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RESEARCH ON ION-MOLECULE REACTIONS AND DISSOCIATIVE RECOMBINATION IN THE UPPER ATMOSPHERE AND IN THE LABORATORY

A. D. DANILOV and G. S. IVANOV-KHOLODNYĬ

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1. INTRODUCTION

AS research methods using rockets and artificial satellites have been developed and perfected, these studies have made an even greater contribution to the study of the earth's ionosphere. In particular, well-known new advances have been made in the elucidation of the structure of the ionosphere. They have established important features of its structure that had been missed in earlier studies made by earthbound means (see, e.g., reviews^[1-5]). At the same time, as experimental data have accumulated, the problem has become more and more pressing that we must interpret the data from the standpoint of elucidating the processes that determine the nature and behavior of the ionosphere.

Recently-performed studies of the upper atmosphere (especially during the IGY and after) using rockets and satellites have made it possible to obtain new data on the physical and chemical properties of the atmosphere at high altitudes. Especially valuable data have been obtained with the mass spectrometer on the ionic and neutral components of the atmosphere at different altitudes and times of day, and also with various detectors of short-wavelength radiation on the intensity and spectrum of the solar radiation. Analysis of the new data on the composition of the upper atmosphere and the intensity of ionizing agencies has led to new concepts on the rates and the nature of the physicochemical processes that occur at altitudes above 100 km. New concepts have arisen on the nature of the ionosphere. For example, the special role has been elucidated of ion-molecule reactions between atomic ions and neutral molecules, which regulate the equilibrium values of the concentrations of molecular and atomic ions in the upper atmosphere; it has been found that reactions of dissociative recombination of molecular ions play the dominant role in the neutral-

ization processes in the ionosphere.

In order to facilitate a grasp of the material below, we present in Table I a summary of the fundamental data on the ionosphere, which is formed and distributed in the upper atmosphere roughly above 50 km. The highest concentration of ions and electrons in the ionosphere is reached at the maximum of the F region at a height of ~300 km. However, the ionized portion of the atmosphere extends considerably higher, up to the boundary with the interplanetary medium (~10-15 Earth radii). The major regions of the ionosphere are distributed below 300 km. As we see, the temperature in the ionosphere in various regions varies from ~200 to 1000-2000°K, while the concentration of neutral particles varies from 10¹⁵ to ~10⁹ per cm³. However, for each region of the ionosphere, these parameters have quite definite values subject to small variations. Above 120 km, the composition of the atmosphere begins to change because of gravitational-diffusional separation, but it is still not clear how greatly the ratio of oxygen atoms to nitrogen molecules at an altitude of 300 km differs from that found in the 120 km region. Several values are given for the electron concentration n_e, since n_e undergoes appreciable variations depending on the phase of the sunspot cycle (maximum or minimum) and the time of day. In addition, n_e depends in a known manner on the latitude of the site and the season, and is altered during ionospheric perturbations. For brevity, we have shown only the seasonal variations in the F (or F2) region. We should note in this regard that in a number of cases the data of Table I (e.g., the altitudes and especially the night values of n_e) are only approximate (and sometimes even provisional) and differ somewhat with different authors. In addition, the altitude of the F2 region undergoes certain variations, usually increasing at night.

Even the first measurements of the ionic composi-

Table I

Region of ionosphere	Altitude, km	T, °K	Particle concentration, cm ⁻³			
			n	day		night
				maximum n _e	minimum n _e	n _e
D	70	220	2 · 10 ¹⁵	150		~ 10
E	110	270	2 · 10 ¹²	2 · 10 ⁵	10 ⁵	~ 4 · 10 ³
F1	180	800-1800	1.5 · 10 ¹⁰	4 · 10 ⁵	3 · 10 ⁵	~ 10 ³
Summer F2	300	800-1800	(0.8 - 1.5) · 10 ⁹	0.8 · 10 ⁶	3 · 10 ⁵	(2 - 5) · 10 ⁵
Winter				2.5 · 10 ⁵	6 · 10 ⁵	~ 1.5 · 10 ⁵

tion of the atmosphere at altitudes of 100–700 km, which were made by V. G. Istomin^[7-9] and independently by Johnson and his associates,^[6] showed that the upper atmosphere contains a considerable quantity of the molecular ions NO^+ and O_2^+ , which cannot be formed through direct ionization events. This fact has sharply raised the question of the ion-molecule processes that take place in the upper atmosphere and can lead to the formation of the stated molecular ions from atomic ions, and also of the dissociative-recombination processes that bring about rapid neutralization in the ionosphere through the disappearance of molecular ions.^[10,11] Ion-molecule reactions and dissociative-recombination processes are of great importance in understanding many processes in the upper atmosphere. However, at present there is no unified viewpoint on the role and efficiency of these processes in the ionosphere. The latter situation is due to the lack of pertinent laboratory studies and of reliable experimental data. Hence various authors assume values of the rate constants of these reactions in accord with their approach to the problem of the nature of the ionosphere in general. In solving this problem there are two tendencies, involving the question of whether one assumes low or high values for the energy flux necessary to maintain the ionization of the upper atmosphere. Owing to the considerable development of rocket and satellite studies, important experimental data have been obtained, and the different points of view have recently converged, although differences of opinion still remain in a number of cases.

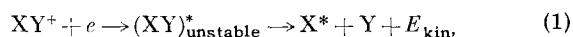
We have tried in this article to collect together all the existing laboratory data on the processes under discussion, and the fundamental studies to determine their role in the upper layers of the atmosphere. Here we shall try to emphasize the fundamental difficulties and contradictions that have arisen in solving these problems, and to reflect the different points of view in the discussion.

2. IONOSPHERIC STUDIES

First we shall discuss the results of the ionospheric studies on the fundamental reactions involving ions.

A. Dissociative Recombination

a) Definition and theoretical calculations. As has been pointed out, in the major portion of the ionosphere neutralization does not take place through the ordinary so-called radiative recombination of ions with electrons, but through the very fast process of dissociative recombination of the molecular ions XY^+ :



where a molecule in the unstable excited state $(\text{XY})_{\text{unstable}}^*$ is formed as an intermediate stage. From this state, the molecule quickly dissociates into its two constituent atoms, which may happen to be in

the excited state X^* . The energy liberated in neutralizing the molecular ion is also partially transformed into radiation energy and kinetic energy E_{kin} of the atoms. The rate r_1 of reaction (1), as for any binary collision process, is

$$r_1 = \alpha^* [\text{XY}^+] n_e, \quad (2)$$

where $[\text{XY}^+]$ and n_e are the concentrations of ions and electrons and α^* is the rate constant for dissociative recombination.

In order to calculate quantitatively the rate constant of the dissociative-recombination process, we must know precisely the potential curves of the molecule and its ion, especially near the intersection points of the curves for the molecular ion and the potential curves of the excited state of the molecules, and also the lifetime of the excited state. As yet, such information is not available either theoretically nor experimentally. However, Bates^[12] has started from some reasonable assumptions and estimated that α^* can be $\sim 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$, which is five orders of magnitude higher than the rate constant for radiative recombination. Bauer and Wu^[13] and Stabler^[14] have tried to calculate the value of α^* for the ion H_2^+ , and Gibbons and Squire (see^[15]) obtained $\alpha^* = 7 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ for NO^+ at the relatively high electron energy of $\sim 1 \text{ eV}$. Stabler^[16] has recently obtained analogous values for the atmospheric ions N_2^+ and O_2^+ at the temperature 300°K . However, the conclusions that one can draw from these theoretical calculations are basically qualitative. At present we can hope to obtain the necessary values of α^* only by experiment. As will be shown below, ionospheric studies can play a great role here.

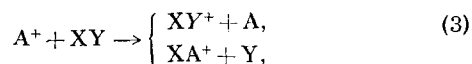
Although in 1937 Massey^[17] raised serious objections against the dissociative-recombination reaction, later Bates and Massey^[18,19] pointed out the possibility of occurrence of such reactions in the ionosphere. However, at that time a definite preference was given to reactions with negative ions. After some successful laboratory experiments on dissociative recombination had given high values of the reaction rate $\alpha^* = 10^{-6} - 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$, Bates^[12] made some theoretical calculations and showed that $\alpha^* \sim 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$. However, after finding that the reaction rate for dissociative recombination is very high, Bates expressed a doubt that this reaction could be occurring in the ionosphere, since according to the data existing then, the effective recombination coefficient even in the E-region is of the order of $10^{-8} \text{ cm}^3 \text{ sec}^{-1}$, or considerably less than α^* .

b) Application of the dissociative-recombination process in ionospheric studies. The relatively high effective recombination coefficient $\alpha' \approx 10^{-8} - 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ found in the ionosphere led ionospheric researchers into an impasse at the time, since the reaction of radiative recombination known at that time has a rate several orders of magnitude

smaller ($\sim 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$). It seemed that the way out of the difficulty lay in the application of the relatively fast reactions with negative ions. However, the occurrence of these reactions requires a high enough atmospheric density. Gerjouy and Biondi^[20] proposed in 1953 that one should replace the negative-ion hypothesis with a "dissociative-recombination" hypothesis in explaining the fast recombination processes in the E region of the ionosphere. Here they pointed out that the results of ionospheric measurements of α' are not reliable enough, and that according to certain data, e.g., those of Piddington,^[21] an even higher value has been measured during eclipses: $\alpha' \sim 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$. Yonezawa^[22, 23] in 1954–1955 expressed analogous ideas of applying the dissociative-recombination reaction to explain the processes in the F region of the ionosphere. Later on, the hypothesis of Bates and Massey using the dissociative-recombination reaction to explain neutralization in the ionosphere became widely accepted, while the explanation in terms of negative ions was kept only for the D region, which is situated in the sufficiently dense layers of the atmosphere.

Ratcliffe^[24] and other authors have discussed the difference in the roles of radiative and dissociative recombination and of ion-exchange reactions in the neutralization of charged particles in the different levels of the ionosphere. Thus, the period before the rocket investigations of the ionosphere marked the solution of one of the fundamental questions of ionospheric physics: the problem of the relation and interaction of the molecular and atomic ions. Mass-spectrometer measurements in rockets showed that in the ionosphere the concentration ratio of molecular to atomic ions varies greatly from the value of 10^2 at altitudes of 130–140 km to a value of 10^{-3} at altitudes of 500–600 km.

c) The effective recombination coefficient and the fundamental reactions involving ions in the ionosphere. It has been established from the data of earth-based ionosphere studies that the rate of time variation of the electron concentration in the E region throughout the day and during various disturbances is high; it is proportional to the square of the electron concentration n_e^2 (the proportionality coefficient is the effective recombination coefficient α'). However, in the F region the rate is considerably smaller in absolute magnitude, and is proportional to n_e . These two facts prove to be interrelated. As Ratcliffe^[24] has shown, in the ionosphere the molecular ions XY^+ are neutralized by the dissociative-recombination reaction (1), which proceeds at a rate $\alpha^* n_e [XY^+]$, where $[XY^+]$ is the concentration of the XY^+ ions, while the atomic ions A^+ are neutralized by the ion-molecule reaction



which proceeds at a rate $\gamma [XY] [A^+]$. Thus, the resul-

tant neutralization rate $r = \alpha' n_e^2$ is determined by the effective coefficient of recombination, which is equal to

$$\alpha' = \alpha^* \frac{[XY^+]}{n_e} = \frac{\alpha^*}{1 + \frac{[A^+]}{[XY^+]}} = \frac{\alpha^*}{1 + \frac{\alpha^* n_e}{\gamma [XY]}}. \quad (4)$$

Consequently, in the lower portion of the ionosphere, where $[XY^+]/[A^+] \gg 1$, $\alpha' = \alpha^*$, and $r \propto n_e^2$, while in the upper portion of the ionosphere, where

$$\frac{[XY^+]}{[A^+]} \ll 1, \quad \alpha' = \alpha^* \frac{[XY^+]}{[A^+]} \ll \alpha^* \text{ and } r \propto n_e.$$

The linear law $r \propto n_e$ has now been confirmed in a number of studies on the time variations in the upper portion of the ionosphere during solar eclipses and at sunrise and sunset. The fact that the linear law of disappearance of electrons in the F region of the ionosphere has been established experimentally confirms the correctness of the choice of the cycle of reactions (1) and (3) as the fundamental reactions for the ionosphere.

The strongest argument in favor of these reactions is that they explain the altitude-dependence of the concentrations of atomic and molecular ions measured with mass spectrometers in rockets. A. D. Danilov^[25-28] has used the data on the variation with altitude of the relative amounts of different ions, and has confirmed the hypothesis of Bates and Massey^[18] that the transformation and annihilation of ions in the ionosphere occurs in such a way that the atomic ions are transformed by ion-molecule reactions into molecular ions, while neutralization takes place by dissociative recombination of the molecular ions. The hypothesis of the dissociative-recombination reaction is an essential element in the explanation of the variation in the relative concentrations of molecular and atomic ions as functions of the altitude and time of day. While references^[25-28] adopted too high values for α^* ($= 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$) and for the rates of these reactions, and also erroneously used certain minor reactions, the fundamental conclusions of these studies remain valid, since the altitude distribution of the relative concentrations of the major ions depends only on the ratio of the reaction rates, rather than on their absolute values. One can advance other arguments in favor of reactions (1) and (3).

It was shown in^[29] that a certain combination of an entire set of experimental values: $([XY^+]/[A^+])(n_e/[XY])$, remains approximately constant at altitudes of 160–400 km. According to Eq. (4), this combination should actually be a constant, since it is equal to the ratio γ/α^* of reaction constants.

S. P. Yatsenko^[30] has discussed the effect that the difference in mechanisms of disappearance of molecular and atomic ions according to (1) and (3) has on the type of altitude-dependence exhibited by the concentrations of these ions (a monotonic increase for the atomic ions, and the existence of a maximum for the

molecular ions). The difference in the altitude-dependence of the ions expected from theory is actually observed in the data of the mass-spectrometer measurements in rockets. This confirms the correctness of the choice of reactions (1) and (3).

It is generally accepted now^[31] that above 90–100 km dissociative recombination is the fundamental reaction for neutralization of ions in the ionosphere. However, there is a great divergence of opinion on the value of α^* . On the one hand, on the basis of the results of laboratory experiments existing at that time, B. A. Bagaryatskiy^[32] and later A. D. Danilov^[25] adopted $\alpha^* = 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$ for all the molecular ions in the ionosphere. On the other hand, through comparison with Yonezawa's^[22,23] earlier ionospheric data, V. I. Krasovskii,^[33] Mitra,^[34] and others have adopted the considerably lower value $\alpha^* = 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$. However, Bates and Nicolet^[35] found that one has to use different constants for different ions: $\alpha_{\text{NO}}^* = 3 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$, and $\alpha_{\text{O}_2^+}^* = 3 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$. They assumed the high value $\alpha_{\text{N}_2^+}^* = 5 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ for the N_2^+ ion, just as Hertzberg did.^[36,37]

d) Measurements of α' in the E and F1 regions of the ionosphere. Since the fundamental conclusions on the mechanism and rates of the elementary processes in the ionosphere are verified by comparison with the values of α' , it is important to discuss in further detail the results of the experimental studies (including rocket studies) of α' in the ionosphere and the determination of the values of α^* from the ionospheric data.

There are several methods of determining the effective recombination coefficient α' in the ionosphere, based on measurement of the variations in n_e during solar eclipses, at sunrise and sunset, throughout the day, and during various ionospheric disturbances. These methods give differing results, which often contradict one another. The most usual method is to determine α' from the diurnal variations in n_e . For example, these data are reviewed in the book of Ya. L. Al'pert^[38] (p. 131). This method gives values of $\alpha' \approx 10^{-9}$ – $10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ for the E region, and $(0.3\text{--}10) \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ for the F region. Bukin and Fligel',^[39] have recently obtained an analogous value $\alpha' = (0.3\text{--}1.2) \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ for the E region based on an interpretation of the effect of the winter anomaly. On the basis of such measurements, it was considered for a long time that $\alpha' \approx 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ in the E region, and $\alpha' \approx 10^{-10}$ in the daytime or $\approx 3 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ at night in the F region. Studies using rockets and satellites have established the existence of diurnal and seasonal variations in the temperature and density of the upper atmosphere. These cannot help but distort the results of determining α' by the method indicated above, especially in the F region.^[40] The nature of the effective recombination coefficient α' and the methods of measuring it differ

in the lower (E and F1 regions) and the upper (F region) portions of the ionosphere. Hence we shall take them up separately.

The most reliable method of determining α' for the E and F1 regions of the ionosphere, which is practically independent of variations in the density of the upper atmosphere, is to measure it during solar eclipses. Ratcliffe^[41] has made an extensive review of the measurements of α' using this method. The values obtained for α' in the E and F1 regions of the ionosphere were $(0.5\text{--}2) \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ and $(0.2\text{--}1.4) \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$, respectively. The value of α' in the F1 region is about one-half as great as in the E region. These results, it seemed, corroborated well the conclusions based on diurnal measurements. However, in obtaining these data, they neglected the effect of the non-uniform distribution of short-wavelength radiation over the sun's disk, as well as the emission of approximately 10–20% of the radiation from outside the sun's limb. These important features of the radiation had been noted a long time ago, and recently have been thoroughly proved in several rocket experiments. Taking this fact into account, a number of authors have determined that in the E region of the ionosphere, $\alpha' = (0.4\text{--}1) \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$.^[21,42-49] Recently the same sort of values were obtained by observations of the solar eclipse of February 15, 1962 by I. N. Odintsova and M. B. Ogir'^[50] ($\alpha' = 10^{-6}\text{--}10^{-7} \text{ cm}^3 \text{ sec}^{-1}$), by Nestorov and Taubenkhaïm^[51-55] ($\alpha' \geq 1 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$), and by Serafimov^[56] ($\alpha' = (0.63\text{--}2.32) \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$). Here the nature of the distribution of the short-wavelength ionizing radiation over the sun's disk and outside it was checked by measuring the decimeter radio emission of the sun during the eclipse. During the same eclipse, Jasinski^[57] obtained the considerably lower value $\alpha' = 1.5 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$. This was due to the fact that he did not use simultaneous measurements of the radio emission to estimate the source brilliance of the ionizing radiation on the sun's disk and especially, outside it.

As of now, it has been confirmed at a series of ionospheric conferences^[58-61] that according to the eclipse data we must take $\alpha' \geq (4\text{--}10) \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$, i.e., 0.5–1 orders of magnitude larger than had been previously thought. Similar values have been obtained recently in measurements during sudden ionospheric disturbances (Whitten and Poppoff,^[62] $\alpha' = 5 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$). One can obtain the same sort of values, $\alpha' \sim 3 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$, from data on the energy of the short-wavelength radiation of the sun (Watanabe and Hinteregger^[63]). In making the latter estimate by the formula $\alpha' = q/n_e^2$ for the E region of the ionosphere, they used too large a value of n_e and too low a value of the rate of ion formation $q = 2 \times 10^3 \text{ cm}^{-3} \text{ sec}^{-1}$ with the sun at the zenith. Here other authors give values for $q \sim 5 \times 10^3 \text{ cm}^{-3} \text{ sec}^{-1}$,^[40] $4.2 \times 10^3 \text{ cm}^{-3} \text{ sec}^{-1}$,^[64] and recently Hinteregger et

Table II

Ion Author	$\alpha_{N_2^+}, \text{cm}^3 \text{sec}^{-1}$	$\alpha_{O_2^+}, \text{cm}^3 \text{sec}^{-1}$	$\alpha_{NO^+}, \text{cm}^3 \text{sec}^{-1}$	Altitude, km	T, °K
Bates and Nicolet ^[35]	$5 \cdot 10^{-7}$	$3 \cdot 10^{-8}$	$3 \cdot 10^{-9}$	~250	1500
Norton et al. ^[64]	$4 \cdot 10^{-7} \frac{300}{T}$	$2 \cdot 10^{-7} \frac{300}{T}$	$6.7 \cdot 10^{-8} \frac{300}{T}$	100— 200	300— 1000
Danilov ^[74]	—	$(1-2) \cdot 10^{-7} \sqrt{\frac{300}{T}}$	$(2-4) \cdot 10^{-8} \sqrt{\frac{300}{T}}$	100—	300—
Holms et al. ^[75]	—	$3.3 \cdot 10^{-8}$ $4.2 \cdot 10^{-8}$ $8.8 \cdot 10^{-8}$	$1.2 \cdot 10^{-8}$ $2.0 \cdot 10^{-8}$ $6.3 \cdot 10^{-8}$	200 130 140 150	1000 420 523 623

al.^[65] obtained $q \approx 7 \times 10^3 \text{ cm}^{-3} \text{ sec}^{-1}$. By comparing the q values with the rocket data on n_e and the ionic composition, it was found in^[40] that $\alpha' \approx 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$, and $\alpha^* = \alpha_0 T^{-1/2} = (1-1.7) \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$. In^[64], they obtained in an analogous way $\alpha' = 1.1 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$, together with the α^* values for various ions given in Table II. During the solar eclipse of July 20, 1963, a series of six rockets was fired to an altitude of 200 km, and a least estimate was obtained of the value of the effective recombination coefficient in the E region: $\alpha' \geq 1 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$.^[66]

Recently Smith^[67] has published an estimate $\alpha' = 2 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ under nighttime conditions in the E region of the ionosphere based on rocket measurements of the electron concentration n_e after sunset in the evening and towards dawn. The decrease in n_e throughout the night corresponds to an effective recombination coefficient $\alpha' = 2 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$, and indicates the absence of a nocturnal source of ionization. A defect in this study is that the two measurements were made on different nights. In essence, this method differs in no way from the terrestrial method of determining α' from the nature of the decline in n_e after sunset. According to the most recent data, the latter method gives $\alpha' = 7 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$.^[68] Titheridge^[69] has applied this method to the $n_e(h)$ profiles constructed from the data of ionosphere stations. He found that after sunset the effective recombination coefficient does not vary during the night, and on the average is $2 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ at altitudes from 100 to 200 km. In addition, Titheridge found that the rate of decline of n_e after sunset in a period of minimum solar activity is two times as large as in a maximum period. The estimates given for α' at night do not agree with the conclusions of Mitra^[70,71] that α' gradually declines during the night from 10^{-8} to $10^{-9} \text{ cm}^3 \text{ sec}^{-1}$. However, Mitra used a greatly lower daytime value $\alpha' = 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$.

Thus, in the E region of the ionosphere at a temperature of $\sim 300^\circ\text{K}$ at night, $\alpha' = 2 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ (provided that a nocturnal ionization source does not exist). In the daytime, $\alpha' = (4-10) \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ (the higher value is more probable), while in the F1 region at a temperature of $\sim 1000^\circ\text{K}$, α' is approxi-

mately half as large. However, the latter estimate for the higher temperature is only tentative, since it is based on not very reliable estimates of α' for the F1 region. In order to estimate α' at higher temperatures, it is better to use the data for the F2 region (see below).

e) Conclusions concerning α^* from the data on α' .

The use of rockets in certain ionospheric studies makes it possible to obtain α^* values for individual ions. However, before presenting the results of these episodic measurements of α^* , we shall discuss the possibility of determining α^* from the numerous and more reliable data on α' .

Mass-spectrometric measurements in rockets^[6-9] have established that there are basically two ions in the daytime in the E region: $\sim 75\%$ NO^+ and $\sim 25\%$ O_2^+ . Then, using the data on α' given above and taking into account the fact that $\alpha' = \sum \alpha_i^* (n_i/n_e)$, we find that $\alpha_{\text{NO}^+}^* \leq (5-13) \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$, and $\alpha_{\text{O}_2^+}^* \leq (1.5-4) \times 10^{-7}$ at the temperature of the E region. Additional information is needed to arrive at more definite conclusions on α^* .

Bates and McDowell^[72] have shown that the value of the effective recombination coefficient determined during a solar eclipse can approximate either the value of the recombination coefficient of the slowly-recombining ion, or that of the quickly-recombining ion in the ionosphere, depending on the method of determination. Using the conclusions of this study, McElhinny^[47] has found from the data on the eclipse of December 25, 1954 that in the E region of the ionosphere, $\alpha_1 = 5 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ for the slowly-recombining ion, while $\alpha_2 = 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ for the quickly-recombining ion, provided that $n_1^+/n_2^+ = 4$. However, if $n_1^+/n_2^+ = 1$ (which is less typical of the E region of the ionosphere), then $\alpha_1 = 1 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ and $\alpha_2 = 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$. We may assume that α_1 pertains to the NO^+ ion, and α_2 to the O_2^+ ion. These estimates of the α_i coefficients lead to a value of the effective recombination coefficient $\alpha' = (2.5-5) \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$. This is close to the value $\alpha' = 4 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ obtained from the data on the same eclipse by taking into account the effect of the radiation of the sun's corona outside the limits of the sun's disk.^[47]

Bowhill^[73] has expanded on^[72], and shown that the different methods of determining the effective recombination coefficient used in ionospheric studies (not only during solar eclipses, but also during twilight and by determining α' from the diurnal variation in n_e) give different results. This is because the ionospheric plasma consists of a mixture of ions having differing rates of recombination. In ionospheric studies, the effective recombination coefficient α' is defined as the coefficient in the formula

$$r = \alpha' n_e^2, \quad (5)$$

which relates the number of recombinations r to the square of the electron concentration n_e . In aeronomy, in studying the photochemical processes in the ionosphere, the recombination per cubic centimeter is defined as the sum of the recombinations of all the ions having concentrations n_i^+ :

$$r = \sum_i \alpha_i n_i^+ n_e = n_e^2 \sum_i \frac{n_i^+}{n_e} \alpha_i, \quad (6)$$

that is, the effective recombination coefficient α' here is the weighted average of the recombination coefficients of all the ions. If the α_i^* values are all equal, we obtain Eq. (2), since for atomic ions $\alpha_i \ll \alpha^*$. Bowhill^[73] showed that only in certain measurements of the variations of n_i in the ionosphere does one obtain the effective recombination coefficient defined by Eq. (6), while in other cases one measures the quantities $(\alpha')^2$ or $(1/\alpha')$, which are the weighted averages of α_i^2 and $1/\alpha_i$, respectively. Here the weights can involve not only the relative concentrations of the ions, as in Eq. (6), but also the relative fractions of the formation of the ions in the overall rate of ion formation q . If the intensity of the ionizing agency and the electron concentration vary, then we must also observe the well-known variations in the effective recombination coefficient as a function of the time, since the concentration of each ion is determined by its own independent equation of equilibrium

$$\frac{dn_i^+}{dt} = q_i - \alpha_i n_i^+ n_e. \quad (7)$$

When this characteristic is correctly taken into account, we can find also the effective recombination coefficient and the recombination coefficient for each ion separately. After sunset or during an eclipse, the ions having high α^* values disappear more rapidly, leading to a decrease in α' .

In general, we cannot draw unambiguous conclusions on α_i^* from analyzing the measured values of α' if we do not know (e.g., from mass-spectrometer measurements) the number of ions in the mixture and their relative amounts. Certain approximate conclusions derived under the simplifying assumption that the mixture consists of two kinds of ions can be useful. Using the decrease in the value of α' in the E region observed after sunset, Bowhill^[73] found that the re-

combination coefficient for the rapidly-recombining ion is at least 6.4 times as great as for the slowly-recombining ion. However, by comparing the results of measurements of the effective recombination coefficient during an eclipse with the diurnal variations in n_e , he found that the recombination coefficients differ by a factor of ten, in agreement with the conclusions of McElhinny^[47] from eclipse data.

Bowhill's study^[73] also showed that one does not get a weighted average of α' by applying the method widespread in ionospheric studies in which one determines the effective recombination coefficient from the lag of the maximum in the diurnal trend in n_e in the E region after noon. Rather, it gives a quantity actually approximating the recombination coefficient of the slowly-recombining ion. Thus, the value $\sim 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ obtained in these measurements must be ascribed to the NO^+ ion, if we neglect the effect of the diurnal variations in the density of the upper atmosphere (which is generally not valid^[29,40]).

By using values of α' measured by various methods for the day and night ionosphere in the E region, Bowhill found that $\alpha_{\text{NO}^+}^* = 6 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$, and $\alpha_{\text{O}_2^+}^* = 6 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$. These values should be considered to be lower estimates, since low values of α' were used as source data. Bates and Nicolet^[35] have obtained by an analogous method even lower estimates for the E region: $\alpha_{\text{NO}^+}^* = 3 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ and $\alpha_{\text{O}_2^+}^* = 3 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$. This is because they used a low value for daytime conditions: $\alpha' = 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$. Using a more reasonable value $\alpha' \sim 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$, we obtain estimates of α_{NO^+} and $\alpha_{\text{O}_2^+}$ an order of magnitude higher.

Bowhill obtained approximate data on α^* by assuming that there are only two kinds of ions having different recombination coefficients in the ionosphere, since he did not consider the concrete processes and chemical reactions in which the various ions are formed and transformed. This problem has been discussed more fully by Bates and Nicolet^[35] and recently by Norton et al.,^[64] A. D. Danilov,^[74] and also Holms et al.^[75] From these studies, in which the entire set of possible reactions in the upper atmosphere is analyzed, conclusions were drawn not only on the value of α' , but also on the concentrations of the major ions at different altitudes. Hence we can compare the theoretically-calculated values, both of α' and of the ion concentrations, with the experimental results of the mass-spectrometer measurements in rockets. The conclusions on the α^* constants given in Table II have been obtained through such comparisons.

Although all the authors have used mass-spectrometer data on the ionic composition, each of them has started with his own system of ionospheric data, and adopted a different temperature-dependence of the constant α^* . This has led to a rather wide divergence in the results of the computations. This divergence

typifies the still-existing uncertainty in many of the data on the ionosphere.

We have given in Table II the data of Holms et al.,^[75] which they obtained by comparing the theoretical decrease in the concentrations of the ions O_2^+ and NO^+ after sunset with the results of the mass-spectrometer measurements made by these authors^[75] on the ionic composition of the atmosphere at altitudes of 100–200 before and after sunset. Here they observed a slower decline in the electron concentration below 150 km than above. Since the temperature of the atmosphere increases with altitude, this fact implies that the value of α^* for the predominant ions O_2^+ and NO^+ must increase with the temperature, provided that there are no supplementary sources of ionization at night. Holms et al.^[75] considered the obtained trend in α^* as a function of T to be real, and discussed the possibility of theoretical explication of this phenomenon. However, the values of $\alpha_{NO^+}^*$ and $\alpha_{O_2^+}^*$ obtained in^[75] are too low for the E region, and do not agree with other ionospheric determinations of this constant. On the other hand, many strong arguments have now been found in favor of the existence at night of a supplementary ionization source in the ionosphere. In view of this, in our opinion, one should treat the results of Holms et al.^[75] from the standpoint of indicating the existence of such a source, rather than indicating an unusual temperature-dependence of α^* .

f) Measurement of α^* in the lower portion of the ionosphere. Whitten and Poppoff^[62,76,77] have obtained a direct estimate $\alpha^* = 5 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ from data on the value of α' in the D region of the ionosphere. This estimate pertains to a temperature $\sim 200^\circ\text{K}$, but it is not clear to which ion, O_2^+ or NO^+ , since we do not know which of these ions predominates in the D region of the ionosphere. In any case, perhaps, the constant α^* must be smaller than the cited value for either of these ions, since apparently their rates of formation in the D region are close to one another.

By analyzing data on the decay of the absorption of cosmic radio noise following a nuclear explosion, LeLevier^[78] has also estimated the coefficient of dissociative recombination of the molecular ions at an altitude $\sim 70 \text{ km}$: $\alpha^* = (3-7) \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$, with a most probable value of $4 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$. As with Whitten and Poppoff, this coefficient pertains either to NO^+ or to O_2^+ at a temperature near 200°K . Recently Narcisi and Bailey^[79] have determined with a mass spectrometer that the NO^+ ion predominates from 64 to 83 km, while the O_2^+ ion appears only above 75 km. Thus, apparently, the data of Whitten and Poppoff and of LeLevier should be ascribed to the NO^+ ion. One can derive a value $\alpha_{NO^+} \sim 3 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ from the data of direct rocket experiments in the upper atmosphere in which nitric oxide vapors were released from the rockets at an altitude of 95 km,^[80,81] on the basis of direct measurements on the rate of decrease of n_e in the cloud.

Wallace and Nidey^[83] have recently estimated $\alpha_{N_2^+} = 7 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ by analyzing data on the emission of the N_2^+ band at 3914 Å in the F1 region of the ionosphere and using Hinteregger's data^[82] on the short-wavelength radiation of the sun. While the authors ascribe this value to 300°K , however, we should perhaps assume a higher temperature, $\sim 1000^\circ\text{K}$, characteristic of the F1 region during a period of minimum solar activity. This is all the more likely since in this experiment the rotational temperature of the 3914 Å band was estimated to be $1200 \pm 200^\circ\text{K}$. We can also obtain an estimate of $\alpha_{N_2^+}^*$ based on the data of Odenrantz et al.^[84] on the exponential decay of a flash of N_2^+ emission at 3914 Å produced in the upper atmosphere by a high-altitude nuclear explosion. Since the decay constant of the primary flash of emission proved to be very small ($\sim 5 \text{ sec}$), this gives a very high value of $\alpha \approx 1/\tau n_e \approx 10^{-6}-10^{-5} \text{ cm}^3 \text{ sec}^{-1}$. After discussing the laboratory data on $\alpha_{N_2^+}^*$, we shall try to give an explanation of this fact.

g) Measurement of α' in the F2 region of the ionosphere and conclusions on α^* . Previously it was assumed for the F region that $\alpha' = (0.8-1) \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ in the daytime and 3×10^{-10} at night, although Bates^[85] has acknowledged a wide spread in values: $\alpha' = 4 \times 10^{-11}-1 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$. Then the papers of Schmerling, Ratcliffe, and Thomas^[86,87] appeared, showing that in the F region the time variations in the electron concentration n_e are proportional to the first power of n_e , rather than the square, with a proportionality coefficient β . For the nighttime ionosphere near a minimum of solar activity, they determined a value

$$\beta = 10^{-4} \exp\left(\frac{300-h}{50}\right) \text{ sec}^{-1}.$$

This value has subsequently been used in many studies on the ionosphere, and has even found its way into textbooks. However, recently several new detailed studies have appeared on the value of β under various conditions. The paper of Van Zandt, Norton, and Stonehocker^[88] is well known; here, during the solar eclipse of October 12, 1958, i.e., at a period of maximum solar activity, they determined the value

$$\beta = 6.8 \cdot 10^{-4} \exp\left(\frac{300-h}{103}\right) \text{ sec}^{-1},$$

which proves to be almost an order of magnitude higher for the F2 region than the value of Schmerling and Ratcliffe for the nighttime ionosphere and 2–5 times as great as the value of β determined from other eclipse data. Possibly the effect of the solar cycle has been manifested here. However, Rishbeth and Setty^[89] have made a detailed analysis of the results of measuring n_e in the F region during sunrise; independently of the solar-activity period, they found that $\beta \approx 3 \times 10^{-4} \text{ sec}^{-1}$ in the summer, and $\approx 1.8 \times 10^{-4} \text{ sec}^{-1}$ in the winter. In this study, they used only

the morning values of β . Besides, a more detailed study of the diurnal variations in the electron-concentration profiles made by V. M. Polyakov^[90] showed that in the morning a little while after sunrise, the value of β (which he denoted as K) sharply diminishes, especially in the winter period. In addition, he found that in the F region the midday value of β in summer is 2–3 times as great as in winter. In the summer it attains the same values that Van Zandt et al.^[88] had measured. However, in^[90] he did not take into account the effect of the diurnal variations in the density of the upper atmosphere, which can distort the results considerably. Nisbet and Quinn (see^[91]) have recently carried out an analogous study, but only analyzing the nighttime ionosphere data. In this study, they established that at an altitude of ~ 300 km, the nighttime values of the coefficient β vary during the solar cycle by a factor of about 30, attaining a value at the maximum period of $\beta \approx 6 \times 10^{-4} \text{ sec}^{-1}$, like that obtained under daytime conditions by Van Zandt et al.^[88] Under conditions that are relatively quiet in the magnetic sense (with index $K_p < 4.5$), the value of β in summer is 1.5–2 times as high as in winter. Bergh^[92] has found sharper seasonal variations in the value of β (from $2 \times 10^{-4} \text{ sec}^{-1}$ in the summer to $(4-5) \times 10^{-5} \text{ sec}^{-1}$ in the winter) under magnetically disturbed conditions in a period of maximum solar activity. Here he also found that on the average the value of the effective recombination coefficient α' in the F region is $7.4 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$, increasing at night to $1.5 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$. In a period shortly before a solar-activity maximum (November 20, 1960), Orsini and Mazzilli^[93] also obtained a high value $\beta = (3.6-5.3) \times 10^{-4} \text{ sec}^{-1}$ from an analysis of a disturbance in the F region of the ionosphere due to a powerful solar flare.

Thus it is important to note that considerable variations in the recombination coefficients β and α are observed in the F region of the ionosphere, depending on the solar activity, the season of the year, and the time of day. Evidently, these variations are due to the well-known temperature fluctuations of the upper atmosphere, which lead to a variation in the density and composition at the level of the F layer and determine the variations in the rate of recombination. One must take these variations into account in a detailed analysis of the conditions of formation of the F layer of the ionosphere.

Theoretical considerations imply that $\beta = \alpha' n_e$, whereas $\alpha' = \Sigma \alpha^* [XY^+]/n_e$. Hence the quantity β turns out to be equal to

$$\beta = \Sigma \alpha^* [XY^+]. \quad (8)$$

In a period of maximum solar activity in the F2 region, n_e is $(1-2) \times 10^6 \text{ cm}^{-3}$, $\beta = 4 \times 10^{-4} \text{ sec}^{-1}$, and according to the mass-spectrometric measurements on the third artificial satellite^[7], $[\text{NO}^+]/n_e \approx 3 \times 10^{-2}$ and $[\text{O}_2^+]/n_e \approx 1.5 \times 10^{-2}$. Using these data and Eq. (8), we

can estimate the rate constant for dissociative recombination for the ions O_2^+ or NO^+ : $\alpha_{\text{NO}^+}^* \leq 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ or $\alpha_{\text{O}_2^+}^* \leq 2 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$. Since $T \sim 2000^\circ\text{K}$ in the F2 region, the obtained estimate of α^* pertains to this temperature. The estimate of α^* is more reliable than that obtained above from unreliable data for the F1 region, where the temperature is only a little lower.

Another possibility of estimating the recombination rate in the ionosphere, and hence estimating also the value of α^* , involves an investigation of the rate of ionization and the energy balance in the ionosphere. In order to do this, one can use data on the intensity of the short-wavelength radiation of the sun that brings about the ionization and heating of the upper atmosphere of the earth, or data on the heat flow from the upper layers of the atmosphere to the lower ones. However, we must bear in mind the fact that the use of these estimates is complicated by the lack of any clear notions on what portion of the radiation is spent in ionization, and what in heating. A study of the rocket data on the spectrum and intensity of the short-wavelength radiation of the sun and the temperature distribution in the upper atmosphere^[29] shows that the intensity of the energy sources in the upper atmosphere at a period of maximum solar activity amounts to $\leq 0.3-1 \text{ erg/cm}^2\text{sec}$ according to some estimates, but $\geq 10 \text{ erg/cm}^2\text{sec}$ according to others.

Recently a tendency has been manifest to bring these extreme viewpoints together. On the one hand, the theoretical estimates of the intensity of the solar radiation have been lowered to $\sim 6 \text{ erg/cm}^2\text{sec}$ (at maximum solar activity) by a series of refinements (G. M. Nikol'skiĭ^[94]). On the other hand, the most recent rocket measurements of Hinteregger et al.^[82,95] for a period of declining solar activity give a higher value than previously for the intensity: $2.7 \text{ erg/cm}^2\text{sec}$. The authors of^[96] have discussed the various estimates of the intensity of the ionization sources in the upper atmosphere. The most reliable estimates are based on data on the solar radiation and the temperature gradients with respect to altitude in the upper atmosphere. They give a value $3-10 \text{ erg/cm}^2\text{sec}$ for a period of maximum solar activity, taking into account the existing uncertainties. This implies that for the most abundant ion NO^+ , the value of $\alpha_{\text{NO}^+}^*$ is $\lesssim 3 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ ^[96] at altitudes of 200–250 km, i.e., at the temperature $\sim 1500^\circ\text{K}$ characteristic of this region of the ionosphere in the daytime during a period of maximum solar activity. This value agrees with the value $\sim 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ obtained above for a somewhat higher temperature from the data on the effective recombination coefficients in the F region of the ionosphere. The coefficients α^* must be greater for the ions O_2^+ and N_2^+ than for NO^+ . We note that for a period of minimum solar activity, when the temperature of the atmosphere is lower, the estimate of $\alpha_{\text{NO}^+}^*$ can differ, since in the E and D

regions this quantity is of the order of $(4-10) \times 10^{-8}$ and $(3-5) \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$, respectively. This indicates a strong temperature-dependence of $\alpha_{\text{NO}^+}^*$.

As has been shown above, we must assume a dissociative-recombination mechanism to explain the processes of intensive neutralization in the bulk of the ionosphere. This process must lead to a rapid disappearance of the molecular ions. At the same time, according to the experimental data, molecular ions exist in appreciable concentrations up to altitudes of 400–500 km and higher. This has posed the problem anew of explaining a mechanism of formation of these ions in the ionosphere capable of balancing their high rate of disappearance through dissociative-recombination reactions.

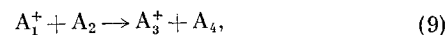
B. Ion-molecule Reactions

Since the discovery of the ionosphere in 1925, the problem of explaining its nature and elucidating the processes occurring in it has always been one of the most difficult problems. Especial difficulties arose, involving the fact that until extensive rocket studies had been conducted, we knew neither the composition of the ionosphere, nor the intensity and spectrum of the short-wavelength ionizing radiation of the sun, nor even the exact distribution of the electron concentration and the atmospheric density as functions of the altitude. Without these, one had to make numerous assumptions and guesses based on all possible indirect data obtained from earthbound observations involving radio-sounding of the ionosphere, propagation of radio waves, night-sky emission, etc.

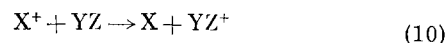
It was previously thought that the formation of the different layers of the ionosphere, E, F1, and F2, involved the ionization of primarily different atmospheric particles having differing ionization potentials. Thus, for example, it was thought that oxygen molecules were responsible for ion formation in the E layer (ionization potential $W_{\text{O}_2} = 12.2 \text{ eV}$), oxygen atoms in the F1 layer ($W_{\text{O}} = 13.5 \text{ eV}$), and nitrogen molecules in the F2 layer ($W_{\text{N}_2} = 15.5 \text{ eV}$). Other models of this sort were also produced. However, the difference in ionization potentials of the different molecules is so small that, given the actual energy distribution in the solar spectrum as determined with rockets, their rates of ionization per particle must be practically identical. In line with the discovery using rockets of a large amount of NO^+ ions in the upper atmosphere, the suggestion began to appear of the presence of a large amount of neutral NO molecules in the atmosphere. However, such suggestions have not been confirmed. Suggestions have also been made that at different altitudes different types of stepwise-ionization processes take place, involving preliminary excitation. This hypothesis also does not agree with the data on the concentrations of these particles in the atmosphere and the solar-spectrum data. In view of this, ion-

molecule reactions have acquired even greater importance in explaining the intensive formation of molecular ions in the ionosphere. We shall first discuss what ion-molecule reactions in general are possible in the upper atmosphere of the earth.

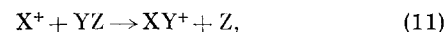
At present there is no strictly established name for processes of the type



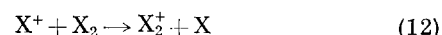
where A_1-A_4 are certain particles (atoms or molecules). The terms "charge transfer," "charge exchange," "ion-exchange reactions," or "reactions between ions and neutral particles" are used. The recently-proposed term "ion-exchange processes" is not exactly felicitous. Hence, following V. L. Tal'roze,^[97] who has discussed this problem in detail, we propose to call processes like (9) ion-molecule reactions, subdividing them (when necessary) into charge-transfer processes (i.e., transfer of an electron without change in the composition of the participating particles)



and processes of transfer of a heavy charged particle

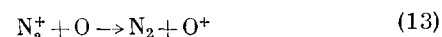


which involve the formation of an intermediate complex. The latter processes can lead either to results analogous to those of the charge-transfer processes or to the formation of new neutral particles and ions. Evidently, for processes such as

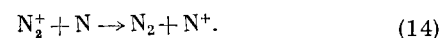


the two types of processes (10) and (11) are indistinguishable.

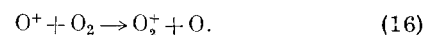
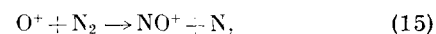
In 1949, Bates^[85] pointed out for the first time the possible role of ion-molecule processes in the upper atmosphere. In discussing the possible pathways for disappearance of N_2^+ ions in the ionosphere, he proposed two ion-molecule processes:



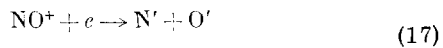
and



Later,^[98] he advanced the hypothesis that processes of "pure" charge transfer like (10) are slow processes, with rare exceptions, since they involve the excitation of electronic levels. On the other hand, ion-molecule processes that involve transfer of a heavy particle (11) are purely chemical processes, and can have high rate coefficients. As fundamental processes of this type that could play an essential role in the upper atmosphere, Bates^[98] cited the reactions

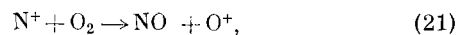
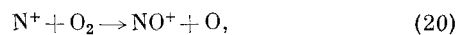
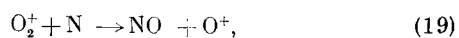
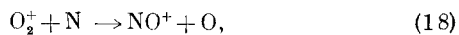


Yonezawa^[22] advanced some interesting ideas in 1955. In discussing the problem of recombination of electrons in the F2 layer of the ionosphere, he proposed that this recombination takes place through dissociative recombination of N_2^+ and O_2^+ ions, with rate constants of the order of $10^{-8} \text{ cm}^3 \text{ sec}^{-1}$. In addition he proposed that O_2^+ ions can be formed through reaction (16). However, this author^[22] could not obtain a satisfactory solution of the problem, evidently because he did not take into account the very important processes



and (15) involving NO^+ ions, whose existence in the ionosphere was not yet known in 1955.

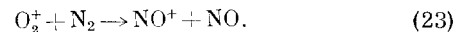
In a search for pathways of formation of molecular ions in the E and F regions of the ionosphere, V. I. Krasovskii^[33] has examined all possible ion-molecule reactions in the oxygen-nitrogen system. Upon rejecting the endothermic processes, he obtained the following system of possible reactions: (14)–(16) and



In that author's opinion, processes (20)–(22) and (14) are not very effective in comparison with processes (15) and (16), since the amount of N^+ and N_2^+ ions in the upper atmosphere must be less than the amount of oxygen ions. On the other hand, the effectiveness of processes (18) and (19) must also be low, since at the altitudes at which O_2^+ ions can exist there is little atomic nitrogen. Thus, according to V. I. Krasovskii^[33] the major ion-molecule processes in the upper atmosphere are again processes (15) and (16), with rate constants of the order of $10^{-10} \text{ cm}^3 \text{ sec}^{-1}$.

One can determine which of the ion-molecule reactions are the most important in the upper atmosphere only by studying the application of these reactions to concrete problems involving the determination of the relation between the concentrations of the different ions and their altitude distributions. It was determined by mass-spectrometer measurements in rockets and in the third Soviet satellite^[7-9] that below 200–250 km there are more molecular than atomic ions. The major molecular ion at all altitudes is the NO^+ ion, the concentration of NO^+ attaining a maximum at an altitude of the order of 200 km. The major atomic ion is the O^+ ion, which attains a maximum concentration at an altitude ~ 300 km in the F region, where the major maximum in the electron concentration occurs.

A study by Hertzberg^[36] that appeared in 1958 emphasized the importance of ion-molecule processes in the upper atmosphere, and pointed out that these processes apparently have cross-sections exceeding the gas-kinetic values. The same study presented a system of ion-molecule reactions involving the O^+ and O_2^+ ions, comprising processes (15), (16), (18), (19), and the reaction



Here, in the opinion of that author, the values of the rate constants of reactions (15), (16), and (19) are approximately of the same order of magnitude: $\gamma_{15} \sim \gamma_{16} \sim \gamma_{19} \sim 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$. Considering that this system is closed with respect to O_2^+ ions, Hertzberg assumed that the rates of formation and disappearance of these ions are equal. Thus he calculated the concentration ratio $[O_2^+]/[O^+]$, and compared his theory with experiment. It turned out that the theory agreed with the experimental data of Johnson and his associates^[6] only if one assumed an anomalously high ratio of concentrations of atomic to molecular nitrogen in the atmosphere ($[N]/[N_2]$ ten times that given by Miller^[99]). The current experimental data on the composition of the atmosphere up to altitudes of 200 km^[100,101] show that the ratio $[N]/[N_2]$ is much less than Hertzberg had to assume to make the theoretical and experimental $[O_2^+]/[O^+]$ ratios agree. This involves the fact that Hertzberg^[36] make an incorrect choice of the fundamental processes regulating the concentration of O_2^+ ions, by not taking into account the very fast process of disappearance of these ions by the dissociative-recombination reaction



In 1959 Bates^[102] confirmed the viewpoint that he had previously expressed^[85,98] on the role of ion-molecule processes in the upper atmosphere, and stated that the NO^+ ions found experimentally at altitudes of 100–400 km must be a product of reaction (15).

In 1959, Yonezawa et al.^[103] discussed the formation of the lower portion of the F layer as arising from the joint action of the following mechanisms: photoionization of oxygen atoms, ion-molecule processes (15) and (16), and the disappearance of the generated NO^+ and O_2^+ ions through the dissociative-recombination reactions (17) and (24). The authors of^[103] obtained agreement between the calculated distributions of the ions O^+ , NO^+ , and O_2^+ and those observed by Johnson et al.^[6] at altitudes of 130–200 km by taking values of the dissociative-recombination coefficients of the O_2^+ and NO^+ ions: $\alpha^* \sim 1.1 \times 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$, and rate constants of reactions (15) and (16): 5.2×10^{-10} and $2.9 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$, respectively. However, as pointed out in^[103], such a high value of the assumed reaction constants requires a considerably greater flux of ionizing radia-

tion than had been previously been assumed in order to maintain the observed electron concentration in the atmosphere.

In discussing possible mechanisms of formation and disappearance of NO^+ ions in the upper atmosphere, A. D. Danilov^[26] showed that the fundamental processes regulating the concentration of NO^+ ions are the ion-molecule reaction (15) and the dissociative recombination (17). Under conditions of equal rates of these processes, he obtained^[26] the ratio

$$\frac{[\text{NO}^+]}{[\text{O}^+]} = \frac{\gamma_{15}}{\alpha_{\text{NO}^+}^*} \frac{[\text{N}_2]}{n_e}. \quad (25)$$

Calculations based on the experimental data on the density and electron concentration in the upper atmosphere have shown that the values of the $[\text{NO}^+]/[\text{O}^+]$ ratio calculated by Eq. (25) agree with the experimental data of V. G. Istomin^[7] and of Johnson et al.^[6] throughout the studied altitude range 100–400 km for a value of $\gamma_{15}/\alpha_{\text{NO}^+}^*$ equal to 10^{-4} . Calculations made by G. S. Ivanov-Kholodnyĭ^[11], based on data somewhat differing from those of^[26] on the density and electron concentration in the upper atmosphere, gave a value $\gamma/\alpha^* = 6 \times 10^{-5}$. The difference in the calculated values involves the existing uncertainty in the original data on the parameters of the upper atmosphere. The value thus obtained, $\gamma_{15}/\alpha_{\text{NO}^+}^* = (5-10) \times 10^{-5}$, is an important experimental quantity for the ionosphere, permitting us to relate firmly the constants of the fundamental processes for theoretical studies (see below).

In^[26] the value of the dissociative-recombination coefficient α^* was taken to be $10^{-6} \text{ cm}^3 \text{ sec}^{-1}$ on the basis of the laboratory data that had been published at that time.^[104,105] This led to the conclusion that the constant γ_{15} for the ion-molecule reaction (15) is of the order of $10^{-10} \text{ cm}^3 \text{ sec}^{-1}$, as Bates^[98] and V. L. Krasovskii^[33] had also assumed. However, this value for the dissociative-recombination coefficient now seems too high, and inadmissible for the ionosphere. As was shown above, the value of $\alpha_{\text{NO}^+}^*$ must amount to about $(1-3) \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ in the major part of the ionosphere in the F1 and F2 regions. In this case, in order to satisfy the relation $\gamma_{15}/\alpha_{\text{NO}^+}^* \approx 10^{-4}$, the rate constant of the ion-molecule reaction (15) must be considerably lower, and amount to several units times $10^{-12} \text{ cm}^3 \text{ sec}^{-1}$.

Bates and Nicolet^[35] have reexamined Bates' previously-expressed opinion^[98] on the high rate of ion-molecule processes in the ionosphere. Upon discussing the possible pathways of disappearance of O^+ ions in the upper atmosphere through ion-molecule reactions, the authors found that

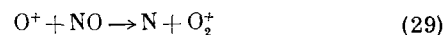
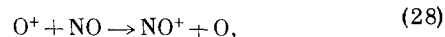
$$n_t(\text{O}^+) = n_0(\text{O}^+) \exp(-\mu t), \quad (26)$$

where $n_0(\text{O}^+)$ is the concentration of O^+ ions at the moment of sunset, $n_t(\text{O}^+)$ is the concentration of these same ions at a time interval t after sunset, and the

quantity μ is given by

$$\mu = \gamma_{15} [\text{N}_2] + \gamma_{16} [\text{O}_2] + (\gamma_{28} + \gamma_{29}) [\text{NO}], \quad (27)$$

where γ_{28} and γ_{29} are the constants of the reactions



respectively. If we assume values of the order of $10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ for the coefficients γ_i in Eq. (27), as Hertzberg^[36] has done, then the value of μ for an altitude of 200 km comes out to be about 3 sec^{-1} . According to Eq. (26), this should lead to a very rapid complete disappearance of O^+ ions immediately after sunset. However, according to the experimental data,^[6] such a pattern is not observed. Using these experimental data and assuming that O^+ ion formation does not occur after sunset, Bates and Nicolet^[35] have obtained an expression for the relation between the constants γ_{15} and γ_{16} :

$$\gamma_{16} + 0.4\gamma_{15} = 1.3 \cdot 10^{-13} \text{ cm}^3 \text{ sec}^{-1}, \quad (30)$$

which implies that process (15) must be three orders of magnitude slower than had been previously assumed.^[98] However, as was pointed out above, the authors of^[35] assumed in the calculations a low value of the effective recombination coefficient in the F region. Since all the other ion-molecule reactions of the same type as (15) and (16) that had been measured up to then in the laboratory have very high rate constants (see^[10]), Bates and Nicolet^[35] consider that the reason why the effectiveness of reactions (15) and (16) can be so low is a high activation energy of these reactions or a high steric factor.

S. P. Yatsenko^[106] has made an analysis of the contaminant ions detected by the mass spectrometer in the third Soviet satellite. By studying the time oscillations of the ion current of contaminants, the author concluded that the observed H_2O^+ ions resulted from ion-molecule processes between neutral contaminant molecules and the ions of the atmosphere. Although no quantitative estimates of the rates were made in^[106], we should expect that fast processes were occurring, since the time of existence of contaminant particles on the surface of the satellite is exceedingly small.

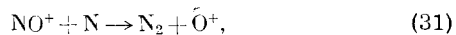
It was shown in^[27] that reaction (16), which has been suggested by many authors (see above), explains well the observed O_2^+ ion distribution only to altitudes of 150–160 km. Here the dissociative-recombination reaction (24) was adopted as the mechanism of disappearance of molecular oxygen ions, with a rate constant not varying with altitude. The assumption that the value of $\alpha_{\text{O}_2^+}$ depends on the temperature (and thus on the altitude) leads to the conclusion^[74] that the ion-molecule reaction can compensate for the disappearance of O_2^+ ions up to altitudes of the order of 190–200 km. However, the question of how these ions

are formed at altitudes of 300–400 km, where there is practically no molecular oxygen, remains open as before. The reaction of association of an oxygen atom and ion discussed in^[27] as well as in the earlier study of Yonezawa^[22] cannot be accepted as a possible mechanism of O_2^+ ion formation above 200 km, since it would have to have too high a rate constant.^[107]

Possibly the existence of O_2^+ ions at great altitudes is due to the diffusion of these ions from the lower layers of the ionosphere. The ion-molecule reaction of formation of N_2^+ ions proposed in^[28] is evidently endothermic, and hence also cannot occur with sufficient effectiveness.^[107]

A study by Hertzberg^[37] gives a more complete list of the ion-molecule processes occurring in the upper atmosphere than his previous study had done.^[36] As Bates and Nicolet^[35] have pointed out, most of the fundamental ion-molecule processes in the atmosphere lead to the rapid disappearance of O^+ ions. Hence, Hertzberg^[37] suggested that these ions must be generated intensively through reaction (19). However, as the author himself pointed out, in order that this process might balance out the high rate of disappearance of O^+ by reactions (15) and (16), too high a content of atomic nitrogen is required at all the altitudes at which O_2^+ ions exist. Hertzberg^[37] points out that one must consider also ion-molecule reactions involving neutral NO molecules, in addition to those involving atoms and molecules of oxygen and nitrogen. Nicolet^[108] has also considered such reactions in the overall balance of formation of the different ions. However, we must note that there is practically no nitric oxide in the atmosphere according to the experimental data^[109] (the fraction of NO amounts to $\leq 10^{-5}$ of the total particle concentration). Therefore, such reactions can make no appreciable contribution to the distribution of the different ions, and we can neglect them.

In 1961 Bates and Nicolet^[110] confirmed their viewpoint^[35] that the ion-molecule processes cannot be very effective in the upper atmosphere, since otherwise all of the O^+ ions would disappear quickly after sunset. In their opinion, reaction (19) proposed by Hertzberg^[37] cannot account for a sufficient rate of the reverse process. In addition, more than half of the ion-molecule processes proposed by Hertzberg^[37] lead to the formation of NO^+ ions, and only the process

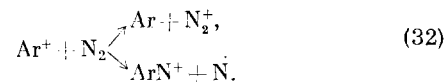


(which according to Bates^[111] should not be very effective) destroys these ions. Therefore, in the opinion of Bates and Nicolet^[110], in line with the high rate constants of the ion-molecule reactions, only NO^+ ions should exist in the atmosphere at night, as contradicted by experiment.^[6] However, the concentration of NO^+ ions is regulated not only by ion-molecule processes, but also by the relatively fast dissociative-recombination reaction. Hence, one should observe

after sunset a certain increase in the relative concentration of NO^+ ions (the same argument holds for O_2^+) as compared with O^+ ions. Such a phenomenon is actually observed according to the experimental data. We must also bear in mind the fact that the diurnal variations in the density and neutral composition of the atmosphere may exert an essential influence on the variation in the ionic composition of the atmosphere from day to night. The problem of why the O^+ ions do not totally disappear at night is part of the more general problem of why the entire ionosphere does not vanish at night, in view of the high dissociative-recombination coefficient measured experimentally, i.e., the problem of the existence of a mechanism sustaining nighttime ionization. For example, according to L. A. Antonova and G. S. Ivanov-Kholodnyi,^[112] currents of low-energy electrons are a possible source of nighttime ionization.

Harteck and Reeves^[113] have discussed the possible ion-molecule processes in the ionosphere, and distinguished between charge-transfer processes and processes involving transfer of a heavy particle. Here the authors drew some conclusions on the relative intensities of the cited processes based on the experiments of Johnson et al.^[6] on the ionic composition. The absence of N_2^+ and N^+ ions at altitudes of 100–200 km indicates evidently that the lifetime of these ions for ion-molecule reactions is very short (of the order of 100 sec). This indicates that the cross-sections of these reactions are high, probably exceeding the gas-kinetic values. The variation from day to night in the concentration of O_2^+ ions permitted these authors^[113] to estimate the rate constant of process (23): $\gamma_{23} < 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$. The nighttime existence of O^+ ions, which were detected in the same experiments of Johnson et al.,^[6] leads to the conclusion that the rate constants γ_{16} and γ_{15} for the processes of destruction of these ions cannot exceed 10^{-12} and $10^{-13} \text{ cm}^3 \text{ sec}^{-1}$, respectively.^[113]

A. D. Danilov^[114] has discussed the problem of ionization of argon in the upper atmosphere. The absence of Ar^+ ions at altitudes of 100–200 km evidently indicates that at these altitudes the cited ions disappear by way of the ion-molecule process



The estimate obtained in^[114] of the rate constant of this reaction, $\gamma_{32} > 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$, involved too high data on the intensity of ionization in the atmosphere, and must be reduced by about an order of magnitude. Thus, we can say at present that the ionospheric data give an estimate: $\gamma_{32} > 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$.

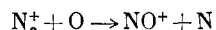
On the basis of the most general considerations, S. P. Yatsenko^[30] has constructed curves of the altitude-variation of the concentrations of ions that disappear through various processes. As the com-

parison of these curves with the experimental trend in the ion concentrations found by V. G. Istomin^[8] showed, the atomic ions O⁺ and N⁺ disappear through ion-molecule reactions with neutral molecules, but the molecular ions disappear through dissociative recombination.

A review article by V. I. Krasovskiĭ,^[115] mainly concerned with studies of reactions involving neutral particles, gives a list of the possible ion-molecule processes occurring in the upper atmosphere, and indicates their energies of reaction. Here he expresses in the article the idea that the fundamental ion-molecule reaction in the ionosphere (16) is reversible, and can proceed in either direction:



Norton et al.^[64] undertook an attempt to construct the theoretical ion-concentration distribution over the altitude range 100–200 km. The authors assumed that photochemical equilibrium was obeyed throughout the altitude range. The neutral composition of the atmosphere was taken under the assumption that the level of separation of O and N₂ occurs at an altitude of 110 km. Such an assumption indicated an essentially atomic atmosphere (at an altitude of 200 km, [O] ~ 4 [N₂]), in disagreement with the data of mass-spectrometer measurements,^[100,101] but in agreement with Hinteregger's data.^[116] An examination of all the existing data on measurements of the neutral composition of the atmosphere shows,^[117] however, that the composition adopted in^[64] is incorrect, and that molecular nitrogen predominates over atomic oxygen up to altitudes of about 300 km. The theoretical and experimental data on the ionic composition were made to agree in^[64] by assuming an intensive destruction of N₂⁺ ions through the reaction



with a rate constant of the order of 10⁻¹¹ cm³ sec⁻¹. However, we must note that the authors carried out the comparison with V. G. Istomin's experimental data given in B. A. Mirtov's book^[118] without taking into account the fact that these data were obtained at differing zenith angles of the sun. Still, the variation in the relative and absolute concentrations of the various ions with the time of day must serve, along with the altitude distribution, as an important criterion of the correctness of reaction systems under discussion (see below).

Nicolet and Swider^[107] have recently reviewed in detail the various processes in the ionosphere and their relative roles in the different regions of the ionosphere. They selected from a large number of possible processes the fundamental ones from the standpoint of the formation or disappearance of the major ions, and gave equations for the equilibrium concentrations. Just like Norton et al.,^[64] they advanced the idea that the process of dissociative re-

combination of N₂⁺ ions cannot be the main mechanism for the disappearance of these ions, and that a faster pathway for the disappearance of N₂⁺ ions must be the ion-molecule reactions with atomic and molecular oxygen.

A. D. Danilov^[74] has discussed in detail the problem of the fundamental processes regulating the ion distribution in the 100–200 km region, based on the experimental data on the variation in the ionic composition with the altitude and the zenith angle of the sun. He derived equations for the equilibrium concentrations of the ions O⁺, O₂⁺, NO⁺, and N₂⁺. These equations practically coincide with the analogous equations given in the cited study by Nicolet and Swider.^[107] The previously-discussed systems of photochemical transformations in the ionosphere had not explained the fact that the number of nitrogen ions amounts to only a small fraction of the total ion density, in spite of the abundance of nitrogen molecules, and hence he discussed this problem in detail. He showed that evidently the main process for disappearance of N₂⁺ ions is their "transformation" by the charge-transfer reaction (13) into O⁺ ions. He also showed that one can choose the system of fundamental processes regulating the altitude distribution of the ions at each instant of time independently of the adoption of any particular set of data on the intensity of the solar ionizing radiation. The latter is related in a definite way to the absolute values of the rate constants of all the reactions. The system of processes comprises ionization of O, O₂, and N₂, the ion-molecule reactions (13), (15), and (16), and the dissociative recombination of the NO⁺ and O₂⁺ ions. This system gives satisfactory agreement between the theoretical and experimental altitude distributions of the studied ion concentrations, and explains well the observed variation in this distribution with the zenith angle of the sun (within the limits of the studied values of Z_⊙ from 90° to 50°). Since we should consider the value ~ 3–10 erg/cm²sec to be at present an apparently quite reliably established value for the flux of ionizing radiation, we can derive the fundamental rate constants of these processes in the atmosphere from a study of the stated system of processes. The following values of the constants were obtained in^[74]:

$$\gamma_{15} = (5 - 10) \cdot 10^{-13} \text{ cm}^3 \text{ sec}^{-1},$$

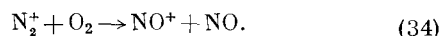
$$\gamma_{16} = (2.5 - 5) \cdot 10^{-12} \text{ cm}^3 \text{ sec}^{-1},$$

$$\gamma_{13} = (3 - 6) \cdot 10^{-11} \text{ cm}^3 \text{ sec}^{-1}.$$

Here it is pointed out that a further refinement in the fundamental parameters of the atmosphere: the neutral and ionic composition, the electron concentration, and the intensity of the sun's ultraviolet radiation, will permit one to obtain more reliable values of the rate constants of these processes based on these data and on the theory of ionospheric processes. The latter is

fully reasonable, since, as will be shown below, the laboratory data still do not provide any reliable and self-consistent information on the rate constants of the fundamental ionospheric processes.

Whitten and Poppoff^[77] have posed an analogous problem: to determine the rate constants of certain ion-molecule processes in the ionosphere by comparing calculated and experimental data on the ionic composition. In distinction from^[74], the authors of^[77] have assumed the rate constants of dissociative recombination of the molecular ions N_2^+ , O_2^+ , and NO^+ and their temperature-dependences to be known from an analysis of the laboratory data. Based on these constants and data taken from Norton et al.^[64] on the neutral composition of the atmosphere and the rates of ionization of the major components, Whitten and Poppoff obtained estimates of the rate constants of the fundamental ion-molecule reactions that they had selected: $\gamma_{16} = 2 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$, $\gamma_{13} = 2 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$, $\gamma_{15} = 2 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$, and $\gamma_{34} = 2 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$, where γ_{34} is the rate constant of the reaction



On studying the existing laboratory data, the authors^[77] consider that none of the obtained values but γ_{15} disagree with the laboratory measurements. As for the obtained value of γ_{15} , Whitten and Poppoff^[77] think that it turned out too low because of a low assumed value of $\alpha_{NO^+}^*$.

In the above-mentioned study of Nisbet and Quinn,^[9] they tried to estimate the rate constant of the fundamental ion-molecule reaction in the region of the maximum of the ionosphere by using the ionospheric values of the coefficient β (see Sec. 2, A, g). Following the experimental data, they took β to be $6.5 \times 10^{-5} \text{ sec}^{-1}$ at an altitude of 300 km. Since the following relation holds in the F2 region, where $[O^+] \gg [NO^+] + [O_2^+]$:

$$\beta = \gamma_{16} [O_2] + \gamma_{15} [N_2], \quad (35)$$

one can estimate the values of γ by assuming the concentrations of the neutral particles. Considering that the main process for disappearance of O^+ at 300 km is reaction (16) and that one can neglect the second term on the right-hand side of Eq. (35), Nisbet and Quinn obtained $\gamma_{16} = (4.5 \pm 1.5) \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$. Here they assumed the value of $[O_2]$ according to the Harris-Priester model. However, in fact this quantity is an upper bound of γ_{16} , since the term $\gamma_{15} [N_2]$ can be comparable to or even (more probably) greater than the term $\gamma_{16} [O_2]$. Analogously, if we take the value of $[N_2]$ at 300 km to be 10^8 , we can obtain an upper estimate for the constant γ_{15} : $\gamma_{15} \leq 6.5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$. Since most probably the contribution of the term $\gamma_{16} [O_2]$ in Eq. (35) is small, the obtained estimate may not differ greatly from the actual value of γ_{15} in the F2 layer of the ionosphere.

Recently Sagalyn and Smiddy^[119] have estimated the value of the rate constant of reaction (15): $\gamma_{15} = (1.6-3.2) \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$, on the basis of their own measurements of the ionic composition of the ionosphere above 230 km and an N_2 concentration taken from the Harris-Priester model^[120] of the atmosphere. However, we must note that the Harris-Priester model gives low values of the N_2 concentration at high altitudes. Evidently, if we take higher values of $[N_2]$, this will give a lower obtained value of γ_{15} .

Thus, on examining the theoretical studies on the significance of ion-molecule processes and dissociative recombination in the ionosphere, we see that, while the determining role of these processes in the formation and behavior of the ionosphere is generally accepted at present, the problem of the values of the rate constants is a topic of active debate. In order to try to solve this problem, we might naturally refer to the laboratory studies of the reactions of interest to us.

3. LABORATORY STUDIES

A. Dissociative Recombination

The first laboratory studies of plasma afterglow, which were performed by Biondi and Brown^[121,122] and by Holt et al.^[123] using a new microwave method, showed that the rates α^* of the recombination processes in the atmospheric gases N_2 and O_2 proved to be unusually large, of the order of $10^{-6} \text{ cm}^3 \text{ sec}^{-1}$ and even larger. The combination of the microwave method with the method of studying the time-dependence of the intensity and spectrum of the afterglow made it possible to eliminate the interfering effect of diffusion, and to conduct an entire series of measurements of the rate of recombination of thermal electrons with positive ions in gases. The first experiments were begun as early as 1946; especially many experiments have been performed in 1950-1952 and recently. The results of all the existing laboratory measurements of recombination coefficients are summarized below. Biondi and Holstein^[124,125] were the first to show, using the example of the inert gases helium and neon, that the large value of α is due to the fact that in a plasma at low enough pressures, what takes place is not the ordinary recombination of ions with electrons, but rather, dissociative recombination of molecular ions to form excited atoms. Hence, the recombination processes are accompanied by the emission of the spectral lines of the atoms. It seems that the process of dissociative recombination can be observed most simply in the afterglow of the inert gases, and hence, these gases have been studied in greater detail.

Bates^[126] has made a theoretical analysis of the high rate of recombination of electrons in helium. He showed that the observed high rate $\alpha = 1.7 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ ^[121] cannot be explained by either

radiative recombination ($\alpha = 4 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$), or by triple recombination, or by electron capture by impurities. He acknowledged the only possible way to explain it to be the dissociative-recombination reaction of the molecular ions He_2^+ , which can be formed in a dense enough plasma through triple collisions. The first theoretical estimates of the magnitude of the rate of such reactions were made by Bates;^[12] they showed that $\alpha^* \approx 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ at $T = 250^\circ\text{K}$. Thus the results of the laboratory experiments were explained. However, subsequent experiments gave results differing from the first data;^[121-125] they showed a strong dependence of α^* on the experimental conditions and even aroused some mistrust in the laboratory data. Bates and Nicolet^[35] expressed the opinion that possibly in the ionosphere dissociative-recombination reactions do occur, but their rates are very low: $\alpha^* \approx 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$. In this regard, it is of special interest to examine the existing data obtained in laboratory experiments.

We should note that the performance of laboratory experiments to determine α^* involves a number of difficulties. For example, in studying a hydrogen plasma Varnerin^[127] found that at low pressure (1–2 mm Hg) $\alpha_{\text{H}_2^+}^* = 3.5 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$. This value is almost one-half an order of magnitude smaller than the value determined originally by Biondi and Brown^[122] and later by Richardson and Holt.^[128] For larger pressures they also obtained lower values of α^* . Varnerin explains this discrepancy in the data by the fact that the authors of^[122,128] used insufficiently purified hydrogen. Persson and Brown^[129] have made a study in specially-purified hydrogen at pressures from 7.5 to 37.6 mm Hg, taking into account the effect of ion diffusion. They discovered here no effect of dissociative recombination, finding that α^* is less than $3 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$. The disappearance of the ions took place through recombination on the walls of the chamber, to which the ions migrated under the action of ambipolar diffusion. Hence Varnerin^[127] ascribed the large values of α^* previously obtained by other authors to the effect of contaminants and impurities in the hydrogen, although apparently the basic difference amounted to differing estimates of the role of diffusion in interpreting the experimental data. A divergence in the data has also been observed for other gases; a marked increase in α^* has been noted upon addition of even very small amounts of water vapor, which shows the high value $\alpha^* \approx 3 \times 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$.^[130] Another important characteristic that Varnerin found^[127] consisted in the fact that the recombination coefficient increased with increasing hydrogen pressure. Since the dissociative-recombination coefficient cannot depend on the pressure p , he ascribed the effect of increase in α^* , which obeyed the law $\alpha^* = \alpha_0 + Ap^2$ (A is a constant), to the influence of negative ions, which are efficiently formed at high enough gas pressures.

A pressure-dependence has also been observed in other gases. Such a dependence has been observed for the N_2^+ ion in the experiments of Bryan et al.,^[104] and of Bialecke and Dougal,^[131] as well as in a recent study by Mentzoni.^[132] This indicates the complexity of the processes that take place in a plasma during the afterglow.

Loeb^[133] has given a detailed summary of all the measurements of α^* coefficients performed up to 1955. Taking into account the fact that the recombination coefficients turned out to be too large in comparison with the previously experimentally-determined radiative-recombination coefficients of the atomic ions, $\sim 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$, he expressed doubt in the correctness of the interpretation of the obtained results as being effects of dissociative recombination. Loeb pointed out that up to that time no one had definitely detected the supposed molecular ions. He emphasized that in a number of experiments at low pressures, insufficient account had been taken of the role of diffusion of ions to the walls of the chamber. At high pressures, they had neglected the role of the process of attachment of electrons to atoms and molecules, as indicated by the pressure-dependence of α^* . He also pointed out difficulties of a theoretical nature in explaining the phenomenon of dissociative recombination. Loeb undertook an attempt to explain all of the experiments that had been performed on the basis of phenomena not involving dissociative recombination. The point of the studies of Loeb^[133] and Persson and Brown^[129] actually consists in the fact that they indicate that one can interpret the experimental data without using the concept of dissociative recombination, but rather, using the hypothesis of ambipolar diffusion. This is likewise the gist of a study by Brömer,^[134] who also studied the afterglow. However, in interpreting the phenomenon of decay of the emission from the plasma in the molecular bands, he gave greater weight to diffusion than to the phenomenon of dissociative recombination of molecular nitrogen ions. He estimated the value of $\alpha_{\text{N}_2^+}^*$ to be $\leq 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$. The data on ambipolar-diffusion coefficients are at present even more uncertain than those on the rate constants for dissociative recombination. Hence, the greater the diffusion rates that one assumes in interpreting the laboratory data, the smaller the values of α^* that one gets. This dilemma has recently been studied by Gray and Kerr,^[135,136] who showed how an insufficient account of one of the phenomena (recombination or diffusion) leads to an overestimate of the other. A study by Kenty^[137] is an example of a concrete analysis along this line. Here he showed how the relation between the rates of the above-cited processes determines the nature of the distribution of the concentration of ions and electrons in the positive column of a discharge. The quantitative study of this phenomenon can serve as a good method of determining rate constants of recombination and diffusion.

Especially intensive study has begun recently on the rates of the diffusion and dissociative-recombination processes (see the most recent reviews by Dalgarno,^[138] Bates and Dalgarno,^[139] Biondi,^[140-145] Mentzoni,^[132] and Whitten and Poppoff^[77]). Several attempts have been undertaken to study the problem of whether volume recombination of electrons and ions actually took place in the cited laboratory experiments, rather than attachment of electrons to neutral molecules or diffusion of ions to the walls of the chamber, and whether the proposed molecular ions take part in the dissociation.

Biondi^[125] tested the hypothesis that molecular ions participate in dissociation, but not atomic ions. He set up two different experiments: in pure argon, and in helium or neon having an admixture of $\sim 0.1\%$ argon. In the first case, he observed the fast recombination characteristic of molecular ions, with $\alpha^* = 8.8 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$. This was apparently due to the process $\text{Ar}_2^+ + e \rightarrow \text{Ar}^* + \text{Ar}$. However, in the second case, in contrast with the conditions in the pure gas, there was no rapid recombination, and the resorption of the electrons occurred three orders of magnitude more slowly through diffusion. In the second case, the argon atoms quickly removed the charge from the molecular ions He_2^+ or Ne_2^+ through charge-transfer processes, owing to the high gas density, and slowly recombined; here Ar_2^+ ions were not formed because of the low Ar concentration. Thus he demonstrated that fast recombination processes are actually due to molecular ions.

Biondi^[143] considers that one of the fundamental arguments in favor of the occurrence of the dissociative-recombination reaction to form excited atoms is the presence of intense atomic emission lines in the afterglow spectrum, e.g., of neon and argon. The intensity of these lines is several orders of magnitude greater than could arise from ordinary radiative recombination.

Another method of testing the fundamental hypothesis has also been applied. If the excitation of atoms in a plasma involves the dissociative-recombination reaction (1), then the atoms formed must have a certain velocity of motion, owing to the transformation of part of the dissociation energy into kinetic energy, and the observed emission lines should be broadened (Biondi^[144]). Rogers and Biondi^[145-147] have studied the 5876 Å He line with a Fabry-Perot interferometer, and it actually proved to be broadened. The equivalent kinetic energy of the atom was determined to be 0.8 eV, in agreement with the hypothesized value. Thus, they confirmed the effect predicted on the basis of the dissociative-recombination theory. As Biondi has emphasized,^[140] negative ions were not detected in the cited experiment. It was reported in^[143] that a broadening of the 5852 Å line was recently found in the afterglow in neon. The line broadening corresponds to a kinetic energy of dissociation of ~ 1 eV,

as was expected theoretically.

The opinion^[133] has been expected that the molecular ions assumed in the experiments of Biondi et al. were not actually detected (see also Olsen and Huxford^[148]). However, the bands of the molecular ions have actually been established in the afterglow spectrum,^[104,134] as discussed above. In addition, Phelps and Brown^[149] have detected the ions He^+ and He_2^+ directly with the mass spectrometer in a study of the afterglow in helium, and Kasner et al.^[150] have detected N_2^+ ions, and Kerr and Leffel^[151] have found that He_2^+ ions are formed more efficiently at pressures > 3 mm Hg.

We shall discuss the fundamental results of the laboratory studies of the dissociative-recombination coefficient for the atmospheric ions N_2^+ , O_2^+ , and NO^+ . All of the published results are compiled in the summary Table III. This table also gives the most reliable estimates of α^* based on ionospheric data.

The N_2^+ ion. The early experiments up to 1958 were performed at relatively high pressures, resulting in a pressure-dependence arising from the effect of negative-ion formation and other effects.

The influence of the negative-ion effect must be greatly diminished at low pressures. However, one cannot advance very far in this direction experimentally, since the effect of diffusion increases sharply with decreasing pressure in inverse proportion to the pressure. This complicates and even renders impossible the measurement of α^* . Faire et al.^[168] have avoided this difficulty by using an ingenious method: they diluted the N_2 , so to speak, by adding a large amount of inert helium. Thus they were able to make measurements of $\alpha_{\text{N}_2^+}^*$ at partial pressures of N_2 down to 0.01 mm Hg.^[105] In the final discussion of the results of their study, Faire et al.^[153] pointed out that one still has to take into account a certain diffusion effect, which had previously resulted in a certain increase in α . They found that the value of α decreases with decreasing pressure, but at N_2 pressures below 4 mm Hg it remains approximately constant at the relatively low value of $3.9 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ at $T = 400^\circ\text{K}$.

Mentzoni et al.^[132,157] have recently conducted an extensive study on $\alpha_{\text{N}_2^+}$ at various temperatures (300–735°K) and pressures (0.5–6.0 mm Hg). They drew the important conclusion that $\alpha^* \propto T^{-3/2}$ at temperatures $< 600^\circ\text{K}$, in agreement with the theoretical calculations. However, with further temperature increase, the constant α^* begins to decline very sharply. At a temperature 735°K, they obtained α^* values even smaller than Sayers and King found at temperatures 1600–3200°K. The most unpleasant feature in these data, as in those of Faire et al., is that they found the value of α^* to be pressure-dependent, which should not be the case.

A study by Kretschmer and Petersen^[169] has recently appeared, in which they reported on the results

Table III

Reaction	Author	Year	Rate constant α^* , $\text{cm}^3 \text{sec}^{-1}$	Temperature, $^\circ\text{K}$	
$\text{N}_2^+ + e \rightarrow \text{N} + \text{N}$	Biondi et al. ^[122]	1949	$1.4 \cdot 10^{-6}$	300	
	Sayers ^[152]	1956	$1.1 \cdot 10^{-7}$	3200	
	Sayers (according to ^[138])	1956	$4.4 \cdot 10^{-7}$	2500	
	Bryan et al. ^[104]	1957	$(3-23) \cdot 10^{-7}$	(300)	
	Bialecke et al. ^[131]	1958	$7 \cdot 10^{-7}$	200-300	
			$2 \cdot 10^{-6}$	92	
	Faire et al. ^[105]	1958	$4 \cdot 10^{-7}$	300	
	Faire et al. ^[153]	1959	$3.9 \cdot 10^{-7}$	400	
	Brömer ^[134]	1960	$\sim 10^{-10}$		
	Biondi, Kasner, Rogers ^[143, 150, 154, 155]	1961-	$(2.8 \pm 0.5) \times 10^{-7}$	300	
		1964	$\times 10^{-7}$		
	King ^[156] †	1961	$5 \cdot 10^{-7}$	1600	
			$6.5 \cdot 10^{-7}$	2000	
	Mentzoni, Montgomery, Row ^[132, 157]	1962	$1 \cdot 10^{-8}$	725	
			$1 \cdot 10^{-7}$	525	
		$2 \cdot 10^{-7}$	300		
	Ionospheric data		$7 \cdot 10^{-7}$	{ 300 (?) (1000)	
			$10^{-6} - 10^{-5}$	~ 1000	
$\text{O}_2^+ + e \rightarrow \text{O} + \text{O}$	Biondi et al. ^[122]	1949	$3 \cdot 10^{-7}$	300	
	Sayers ^[152]	1956	$4 \cdot 10^{-8}$	(2000)	
	Holt ^[158]	1959	$3 \cdot 10^{-7}$	300	
	Sayers (according to ^[138, 159])	1960	$(2-3) \cdot 10^{-7}$	2500	
	Biondi, Kasner, Rogers ^[143, 150, 154, 155]	1961-	$(1.7 \pm 1) \times 10^{-7}$	300	
		1964	$\times 10^{-7}$		
	Mentzoni ^[160]	1964	$3.7 \cdot 10^{-7}$	300	
			$(1.7 \cdot 10^{-7})$	569	
		$1.4 \cdot 10^{-7}$	894		
	Ionospheric data		$\leq (1.5-4) \times 10^{-7}$	~ 270	
			$\geq 5 \cdot 10^{-7}$	200	
			$3.3 \cdot 10^{-8}$	420	
			$8.8 \cdot 10^{-8}$	623	
			$\leq 2 \cdot 10^{-8}$	~ 2000	
$\text{NO}^+ + e \rightarrow \text{N} + \text{O}$	Lamb et al. ^[161]	1957	$10^{-6} - 10^{-7}$	300	
	Low et al. ^[162]	1959	10^{-6}	(4000)	
	Lin (according to ^[183])	1961	10^{-9}	4000	
	Günton, Inn, Shaw ^[163, 164]	1961	$1.3 \cdot 10^{-6}$	450	
	Doering, Mahan ^[165]	1961	$(0.4-2) \times 10^{-6}$	300	
	Sugden (see ^[165])		$\times 10^{-6}$		
	Syverson et al. ^[167]	1961	10^{-7}	2000	
	Stein et al. (see ^[77])	1962	$1.3 \cdot 10^{-7}$	3000	
		1963	$4 \cdot 10^{-8}$	3000	
		Ionospheric data		$3-5 \cdot 10^{-7}$	~ 200
				$(5-13) \times 10^{-8}$	~ 300
			$\times 10^{-8}$		
			$\leq 3 \cdot 10^{-8}$	~ 1500	
			$1 \cdot 10^{-8}$	~ 2000	
			$\leq 1.2 \cdot 10^{-8}$	420	
			$6.3 \cdot 10^{-8}$	623	

† [Translator's note: The above two values of α^* were misread from a graph in^[156]. They should be 5×10^{-8} and 6.5×10^{-8} , respectively.]

of studying dissociative recombination of the ions Ar^+ , O_2^+ , N_2^+ , etc., as measured in gas discharges with a Langmuir probe. The measurements were made at relatively high gas pressures from 0.1 to 20 mm Hg. The rate constants for recombination in the atmospheric gases, nitrogen and oxygen, also proved to depend on the pressure; this indicates the complexity of the processes occurring in the plasma and the effect of various ion-molecule reactions in these experiments. The value of $\alpha_{\text{O}_2^+}^*$ extrapolated to zero pressure proved to be $2 \times 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$, while a lower limit on

$\alpha_{\text{N}_2^+}^*$ was $1.7 \times 10^{-7} \text{ p cm}^3 \text{ sec}^{-1} \text{ torr}^{-1}$, where p is the pressure in mm Hg (torr), whereas at lower pressures they obtained the very high value $\alpha_{\text{N}_2^+}^* = 5 \times 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$.

A study conducted under Biondi's direction^[141] has cast much light on the problem of the pressure-dependence of α^* , and also in general on the problem of the relatively high α^* values obtained in the first experiments on the atmospheric ions. Mass-spectrometric measurements showed that at high enough pressures the more complex ions N_3^+ , N_4^+ , and O_3^+ are

formed in addition to the diatomic ions N_2^+ and O_2^+ . The former show higher recombination rates than the diatomic ions. Knewstubb and Tickner^[170] and Curran^[171] have also studied the formation of complex ions in a plasma at a pressure of ~ 1 mm Hg using the mass spectrometer. They discovered the formation of even more complex ions, besides those cited.

Some papers by Kasner, Rogers, and Biondi^[150,154,155] and the reviews of Biondi^[141-143] have presented the detailed results of studying recombination coefficients using mass spectrometers. The diatomic molecular ions N_2^+ and O_2^+ appeared in the pure form without admixtures of N_3^+ , N_4^+ , and O_3^+ only at pressures below 10^{-2} mm Hg. In nitrogen-helium mixtures at pressures 0.1–7 mm Hg, the major ions were N_3^+ and N_4^+ , with a recombination coefficient $\geq 10^{-6}$ $\text{cm}^3 \text{sec}^{-1}$. In line with this, they observed considerable variations in the recombination coefficient of electrons and ions in nitrogen-helium mixtures between the cited pressures. Thus, one can explain naturally the high α^* values in almost all the previous experiments, as well as the pressure-dependence of α^* . At very low pressures, the main mechanism of loss of ions from the plasma was ambipolar diffusion to the chamber walls. Through these experiments they determined more precisely the ambipolar-diffusion coefficients. They found that it was better to choose neon as an additive to avoid the effect of diffusion, rather than helium, which had been used previously. They obtained new values of the α^* coefficients for the ions N_2^+ and O_2^+ . These values have been recommended as the most reliable ones for atmospheric studies.^[68] However, we should note that in the literature people have repeatedly used the previously published values, $\alpha_{N_2^+}^* = (5.9 \pm 1) \times 10^{-7}$ and $\alpha_{O_2^+}^* = (3.8 \pm 1) \times 10^{-7}$, which are higher than those given in Table III. These values have turned out to be too high on account of calibration errors in making the measurements of the electron concentration by the microwave method.^[142,143]

Whitten and Poppoff^[77] have compiled the results of various measurements of $\alpha_{N_2^+}^*$ on a single graph as a function of the temperature, and concluded that $\alpha_{N_2^+}^* = 5 \times 10^{-5} T^{-3/4}$, although the exponent of T could lie between the limits of -1 and -0.5 , owing to the wide scatter of the data. Reference^[77] did not take into account all the data given in Table III. The new α^* values obtained by Kasner et al., as well as by Mentzoni et al., prove to be considerably lower, while King's data are considerably higher than those of other measurements, especially in the high-temperature range. These values do not agree with the formula derived by Whitten and Poppoff. [Translator's note: The authors of this review have misread King's^[156] values from a graph. When corrected, these values are on the low side. See Table III for the

corrections.]

Strangely, the ionospheric estimates of $\alpha_{N_2^+}^*$ given on Table III prove to be greatly elevated in comparison with the laboratory measurements, even though other ions exhibit the opposite pattern. Lytle and Hunten^[172] have found a very high rate of disappearance of N_2^+ ions by studying the twilight emission of the N_2^+ band at 3914 Å. This rate exceeded the rate of dissociative recombination by an order of magnitude or more. They also found the rate to be proportional to the concentration of neutral particles in the upper atmosphere. The mechanism [reaction (22)] which they proposed for the rapid destruction of N_2^+ does not show a sufficient rate. The analogous reactions of N_2^+ with O_2 (34) and with N (14) are not effective enough, owing to the low concentrations of O_2 and N; Hunten^[173] also considered reaction (13), for which a rate constant $\sim 0.1\%$ of the gas-kinetic value would be required. In photochemical studies of the ionic composition of the upper atmosphere, Norton et al.,^[64] Whitten and Poppoff,^[77] Nicolet and Swider,^[107] and Danilov^[74] (see Sec. 2, B) have discussed the analogous problem of the necessity of rapid removal of N_2^+ ions by reactions (22) and (13), since dissociative recombination does not show a sufficient rate. Thus, the ionospheric data on the rate of destruction of the N_2^+ ion cannot be compared with the laboratory data on $\alpha_{N_2^+}^*$, since in the lower part of the ionosphere the N_2^+ ion is destroyed more rapidly by reaction (22), or more probably, by reaction (13).^[74,77]

The divergence in the data in Table III is so great that it is hard to draw any definite conclusions on the temperature-dependence of $\alpha_{N_2^+}^*$. We can only estimate approximately the value of $\alpha_{N_2^+}^*$ for a temperature of $\sim 300^\circ\text{K}$. On the basis of a number of recent laboratory experiments, we should apparently adopt for $T = 300\text{--}400^\circ\text{K}$ the rate constant of the reaction $N_2^+ + e \rightarrow N' + N$ as being $\alpha_{N_2^+}^* = (2.5\text{--}4) \times 10^{-7}$ $\text{cm}^3 \text{sec}^{-1}$. Chamberlain and Sagan^[174] had previously drawn an analogous conclusion from the data of^[131], as had Hertzberg^[36] from the data of^[105,122,123].

The O_2^+ ion. As we see from Table III, fewer data have been obtained for the dissociative recombination of O_2^+ than for N_2^+ . However, we should note that the data obtained by Biondi and Brown^[122] have also been confirmed in Bryan's experiments, as was reported in^[104]. Holt^[158] has also obtained an analogous value. After^[152], the large review paper of Dalgarno^[138] appeared, reporting on Sayer's new results in determining $\alpha_{O_2^+}^*$ (given in Table III). The studies of Kasner, Rogers, and Biondi gave a value of $\alpha_{O_2^+}^*$ at $T = 300^\circ\text{K}$ of $(1.7 \pm 1) \times 10^{-7}$ $\text{cm}^3 \text{sec}^{-1}$. Mentzoni has recently reported new data for three temperatures: 300° , 569° , and 894°K .

Whitten and Poppoff^[77] have collected the laboratory determinations of $\alpha_{O_2^+}^*$ on a graph analogous to that for N_2^+ as a function of the temperature, and found

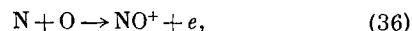
that they agree well with the various ionospheric data. Here they found $\alpha_{O_2^+}^* = 7 \times 10^{-5} \text{ T}^{-1}$, giving a value $\alpha_{O_2^+}^* \approx 3 \times 10^{-7}$ at a temperature of 300°K, practically differing very little from the value of $\alpha_{N_2^+}^*$ at the same temperature. The temperature-dependence of α^* was determined more definitely for the O_2^+ ion than for N_2^+ ; it even fits well all the new data on $\alpha_{O_2^+}^*$ not used in^[77], as well as Sayers' data (of 1960). Thus, the laboratory experiments gives values and temperature-dependences of α^* that agree well among themselves for the O_2^+ ion, for which there exists the least amount of all of ionospheric data.

The NO⁺ ion. The main molecular ion at altitudes ≤ 500 km is the NO⁺ ion. Hence it is important to know α^* for reaction (17) in particular. Many experimental data give about the same value for this reaction as for the dissociative-recombination reaction of the other molecular ions, i.e., 10^{-6} – $10^{-7} \text{ cm}^3 \text{ sec}^{-1}$. Very recently several experimental studies have appeared^[163-167] in which just such values have been obtained for $\alpha_{NO^+}^*$. However, one would like to see these values made more precise. This is all the more important, in that Doering and Mahan^[166] obtained a value of $2 \times 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$ by determining $\alpha_{NO^+}^*$ from probe measurements of the equilibrium value of n_e formed by photoionization with the short-wavelength ultraviolet radiation of a krypton lamp at 1236 Å. On the other hand, by measuring the decay time of n_e after the irradiation had ceased, they obtained the value $4 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$. The reason for this great divergence in the data has not been completely elucidated, but the second method is considered more reliable.

A wide scatter in values of $\alpha_{NO^+}^*$ has been obtained at high temperatures. Lin found that the constant for process (17) $\alpha^* = 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ at $T = 5000^\circ\text{K}$. This is considerably lower than Low had previously estimated for $T = 4000^\circ\text{K}$, and Sugden (see^[165]), Syverson et al.,^[167] and Stein et al. (see^[77]) had obtained at a somewhat lower temperature. Here the latter data are too high, even in comparison with the ionospheric data. If Lin's data are correct (see^[135,138,107]), then when combined with the laboratory data giving $\alpha_{NO^+}^* \approx (3-10) \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ at $T = 300-450^\circ\text{K}$, they indicate the existence of a very sharp variation having $\alpha_{NO^+}^* \propto T^{-3}$, as the ionospheric data also imply (see Sec. 2, A). Then, in the F region of the ionosphere, where the temperature varies over the range from 1800° to 800°K, the value of $\alpha_{NO^+}^*$ should vary over the range from 5×10^{-9} to $5 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$. The value of $\alpha_{NO^+}^*$ should thereby undergo appreciable diurnal variations. While these conclusions on the value of $\alpha_{NO^+}^*$ are not in strong contradiction with the ionospheric estimates given in Table III, however, no signs of the existence of diurnal variations in $\alpha_{NO^+}^*$ in the upper atmosphere have yet been obtained.

Whitten and Poppoff in^[77] adopted a certain generalized formula $\alpha_{NO^+}^* = 1.5 \times 10^{-3} \text{ T}^{-3/2} \text{ cm}^3 \text{ sec}^{-1} \text{ deg}^{2/3}$,

which hardly differs from the formula $\alpha_{NO^+}^* = 3 \times 10^{-3} \text{ T}^{-3/2} \text{ cm}^3 \text{ sec}^{-1} \text{ deg}^{2/3}$ obtained by Lin and Teare^[175]. The latter authors used, on the one hand, the experimental data on the reaction



which is the reverse reaction of the dissociative recombination of the NO⁺ ion, and on the other hand, the equilibrium constant for these two reactions. Here they used only the weakest temperature-dependence, whereas the experimental data permit also a steeper temperature-dependence. The proposed formulas give $\alpha_{NO^+}^*$ values of 200°, 300°, and 2000°K of approximately $(0.5-1) \times 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$, $(3-6) \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$, and $(1.5-3) \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$. That is, the values differ greatly both from the high-temperature laboratory data and from the ionospheric determinations of $\alpha_{NO^+}^*$. However, it is important to note that, just as in our previous discussion, this formula reflects a considerably stronger temperature-dependence of $\alpha_{NO^+}^*$ than one might expect for the ions O_2^+ and N_2^+ .

Thus, a comparison of the ionospheric and laboratory data on α^* shows satisfactory agreement between them only for the O_2^+ ion. There are practically no ionospheric data for the N_2^+ ion, and for the NO⁺ ion most of the laboratory data give values of α^* too high as compared with the more reliable ionospheric values. At present the laboratory studies give a larger scatter in the data than is observed in the various ionospheric studies, which confirms the lower reliability of the laboratory data.

B. Ion-molecule Processes

The laboratory experiments studying ion-molecule processes pertain mainly to reactions involving hydrogen, inert gases, and hydrocarbons. At present there exists a very large number of studies of this sort, among which a series of experiments by Stevenson and Schissler^[176-178] occupies a key spot. However, we shall spend no time here on these laboratory studies, since recent detailed reviews have been published by V. L. Tal'roze^[97] and by Giese and Maier.^[179,180] Charge-transfer between ions and complex molecules has been studied in detail by G. K. Lavrovskaya et al.^[181] We shall mention only one important result obtained in the experiments with inert gases,^[178] namely, that the cross-section of these reactions depends on the temperature as $\sigma \sim T^{-1/2}$. The latter fact implies that for the relatively simple processes studied, the reaction constant γ , which is proportional to $\sigma T^{1/2}$, is practically independent of the temperature.^[97] However, this situation may not hold for the more complex actual processes occurring in the atmosphere.

We shall discuss the relatively small number of experiments on the rate constants of the processes occurring in the ionosphere.

A study by Potter^[182] appeared in 1955 on determining the constant of reaction (15) from data of mass-spectrometer measurements. In mass-spectrometer studies, he observed an ion of mass number 30 in the spectrum of air. The appearance potential of this ion was close to that of the oxygen ion, rather than that of the nitric oxide molecule. On the basis of this, as well as of the study of Bates^[98] that had appeared shortly before, predicting a high rate for ion-molecule processes like (11), the author ascribed the appearance of the NO⁺ ions to reaction (15). Making some assumptions on the geometry of the chamber in which the O⁺ and N₂⁺ interacted, Potter^[182] obtained the very high value of the rate constant of reaction (15) of $(1.0 \pm 0.25) \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$, based on the time-variation of the ratio of ion currents of O⁺ and NO⁺.

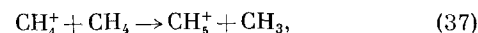
Bates and Nicolet^[35] have expressed doubt in whether Potter's results^[182] are trustworthy. In their opinion, it is doubtful that process (15) was responsible in this case for the formation of NO⁺ ions. Hence, in the opinion of the authors of^[35], the cited experiment does not even give us grounds to suppose that process (15) is in general a fast process.

An experiment by Dickinson and Sayers^[183] is of great interest in the study of the upper atmosphere. Here they studied the rate of the ion-molecule process (16) in terms of the disappearance of O⁺ ions produced by a gas discharge. The first mention of this experiment occurs in an article by Sayers,^[152] where he states that the rate constant of process (16) is of the order of $10^{-10} \text{ cm}^3 \text{ sec}^{-1}$. In a later paper,^[183] the authors give a detailed description of the technique and results. As has been pointed out, process (16) can occur either through charge-transfer (10), or through transfer of a heavy particle (11). In this case the two pathways are indistinguishable. However, the authors consider on theoretical grounds (Bates^[98]) that their measurements pertain to the faster process involving heavy-particle transfer. At pressures from 2×10^{-3} to 2.5×10^{-5} mm Hg, Dickinson and Sayers^[183] obtained a value of $(2.5 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ for the rate constant of reaction (16). Upon varying the temperature from 200° to 300°K, the authors obtained no systematic dependence of the constant γ_{16} on T.

S. Ya. Pshezhetskiĭ and M. T. Dmitriev^[184] have found that the activation energy of reaction (34) is large, amounting to 7 kcal/mole. This means that the given reaction cannot occur with a high rate constant. The latter has been confirmed by the experiments of V. L. Tal'roze and E. L. Frankevich^[185] studying the formation of NO⁺ ions in the ion source of a mass spectrometer using an oxygen-nitrogen mixture.

In an experiment V. L. Tal'roze and his associates^[186] studied the rate constant of the ionosphericly very important process (15). They determined the rate constant from the slope of the curve of the variation of the NO⁺ ion current as the O⁺ ion current

was varied. Since the experiments gave no appreciable change in I₃₀ as I₁₆ increased, they took the maximum possible error in the slope of the I₃₀/I₁₆ curve to get an upper estimate of the rate constant. In order to take into account a possible "removal" of NO⁺ ions from the ion source, they used the reaction



whose rate constant is rather well known. In the paper that these authors presented at a discussion of the Faraday Society,^[186] they gave an estimate of the constant γ_{15} obtained in the above-mentioned way: $\gamma_{15} < 6.75 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$. However, a misprint has slipped into this value. As we can easily see directly from the graph of the experimental data given in the cited study,^[186] the upper limit of the rate constant is equal to $6.75 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$.

At the same session of the Faraday Society where V. L. Tal'roze et al.^[186] presented their paper, there was also a brief report on two experimental studies on ion-molecule processes of importance in the upper atmosphere. Using the same method as in the cited study by Dickinson and Sayers,^[183] Langstroth and Hasted^[187] obtained the following values of the rate constants of the fundamental processes (15) and (16) in the ionosphere: $\gamma_{16} = (1.8 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$, and $\gamma_{15} = (4.7 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$. Fite and his associates^[188] reported that according to their measurements, the rate constant of process (16), γ_{16} is within the range 10^{-10} – $10^{-11} \text{ cm}^3 \text{ sec}^{-1}$, while the rate constant γ_{20} of reaction (20) is approximately $5 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$.

A. D. Danilov and S. P. Yatsenko^[189] have described the first tentative experiment to study the rate constants of the fundamental ionospheric processes directly in the upper atmosphere. They studied the ion currents of NO⁺ and O₂⁺ in a mass spectrometer, as formed through the interaction of atmospheric O⁺ ions with the N₂ and O₂ molecules of air released from the rocket by means of a special attachment. Thus they found that in the atmosphere the ratio of the rate constants of processes (15) and (16) is

$$\frac{\gamma_{15}}{\gamma_{16}} \leq 0.1.$$

As was shown in^[74], we must assume such a ratio of the constants γ_{15}/γ_{16} to get the best agreement between the theoretical and experimental data on the concentration distribution of the major ions in the ionosphere.

Stebbing et al.^[190] have measured the cross-sections for charge-transfer of the ions N⁺, N₂⁺, NO⁺, and O₂⁺ with oxygen atoms and molecules, and of He⁺ ions with O₂ and N₂ molecules. The curves given in these studies give a detailed picture of the behavior of the charge-transfer cross-sections of the cited ions over the energy range 10–6500 eV. However, the lack of data on the cross-sections of the discussed proces-

Table IV

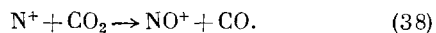
Author	$O^+ + N_2 \rightarrow NO + N$	$O^+ + O_2 \rightarrow O_2^+ + O$
Potter ^[182]	$\sim 10^{-8}$	
Dickinson and Sayers ^[183]		$2.5 \cdot 10^{-11}$
Talrose et al. ^[186]	$\leq 6.7 \cdot 10^{-11}$	
Langstroth and Hasted ^[187]	$4.7 \cdot 10^{-12}$	$1.8 \cdot 10^{-12}$
Fite et al. ^[188]	$10^{-10} - 10^{-11}$	
Volpi et al. ^[193]	$2.2 \cdot 10^{-11}$	
Sayers and Smith ^[194]	$2.7 \cdot 10^{-11}$	$1.6 \cdot 10^{-11}$
Paulson (according to ^[192])	$\leq 5 \cdot 10^{-11}$	

Table V

Reaction	Fite et al. ^[188]	Volpi et al. ^[191]
$N_2^+ + O_2 \rightarrow NO^+ + NO$	$2.1 \cdot 10^{-13}$	$2.1 \cdot 10^{-13}$
$N^+ + O_2 \rightarrow NO^+ + O$	$5 \cdot 10^{-10}$	$1 \cdot 10^{-10}$
$O_2^+ + N_2 \rightarrow NO^+ + NO$		$2.1 \cdot 10^{-13}$
$N_2^+ + O_2 \rightarrow N_2 + O_2^+$	$2 \cdot 10^{-10}$	

ses at thermal ion energies prevents us from directly applying the results of this work in studying the rates of ion formation in the upper atmosphere.

Using the same method as in the described study of Tal'roze et al.,^[186] Volpi and his associates^[191] have studied the formation of NO^+ ions through ion-molecule processes. In spite of the conclusions of^[186], Volpi et al.^[191] found that the role of neutral NO molecules in the formation of NO^+ is small and can be neglected. In studying processes (34) and (23), they found a slight dependence of the current intensity I_{30} on the currents I_{28} and I_{32} . This permitted them to estimate the upper limits of the rate constants of these reactions: $\gamma_{34} \leq 2.1 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$, and $\gamma_{23} \leq 2.1 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$. The small value of the constant for (34) is in accord with the high activation energy of this reaction obtained by Pshezhetskiĭ and Dmitriev.^[184] The study of process (15) showed^[191] that the appearance potential of the NO^+ ion coincided with that of O^+ . However, the authors found that the slope of the curve giving the dependence of I_{30} on I_{16} depended considerably on the energy of the electron beam. The authors explain the latter by the effect of the formation of NO^+ ions by reactions (20) and (38):



The authors' estimates based on the same experimental data gave values for the rate constants of these reactions: $\gamma_{20} \approx 1 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$, and $\gamma_{38} \approx 3 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$. The value of γ_{20} obtained agrees with the data obtained by Fite and his associates.^[188] As the authors of^[191] themselves point out, there is a certain uncertainty in interpretation involving the possible role of electronically-excited O^+ ions of high kinetic energy. With these reservations, the authors estimated the value of the rate constant of process (15) from the variations in the ratio I_{30}/I_{16} : $\gamma_{15} \approx 2.2 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$. This value does not disagree with

the estimate of Tal'roze et al.,^[186] but it disagrees with the data of Hasted.^[187] The authors do not discuss possible reasons for the discrepancy.

A recent review by Paulson^[192] describes in detail and compares the three fundamental methods applied in laboratory studies of ion-neutral particle reactions; the primary ionization method, the afterglow method, and the ion-beam method. This article gives a summary table of the results obtained by all three methods for reactions involving hydrogen, deuterium, helium, nitrogen, and oxygen. It is also reported in^[192] that according to unpublished measurements of Paulson and Mosher, the constant γ_{15} is less than $5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ for energies $\leq 1 \text{ eV}$.

An article by Fite^[193] gives an extensive review of studies on charge-transfer reactions, but the author discusses only experiments performed at high particle energies.

We can summarize all that we have said about laboratory studies of ion-molecule processes of importance in the ionosphere in the form of Tables IV and V.

As we see from Tables IV and V, the greatest number of laboratory studies have been made on the fundamental ionospheric ion-molecule reaction (15). However, these studies do not yet permit one to obtain (even within an accuracy of a factor of 2-3) any definite value for γ_{15} , since the results of the experiments vary greatly among themselves. Judged by comparison with the ionospheric data described above, the value closest to actuality seems to be the smallest one: $\gamma_{15} = 4.7 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$, obtained by Langstroth and Hasted.^[187] However, we must bear in mind the fact that this value diverges most of all from the results of the other laboratory measurements of the rate constant of reaction (15), which give γ_{15} values of the order of several times $10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ (see Table IV). The results of the laboratory measurements of γ_{16} also differ greatly among themselves. Thus the data from the laboratory experiments cannot serve as a basis for corresponding calculations in the ionosphere. In view of this, the attempt undertaken in^[74,77] to obtain more reliable information on the rate constants of the ionospheric processes from data on the parameters of the upper atmosphere becomes understandable.

4. CONCLUSION

The successful development of satellite and rocket studies has brought a set of geophysical and astrophysical problems involving the study of the earth's upper atmosphere closer to terrestrial physics and chemistry. One of the interesting problems posed by the ionospheric studies is to elucidate the role and the relative effectiveness of the various elementary processes involving charged particles. In solving this problem, the leading role has been ascertained of the processes of dissociative recombination and ion-mole-

cule reactions in the ionosphere, and a great need has arisen for the development of laboratory studies of these reactions.

It is now evident that we know from analyzing the various ionospheric data what are the fundamental processes involving charged particles occurring in the upper atmosphere. A further refinement of the parameters of the upper atmosphere and their variations is being conducted very actively now, and will evidently permit us to elucidate in a very short time the relative roles of the different reactions in the formation and disappearance of ions and electrons, and to give reliable estimates of the reaction constants. Naturally, an essential check on the obtained results here would be to compare the constants obtained from the ionospheric data with laboratory measurements of the same quantities. However, unfortunately, the laboratory data on the fundamental processes (ion-molecule reactions and dissociative recombination) continue even now to be sparse and contradictory. For the fundamental ion-molecule reaction in the ionosphere, the divergence of results of the laboratory measurements of the rate constant is very large, and does not permit us to choose any more or less reliable mean value with an accuracy any better than an order of magnitude. Although rather many measurements exist on dissociative recombination, the problem is uncertain, as before, concerning the temperature-dependence of the rate constants. Evidently, painstaking measurements are required over a broad temperature range in order to solve this problem finally.

A successful solution of the cited problems in the laboratory will make it possible to take an entire series of important steps in studying the elementary processes occurring in the upper layers of the earth's atmosphere.

¹K. I. Gringauz, DAN SSSR 120, 1234 (1958), Soviet Phys. Doklady 3, 620 (1959).

²K. I. Gringauz, *Iskusstvennye sputniki Zemli*, No. 1, 62 (1958).

³V. I. Krasovskiĭ, *ibid.*, No. 2, 36 (1958).

⁴Ya. L. Al'pert, UFN 71, 369 (1960), Soviet Phys. Uspekhi 3, 479 (1961).

⁵H. E. Newell, in collected volume *Physics of the Upper Atmosphere*, Ed. J. A. Ratcliffe, Academic Press, New York (1960); Russ. transl. in collected volume *Fizika verkhnei atmosfery (Physics of the Upper Atmosphere)*, M., IL, 1963, p. 74.

⁶Johnson, Meadows, Holmes, and Heppner, in collected volume *Issledovaniya verkhnei atmosfery s pomoshch'yu raket i sputnikov (Upper-Atmosphere Studies Using Rockets and Satellites)*, M., IIL, 1961, pp. 254, 257. [This reference may be a Russ. transl. of the following two papers: Johnson, Heppner, Holmes, and Meadows, *Ann. geophys.* 14, 475 (1958);

Johnson, Meadows, and Holmes, *J. Geophys. Res.* 63, 443 (1958).]

⁷V. G. Istomin, *Iskusstvennye sputniki Zemli*, No. 4, 171 (1960); DAN SSSR 129, 81 (1959).

⁸V. G. Istomin, *Iskusstvennye sputniki Zemli*, No. 7, 64 (1961).

⁹V. G. Istomin, *ibid.*, No. 11, 95 (1962).

¹⁰A. D. Danilov, *ibid.*, No. 17, 19 (1963).

¹¹G. S. Ivanov-Kholodnyĭ, DAN SSSR 137, 327 (1961).

¹²D. R. Bates, *Phys. Rev.* 78, 492 (1950).

¹³E. Bauer and T. Y. Wu, *Can. J. Phys.* 34, 1436 (1956).

¹⁴R. C. Stabler, *Bull. Am. Phys. Soc.* 7, 313 (1962).

¹⁵S. N. Ghosh and S. P. Khare, *J. Sci. and Industr. Res. (India)* A21, 365 (1962).

¹⁶R. C. Stabler, *Phys. Rev.* 131, 1578 (1963).

¹⁷H. S. W. Massey, *Proc. Roy. Soc.* A163, 542 (1937).

¹⁸D. R. Bates and H. S. W. Massey, *Proc. Roy. Soc.* A187, 261 (1946).

¹⁹D. R. Bates and H. S. W. Massey, *Proc. Roy. Soc.* A192, 1 (1947).

²⁰E. Gerjouy and M. A. Biondi, *J. Geophys. Res.* 58, 295 (1953).

²¹J. H. Piddington, *J. Geophys. Res.* 56, 409 (1951).

²²T. Yonezawa, *Rep. Ionosph. Res. Japan* 9, 17 (1955).

²³T. Yonezawa, *J. Radio Res. Labor.* 3, 1 (1956).

²⁴J. A. Ratcliffe, *J. Atm. Terr. Phys.* 8, 260 (1956).

²⁵A. D. Danilov, DAN SSSR 137, 1098 (1961).

²⁶A. D. Danilov, *Iskusstvennye sputniki Zemli*, No. 5, 60 (1960).

²⁷A. D. Danilov, *ibid.*, No. 7, 56 (1961).

²⁸A. D. Danilov, *ibid.*, No. 8, 72 (1961).

²⁹G. S. Ivanov-Kholodnyĭ, *Geomagnetizm i aëronomiya* 2, 377 (1962).

³⁰S. P. Yatsenko, *Geomagnetizm i aëronomiya* 2, 873 (1962).

³¹J. A. Ratcliffe and K. Weekes, see Ref. [5], p. 338.

³²B. A. Bagaryatskiĭ, *Izv. AN SSSR, ser. Geofiz.*, No. 9, 1359 (1959).

³³V. I. Krasovskiĭ, *ibid.*, No. 4, 504 (1957).

³⁴A. P. Mitra, *J. Geophys. Res.* 64, 733 (1959).

³⁵D. R. Bates and M. Nicolet, *J. Atm. Terr. Phys.* 18, 65 (1960).

³⁶M. Hertzberg, *J. Geophys. Res.* 63, 856 (1958).

³⁷M. Hertzberg, *J. Atm. Terr. Phys.* 20, 177 (1961).

³⁸Ya. L. Al'pert, *Rasprostranenie radiovoln i ionosfera (Radio Wave Propagation and the Ionosphere)*, M., Izd-vo AN SSSR, 1960; Engl. transl., Consultants Bureau, New York, 1963.

³⁹G. V. Bukin and M. D. Fligel', *Geomagnetizm i aëronomiya* 2, 1103 (1962).

⁴⁰G. S. Ivanov-Kholodnyĭ, *ibid.* 2, 674 (1962).

⁴¹J. A. Ratcliffe, *Suppl. J. Atm. Terr. Phys.* 6, 1 (1956).

⁴²K. Bibl and F. Delobbeau, *Z. Geophys.* 21, 215 (1955).

⁴³J. Hunaerts and M. Nicolet, *J. Geophys. Res.* 60,

537 (1955).

⁴⁴ C. M. Minnis, *Nature* 178, 33 (1956).

⁴⁵ Bonnet, Hunaerts, and Nicolet, *Bull. des. Seances, Acad. Roy. Sci. Coloniales*, n. s. III, 4, 964 (1957).

⁴⁶ J. A. Ratcliffe, *Suppl. J. Atm. Terr. Phys.* 6, 306 (1956).

⁴⁷ M. W. McElhinny, *J. Atm. Terr. Phys.* 14, 273 (1959).

⁴⁸ J. A. Gledhill, *ibid.* 16, 367 (1959).

⁴⁹ Chubb, Friedman, Kreplin, Blake, and Unzicker, *Mem. Soc. Roy. Liege* 4, 228 (1961); *Russ. Transl., Ul'traioletovoe izluchenie Solntsa i mezplanetnaya sreda (Ultraviolet Radiation of the Sun and the Interplanetary Medium)*, M., IL, 1962, p. 129.

⁵⁰ I. N. Odintsova and M. B. Ogir', *Izv. Krymskoĭ astrofiz. abs.* 29, 175 (1963).

⁵¹ G. Nestorov and Yu. Taubenkhaim, *Izv. Geofiz. in-ta Bolg. AN* 3, 259 (1962).

⁵² G. Nestorov and Yu. Taubenkhaim, *Geomagnetizm i aëronomiya* 3, 277 (1963); *Engl. Transl.*, 3, 224 (1963).

⁵³ G. Nestorov and J. Taubenheim, *Dokl. Bolg. AN* 15, 131 (1962).

⁵⁴ G. Nestorov and J. Taubenheim, *Monatsber. Dtsch. Akad. Wiss. Berlin* 4, 191 (1962).

⁵⁵ G. Nestorov and J. Taubenheim, *J. Atm. Terr. Phys.* 24, 633 (1962).

⁵⁶ K. B. Serafimov, *Pure and Appl. Geophys.* 57, 133 (1964).

⁵⁷ S. Jasinski, *Prace Inst. Iaczn.* 9, 23 (1962).

⁵⁸ *Solar Eclipse and the Ionosphere*, Ed. W. J. G. Beynon and G. M. Brown, Pergamon Press, London-N. Y., 1956.

⁵⁹ *Advances in Upper Atmosphere Research*, Ed. B. Landmark, Pergamon Press, Oxford-New York, 1963.

⁶⁰ *Electron Density Profiles in the Ionosphere and Exosphere*, Ed. B. Maehlum, Pergamon Press, 1962.

⁶¹ *Proceedings of the International Conference on the Ionosphere*, Ed. A. C. Stickland, *Inst. Physics and Phys. Soc.*, Chapman and Hall, London, 1963.

⁶² R. C. Whitten and I. G. Poppoff, *J. Geophys. Res.* 66, 2279 (1961).

⁶³ K. Watanabe and H. E. Hinteregger, *ibid.* 67, 999 (1962).

⁶⁴ Norton, Van Zandt, and Denison, see Ref. 61, p. 26.

⁶⁵ Hinteregger, Hall, and Schmidtke, in collected volume *Solar XUV Radiation and Neutral Particle Distribution in July 1963 Thermosphere*, 5th COSPAR Intern. Conference, Florence, 1964 (preprint).

⁶⁶ Smith, Accardo, Weeks, and McKinnon, in collected volume *Rocket Measurements in the Ionosphere during the Eclipse of 20 July 1963*, 5th COSPAR Intern. Conference, Florence, 1964 (preprint).

⁶⁷ L. G. Smith, *J. Geophys. Res.* 67, 1658 (1962).

⁶⁸ *Trans. Amer. Geophys. Union* 44, 965 (1963).

⁶⁹ J. E. Titheridge, *J. Atm. Terr. Phys.* 17, 126 (1959).

⁷⁰ A. P. Mitra, *ibid.* 10, 140 (1957).

⁷¹ A. P. Mitra, see Ref. 59, p. 57.

⁷² D. R. Bates and M. R. C. McDowell, *J. Atm. Terr. Phys.* 10, 96 (1957).

⁷³ S. A. Bowhill, *ibid.* 20, 19 (1961).

⁷⁴ A. D. Danilov, *Kosmicheskie issledovaniya* 2(6), 865 (1964).

⁷⁵ Holms, Johnson, and Young, *Ionospheric Chemistry*, 5th COSPAR Intern. Conference, Florence, 1964 (preprint).

⁷⁶ R. C. Whitten and I. G. Poppoff, *J. Geophys. Res.* 67, 3000 (1962).

⁷⁷ R. C. Whitten and I. G. Poppoff, *J. Atm. Sci.* 21, 117 (1964).

⁷⁸ R. E. LeLevier, *J. Geophys. Res.* 69, 481 (1964).

⁷⁹ R. S. Narcisi and A. D. Bailey, *Mass Spectrometric Measurements of Positive Ions at Altitude from 64 to 112 Kilometers*, 5th COSPAR Intern. Conference, Florence, 1964 (preprint).

⁸⁰ Marmo, Pressman, Aschenbrand, Jursa, and Zelikoff, *Threshold of Space*, Pergamon Press, 1957, p. 232.

⁸¹ Marmo, Aschenbrand, and Pressman, *Planet and Space Sci.* 1, 227 (1959).

⁸² H. E. Hinteregger and K. Watanabe, *J. Geophys. Res.* 67, 3373 (1962).

⁸³ L. Wallace and R. A. Nidey, *J. Geophys. Res.* 69, 471 (1964).

⁸⁴ Odencrantz, Saint-Amand, and Moore, *ibid.* 67, 4091 (1962).

⁸⁵ D. R. Bates, *Proc. Roy. Soc. A* 196, 562 (1949).

⁸⁶ Ratcliffe, Schmerling, Setty, and Thomas, *Phil. Trans. Roy. Soc. A* 248, 621 (1956).

⁸⁷ E. R. Schmerling and J. O. Thomas, *ibid.* A248, 609 (1956).

⁸⁸ Van Zandt, Norton, and Stonehocker, *J. Geophys. Res.* 65, 2002 (1960).

⁸⁹ H. Rishbeth and C. S. G. K. Setty, *J. Atm. Terr. Phys.* 20, 263 (1961).

⁹⁰ V. M. Polyakov, *Geomagnetizm i aëronomiya* 3, 868 (1963); *Engl. Transl.* 3, 702 (1963).

⁹¹ J. S. Nisbet and T. P. Quinn, *J. Geophys. Res.* 68, 1031 (1963).

⁹² H. W. Bergh, *J. Atm. Terr. Phys.* 24, 949 (1962).

⁹³ L. Q. Orsini and R. H. Mazzilli, *Nature* 193, 462 (1962).

⁹⁴ G. M. Nikol'skiĭ, *Geomagnetizm i aëronomiya* 3, 793 (1963); *Engl. Transl.* 3, 643 (1963).

⁹⁵ Hall, Damon, and Hinteregger, *Space Research*, Vol. 3, Amsterdam, 1963, p. 745; *Russ. Transl.: Korotkovolnovoe izluchenie nebesnykh tel (Short-Wavelength Emission of Celestial Bodies)*, M., IL, 1963, p. 101.

⁹⁶ A. D. Danilov and G. S. Ivanov-Kholodnyĭ, *Geomagnetizm i aëronomiya* 3, 850 (1963); *Engl. Transl.*, 3, 688 (1963).

⁹⁷ V. L. Tal'roze, *Pure Appl. Chem.* 5, 455 (1962).

⁹⁸ D. R. Bates, *Proc. Phys. Soc. A* 68, 344 (1955).

- ⁹⁹ L. E. Miller, *J. Geophys. Res.* **62**, 351 (1957).
- ¹⁰⁰ A. A. Pokhunkov, *Iskusstvennye sputniki Zemli*, No. 7, 89 (1961).
- ¹⁰¹ A. A. Pokhunkov, *ibid.*, No. 13, 110 (1962).
- ¹⁰² D. R. Bates, *Proc. Roy. Soc. A253*, 451 (1959).
- ¹⁰³ Yonezawa, Takahashi, and Arima, *J. Radio Res. Labor.* **6**, 21 (1959).
- ¹⁰⁴ Bryan, Holt, and Oldenberg, *Phys. Rev.* **106**, 83 (1957).
- ¹⁰⁵ Faire, Fundingsland, Aden, and Champion, *J. Appl. Phys.* **29**, 928 (1958).
- ¹⁰⁶ S. P. Yatsenko, *Iskusstvennye sputniki Zemli*, No. 7, 61 (1961).
- ¹⁰⁷ M. Nicolet and W. Swider, Jr., *Planetary and Space Sci.* **11**, 1459 (1963).
- ¹⁰⁸ M. Nicolet, *Aeronomy, Russ. Transl. M., Izd-vo "Mir"*, 1964.
- ¹⁰⁹ Jursa, Tanaka, and LeBlanc, *Planetary and Space Sci.* **1**, 1 (1959).
- ¹¹⁰ D. R. Bates and M. Nicolet, *J. Atm. Terr. Phys.* **21**, 286 (1961).
- ¹¹¹ D. R. Bates, *Some Problems on the Upper Atmosphere*, in collected volume 13th Astronautical Congress (Varna, 1962), Springer Verlag, Vienna-New York, 1964.
- ¹¹² L. A. Antonova and G. S. Ivanov-Kholodnyĭ, *Geomagnetizm i aeronomiya* **1**, 164 (1961); *Engl. Transl.*, **1**, 161 (1961).
- ¹¹³ P. Harteck and R. R. Reeves, in collected volume *Chemical Reactions in the Lower and Upper Atmosphere*, Interscience, New York, 1961, p. 219.
- ¹¹⁴ A. D. Danilov, *Kosmicheskie issledovaniya* **1** (2), 256 (1963).
- ¹¹⁵ V. I. Krasovskii, *Iskusstvennye sputniki Zemli*, No. 17, 3 (1963).
- ¹¹⁶ H. E. Hinteregger, *J. Atm. Sci.* **19**, 351 (1962).
- ¹¹⁷ A. D. Danilov, *Kosmicheskie issledovaniya* **4** (2), (1964).
- ¹¹⁸ B. A. Mirtov, *Gazovyĭ sostav atmosfery i metody ego issledovaniya (Gas Composition of the Atmosphere and Methods of Studying It)*, M., Izd-vo AN SSSR, 1961.
- ¹¹⁹ R. C. Sagalyn and M. Smiddy, *J. Geophys. Res.* **69**, 1809 (1964).
- ¹²⁰ I. Harris and W. Priestler, *Space Research*, Vol. 3, Ed. W. Priestler, Amsterdam, 1963, p. 53.
- ¹²¹ M. A. Biondi and S. C. Brown, *Phys. Rev.* **75**, 1700 (1949).
- ¹²² M. A. Biondi and S. C. Brown, *ibid.* **76**, 1697 (1949).
- ¹²³ Holt, Richardson, Howland, and McClure, *ibid.* **77**, 239 (1950).
- ¹²⁴ M. A. Biondi and T. Holstein, *ibid.* **82**, 962 (1951).
- ¹²⁵ M. A. Biondi, *Phys. Rev.* **83**, 1078 (1951).
- ¹²⁶ D. R. Bates, *ibid.* **77**, 718 (1950).
- ¹²⁷ L. J. Varnerin, Jr., *ibid.* **84**, 563 (1951).
- ¹²⁸ J. M. Richardson and R. B. Holt, *ibid.* **81**, 153 (1951).
- ¹²⁹ K. B. Persson and S. C. Brown, *Phys. Rev.* **100**, 729 (1955).
- ¹³⁰ S. Takeda and A. A. Dougal, *Bull. Am. Phys. Soc., Ser. 2*, **4**, 113 (1959).
- ¹³¹ E. P. Bialecke and A. A. Dougal, *J. Geophys. Res.* **63**, 539 (1958).
- ¹³² M. H. Mentzoni, *J. Geophys. Res.* **68**, 4181 (1963).
- ¹³³ L. B. Loeb, *Basic Processes of Gaseous Electronics*, University of Calif. Press, Berkeley, 1955, p. 563.
- ¹³⁴ H. H. Brömer, *Z. Phys.* **158**, 133 (1960).
- ¹³⁵ E. P. Gray and D. E. Kerr, *Proceedings of the 4th International Conference on Ionization Phenomena in Gases*, Amsterdam, Vol. 1, 1960, p. 84.
- ¹³⁶ E. P. Gray and D. E. Kerr, *Annals of Physics* **17**, 276 (1962).
- ¹³⁷ C. Kenty, *Phys. Rev.* **126**, 1235 (1962).
- ¹³⁸ A. Dalgarno, *Ann. Géophys.* **17**, 16 (1961); *Russ. Transl.: UFN* **79**, 115 (1963).
- ¹³⁹ D. R. Bates and A. Dalgarno, in collected volume *Atomic and Molecular Processes*, Ed. D. R. Bates, Academic Press, New York, 1962, p. 244.
- ¹⁴⁰ M. A. Biondi, *Planetary and Space Sci.* **3**, 104 (1961).
- ¹⁴¹ M. A. Biondi, see Ref.^[113], p. 353.
- ¹⁴² M. A. Biondi, *Adv. Electronics and Electr. Phys.* **18**, 67 (1963).
- ¹⁴³ M. A. Biondi, *Ann. Géophys.* **20**, 34 (1964).
- ¹⁴⁴ M. A. Biondi, *Phys. Rev.* **93**, 650 (1954).
- ¹⁴⁵ W. A. Rogers and M. A. Biondi, *Phys. Rev.* **99**, 1657 (1955).
- ¹⁴⁶ W. A. Rogers and M. A. Biondi, *Bull. Am. Phys. Soc. Ser. 2*, **2**, 87 (1957).
- ¹⁴⁷ W. A. Rogers and M. A. Biondi, *ibid.* **4**, 113 (1959).
- ¹⁴⁸ H. N. Olsen and W. S. Huxford, *Phys. Rev.* **87**, 922 (1952).
- ¹⁴⁹ A. V. Phelps and S. C. Brown, *Phys. Rev.* **86**, 102 (1952).
- ¹⁵⁰ Kasner, Rogers, and Biondi, *Phys. Rev. Letters* **7**, 321 (1962).
- ¹⁵¹ D. E. Kerr and C. S. Leffel, *Bull. Am. Phys. Soc., Ser. 2*, **4**, 113 (1959).
- ¹⁵² J. Sayers, *Suppl. J. Atm. Terr. Phys.* **6**, 212 (1956).
- ¹⁵³ A. C. Faire and K. S. W. Champion, *Phys. Rev.* **113**, 1 (1959).
- ¹⁵⁴ Kasner, Rogers, and Biondi, *Bull. Am. Phys. Soc.* **7**, 131 (1962).
- ¹⁵⁵ W. H. Kasner and M. A. Biondi, *ibid.* **9**, 184 (1964).
- ¹⁵⁶ I. R. King, *J. Chem. Phys.* **35**, 380 (1961).
- ¹⁵⁷ Mentzoni, Montgomery, and Row, *Bull. Am. Phys. Soc.* **7**, 636 (1962).
- ¹⁵⁸ E. H. Holt, *Bull. Am. Phys. Soc.* **4**, 112 (1959).
- ¹⁵⁹ A. Dalgarno, *Trans. Am. Geophys. Union* **41**, 624 (1960).
- ¹⁶⁰ M. H. Mentzoni, *Bull. Am. Phys. Soc.* **9**, 184 (1964).
- ¹⁶¹ L. Lamb and S. C. Lin, *J. Appl. Phys.* **28**, 754 (1957).
- ¹⁶² W. Low and Y. Manheimer, 11th International Astronautical Congress (Amsterdam, 1958), Vienna,

- 1959, p. 20.
- ¹⁶³R. C. Gunton and E. C. Y. Inn, *J. Chem. Phys.* **35**, 1896 (1961).
- ¹⁶⁴Gunton, Inn, and Shaw, *Bull. Am. Phys. Soc.* **7**, 132 (1962).
- ¹⁶⁵J. P. Doering and B. H. Mahan, see Ref.^[113], pp. 327, 329.
- ¹⁶⁶J. P. Doering and B. H. Mahan, *J. Chem. Phys.* **36**, 669 (1962).
- ¹⁶⁷Syverson, Stein, Shaw, Scheibe, and Gunton, *Bull. Am. Phys. Soc.* **7**, 378 (1962).
- ¹⁶⁸Faire, Fundingsland, and Aden, *Phys. Rev.* **93**, 650 (1954).
- ¹⁶⁹C. B. Kretschmer and H. L. Petersen, *J. Appl. Phys.* **34**, 3209 (1963).
- ¹⁷⁰P. F. Knewstubb and A. W. Tickner, *J. Chem. Phys.* **37**, 2941 (1962).
- ¹⁷¹R. K. Curran, *J. Chem. Phys.* **38**, 2974 (1963).
- ¹⁷²E. A. Lytle and D. M. Hunten, *Can. J. Phys.* **40**, 1370 (1962).
- ¹⁷³D. M. Hunten, *Planetary and Space Sci.* **10**, 37 (1963).
- ¹⁷⁴J. W. Chamberlain and C. Sagan, *Planetary and Space Sci.* **2**, 157 (1960).
- ¹⁷⁵S. C. Lin and J. D. Teare, *Phys. Fluids* **6**, 355 (1963); *Russ. Transl., Voprosy raketnoĭ tekhniki*, No. 5, 16 (1964).
- ¹⁷⁶D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.* **23**, 1353 (1955).
- ¹⁷⁷D. P. Stevenson and D. O. Schissler, *ibid.* **24**, 924 (1956).
- ¹⁷⁸D. P. Stevenson and D. O. Schissler, *ibid.* **29**, 292 (1958).
- ¹⁷⁹C. F. Giese and W. B. Maier, *J. Chem. Phys.* **35**, 1913 (1961).
- ¹⁸⁰C. F. Giese and W. B. Maier, *ibid.* **39**, 739 (1963).
- ¹⁸¹Lavrovskaya, Markin, and Tal'roze, *Kinetika i kataliz* **2**, 21 (1961).
- ¹⁸²R. F. Potter, *J. Chem. Phys.* **23**, 2462 (1955).
- ¹⁸³P. H. D. Dickinson and J. Sayers, *Proc. Phys. Soc.* **76**, 137 (1960).
- ¹⁸⁴S. Ya. Pshezhetskiĭ and M. T. Dmitriev, *DAN SSSR* **103**, 647 (1950).
- ¹⁸⁵V. L. Tal'roze and E. L. Frankevich, *Zhur. Fiz. Khim.* **36**, 2709 (1960).
- ¹⁸⁶Tal'roze, Markin, and Larin, *Disc. Faraday Soc.* **33**, 257 (1962).
- ¹⁸⁷G. F. O. Langstroth and J. B. Hasted, *ibid.* **33**, 298 (1962).
- ¹⁸⁸Fite, Rutherford, Snow, and Van Lint, *ibid.* **33**, 264 (1962).
- ¹⁸⁹A. D. Danilov and S. P. Yatsenko, *Kosmicheskie issledovaniya* **2** (2), 276 (1964).
- ¹⁹⁰Stebbins, Smith, and Ehrhardt, *J. Chem. Phys.* **39**, 968 (1963).
- ¹⁹¹Galli, Giardini-Guidoni, and Volpi, *ibid.* **39**, 518 (1963).
- ¹⁹²J. F. Paulson, *Ann. Géophys.* **20**, 75 (1964).
- ¹⁹³W. L. Fite, *Ann. Géophys.* **20**, 47 (1964).
- ¹⁹⁴J. Sayers and D. Smith, 3rd International Conference on Physics of Electronic and Atomic Collisions, London, 1963.

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