_9[O_2^+][N_2] + k_{10}[O_2^+][NO] \\ & + k_{11}[O_2^+][N] \\ & + k_{12}[N^+][O_2] + k_{14}[N^+][NO]\end{aligned}$$

Reactions 8 and 9, involving the breaking of two bonds, are too slow to be significant in the NO^+ production in the range covered by the NRL positive ion data. The N^+ concentration is too small for reaction 12 or 14 to contribute significantly. Reaction 7 can be neglected, since both $[N_2^+]$ and [NO] are small. Reactions 10 and 11 have large rate constants, so that, even though the atomic nitrogen and NO concentrations are small (and unfortunately not well known, particularly in the case of [N]), they cannot obviously be neglected. Reaction 3 does not make a significant contribution. If only reactions 1 and 5 are considered, the NO^+ equation (for 120 km) gives $\alpha(NO^+) = 2.6 \times 10^{-7}$ cm^3 s^{-1}, probably within the range of uncertainty of this rate constant at 300 K, although a higher rate is often quoted [Donahue, 1965], e.g. 4–20 $\times 10^{-7}$ cm^3 s^{-1}. The contributions of different reactions to NO^+ production are shown in Table 5. Note that the $N_2^+ + O$ reaction 5 is more important than the $O^+ + N_2$ reaction 1 for NO^+ production at this altitude. Reaction 10, the charge transfer of O_2^+ with NO, may well make a significant contribution. Using Barth's [1965] NO value of $\sim 10^7$ cm^{-3} at 120 km, we have from this process $d[NO^+]/$

Table 5

Altitude	NO^+ production, cm^{-3} s^{-1}, by reaction					
km	1. $O^+ + N_2$	5. $N_2^+ + O$	10. $O_2^+ + NO$	11. $O_2^+ + N$	$\alpha(NO^+)$	T, deg K
120	135	500	500	1.5×10^{-5} [N]	4.4×10^{-7}	280
140	480	1240			3.3×10^{-7}	420
160	1000	1270			1.3×10^{-7}	600
220	400	210			9×10^{-8}	1000

$dt = 500$ cm^{-3} s^{-1}, a production comparable with that from the other two reactions! This contribution would raise the value of $\alpha(NO^+)$ to 4.4×10^{-7} cm^3 s^{-1}. Nicolet's [1965] estimate of the NO concentration at 120 km is somewhat lower than the one used here, 2–5 $\times 10^6$ cm^{-3}.

The contribution of reaction 11 is difficult even to estimate, because the atomic nitrogen concentration is so poorly known. The contribution at 120 km will be

$$d[NO^+]/dt = 1.1 \times 10^{-5}[N]$$

and will become significant if $[N] \gtrsim 3 \times 10^7$, corresponding to $[N]/[N_2] \sim 10^{-4}$. The possibility of [N] being this large at 120 km does not appear to be definitely excluded. Bates [1952] estimated [N] to be of the order of 2×10^8 at around 120 km. An [N] concentration this large would produce a major part of NO^+ by reaction 11. However, Nicolet [1965] argues that $[N] < [NO]$, so that on this basis we can perhaps exclude this reaction.

Above 140 km, both NO and N can be neglected as NO^+ sources. The relative contributions to NO^+ production by reactions 1 and 5 are shown in Table 5 for the four representative altitudes discussed in this paper. The value of $\alpha(NO^+)$ which gives the NO^+ concentration at these altitudes and with these production rates is also given. It seems clear that the dissociative recombination rate for NO^+ is very similar to that for $N_2{}^+$ and $O_2{}^+$ at 300 K, several times 10^{-7} cm^3 s^{-1}, and it seems most likely that this rate decreases with an increase in temperature.

It seems that there are no obvious inconsistencies between daytime ionospheric observations and the recent laboratory measurements. The largely unconsidered reaction $N_2{}^+ + O \rightarrow NO^+ + N$ clearly plays a strong role both in $N_2{}^+$ loss and NO^+ production.

NIGHTTIME IONOSPHERE

At nighttime the density of all positive ions and the density of electrons decrease, owing to removal of the dominant ionization source, photoionization. The NRL data show a measured nighttime ion distribution. It has been widely recognized that a difficulty exists in the persistence of the nighttime ionosphere [Bates and Nicolet, 1960; and Fehsenfeld *et al.*, 1965]. Rate constants as large as those measured in the laboratory (and which appear to be necessary to explain the equilibrium daytime ionosphere) would effectively deplete the ionosphere rapidly after sunset in the absence of an ionization source. For example, the O^+ concentration of 220 km from the NRL flight was around 10^3 cm^{-3} at 0106 local time, down from the daytime (0934) density by a factor 360. This would correspond to a decay rate δ such that $e^{\delta t} \approx 360$ at $t = 2 \times 10^4$ sec or $\delta \approx 3 \times 10^{-4}$ sec^{-1}. This would give $k_1[N_2] + k_2[O_2] = 3 \times 10^{-4}$ sec^{-1} at 220 km. However, the laboratory rates and the daytime atmospheric model give $3 \times 10^{-12} \times 3.3 \times 10^8 + 4 \times 10^{-11} \times 1.7 \times 10^7 = 2 \times 10^{-3}$ sec^{-1}. This discrepancy cannot be explained as the result of a temperature effect on the reaction rate constants, since the nighttime ionospheric temperature is closer to the laboratory temperature than is the daytime ionospheric temperature.

The situation is even more difficult in the case of $N_2{}^+$ and $O_2{}^+$. Donahue [1965] has considered this problem in detail and concludes that a night time source of 6–8 ion pairs/cm^{3}s in the 220 km region at night is required. This value is small, being equivalent to about 3×10^{-10} ergs/cm^3, or about 10^{-3} ergs/cm^2 s flux. If the source of this ionization were electron impact, it is estimated that approximately 5×10^{-2} Rayleigh of 3914 A $N_2{}^+$ emission would be excited from the same source—an amount that is not excluded by night time airglow observations. A recent statement [Gintzburg, 1965] that the ionization of the ionosphere during the night is caused by a stream of electrons ($E \sim 1$ keV) with energy flux 1–10 ergs/cm^2 s does not satisfy the observational criteria of low (or zero) night time 3914 A emission. This problem has been discussed in some detail by Dalgarno [1964], who sets an upper limit of 0.3 ergs/cm^2 s and gives results which strongly suggest an even lower upper limit.

In view of this uncertain nature of night time ionization sources and other possible complications such as diffusion and neutral atmosphere changes, we cannot very usefully test the laboratory rates by consideration of night time ion profiles. The following general comments can be made, however. The major night time ion below 200 km as shown in the NRL rocket data is NO^+. This of course reflects the role of chemical reaction sources of NO^+ which do not turn off abruptly at sunset. In addition, a substantial $O_2{}^+$ concentration nearly constant with height at about 100 ions/cm^3 between 130 and 190 km remains at night. In view of the almost complete lack of chemical $O_2{}^+$ sources (the O^+ and $N_2{}^+$ concentrations are negligible in the E and F_1 regions at night), a local night time ionization source is required, as Donahue [1965] pointed out. The dissociative recombination loss alone at 120 km is 0.15 ion/cc s with $\alpha(O_2{}^+) = 2 \times 10^{-7}$ cc s^{-1}, requiring a similar local ionization production rate. The fast charge-transfer of $O_2{}^+$ with NO greatly aggravates this problem, since an NO concentration of 10^7 cc^{-1} at 120 km leads to an $O_2{}^+$ loss rate of 1.3 ions/cc s. This suggests that a night time $O_2{}^+$ measurement down to lower heights (e.g. 100 km) might lead to a deduction of the NO distribution or, more precisely, a constraint on the coupled NO distribution and the night time ionization source.

If the atomic nitrogen concentration is as large as 10^3 times the electron density, reaction 11 will also compete with electron loss of $O_2{}^+$ at night.

REFERENCES

Barth, C. A. Rocket measurements of the nitric oxide dayglow, *Space Res.*,**5**, 767 (1965).

Bates, D. R. Some reactions occurring in the earth's upper atmosphre, *Ann. Geophys.* **8**, 194 (1952).

Bates, D. R. and Nicolet, M. Ion-atom interchange, *J. Atmospheric Terrest. Phys.* **18**, 65 (1960); **21**, 286 (1961).

Dalgarno, A. Corpuscular radiation in the upper atmosphere, *Ann. Geophys.* **20**, 67 (1964).

Donahue, T. M. Ionospheric reaction rates in the light of recent measurements in the ionosphere and the laboratory, *Planetary Space Sci.*, **13** (1965) in press.

Fehsenfeld, F. C., Goldan, P. D., Schmeltekopf, A. L. and Ferguson, E. E. Laboratory measurements of the rate of the reaction $O^+ + O_2 \rightarrow O_2{}^+ + O$ at thermal energy, *Planetary Space Sci.*, **13**, 579 (1965).

Gintzburg, M. A. Interpretation of Pioneer 1 magnetic field measurements, *Phys. Rev. Lett.*, **14**, 625 (1965).

Hinteregger, H. E., Hall, L. A. and Schmidtke, G. S. Solar XUV radiation and neutral particle distribution in July 1963 thermosphere, *Space Res.*, **5**, 1175 (1965).

Holmes, J. C., Johnson, C. Y. and Young, J. M. Ionospheric chemistry, *Space Res.*, **5**, 756, (1965).

Kasnar, W. H. and Bionid, M. A. Electron-ion recombination in nitrogen, *Phys. Rev. A*, **137**, 317 [1965].

Nicolet, M. Ionospheric processes and nitric oxide, *J. Geophys. Res.*, **70**, 691 (1965).

Nier, A. O., Hoffman, J. H., Johnson, C. Y. and Holmes, J. C. Neutral composition of the atmosphere in the 100–200 kilometer range, *J. Geophys. Res.*, **69**, 979 (1964).

Norton, R. B., VanZandt, T. E. and Denison, J. S. A model of the atmosphere and ionosphere in the E and F_1 regions, *Proc. Inter. Conf. Ionosphere*, p. 26, Physical Society, London (1963).

Paulson, J. F. Low energy charge exchange and ion-molecule reactions, *Ann. Geophys.*, **20**, 18 (1964).

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

Zipf, E. C. Rocket measurements of the visible dayglow, *J. Geomag. Geoelec. Kyoto*, (1965) in press.