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Ionospheric Composition and Reactions

Our present knowledge of what ions are in the ionosphere, and why, is summarized.

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The ionosphere is the electrically charged part of the earth's atmosphere. It extends from the surface of the earth to the boundary between the earth's magnetic field and the interplanetary medium. I confine myself here to a description of the properties of the ionosphere from about 60 to about 1000 kilometers above the earth's surface. My objective is to outline what we know about the constituents of the ionosphere and the processes by which the ions are created, transformed, transported, and destroyed, and to discuss the many problems which have been created and in some cases resolved by measurements made recently in space vehicles and in terrestrial atomic physics laboratories. In this discussion I restrict myself to the mid-latitude ionosphere. I avoid thereby the great complexities associated with equatorial and polar regions.

As almost everyone knows, the ionosphere was discovered as a result of the high reflectivity that the free electrons in the upper atmosphere exhibit for radio waves. The fact that electrons become almost perfectly reflecting below a critical frequency set by the electron density has enabled us to probe, from the surface of the earth, the electron density as a function of altitude. This we do by varying the frequency of our transmitters and measuring the time between the transmission and reception of pulsed waves of a given frequency. With this method of sounding we can reach only as high as the altitude of maximum electron density, which lies between 200 and 400 kilometers. To probe above that maximum we must place the sounder in a satellite and let it orbit at an altitude above the maximum so that it can send the probing radiation downward.

In the early years some remarkable progress was made in accounting for the properties of the ionosphere from a knowledge of electron density alone. However, it was not until sounding rockets and satellites began to deliver information concerning the ionic and neutral composition of the atmosphere and the nature of the sun's ultraviolet spectrum that the full complexity of the problems presented by the ionosphere could be appreciated. So many kinds of ions were present, and so many kinds of interactions were possible, that the help of the laboratory in measuring rates of reactions between ions, electrons, and molecules was needed to identify the dominant processes. Unfortunately these measurements raised some serious new problems in the course of solving some old ones. Today we are still looking for missing elements of physics and chemistry to remove major discrepancies between observation and our understanding of what should be going on in the earth's ionosphere.

Creation of the Ionosphere and Its Composition

The ionosphere is created mainly by the ultraviolet and x-radiation from the sun—radiation of wavelength shorter than 1027 angstroms. This radiation frees electrons from atoms and molecules of the upper atmosphere. Some of these photoelectrons, in turn, have sufficient energy to cause further ionization before they reach thermal equilibrium. The thermalized electrons constitute the bulk of the ionospheric electron gas. They endure as free electrons until they encounter positive ions with which they can recombine. Usually the ion is diatomic, and the process of recombination normally causes it to dissociate into two fast atoms. In this way the absorption of ultraviolet solar energy eventually heats the neutral gas. The temperature of the atmosphere can, consequently, be as high as 2000°K above 200 kilometers.

The atmosphere in which this absorption of energetic solar radiation occurs differs rather strikingly from air at sea level. This is partly because of the absorption of ultraviolet radiation of wavelength greater than 1100 angstroms. At altitudes above 90 kilometers this radiation is expended mainly in dissociating oxygen molecules. A little higher, the turbulent mixing of the atmosphere ceases and the gases diffuse freely in the gravitational field. The density of the lighter gases falls off more slowly than that of the heavy ones. At 120 kilometers atomic oxygen dominates molecular oxygen. Near 200 kilometers it is even more abundant than molecular nitrogen. Finally, above about 1000 kilometers, atomic hydrogen and helium—very minor constituents lower down—are the major constituents (molecular nitrogen, which is very stable, is not appreciably dissociated by ultraviolet radiation).

The distribution of gases during a typical day at middle latitudes is shown in Fig. 1. The densities of nitrogen

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and molecular oxygen are measured by mass spectrometers or optical spectrometers carried aloft on sounding rockets and satellites (*1*). The densities of atomic oxygen, helium, and hydrogen are difficult to measure. Various measurements—some made with similar instruments—have given densities for atomic oxygen that spread over a wide range, some of them falling below the values plotted in Fig. 1 by a full order of magnitude. The variation may be real; it may be instrumental. No creditable densities for atomic oxygen have been obtained below 120 kilometers. The hydrogen densities are deduced from optical observations of scattered—or diffused—solar hydrogen radiation (*2*). Recent mass-spectrometric measurements have given densities that exceed these by a factor of 4 (*3*). Uncertainties such as these lead us, in many cases, to consider that observation and theory are in agreement if the results differ by no more than a factor of 2.

The intensity of the ultraviolet spectrum of the sun has been measured with care and precision by groups at the Naval Research Laboratory, the Air Force Cambridge Research Laboratory, and the Goddard Space Flight Center (*4*). Cross sections for ionization of atmospheric gases by ultraviolet radiation and fast electrons have been measured in the laboratory or calculated by theoreticians (*5*). From the atmospheric density distribution, the solar flux, and these cross sections we calculate the rate at which N_2, O_2, oxygen, helium, and hydrogen are ionized as functions of altitude for any specified direction of the sun. As the ultraviolet radiation penetrates the atmosphere the increasing density causes the rate of ionization to increase at first. However, as the radiation is absorbed the rate passes through a maximum and finally decreases. In Fig. 2 the rates of production of N_2^+, O_2^+, and O^+ are plotted for the atmosphere depicted in Fig. 1 (right) when the sun is 60 degrees from the zenith. The ionization of nitrogen requires radiation of wavelength shorter than 796 angstroms; ionization of atomic oxygen and of molecular oxygen requires wavelengths shorter than 911 and 1027 angstroms, respectively. It is the strong solar hydrogen Lyman-β radiation which, penetrating to the 110-kilometer region, causes the ionization of O_2 to dominate at that altitude. Below 100 kilometers, weakly absorbed x-rays from the solar corona penetrate the atmosphere and ionize nitrogen (predominantly). The production rates shown in Fig. 2 include the contribution not only of photons but of fast photoelectrons as well.

Table 1. Dissociative recombination coefficients.

Ion	α(300°K) (10^{-7} cm^3 sec^{-1})	Temperature dependence
N_2^+	2.9 ± 0.3	$T_e^{-1/3}$ ($T_+ = T_{gas} = 300°K$) $T^{-1/50}$
NO^+	5 ± 1	$T^{-(1.2 \pm 0.3)}$
O_2^+	2.2 ± 0.5	$T^{-0.5}$

$\left.\right\}$ $T_e = T_+ = T_{gas}$

The variation of the ionospheric electron density bears little resemblance to the production-rate curves shown in Fig. 2. The density rises sharply from a ledge between 75 and 80 kilometers to a second ledge near 110 kilometers, where it reaches 10^5 electrons per cubic centimeter. Sometimes there is another plateau between 150 and 200 kilometers, but despite the decrease in production of electrons above 160 kilometers, the density goes on rising, to a maximum between 220 and 250 kilometers. Above that altitude it decreases steadily, falling by a factor of 0.37 every 100 kilometers up to about 500

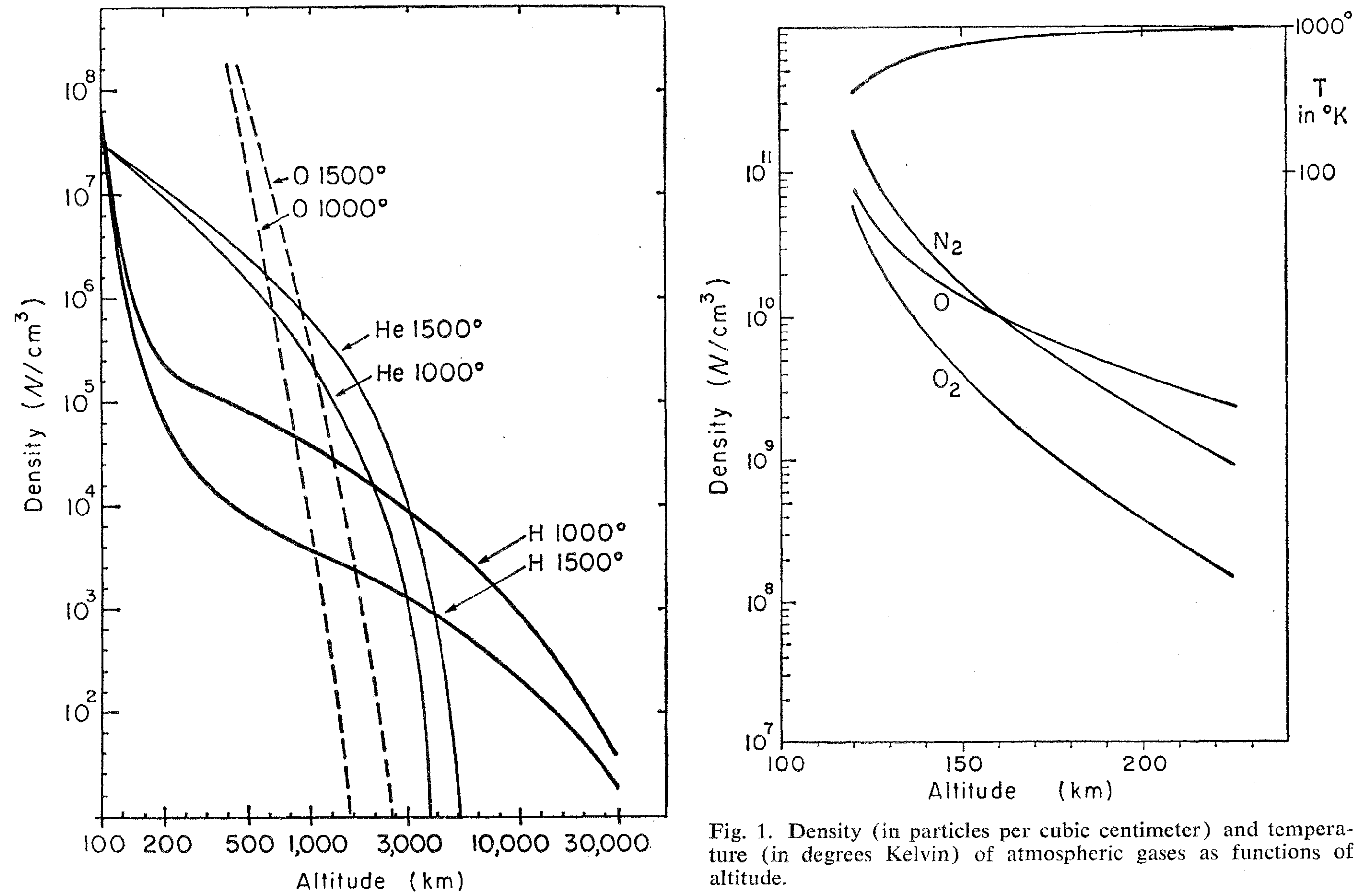

Fig. 1. Density (in particles per cubic centimeter) and temperature (in degrees Kelvin) of atmospheric gases as functions of altitude.

kilometers, where the decrease becomes much more gradual. The part of the ionosphere below 90 kilometers is called the *D* region. The part from 90 to about 120 kilometers, where ionization by x-rays and ionization of O_2 by Lyman-β radiation predominates, is called the *E* region. The part where the principal ionization occurs—from 120 to 180 kilometers—is called the *F1* region. The part above that, where diffusion begins to control the distribution, is called the *F2* region.

The species of positive ions which accompany the electrons change with altitude. In recent years many experimenters have sampled the ion densities by means of mass spectrometers placed aboard sounding rockets and satellites (*6–9*). Figure 3 is a composite of daytime measurements representative of conditions during the recent minimum of solar activity. It is rather shocking to note that this composite must rely on a single experiment—that of Holmes Johnson, and Young (*6*)—for the region from 120 to 250 kilometers. For N_2^+, data are also available from the behavior of sunlight scattered by these ions and observable from rockets (*10*). There are so many interesting experiments to be performed and so few experimenters in this field that routine and systematic repetition of an experiment is rarely the practice. Since the sun presents phenomena that vary enormously, and the variation has an 11-year period, there is often a long wait between the time an experimental result is obtained and the time of its confirmation. Rocket experimentation did not get well under way until 1956, so in most cases we are still waiting for the first repetition of a space experiment.

With modern techniques, obtaining data on ion densities—at least for the more abundant ions—above 120 kilometers presents no obvious serious problem. At low altitudes, however, the high speed of the vehicle in a medium of relatively high density sends gas through the orifices of the mass spectrometer at a high flow rate. This necessitates the use of pumps—usually cryogenic—on board the rocket. Furthermore, no one has yet solved the problem of sampling negative ion densities, because the rocket itself builds up a negative charge in flight and repels the ions which we wish to collect.

Let us consider first the *E* region and the *F* region up to 300 kilometers. At these altitudes the properties of the ionosphere which stand out in a comparison of the actual ion densities with the rates of ion production are the following.

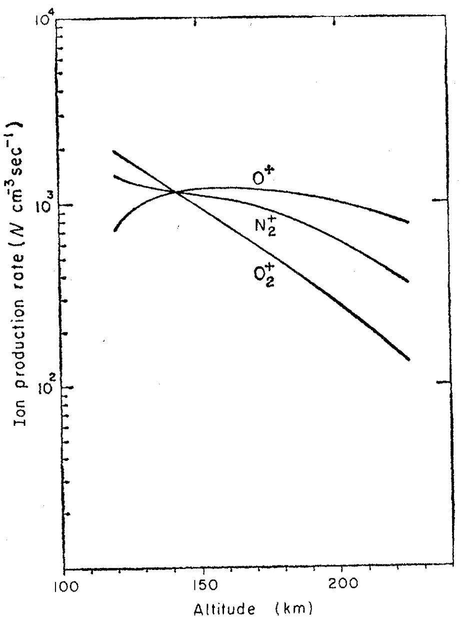

Fig. 2. Rate of ionization (in ions per cubic centimeter per second) of N_2, O_2, and O at altitudes between 120 and 220 kilometers by solar ultraviolet radiation and photoelectrons. The sun is 60 degrees from the zenith and the atmosphere is that of Fig. 1, right, referred to in the text as model 1.

1) The increasing predominance of O^+ with increasing altitude. To a certain extent this is reflected in the production rates too, as a consequence of atomic oxygen's becoming the major atmospheric constituent. However, the O^+ density and the electron density as well reach a maximum near 250 kilometers, some 100 kilometers above the region of greatest O^+ production.

2) The minor role of N_2^+, despite the fact that it is produced in greater abundance than any other species.

3) The appearance of the nitric oxide ion as a major species, despite the fact that nitric oxide itself is a minor atmospheric constituent.

Ionic Reactions

To understand these anomalies we must understand something about the history of ions after they are created. Eventually, of course, a positive ion will collide with an electron and be neutralized. The simplest recombination process to visualize is the radiative capture of an electron, in which an electron radiates a photon as it gets rid of its kinetic energy and drops into a bound state of the neutral atom or molecule. This process is, however, a rather unlikely one, its probability per collision being governed by the ratio of the time the electron spends near the ion, as it passes by, to the characteristic lifetime of an electron that is undergoing an electronic transition. Only about one collision in 10^5 would be expected to lead to recombination. Much more effective is dissociative recombination, in which an electron encounters a molecular ion and forms an unstable neutral molecule. Only a very short time is required for the atoms in this complex to move apart far enough to render unlikely the restoration of the bound-molecular-ion, free-electron state. Thus this type of recombination can be very efficient. It can be described schematically as follows:

$$XY^+ + e \rightarrow X + Y + \text{kinetic energy} \quad (1)$$

The rate at which such a reaction occurs determines the rate of loss of electrons. Thus

$$\frac{dn_e}{dt} = \sum_i q_i - \sum_i \alpha_i n_e n_i^+ \quad (2)$$

where q_i is the production rate of the *i*th kind of ion, n_e is the electron density, n_i^+ is the ion density, α_i is the so-called recombination coefficient, and t is the time. The dissociative recombination coefficients are about the best-measured rate coefficients available for ionospheric analysis. Much of the measurement work has been done in the laboratories of the University of Pittsburgh and in the Westinghouse Research Laboratories, under the leadership of M. A. Biondi (*11*). For ions such as N_2^+, O_2^+, and NO^+, this coefficient, at 300°K, is of the order of a few times 10^{-7} cm^3 sec^{-1} (see Table 1) as compared to something like 10^{-12} cm^3 sec^{-1} for radiative recombination of O^+ and electrons. It is, therefore, not surprising that, where O^+ is the ion most abundantly created, the plasma density should be relatively high, even as compared to the value at lower altitudes, where the total production is larger but the ions created are predominantly diatomic. This is not the whole story, however. Since at 220 kilometers the production rate $q(O^+)$ is about 10^3 ions per cubic centimeter per second and the electron density is about 5×10^5 electrons per cubic centimeter, the apparent value of α is 4×10^{-9} cm^3 sec^{-1}—a value much too large for radiative recombination of O^+ and too small for dissociative recombination. The reason for this behavior seemed apparent long ago (*12*):

the O^+ ions are apparently being converted to diatomic ions in collisions with oxygen and nitrogen. Such reactions are called ion-molecule reactions either of charge exchange, such as the reaction which I call reaction *b*

$$(b) \qquad O^+ + O_2 \rightarrow O_2^+ + O \qquad k_b = 2 \times 10^{-11}\ \text{cm}^3\ \text{sec}^{-1}, \qquad (3)$$

or of ion-atom interchange, such as the reaction I designate reaction *c*

$$(c) \qquad O^+ + N_2 \rightarrow NO^+ + N \qquad k_c = 1 \times 10^{-12}\ \text{cm}^3\ \text{sec}^{-1}. \qquad (4)$$

The rate constants k_b and k_c given above determine the rate at which the original ions are converted to the product ions in collisions with a species whose density is $n(X)$. When no other processes intervene, this rate is governed by the equation of continuity

$$\frac{dn_i^+}{dt} = q_i(n_i^+) - kn_i^+n(X) \qquad (5)$$

(Note that the dimensions of a rate constant are those of volume per unit time, since the rate constant converts the product of *two* number densities into a rate per unit volume.) For years laboratory physicists have busied themselves measuring the rates of these reactions, with results that were widely scattered. During the past few years a group under the leadership of E. Ferguson at the Environmental Science Services Administration (ESSA), in Boulder, Colorado, has developed a powerful technique for measuring rates of reactions such as these, and there is growing confidence that the measurements are now accurate certainly to within a factor of 2 (*13*). Even the temperature dependences of the two O^+ reactions have been measured (*14*).

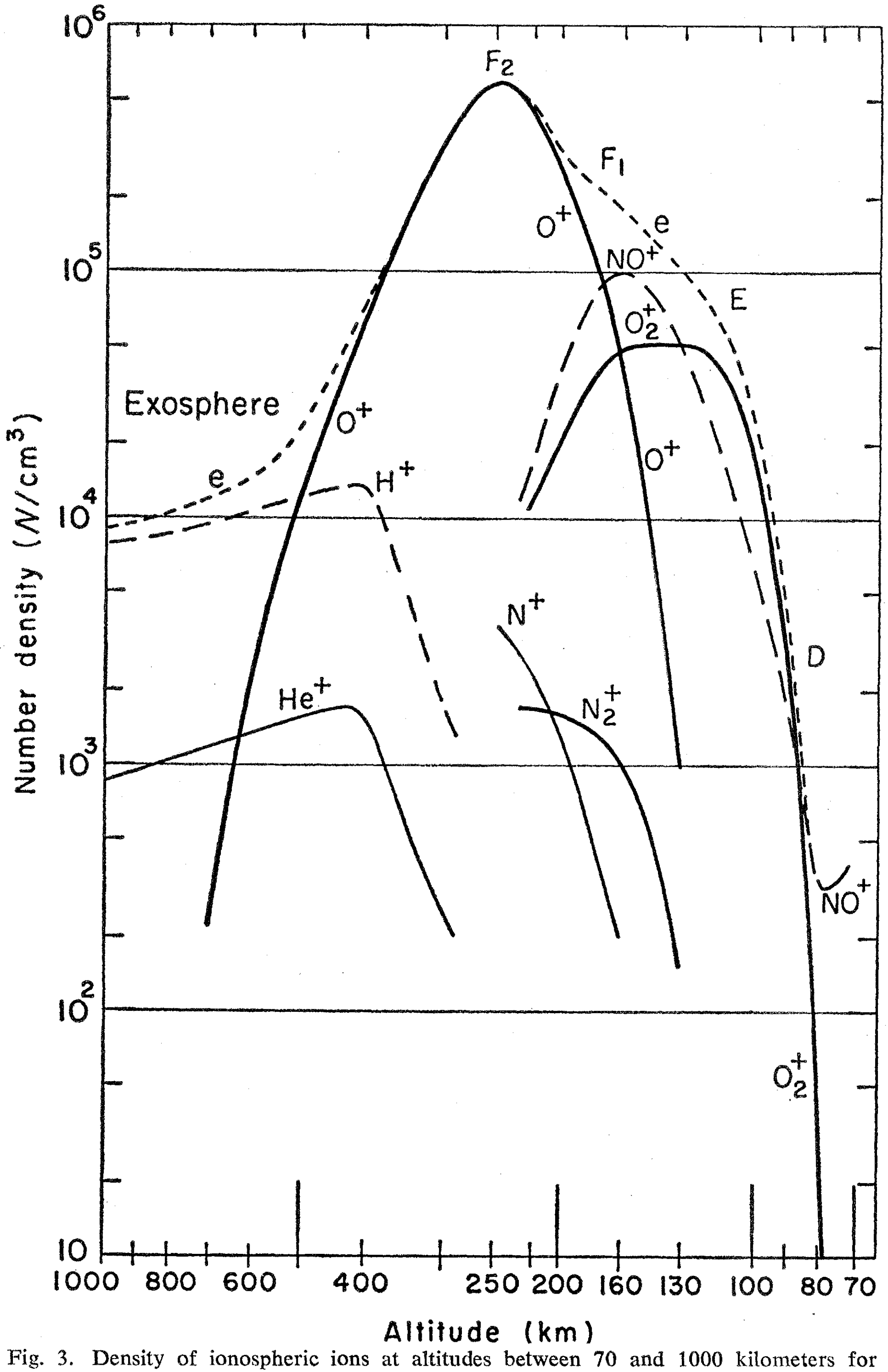

Fig. 3. Density of ionospheric ions at altitudes between 70 and 1000 kilometers for the atmosphere of Fig. 1, right (model 1), in the daytime.

There is a long list of ion-molecule reactions that might possibly intervene between the creation of an atmospheric ion and the neutralization of that ion or its progeny. Thanks to the laboratory measurements of rate constants we can now identify a handful as truly important. In addition to reactions *c* and *b* involving O^+ there are two others which rapidly convert N_2^+ to O_2^+ or NO^+. These reactions, *a* and *d*, and their rates are as follows:

$$(a) \qquad N_2^+ + O_2 \rightarrow O_2^+ + N_2 \qquad k_a = 1\text{–}2 \times 10^{-10}\ \text{cm}^3\ \text{sec}^{-1} \qquad (6)$$

$$(d) \qquad N_2^+ + O \rightarrow NO^+ + N \qquad k_d = 2.5 \times 10^{-10}\ \text{cm}^3\ \text{sec}^{-1} \qquad (7)$$

These reactions are responsible for the rapid depletion of N_2^+ and for its low steady-state density. Reactions *c* and *d* together account for the great abundance of NO^+. Much of the O^+ and N_2^+ created is converted to NO^+. Because of the low ionization potential of NO, its ion cannot react with N_2, O_2, or O but must wait for an electron to come along and neutralize it.

Comparison of Theory and Experiment: E and F1 Regions

In the daytime the rate of ionization and the rates of the four reactions (*a–d*) are so high, in comparison with the rates at which ion densities change because of the changing zenith angle of the sun or because of diffusive flow, that a steady state prevails. The O^+ density at a given altitude is thus determined by the rate at which O^+ is created relative to the rate at which it disappears in channels *b* and *c*. Similarly, the rates of creation of the diatomic ions by photoionization and by ion-molecule reactions balance the rates of loss in other reactions and in recombination. The total production rate must also balance the recombination rate, and the positive-ion density must equal the electron density. The result of calculating the transfer rates, the loss rates, and the densities (*15*) can be represented in a flow diagram of the kind shown in Fig. 4. The four circles at the vertices of Fig. 4 represent the ion reservoirs, and the ion densities are noted inside the circles. The arrows directed in toward the circle and the numbers beside the arrows represent the rates of production by solar flux and by ion-molecule reactions *a*, *b*, *c*, and *d*. The arrows directed away from the circle represent losses either by reactions or by recombination. Model 1 is the model, described above, for the earth's atmosphere. Model 2 is another model, poorer in atomic oxygen by a factor of 4 and poorer in O_2 but richer in N_2. It is based on mass-spectrometric measurements.

The great importance of channel *d*, which converts N_2+ to NO+ by means of atomic oxygen, is apparent. This reaction was once thought by some to be, in effect, endothermic, although there were others who considered the solution of the ionospheric problem to be impossible unless the reaction were not only exothermic but fast (*16*). The debate was settled in the laboratory at Boulder when the reaction was found to be very fast indeed.

In Figs. 5 and 6 the ion densities predicted by these calculations are compared with the measured values. Whether the agreement is poor or good is almost a matter of personal opinion. I do not consider it to be really satisfactory. While uncertainties of measurement can easily force toleration of a factor-of-2 disagreement in absolute values, the calculated *relative* variations in altitude for single ionic species and for the electron density should resemble the experimental values more closely than they do. The calculated O+ density increases much too slowly between 130 and 220 kilometers, even in model 1. There is something obviously wrong about the behavior of NO+ above 160 kilometers. In model 1 the N_2+ density is intolerably low except near 130 kilometers. In model 2 the N_2+ density is satisfactory, but above 130 kilometers the O_2+ density is too low. The agreement between calculated and observed O_2+ and NO+ densities is improved near 130 kilometers—and in fact becomes excellent for model 2—if we take into account the transformation of O_2+ into NO+ by charge exchange with NO. The laboratory rate is 3×10^{-10} cm^3 sec^{-1}, but the NO density must be taken to be 10^7 molecules per cubic centimeter. This is actually the measured value (*17*), although many ionosphericists are reluctant to accept it because they feel it creates difficulties in the *D* region, as we shall see.

The predicted NO+ density holds up at high altitude because, in the calculation, I have used the strong dependence on electron temperature of its recombination coefficient (Table 1). Above 200 kilometers the electron temperature rises to more than 2000°K. There is evidence, from the laboratory studies of recombination of N_2+, that the recombination coefficient increases with vibrational excitation of the ion (*11*). Perhaps the NO+ formed by ion-molecule reactions is highly excited vibrationally. If its recombination coefficient decreased only to 1.5×10^{-7} cm^3 sec^{-1} at 200 kilometers, the calculated NO+ profile would follow the observed trend very well. However, this would reduce the predicted electron density appreciably, and the calculated value would be too low by a factor of 2 at 220 kilometers. Most of the disagreement between calculated and observed ion densities would disappear if only the reaction rate coefficients would de-

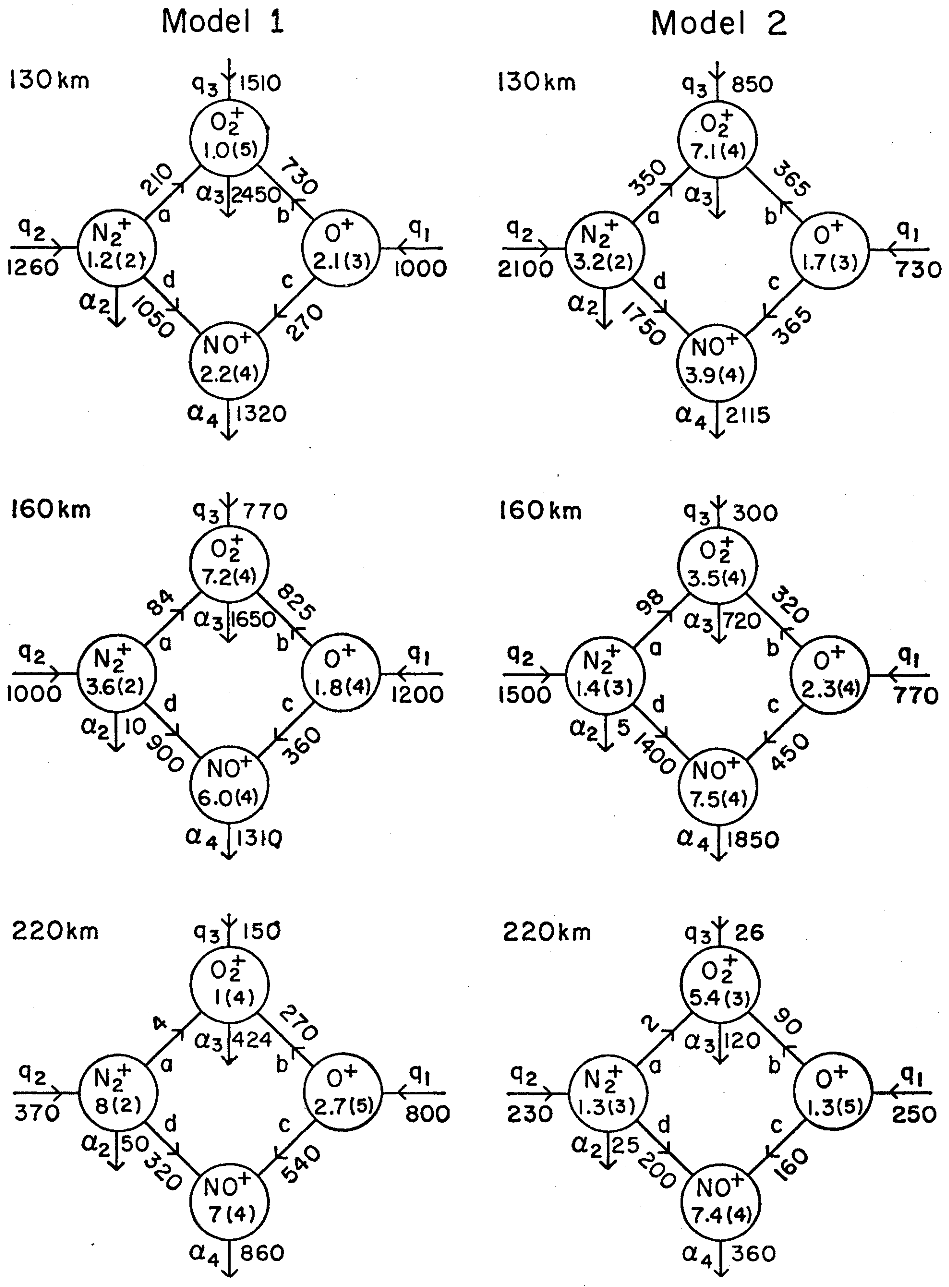

Fig. 4. Flow diagrams showing rates of creation, transfer, and removal of species N_2^+, O_2^+, O^+, and NO^+, together with their densities at various altitudes (see text).

crease with temperature. If we assume that they do not, we must look elsewhere for solutions to our problems.

Because of the low values calculated for N_2^+ the suspicion is strong that either the N_2 densities in model 1 are too low or the ionizing source is stronger than had been assumed. It must be realized that nitrogen and atomic oxygen compete for the same ionizing photons, and that increasing the density of one will reduce the ionization rate of the other. Thus, improving the N_2^+ situation in this way creates a more serious O^+ deficiency—particularly since it also increases the drain of O^+ through channel *c*. If the ionizing flux is increased, a problem will develop with O_2^+ in model 1. Its density will be excessive. With the charge transfer to NO included in the budget, the O_2^+ density now follows the measured value closely. Thus, changing a single parameter solves some of our problems at the price of creating some new ones.

The cross sections used to calculate the rates of O^+ production are not measured. They are theoretical estimates and may be much too low. If that is the case, the situation with O^+ may be saved by arranging an upward shift of 20 or 30 kilometers in the altitude of maximum O^+ production. It would be much better were $q(O^+)$ higher by a factor of 2 at 200 kilometers and lower by a factor of 2 at 130 kilometers (*18*). It must be remembered that changing cross sections without changing the solar flux will not change the total number of ions created; it will only change the altitude at which the ions are manufactured. With the help of secondary ionization all of the solar energy available is already being used up in producing ions. The problem is really one of integrated rates of creation and loss, and integrated densities. We need to move the production region higher, to altitudes where, because of the lower densities of neutral particles, loss rates, particularly for O^+ and N_2^+, are lower. This we must do without increasing the oxygen density. Increasing it has the effect of keeping the density of N_2^+ down, because of the importance of channel *d*.

The F2 Maximum

The increase with altitude in the densities of O^+ and of electrons will not continue indefinitely. The ions are, after all, diffusing, and the continuity equation does contain transport terms such as

$$-n(X^+)v_D \qquad (8)$$

where v_D is a diffusion velocity. Since the diffusion coefficient increases inversely as the atmospheric density, and the chemical rate of loss of O^+ to N_2 in channel *c* decreases with the nitrogen density, diffusion will eventually compete successfully with chemical transformation of O^+ to NO^+. Near the altitude where this happens, the O^+ density will be a maximum. Above that altitude the distribution will be increasingly diffusion-controlled and the density of O^+ will decrease with altitude (*19*). The electron-density maximum is called the *F2* maximum. The mean-square distance an ion diffuses in a time *t* is approximately $(2\ Dt)^{\frac{1}{2}}$ (here *D* is the diffusion coefficient), and the lifetime against loss of O^+ to N_2 is $[k_c n(N_2)]^{-1}$. The *F2* maximum will occur, then, where

$$k_c n(N_2) = 2D/H^2 \qquad (9)$$

where *H* is the nitrogen scale height. This is so because, from that altitude, an ion can diffuse upward into a region where the density of nitrogen has decreased by e^{-1} before the nitrogen can react. Since the diffusion coefficient varies in the following way

$$D = 10^{17}\sqrt{T}/n(O), \qquad (10)$$

this condition puts the *F2* maximum where the product of nitrogen and oxygen densities is 20×10^{17} cm^{-6}. This occurs at 230 kilometers in model 1, and that is where the *F2* maximum did occur on the day the ion data were obtained. At the peak the O^+ density should be given by

$$n(O^+) = q(O^+)/k_c n(N_2) \qquad (11)$$

or 4×10^5. This is a trifle low relative to the measured density, as are all O^+ densities computed in the *F* region. Certainly at this altitude the discrepancy is not serious. If k_c were slightly lower the agreement would be perfect.

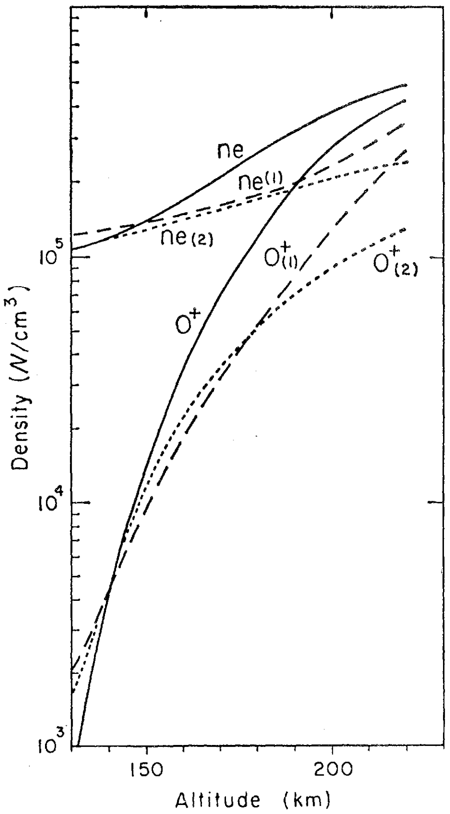

Fig. 5. Calculated and observed daytime densities of ionospheric ions (O^+ and electrons). (Dashed line) Calculated densities for the atmosphere of model 1; (dotted line) calculated densities for the atmosphere of model 2; (solid lines) observed densities.

Exospheric Ions

Eventually helium and hydrogen prevail over oxygen as major components of the atmosphere. Actual data on helium densities have only recently become available (*20*). Helium is an enigma (*21*). It is produced inside the earth as a product of radioactive decay processes. The amount in the atmosphere is far lower than one would expect in view of the strength of the source and the billions of years it has been active. This is because helium, although light, cannot escape by evaporation at high altitude at a rate anything like the rate (2×10^6 ions per square centimeter per second) at which it is created. The rate of escape by evaporation is too small by an order of magnitude to account for the low residual density. On the other hand, helium atoms are ionized in the upper atmosphere at about the same rate at which they are produced in the earth. If each ion could be transformed into a fast atom it could escape and the loss rate would be high enough to balance the production rate. It has been proposed (*22*) that the reaction of He^+ with O_2 which produces He, O, and O^+ plus 5.9 electron volts of excess energy might pass through an intermediate stage involving the complex HeO^+ ion, so that an important fraction of the 5.9 electron volts might be taken away by helium atoms. The helium atoms would then be fast enough to escape. The rate of the reaction has been measured and is very high. Unfortunately, the rate of the reaction of He+ with N_2, which has also been measured recently (*13*), is found to be as high as the rate of reaction with O_2.

Nitrogen is much more abundant than oxygen, particularly near 500 kilometers, where the fast helium atoms can escape before they thermalize. And the reaction with nitrogen does not release much energy for the helium atom to carry off, so we are still left with the problem of accounting for the apparently high rate of helium escape from earth.

Another problem created by the strong interaction of helium ions with nitrogen (with a rate constant of 1 to 3×10^{-9} cm^3 sec^{-1}) is that the interaction depletes the He+ population rapidly in the ionosphere. The only direct, mass-spectrometric observations of helium ions that have been made were made during the recent period of reduced solar activity (1963–1966), when the temperature in the upper atmosphere was relatively low (1000°K and lower) (*7, 23*). Low temperatures mean a relatively rapid drop in helium density with altitude. They also, paradoxically, mean relatively large hydrogen densities. This is because important amounts of hydrogen can escape by a kind of thermal evaporation from the atmosphere. Since the escape rate increases with temperature, the hydrogen content of the upper atmosphere decreases with increasing temperature. During solar minimum the realm of hydrogen supremacy spreads down into the atmosphere, and this hydrogen buildup is reflected in the ionosphere, where O+ eventually gives way to H+, and He+ remains a minor ion. During the last solar maximum there was indirect evidence, from the changing slope of electron density with altitude, that there was a clear-cut He+ belt between the O+ and H+ zones. At that time the observed He+ densities were higher by almost three orders of magnitude than they should have been if we have used correct values for helium densities, solar flux, and ionization cross sections in our calculations and if the loss of He+ to N_2 is as rapid as the laboratory measurements indicate. If there is no mistake in these assumptions we are presumably ignorant of some important facet of the physics of He+. Thus there is a twofold helium problem—the escape problem and the ion density problem. Both of these are aggravated if not generated by the very large cross section obtained in the laboratory for the interaction of helium ions and nitrogen.

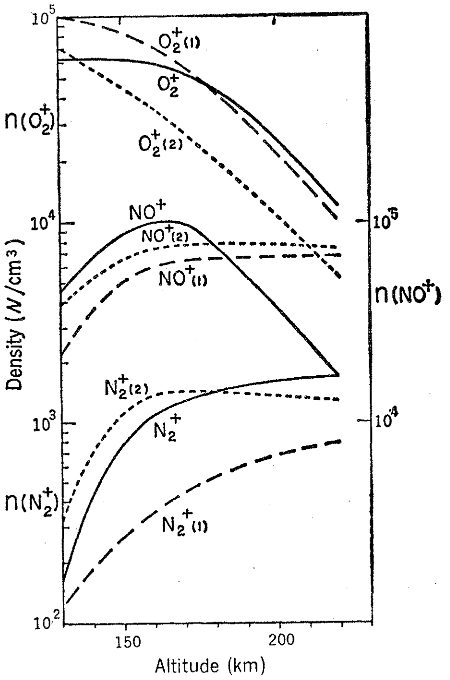

Fig. 6. Calculated and observed daytime densities of ionospheric ions O_2^+, NO^+, and N_2^+. (Dashed line) Calculated densities for the atmosphere of model 1; (dotted line) calculated densities for the atmosphere of model 2; (solid lines) observed densities.

Somewhere I should insert, in the course of these excursions between the laboratory and the ionosphere, a standard caveat. There is always the possibility that the ions, atoms, and molecules in the ionosphere and their counterparts in the laboratory are distributed over entirely different sets of electronic and vibrational states. The cross sections may depend sensitively on these states, and our conclusions correspondingly may be invalidated.

The H+ densities shown in Fig. 3 are representative of those being obtained these days (*24*). They are a bit too high to be understandable in terms of the atmosphere as we thought we understood it. Until recently, when mass spectrometers aboard satellites began to measure hydrogen densities, we had obtained all our information concerning hydrogen in the earth's atmosphere from optical observations. These involved studying the effect of the hydrogen in the earth's atmosphere on bright radiation emitted in the ultraviolet by hydrogen atoms on the sun (*2*).

For the most part that radiation is the so-called Lyman-α radiation emitted by a hydrogen atom when its electron drops from the second to the first Bohr orbit. The optical observations are difficult, and their implications are not often clear-cut; as a whole they indicated that, at 100 kilometers, there were about 3×10^7 atoms per cubic centimeter; that the density dropped rapidly at first and then slowly; and that at 500 kilometers there were about 1.5×10^5 atoms per cubic centimeter if the temperature was 1000°K (*2*). They also indicated a strong variation in density with temperature, in the sense appropriate to an escaping gas. The density apparently increases at night (at low temperature) and also is much higher during solar minimum than during solar maximum. At temperature of 700°K, the indicated density at 500 kilometers was 1.5×10^6 atoms per cubic centimeter. Some of these measurements definitely put upper limits to the hydrogen content of the atmosphere. The values given here cannot be too low by as much as 100 percent. Now mass spectrometers have detected hydrogen and have registered 2.5×10^6 hydrogen atoms per cubic centimeter at 500 kilometers for 800°K and 5×10^5 per cubic centimeter for 900°K, five and two times higher, respectively, than the densities implied by the Lyman-α observations. These measurements are apparently supported by samplings of the ionic H+ densities, which also seem to indicate rather high hydrogen abundances.

To deduce neutral hydrogen densities from measured hydrogen ion densities, it is necessary to employ the following argument (*25*). Oxygen and hydrogen have ionization potentials that differ by only 0.019 volt. Thus the charge exchange process

$$H^+ + O \leftrightarrows O^+ + H \qquad (12)$$

can proceed in either direction down to very low energy. The charge-transfer cross reaction increases rapidly as the energy of the reactants approaches zero if there is true energy resonance, as is the case for H+ and H. If this is true also for an accidentally resonant process such as reaction 12 at energies that are as small as the kinetic energies of the particles in the upper atmosphere, reaction 12 will be fast in both directions as compared to diffusion times and the H+ and O+ will be in chemical equilibrium. Furthermore, if the reaction remains truly reversible and if we take account of statistical weights, this means that we should have

$$8n(H^+)n(O) = 9n(O^+)n(H) \qquad (13)$$

The cross sections have been measured at energies down to 1 electron volt and have been found to be increasing steadily with decreasing energy (*23*). Whether they are still large at thermal energies remains to be determined. If we assume that they retain a full resonant character at thermal energies we have

$$n(\mathrm{H}) = \frac{8}{9}\, n(\mathrm{O}) \frac{n(\mathrm{H}^+)}{n(\mathrm{O}^+)} \qquad (14)$$

below the region of diffusive control. The measurements plotted in Fig. 3 were made at night in 1964 when the exospheric temperature was 700°K. The oxygen density at 350 kilometers was probably between 10^7 and 10^8 atoms per cubic centimeter. The ratio of H^+ to O^+ was 0.1, so the inferred hydrogen density was about 4×10^6 atoms per cubic centimeter. Now the optical model for 700°K calls for only 1.5×10^6 hydrogen atoms per cubic centimeter, so there is a discrepancy. It is peculiar, however, that whereas the density of hydrogen should have decreased with altitude as $e^{-h/H}$ where H, the scale height, should have been 590 kilometers, the measured ratio of H^+ to O^+ has a scale height of −31 kilometers; this measurement, in combination with the scale height for oxygen of 37 kilometers, calls for a scale height of hydrogen of −200 kilometers if the hydrogen is indeed following Eq. 14. In my opinion the assumption of a simple equilibrium, given by Eq. 14, is called into question by these results. In place of the factor 8/9, a ratio of temperature-dependent rate constants may be required. The failure of Eq. 14 to give a reasonable altitude variation for hydrogen even near 350 kilometers indicates trouble. Perhaps for ionospheric temperature Bates is right and polarizing effects destroy the resonance. The reactions may be slow, and the rates in opposite directions different.

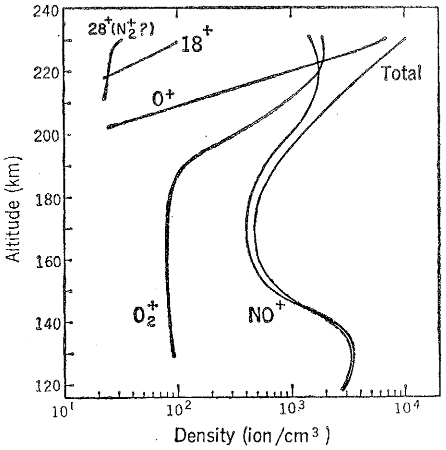

Fig. 7. Densities of atmospheric ions observed at night at White Sands, New Mexico, on 1 August 1963.

The D Region and the Lower E Region

In the lower part of the daytime *E* region ionization is primarily by solar x-rays. Atomic oxygen is a minor constituent, and the primary ions are N_2^+ and O_2^+. The N_2^+ is quickly coverted to O_2^+ by charge transfer. The O_2^+ densities which have been measured between 75 and 85 kilometers are so high that they imply production rates far above the expected level (*27*). This is true even if dissociative recombination is the only loss process important for O_2^+ and the recombination coefficient has its laboratory value of 2×10^{-7} cm^3 sec^{-1}. For example, at 85 kilometers, O_2^+ ions are being lost at a rate of 10 per cubic centimeter per second, although the rate of production of N_2^+ and O_2^+ together is apparently only 0.5 ion per cubic centimeter per second. The situation is even worse if there is as much nitric oxide in the mesosphere as measurements indicate, for O_2^+ has a large cross section for charge exchange with NO. Even the very slow double-bond-breaking reaction

$$O_2^+ + N_2 \rightarrow NO^+ + NO \qquad (15)$$

can represent an appreciable drain on O_2^+ (and an important source of NO) unless its rate is less than 10^{-17} cm^3 sec^{-2} at 200°K.

The strong solar Lyman-α radiation slips through a famous window in the O_2 absorption spectrum to penetrate to the 70- to 80-kilometer region, where it ionizes nitric oxide (*28*). This produces a noticeable ledge in electron density in the *D* region. There is disagreement among experts as to whether the nitric oxide density of 4×10^7 molecules per cubic centimeter measured by Barth implies a rate of ionization too high for dissociative recombination to cope with; I am one who believes that it does not, and that, while a recombination coefficient of 1 to 2×10^{-6} cm^3 sec^{-1} is required, this is the value indicated by laboratory measurements at low temperatures.

Sporadic E Layer

Some very strange ions show up in the *D* and *E* regions of the ionosphere, according to data obtained by R. Narcisi of the Air Force Research Laboratories (*8*). There is a great and sharp peak of atomic ions such as Si^+, Ca^+, Mg^+, and Na^+ between 90 and 95 kilometers.

This is just where there is a similarly thin layer of neutral sodium. The source is probably meteoric dust, from which atoms such as sodium are evaporated. As they diffuse away they are ionized or oxidized by ozone. The removal process for ions such as Mg^+ may be

$$\mathrm{Mg}^+ + O_3 \rightarrow \mathrm{MgO}^+ + O_2 \qquad (16)$$

followed by dissociative recombination (*27*).

When these meteoric oxides diffuse into the *E* region they are dissociated, ionized again, and swept into thin ionized layers by electric fields which result from their being carried by winds across the earth's magnetic field (*29*). Great wind shears known to exist in this region produce fields that change direction abruptly and hence can concentrate the atomic ions. The transport times are short compared to recombination times for these ions, which must first form diatomic species before they recombine. Sometimes, particularly at night, an especially strong shear or a large influx of meteoric ions can cause the density in this sharp layer to exceed the ambient NO^+, O_2^+ population. The result is a phenomenon called a "sporadic *E*" layer. Recently mass spectrometric measurements (*30*) have show that the ions in a sporadic *E* layer are indeed these meteoric ions and that the density of the normal ionospheric ions is decreased in this layer because of the rapid recombination of these ions in the presence of anomalously high electron densities.

The Nighttime Ionosphere

At nightfall when the sun—the source of ionizing radiation—goes down, the electron density should decrease rapidly. If the ions are predominantly diatomic and transport is unimportant, the rate of decay is governed by the differential equation.

$$\frac{dn_e}{dt} = -\alpha n^+ n_e = -\alpha n_e^2 \qquad (17)$$

where, when more than one kind of ion is present, α is an effective recombination coefficient. The solution of this differential equation is

$$n_e^{-1} = n_{eo}^{-1} + \alpha t$$

where n_{eo} is the density when the source vanished. The time required for the density to be halved is $1/\alpha n_{eo}$, only of the order of 100 seconds.

The ion density near midnight, actually measured in 1963 by Holmes, Johnson, and Young (*6*), is depicted in Fig. 7. Near 160 kilometers it is just what we expect to find if there is no source of ionizing radiation: the O^+ and N_2^+ are converted to O_2^+ and NO^+ by reactions *a, b, c,* and *d,* and these ions recombine at their daytime rates.

Near 130 kilometers, however, something is amiss. The NO^+ density has diminished from its daytime value by only a factor of 10. The O_2^+ density, which should have gone down by e^{-20}, has decreased by a factor of only 400. A source of ions is needed to explain these results.

Nightglow ultraviolet radiation may be such a source. However, Lyman-α radiation, the strongest nightglow emission, will ionize only NO, and that at a rate of 0.2 ion per cubic centimeter per second, whereas a rate of 13 ions per cubic centimeter per second is needed to account for the observations. The presence of the Balmer-α line in the spectrum of the night sky implies that the ultraviolet Lyman-β radiation is there too at high altitude. Calculations indicate that this radiation will ionize O_2 at altitudes between 100 and 130 kilometers, and that some of the O_2^+ will produce NO^+ by charge exchange with NO, provided there are about 10^7 nitric oxide molecules present per cubic centimeter (*31*).

Something odd seems to be going on in the *F* region also (*12*). The crucial issue is the identity of the ion of mass 28. If this is N_2^+, there is no escaping the conclusion that there must be a nocturnal source of ionization near 200 kilometers. N_2^+ is too quickly converted to NO^+ to be around 6 hours after sunset unless it is being made at the time it is observed. To assess the source requirements properly, we must take account of the diffusive flow of O^+ into the 200-kilometer region from above. If the mysterious ion is N_2^+, five to ten ions per cubic centimeter must be produced by some source. Even if the ion of mass 28 is not atmospheric N_2^+, diffusion may not be fast enough to explain all the O_2^+ and NO^+ observed.

Negative Ions in the D Region

Last, I discuss one of the most baffling of the ionospheric problems. In the *D* region, atmospheric density is so high that negative ions of O_2 are formed in large numbers as a result of three-body collisions involving electrons and oxygen molecules. In sunlight the electrons are quickly detached and the population of negative ions is not high. However, at night many of the electrons are bound as negative ions (*32*). This is most noticeable in polar regions during periods of great solar activity, where large fluxes of fast protons pouring into the atmosphere can produce ionization in the lower *D* regions even at night. The trouble is that there are many more free electrons around at night than, theoretically, there should be. Recently it has been found that, when O_2^- collides with atomic oxygen, an ozone molecule is easily formed and the electron is freed (*13*). This could explain the detachment observed, except for the fact that atomic oxygen at night is supposed to combine with molecular oxygen to form ozone and there should, therefore, not be enough O around to act as a sufficiently efficient reaction partner for O_2^-.

There are other negative-ion reactions, recently discovered in the laboratory (*33*), which have the effect of converting the O_2^- first into O_3^- by charge exchange and then into NO_3^- after reaction with NO. Another chain in which CO_2 and NO are used in succession changes the O_3^- to CO_3^- and then to NO_2^-. These reactions are fast and probably mean that NO_3^- and NO_2^- are the dominant negative ions. However, there is much about the *D*-region chemistry, involving hydrogen compounds and radicals, ozone, oxides of carbon and nitrogen—even ice and dust—that we have to understand before we can with confidence predict the properties of this complex region. And we are not even sure yet what it is we must explain, since, as I have pointed out, it is difficult to obtain data by direct probe, particularly data pertaining to negative ions, in the region of high atmospheric density below 90 kilometers.

Summary

Recent measurements of ion densities in the ionosphere seem to be more or less compatible with current data for ion-molecule reaction rates in some parts of the ionosphere under conditions in which a steady state prevails. There is no such agreement for the upper ionosphere, where the densities of He^+ and H^+ are difficult to understand in terms of present concepts concerning the relevant production and loss processes. Sources of ionizing radiation are needed to explain nighttime observations in the *E* region and perhaps also in the *F* region. The *D* region remains a poorly understood laboratory of negative-ion and positive-ion chemistry, where neither observation nor theory is as yet adequate.

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Biosynthesis of Surface Lipids

Biosynthesis of long-chain hydrocarbons and waxy esters is discussed.

P. E Kolattukudy

Lipids are responsible for the familiar water-repellent character of the surfaces of plants, animals, and insects. In chemical composition the surface lipids differ from the internal lipids. Collectively they are called waxes because of their peculiar physical properties, although in strict chemical terms, wax refers to esters of long-chain alcohols with long-chain acids. Identification of wax components has been progressing at a rapid rate because of modern analytical techniques. The biosynthesis of such compounds has been the subject of much conjecture, but only in the past few years have we gained any knowledge based on experimental evidence concerning the formation of surface lipids in nature.

Chemistry

In that several reviews on the chemistry of plant waxes (*1*) and animal surface lipids (*2*) have recently appeared, I shall discuss this aspect only briefly. The surface lipids usually contain hydrocarbons, waxy esters (long-chain alcohol esters of long-chain acids), primary alcohols, and fatty acids. Generally, the hydrocarbons are *n*-paraffins (10 to 50 percent in plants, 1 to 10 percent in animals, and up to 75 percent in insects) containing 21 to 35 carbon atoms in chains with an odd number of carbon atoms predominating. In most cases (especially in plants) one paraffin predominates; for example, in *Brassica oleracea* (broccoli, cabbage) more than 90 percent of the paraffin fraction is a C_{29} alkane, and in *Senecio odoris* it is a C_{31} alkane that predominates.

The waxy esters are usually made up of fatty acids and fatty alcohols with an even number of carbon atoms; the chain usually contains from 10 to 30 carbon atoms. Several dominant waxy esters together with a few minor components are usually found. The free alcohols and free fatty acids of the surface lipids also usually have an even number of carbon atoms and a chain length from C_{10} to C_{30}.

Many waxes are much more complex than this oversimplified picture. Some waxes contain branched hydrocarbons, primarily 2-methyl (*iso*) and 3-methyl (*anteiso*) (*3*), unsaturated hydrocarbons (*4, 5*), and even cycloparaffins (*6, 7*). Other classes of compounds such as ketones (*8, 9*), aldehydes (*10, 11*), diols (*12*), glycerides (*2, 13*), terpenes (*10, 14*), and flavones (*9, 15*) are also occasionally found in waxes.

Possible Significance

The surface lipids are of great importance in conserving water in the organism. In plants as well as in animals, because the surface lipid is the barrier between the organism and its environment, the nature of the surface lipid plays an important role in the interaction between the two. For example, in plants the cuticular wax controls the entry of agricultural chemicals and possibly pathogenic organisms (*16*). Furthermore, the following observations suggest that long-chain hydrocarbons may be of greater importance to organisms than is generally realized. The hydrocarbons usually found in waxes can be catabolized by microorganisms (*17*) and by animals (*18*). Hydrocarbons are found not only in the surface lipids of plants, insects, and animals but also in microorganisms (*19*). They are also found in a variety of animal tissues (other than skin), such as human arterial tissues and plaques (*20*), lymph nodes, spleen, portal triads of liver (*21*), and brain (*22*). Under certain pathological conditions, human spleen is reported to accumulate fat globules consisting mostly of long-chain (C_{25} to C_{28}) hydrocarbons (*23*). Livers of patients dying from malignant disorders have been reported to contain saturated hydrocarbons. Certain fungal infections in plants seem to

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