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ATMOSPHERIC PHOTOCHEMISTRY CASE FILE COPY

by Sir HARRIE MASSEY
and
A. E. POTTER

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ATMOSPHERIC PHOTOCHEMISTRY

BY

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ATMOSPHERIC PHOTOCHEMISTRY

The upper atmosphere offers a vast photochemical laboratory free from solid surfaces, so all reactions take place in the gaseous phase. At 30 km altitude the pressure has fallen to about one-hundredth of that at ground level, and we shall, rather arbitrarily, regard the upper atmosphere as beginning at that height. By a little less than 100 km the pressure has fallen to 10^{-3} mm Hg and is decreasing by a power of ten for every 15 km increase in altitude (*see* Table I). Essentially we are

TABLE I
VARIATION OF ATMOSPHERIC DENSITY WITH ALTITUDE

| Height above sea level (km) | Density (g/cc) | Pressure (mm Hg) | Number of particles/cc | Temperature °K |
|-----------------------------|-----------------------|----------------------|------------------------|-----------------|
| 50 | 1.1×10^{-6} | 6.7×10^{-1} | 2.4×10^{16} | 274 |
| 60 | 3.5×10^{-7} | 1.9×10^{-1} | 7.3×10^{15} | 253 |
| 70 | 9.9×10^{-8} | 4.5×10^{-2} | 2.1×10^{15} | 210 |
| 80 | 2.1×10^{-8} | 8.7×10^{-3} | 4.3×10^{14} | 200 |
| 90 | 3.7×10^{-9} | 1.6×10^{-3} | 7.6×10^{13} | 200 |
| 100 | 6.6×10^{-10} | 3.0×10^{-4} | 1.4×10^{13} | 210 |
| 200 | 3.8×10^{-13} | — | (1.5×10^{10}) | } (1200–1500 ?) |
| 300 | 6.7×10^{-14} | — | (2×10^9) | |
| 400 | 10^{-14} | — | (4×10^8) | |
| 500 | 2×10^{-15} | — | (10^8) | |

concerned then with the photochemistry of a nitrogen–oxygen mixture under low-pressure conditions in which photo-ionization, as well as photodissociation, plays an important part. Account must also be taken of the presence of rare constituents, such as water vapour and its decomposition products, including particularly hydroxyl, oxides of carbon, methane and, strangely enough, sodium, lithium and calcium.

Many curious and unfamiliar reactions occur in the upper atmosphere. Some of them are luminescent, causing the atmosphere to emit a dim light called the airglow. Others, between gaseous ions and neutral molecules, are almost a complete mystery at this time. Similar interesting phenomena must occur in other planetary atmospheres, and they might be predicted if sufficient chemical information were available.

Some Characteristics of the Upper Atmosphere

An adequate discussion of the photochemistry of the upper air must be based on knowledge of (a) the structure and composition of the atmosphere out to great distances from the earth, (b) the intensity of the solar radiation at all wavelengths incident on the atmosphere and, (c) the rates of the various reactions which may occur. Naturally, at present, information on all these aspects is far from complete. A good deal is known about structure and composition up to 200 km altitude or so,

but data are increasingly sparse for greater altitudes. The variability of the atmosphere above 100 km is also very much more marked. Much new information relating to heights above 150 km is now available from study of the drag force exerted by the upper air on the orbits of satellites circulating through it.

The use of vertical sounding rockets and satellites has made possible the observation of solar radiation in the ultraviolet and X-ray regions, and information is increasing steadily (see Fig. 1). The subject is so vast, however, that it will be a very long time before we have adequate data.

Perhaps the least adequate are the basic data regarding the rates of the relevant reactions. Very few of the chemical reactions have been studied quantitatively as they all occur in the gaseous phase. There is here a wide field for chemical research, albeit a difficult one.

Table I shows how the atmospheric density varies with altitude from 50 to 500 km. As remarked above, the values given for above 100 km are averages only and not very definite averages at that. Pressure, temperature and number of particles per unit volume are also given up to 100 km inclusive. Bracketed values given for higher altitudes indicate order of magnitude only.

TABLE II
COMPOSITION OF THE ATMOSPHERE AT GROUND LEVEL

| Atom or Molecule | Concentration (nr/cc) | Fractional Concentration |
|------------------|-----------------------|--------------------------|
| N ₂ | 2.1×10^{19} | 0.78 |
| O ₂ | 5.6×10^{18} | 0.21 |
| Ar | 2.5×10^{17} | 9×10^{-3} |
| CO ₂ | 8.9×10^{15} | 3.3×10^{-3} |
| He | 1.4×10^{14} | 5.2×10^{-6} |
| Na | 4.9×10^{14} | 1.8×10^{-5} |
| Kr | 3.1×10^{13} | 1.1×10^{-6} |
| Xe | 2.3×10^{12} | 8.7×10^{-8} |

The composition of the atmosphere at ground level is given in Table II. In addition to the constituents listed, there are a number of minor ones, such as water vapour, methane, carbon dioxide, nitrogen oxides (N₂O, NO₂ and NO) and ozone. Of these, water vapour is by far the most abundant (a fractional concentration between 10⁻² and 10⁻⁵ by volume). The others are present to a fractional volume concentration between 10⁻⁶ and 10⁻⁸.

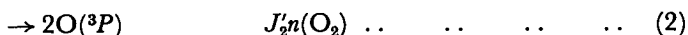
The composition of the main atmosphere remains effectively constant to an altitude of 100 km, although there is some diffusive separation out of the heavier rare gases. Above 100 km the oxygen becomes mainly monatomic as discussed in the next section, while it is likely that at about 150 km diffusive separation out of nitrogen, which is still predominantly diatomic, begins to be effective. The proportion of the minor constituents (see p. 10) also falls off at high altitudes owing to photodissociation. In their place, radicals such as OH are present.

THE EQUILIBRIUM BETWEEN OZONE AND DIATOMIC AND MONATOMIC
OXYGEN

The simplest photochemical problem is the variation, with height, of the relative proportions of oxygen in the monatomic, the diatomic and the triatomic form, account being taken of photodissociation by sunlight. We can consider this problem without allowing for the presence of nitrogen, because the production of atomic nitrogen by photodissociation is very slow and its concentration is never high enough to influence the oxygen reactions.

The reactions which determine the equilibrium, with the corresponding reaction rates, are as follows :

Photodissociation



The first of these is produced through the Schumann-Runge continuum, the threshold wavelength being 1760 Å, while the second begins at 2420 Å. The absorption coefficient is much higher for the first, and as

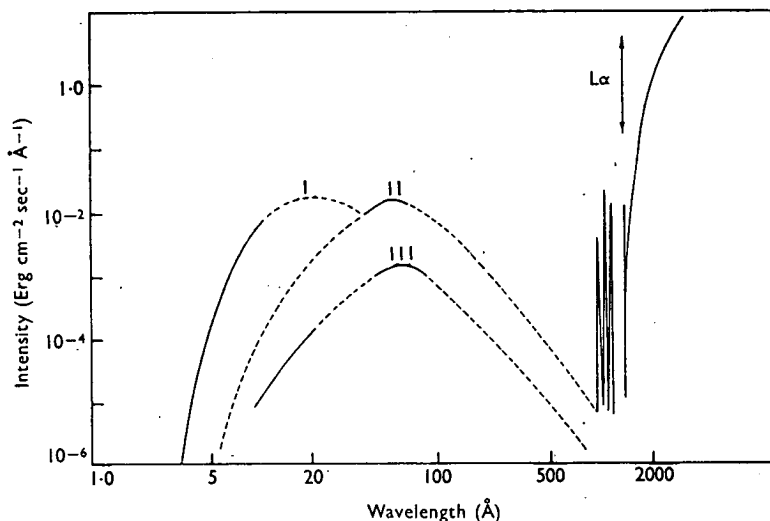


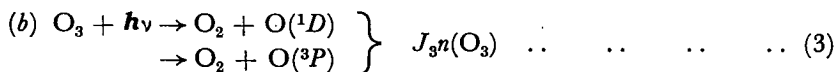
FIG. 1. Illustrating the present state of knowledge of the intensity distribution in the solar spectrum in the ultraviolet and X-ray region, derived from observations with detectors in vertical sounding rockets.

Full lines refer to actual observations, dotted lines to extrapolations. Curves I, II and III refer to three different rocket flights. The first of these took place very shortly after a strong solar disturbance and this is responsible for the increased intensity at very short wavelengths (from H. Friedman⁸).

a result, the radiation from the sun in this short-wavelength region is absorbed quite high in the atmosphere and does not penetrate much below 100 km. On the other hand, the radiation beyond 2420 Å penetrates almost to ground level (the wavelength cut-off at ground is

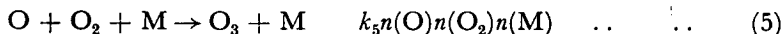
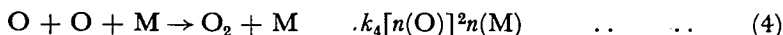
at 2900 Å). Because of these opposing factors, the rate of photodissociation of molecular oxygen has two maxima, one near 100 km and the other near 30 km altitude¹. From a knowledge of the absorption coefficient and of the incoming intensity of solar radiation in each wavelength region, it is possible to determine the coefficients J_2 and J_2' above, as functions of height. The absorption coefficients of atmospheric gases have been extensively studied, and much information concerning them is now available.² It is only in recent years, from observations made with vertical sounding rockets, that information about the incident intensity of solar radiation has been forthcoming.³

Rough estimates indicate that the rate of production of atomic oxygen by the process (1) is about $10^7 \text{ cm}^{-3} \text{ sec}^{-1}$ at its maximum, near 100 km, and about five times greater for (2), near its maximum at 30 km.

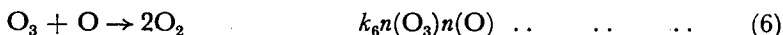


Of these processes, the first, which takes place through the Hartley continuum, near 2550 Å, is much the stronger.

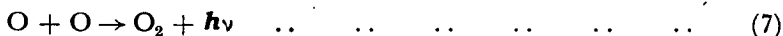
Three-body Recombination



Rearrangement



Apart from the radiative recombination:



which we can ignore as being too slow to affect the equilibrium, except at very high altitudes, these are all the effective reactions.

We now have the equations for the concentrations of the separate allotropes:

$$\begin{aligned} \frac{dn(\text{O})}{dt} = & 2(J_2 + J_2')n(\text{O}_2) + J_3 n(\text{O}_3) - 2k_4 [n(\text{O})]^2 n(\text{M}) \\ & - k_5 n(\text{O}) n(\text{O}_2) n(\text{M}) - k_6 n(\text{O}_3) n(\text{O}) \quad \dots \dots (8) \end{aligned}$$

$$\begin{aligned} \frac{dn(\text{O}_2)}{dt} = & -(J_2 + J_2')n(\text{O}_2) + J_3 n(\text{O}_3) + k_4 [n(\text{O})]^2 n(\text{M}) \\ & - k_5 n(\text{O}) n(\text{O}_2) n(\text{M}) + 2k_6 n(\text{O}_3) n(\text{O}) \quad \dots \dots (9) \end{aligned}$$

$$\frac{dn(\text{O}_3)}{dt} = -J_3 n(\text{O}_3) + k_5 n(\text{O}) n(\text{O}_2) n(\text{M}) - k_6 n(\text{O}_3) n(\text{O}) \quad (10)$$

At high altitudes, we can ignore the ozone in considering the concentration of O_2 and O and we find that, for equilibrium,

$$\frac{n(\text{O})}{n(\text{O}_2)} = \left\{ \frac{J_2}{k_4 n(\text{M}) n(\text{O}_2)} \right\}^{\frac{1}{2}} \quad \dots \dots (11)$$

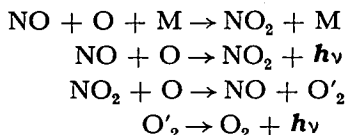
This shows clearly that, under these conditions, as the height increases the proportion of oxygen in the monatomic form increases rapidly, because both $n(\text{M})$ and $n(\text{O}_2)$ fall off rapidly with height.

The calculation of the altitude at which $n(\text{O})$ becomes equal to $n(\text{O}_2)$ depends upon a knowledge of the magnitude of the rate coefficient k_4 . Recent measurements⁴ of k_4 yield about $3 \times 10^{-33} \text{ cm}^6 \text{ sec}^{-1}$. From this value, one finds that the altitude at which the oxygen changes from being primarily diatomic to primarily monatomic is not far from 100 km.

At the transition altitude, the two-body radiative association reaction (7) is certainly unimportant, although at sufficiently great heights it must become more important than (4). This does not affect the general argument, as it is only necessary to replace $k_4 n(\text{M})n(\text{O}_2)$ in (11) by $[k_4 n(\text{M}) + \lambda]n(\text{O}_2)$, where λ is the rate coefficient for (7).

If photochemical equilibrium prevails, then, according to (11), the concentration of O_2 would fall to less than one-hundredth of that of O in going from 100 to 110 km, and would be quite negligible at 150 km. In fact, observations⁵ of the variation with height of the intensity of solar radiation in the wavelength region 1445–1500 Å (which is absorbed exclusively by O_2) showed that, even at 150 km, $n(\text{O}_2)$ is not much less than $0.1n(\text{O})$. The reason for this becomes clear when account is taken of the possibilities of diffusion and mixing. At 150 km the mean lifetime of a molecule in day-time is as long as 15 days, whereas the characteristic diffusion time is less than one day.⁶ This shows quite definitely that, at such an altitude, diffusive rather than photochemical equilibrium prevails, and this would account for the relatively slow decrease of diatomic concentration above the transition altitude. Account must also be taken of mixing due to atmospheric motion, the characteristic times for which are difficult to estimate. There is great scope here for further rocket observations.

A direct demonstration of the presence of atomic oxygen in considerable concentration in the high atmosphere was provided⁷ by a night-time rocket flight from White Sands, New Mexico, during which 18 lb of nitric oxide were released into the atmosphere at a height of 105 km. This produced a pale green glow in which the peak luminous power was no less than 45 kW. There seems little doubt that the light was emitted through the reactions:



in which the nitric oxide catalyses the recombination of oxygen.

Turning now to the situation in the region below 100 km, in which ozone must be considered, we see from (10) that, in equilibrium,

$$n(\text{O}_3) = \frac{k_5 n(\text{M})n(\text{O})n(\text{O}_2)}{J_3 + k_6 n(\text{O})} \quad \dots \quad (12)$$

At altitudes below 70 km we may neglect the term involving k_6 in the denominator. On substitution in (9) for $n(\text{O}_3)$, we then obtain:

$$n(\text{O}) = \left\{ \frac{J_2 J_3 n(\text{O}_2)}{k_4 J_3 + 2k_6 k_5 n(\text{O}_2)n(\text{M})} \right\}^{\frac{1}{2}} \quad \dots \quad (13)$$

J_2 being negligible in comparison with J'_2 . Below about 60 km, the term $k_4 J_3$ may be neglected in comparison with $k_6 k_5 n(\text{O}_2)$ and in these circumstances

$$\frac{n(\text{O}_3)}{n(\text{O}_2)} = \left\{ \frac{k_6 J'_2 n(\text{M})}{2k_8 J_3} \right\}^{\frac{1}{2}} \quad \dots \quad (14)$$

This shows that we would expect the term $n(\text{O}_3)$ to pass through a maximum value at some altitude in this range, the increase of $n(\text{M})n(\text{O}_2)$ in a downward direction being overcompensated by the rapid increase of J'_2 , as absorption of the effective radiation becomes strong.

The existence of an ozone layer, centred around an altitude of 30 km, is well established; but any comparison between the distribution as given by (14) and observed results must allow for the importance of mixing.

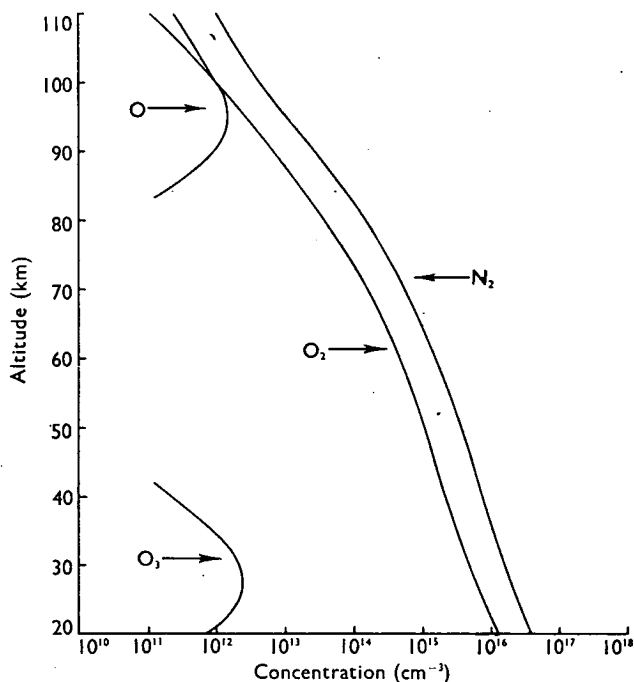


FIG. 2. General features of the distribution of the oxygen allotropes with altitude in the terrestrial atmosphere.

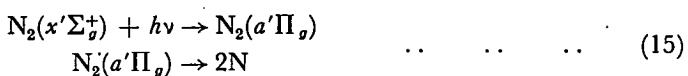
Nicolet⁸ has estimated that the time to attain photochemical equilibrium between O_2 and $\text{O} + \text{O}_3$ is about a month at 30 km and several years at 20 km. Under such conditions, there will be no appreciable variation in ozone content between day and night. Further estimates suggest that in the altitude range between 40 and about 70 km photochemical equilibrium can be maintained. The first measurements⁹ of ozone concentration up to 70 km, made with rocket-borne instruments, provide some support for this view.

In order to show graphically the topic of the preceding paragraphs, a representation of the distribution of the oxygen allotropes with altitude is given in Fig. 2. It is a composite of results from several sources^{10,11,9} and must not be taken too literally, as atmospheric heating and winds frequently alter the picture somewhat.

NITROGEN AND NITROGEN OXIDES

Atomic and Molecular Nitrogen

The essential difference between nitrogen and oxygen, from the viewpoint of atmospheric photochemistry, is the very small cross-section of the nitrogen molecule towards dissociation by ultraviolet radiation. Only one such process is known, which involves radiation in the wavelength region 1200–1250 Å. This is the weak predissociation :



which was pointed out by Herzberg and Herzberg.¹² There are some other processes which lead to dissociation but these involve rare constituents, such as positive ions. For example, we have the dissociative recombination



(where the primes indicate that electronically excited atoms may be formed) and the ion-atom interchange reactions



and



These reactions are of considerable interest, as rocket observations with mass spectrographs¹³ show that NO⁺ is the main positive ion in the ionosphere up to 150 km. The principal reaction whereby atomic nitrogen is removed in the atmosphere is thought¹⁴ to be



It is possible to equate the rates of formation and removal of N, and arrive at an expression for its concentration in terms of rate constants and reactant concentrations. Unfortunately, these are not known in most cases, and in addition, the reactants are so dilute that the reactions are probably so slow that diffusion and mixing should not be neglected. We are not, therefore, in a position to calculate with confidence the concentration of atomic nitrogen at any altitude.

Nicolet has estimated¹⁴ that the atomic nitrogen concentration might be about 5×10^6 atom/cm³ at 100 km.

Another attempt to estimate the nitrogen abundance¹⁵ has been shown to be incorrect.¹⁶ As far as observation goes, there is no indication of molecular nitrogen bands arising from atomic nitrogen recombination in the night airglow, whereas oxygen bands from atomic oxygen recombination are prominent. However, a line from atomic nitrogen does

appear faintly during part of the night in the night airglow,¹⁷ probably¹⁸ from excited atoms produced by the dissociative recombination reaction (16). Atomic nitrogen lines also occur in auroral spectra, but these may arise from atoms produced by bombardment of molecular nitrogen during the auroral display, and do not give any information as to the normal atomic nitrogen content of the atmosphere. It is clear that atomic nitrogen is a very rare constituent of the upper atmosphere. Indeed, the strongbands of molecular nitrogen in auroral spectra show that molecular nitrogen is abundant at altitudes up to several hundred kilometres.

The Nitrogen Oxides

As is well known, the chemistry of the nitrogen oxides is extremely complex, and in order to estimate the concentration of the various oxides in the upper atmosphere, gross simplifications must be made by neglecting all but the fastest reactions. This implies a complete knowledge of the kinetics of all possible reactions in the nitrogen-oxygen system. Clearly, this knowledge does not exist, and simplifications run the risk that important reactions may be neglected. A summary of kinetic data has been given by Harteck.¹⁹

Of the nitrogen oxides, particular interest attaches to nitric oxide, and for two reasons. One has already been mentioned. The second is that it has long been supposed that ionization in the D region of the ionosphere, located near 80 km, arises from photo-ionization of nitric oxide.²⁰ Originally, this conclusion was reached because it was thought that all radiation capable of ionizing the major atmospheric constituents was completely absorbed before penetrating to the 80 km level.

Nitric oxide has an ionization potential less than any of the other important species, and the Lyman- α radiation from the sun, which is short enough to ionize it, could penetrate far enough. It is now known²¹ that solar X-rays from 1 to 10 Å exist, penetrate thus far and are responsible for some of the ionization, as are also cosmic rays. However, nitric oxide is still important, and the recent discovery that the Lyman- α line is more intense than was first thought, makes the amount needed to explain the D-layer less than before. Nicolet²² has calculated theoretically the daytime nitric oxide concentration as follows.

The principal source of nitric oxide is believed to be the reaction of atomic nitrogen with molecular oxygen, as in reaction (19). The most important process which removes nitric oxide is the reaction



In the steady state, these two reactions lead to an expression for the nitric oxide concentration as follows:

$$n(\text{NO}) = \frac{k_{19}n(\text{O}_2)}{k_{20}} \quad \dots \quad \dots \quad \dots \quad (21)$$

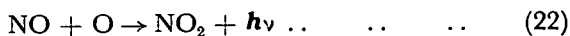
where k_{19} and k_{20} are the rate coefficients for the respective reactions (19) and (20).

Atomic nitrogen does not appear explicitly in this formula, but the formula is invalid in its absence. Also, reactions involving NO_2 have been neglected, which is permissible in the daytime, owing to the rapid photodissociation of NO_2 which occurs then. At night, reactions involving NO_2 must be included. The expression (21) will therefore only be valid if the concentration of atomic nitrogen is high enough for equilibrium to be reached in the daytime. With the rather uncertain rate constants now available,²³ equation (21) yields a value for the daytime nitric oxide concentration of $10^{4\pm 1}$ molecules/cm³ at 85 km. This is much less than the previous estimates of the minimum NO concentration needed to explain the D-layer, but it is consistent with the rocket observation, by absorption spectroscopy, that the concentration cannot exceed 10^8 molecules/cm³. Even so, according to Nicolet,²¹ nitric oxide still can account for most of the ionization near 85 km, although it now appears that ionization of oxygen and nitrogen by solar X-rays may also be important, especially at lower altitudes.

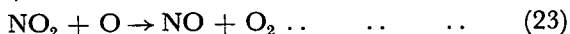
At night, NO and O react to form NO_2 , which in turn re-forms NO by reaction with O and N. The net result¹⁹ is that the night concentration of NO is about one order of magnitude larger than the day concentration.

Other oxides of nitrogen exist in the upper atmosphere, in particular nitrogen dioxide and nitrous oxide. Experimental studies, summarized by Harteck,¹⁹ show that the following reactions are important in determining their concentrations. As in the case of nitric oxide, only the fastest reactions are considered.

Nitrogen dioxide is rapidly photolysed by sunlight in the daytime, and its concentration during the day is thought to be several orders of magnitude less than that of nitric oxide. At night, the major reaction by which NO_2 is produced is

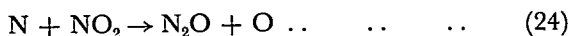


It is destroyed rapidly by reaction with atomic oxygen,



and slowly by reactions with atomic nitrogen. The rate constants for the formation and destruction reactions are thought to be approximately equal, so that if the steady state is reached in the night, the concentrations of NO and NO_2 are of equal magnitude.

Nitrous oxide is usually regarded as a permanent atmospheric constituent, present to the extent of 0.5 parts per million. It is rapidly destroyed by photodecomposition in the upper atmosphere, so rapidly that it is difficult to find a chemical process fast enough to replace that lost.²⁴ The most likely reaction yet considered¹⁹ is



All other reactions appear to be too slow. It seems possible²⁵ that soil micro-organisms may provide a large fraction of the atmospheric N_2O .

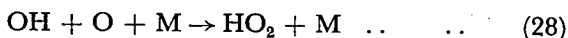
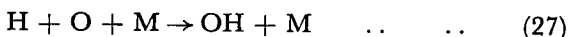
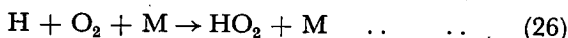
It is clear that the chemistry of the atmospheric nitrogen oxides is still in a primitive state, owing largely to the lack of accurate rate constants for the multitude of fast reactions which occur.

MINOR ATMOSPHERIC CONSTITUENTS

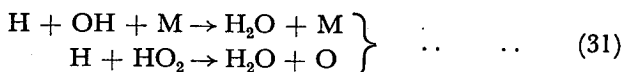
Water Vapour

In spite of its importance, little is known about the photochemistry of water vapour in the atmosphere. Nearly all our present knowledge is contained in a theoretical study by Bates and Nicolet.²⁶ Current rocket studies promise some experimental information; these will be discussed after the theoretical part.

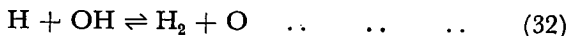
Water vapour is decomposed to H and OH by radiation shorter than 2400 Å, with the most effective wavelengths below 1800 Å. The most effective radiation is thus absorbed strongly by molecular oxygen, so that the altitude at which water is photodissociated is controlled by the molecular oxygen concentration. The products of photodissociation enter into a variety of fast reactions, which can be classified either as oxidation, (25) to (28), or reduction, (29) and (30).



With the exception of the ozone reaction, all the oxidation reactions are termolecular, so that their rates decrease with the cube of the pressure. The reduction reactions are bimolecular, so that their rates change only as the square of the pressure. Hence, at sufficiently high altitudes, where the pressure is very low and the ozone concentration is negligible, the reduction reactions predominate and the abundance of hydroxyl and perhydroxyl relative to atomic hydrogen diminishes. This in turn hinders the re-formation of water vapour by the reactions



The gradual dominance of the reduction reactions over all others as altitude increases leads to the result that water is almost entirely dissociated to atomic hydrogen and atomic oxygen above 80 km. Slightly below this altitude, a layer of molecular hydrogen is to be expected, arising from the reactions

*Atomic Hydrogen*

The calculated atomic hydrogen concentration arising from dissociated water vapour²⁶ ranges between 10^9 and 10^{10} atom/cm³ from 65 to 95 km. Almost needless to say, only the general outlines of the calculated

distribution can be considered correct, owing to the nearly total lack of rate data. As reliable results accumulate, the distribution will be modified. Also, since atomic hydrogen has an exceptionally large diffusion coefficient, it can be expected that diffusion will greatly influence its distribution.

The distribution of atomic hydrogen is of special interest since, as Chapman²⁷ has pointed out, the predominant species in the outermost fringes of the atmosphere must be atomic hydrogen. Some of it comes from below, where water vapour and hydrogen are dissociated by sunlight. The altitude at which the atmosphere is predominantly atomic hydrogen could probably be estimated if the hydrogen distribution at lower levels were accurately known. Recent rocket experiments give hope that measurement of this distribution will be possible soon.

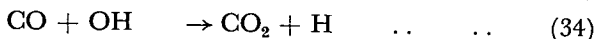
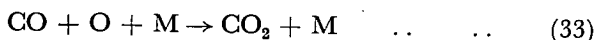
Atomic hydrogen strongly scatters the Lyman- α line at 1216 Å. Consequently, observations of solar Lyman- α scattered or absorbed by atomic hydrogen can yield information on its abundance and altitude distribution. Since radiation of this wavelength does not penetrate below an altitude of 65 km, all observations must be made from rockets. Two experiments have been performed to date. The first of these demonstrated the existence of appreciable atmospheric hydrogen, the second yielded some information on its distribution and amount. First, Lyman- α detectors were flown to 146 km altitude at night.²⁸ The rocket rolled slowly during the flight so that the detectors alternately pointed up and down. Above 85 km, radiation was observed from below the rocket, indicating emission of Lyman- α by the atmosphere. At the peak of the flight, the emission from the atmosphere below the rocket amounted to nearly half that from space above the rocket. The flux from space above the rocket is believed to come from sunlight scattered by hydrogen atoms in space, and the radiation from below to originate from hydrogen atoms in the earth's atmosphere. It appears that the Lyman- α flux from space excites Lyman- α resonance radiation of the terrestrial hydrogen. If this were the only process operative, intensity of the atmospheric Lyman- α could be used to calculate the abundance and altitude distribution of hydrogen. Unfortunately, the intensity of the atmospheric radiation is so high as to suggest the presence of a source of Lyman- α other than resonant scattering.²⁹ Possibly, bombardment of the atmosphere with energetic particles is the cause.

The second, and most significant, experiment is the measurement of the absorption of solar Lyman- α by atomic hydrogen in the atmosphere.³⁰ The solar Lyman- α line is about 1 Å wide. Absorption by cool (less than 3000 °C) terrestrial hydrogen removes 50–60 per cent of the intensity over a 0.1 Å region in the centre of the emission line. The absorption corresponds to an absorbing column of between 10^{12} and 10^{13} atom/cm². Almost no measurable variation in the amount of absorption between 95 and 200 km was observed. This seems to indicate that most of the hydrogen observed in this experiment lay above 200 km.

It may be anticipated that refinements of this experiment eventually will yield an accurate knowledge of the distribution of atomic hydrogen in the atmosphere.

Carbon Dioxide

As will be seen later, the photochemistry of carbon dioxide in the atmospheres of Mars and Venus is of great interest. It is less important in the terrestrial atmosphere. Carbon dioxide is dissociated to CO and O (¹D) by wavelengths shorter than 1690 Å. As in the case of water vapour, the altitude at which CO₂ is dissociated by sunlight is controlled by the molecular oxygen concentration, and is probably¹ above 100 km. At higher altitudes, ionization of CO₂, and ionization and dissociation of CO, may be expected. Oxidation of CO occurs through



and possibly



The oxidation by ozone does not seem to be important.³¹ The atmospheric chemistry of CO₂ is seen to be closely linked to that of water vapour through reactions (34) and (35). These oxidation processes are slow,³² and their rates are so small above 100 km that it is likely that CO formed above 100 km must diffuse down to altitudes around 70 km where the pressure is higher, and OH abundant, before oxidation occurs.

The slowness of oxidation of CO in the atmosphere raises a question as to how carbon-14 formed in the atmosphere from nitrogen by cosmic rays gets into the photosynthetic cycle.³² It was first thought that the high-energy radiogenic carbon must react directly with oxygen to form ¹⁴CO₂, since carbon must be in the tetravalent state to enter the photosynthetic cycle. However, the primary product of neutron-irradiated air is found to be carbon monoxide, rather than the dioxide. The slowness of atmospheric oxidation of CO makes it appear that much of the radioactive CO is oxidized biologically by soil bacteria. This conclusion applies equally well to non-radioactive CO, and it is possible that the rate of dissociation of CO₂ always exceeds the rate of oxidation of CO, in the upper atmosphere.

Methane

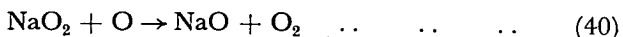
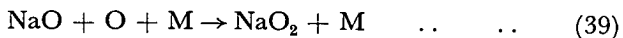
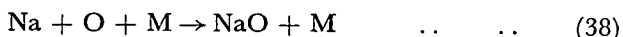
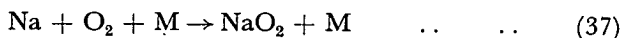
Methane is present in the lower atmosphere at a concentration of about 1.5 parts per million. It is probably entirely destroyed by oxidation with perhydroxyl and atomic oxygen before it can reach altitudes above 100 km, where photodissociation could occur.¹ As the reformation of CH₄ in the upper atmosphere is extremely doubtful, the concentration at any altitude is determined by the relative rates of atmospheric mixing and the destructive oxidation. The methane clearly enters the atmosphere at the earth's surface, and is carried by winds and diffusion up to the levels near 70 km, where its lifetime is only about three hours. The final products of oxidation must be oxides of carbon and hydrogen. The latter will be reduced to atomic hydrogen above 80 km. Hence, the steady flow of methane into the upper atmosphere, and its subsequent destruction there may have an important influence on the distribution of CO and atomic hydrogen. Nicolet¹⁰

has estimated that the loss rate of methane into the upper atmosphere ranges from 10^{10} to 10^{11} molecule cm^{-2} sec^{-1} .

Metals in the Atmosphere: Sodium, Lithium and Calcium

Shortly after sunset, the high atmosphere is sunlit, while the earth below is shadowed. A person on the earth's surface can then see sunlight scattered from the atmospheric gases above. The scattered sunlight is called the twilight glow. Since some atmospheric gases scatter light very strongly, trace concentrations can be determined by spectroscopic analysis of the twilight glow. In this fashion, free sodium, lithium, and ionized calcium have been discovered in the upper atmosphere. These unexpected discoveries have initiated a large amount of observational and theoretical work, much of which has been recently summarized by Bates.³³

The sodium is found in a thin layer, about 14 km thick³⁴ at an altitude near 85 km.^{34,35} The mean concentration of atomic sodium in the layer varies from about 10^3 to 4×10^3 atom/ cm^3 , depending upon whether it is summer or winter.³⁶ The continued life of free sodium in the presence of atomic and molecular oxygen is surprising. Chapman³⁷ first explained this, essentially as follows. Sodium is oxidized through the reactions (36) to (39) and reduced by (40) and (41).



The close formal similarity with the atmospheric chemistry of water vapour is evident. As in the case of water vapour, the bimolecular reduction reactions must predominate over the termolecular oxidation reactions at sufficiently high altitudes. When this occurs, the sodium is predominantly free. It would be possible to calculate the detailed distribution of free and combined sodium, if rate constants for the oxidation and reduction reactions were available. The only reaction that has been studied is the oxidation by molecular oxygen.³⁷ If the reported³⁸ rate constant of 5×10^{-30} cm^6/sec is correct, this reaction is probably the fastest known termolecular reaction.

Various authors have speculated on the origin of atmospheric sodium. The amount required is so minute (one ton in the entire atmosphere) that a number of sources must be considered. Among those suggested are sea salt, volcanic dust and meteors. There is no clear evidence favouring the predominance of any of these.

The lithium resonance line was first observed in the twilight glow over Antarctica in 1957 by Delannoy and Weill.³⁹ Later Antarctic

observations⁴⁰ showed the quantity of lithium over Antarctica in August 1958 to be 3×10^8 atom/cm², decreasing to 3×10^7 atom/cm² a month later (over New Zealand). During these observations, the altitude of the lithium layer appeared to decrease, from a height equal to the sodium layer (about 85 km) to a height 7 km below it. A year later, lithium was sought and found in the northern hemisphere.⁴¹ A careful calculation of the abundance of lithium over Canada yielded a value of 9×10^6 atom/cm². This is a very small amount, being equivalent to about 500 g of lithium dispersed over the entire earth.

The origin of atmospheric lithium is not known with certainty. There appear to be three possibilities; from meteors, sea water or nuclear explosions. The ratio of lithium to sodium in the atmosphere lies between that of meteors and sea water, so that neither is favoured. The suggestion by the IGY committee⁴² that the lithium originates from high-altitude nuclear explosions is a definite possibility, as the dates of the Antarctic observations of large abundances of lithium roughly coincide with the dates of such explosions. The lithium observed in 1957 over Canada may be a remnant of the explosions, or it may represent a permanent atmospheric constituent. Future observations will settle the question.

The continued free life of lithium at high altitudes must be due to reactions similar to those which maintain free sodium.

Another rare constituent of the atmosphere which has been discovered recently⁴³ in the twilight glow is ionized calcium, Ca⁺, the lines of which appear for periods of several days and then disappear. The peak abundance⁴⁴ of Ca⁺ is about 5×10^8 ion/cm² which corresponds to about 200 kg total ionized calcium in the atmosphere. The altitude of the calcium is probably⁴⁵ above 135 km.

The origin of the calcium is possibly meteoric, since its appearance in the atmosphere coincides with the passage of the earth through meteor swarms.^{44,46} It has also been observed during an intense solar flare, which may indicate a solar origin.⁴⁵ In any case, the rather rapid appearance and disappearance of the calcium suggests that it is not a stable constituent of the atmosphere, as is sodium. The fate of the calcium ion is unknown. It appears possible that it is neutralized, and then oxidized to CaO, which is probably stable enough to resist reduction by atomic oxygen.

REACTIONS OF GASEOUS IONS IN THE IONOSPHERE

The rocket-borne spectrographs flown in both the U.S.S.R. and U.S.A. have shown, as previously mentioned, that NO⁺ is the dominant positive ion up to 150 km, particularly at night. As seen below, this discovery opens a new and almost wholly unexplored field—the kinetics of gaseous ionic reactions. Chemists have been traditionally interested in the reactions of ions in solution, but this interest has not extended to gaseous ions, primarily because of experimental difficulties.

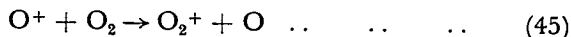
The concentration of NO⁺ far exceeds what could be supplied by the ionization of neutral NO. Furthermore, NO⁺ is least abundant during

the day when solar ionization of NO is fastest. Hence, the ion must arise from ion-atom interchange reactions, such as¹⁶



Reactions (42) and (44) are important in the chemistry of atomic nitrogen, as mentioned above.

A considerable variety of other ion-atom interchange reactions occurs. An important example is



Other than indirect evidence from the rocket observations no reliable information, either theoretical or experimental, is available for the rates of these reactions. It is usually assumed that they are fast, occurring upon every collision, but Bates and Nicolet¹⁶ have shown that this cannot be true. Otherwise, all O^+ and O_2^+ ions in the atmosphere below 150 km would be converted to NO^+ within seconds after sunset, which is contrary to observation. It seems likely that the reactions are slow because of an appreciable activation energy. Experimental and theoretical work on these reactions, while difficult, should yield much new information. In principle, molecular beam and special mass-spectrographic techniques should be well suited for the study of gaseous ionic reactions.⁴⁷

Perhaps more surprising than the predominance of NO^+ is the observation⁴⁸ that NO_2^- is the dominant negative ion* in the daytime around 115 km. This negative ion is evidently very stable, and is easily observed in discharges through air.⁴⁹ Curiously, hardly any NO_2^- is formed by discharges⁴⁹ in, or electron bombardment⁵⁰ of NO_2 . The cross-section for electron attachment to NO_2 is estimated⁵⁰ to be only one-hundredth that for attachment to O. At present, it appears that nothing is known concerning the reactions whereby NO_2^- is formed in the atmosphere.

LUMINESCENT REACTIONS IN THE NIGHT SKY^{33,51,52}

In addition to moonlight and the integrated light from the stars, there is always present a weak glow from the upper atmosphere, about as intense as the light from a candle 300 feet away. It is quite distinct from the very much brighter glow characteristic of aurorae in that it is regular, exhibits relatively little dependence on latitude, and involves relatively low excited states of atoms and molecules. A great deal of attention has been devoted to the study of the airglow spectrum, which includes many rather remarkable features.

The most intense radiation from the night sky falls in the infra-red region near 10,400 Å. It has been identified, quite recently, as arising

* This does not mean that the concentration of NO_2^- is greater than that of the free electrons. Very much the reverse is the true situation. We are using the term negative ion here exclusively to denote a negatively charged atom or molecule.

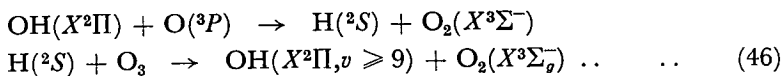
from certain bands of the hydroxyl molecule spectrum. In the visible region the next most prominent features are the green ($^1S \rightarrow ^1D$) and red ($^1D \rightarrow ^3P$) forbidden lines of atomic oxygen, the yellow D lines of sodium, and certain molecular oxygen bands, the whole comprising a very unusual spectrum.

The energy radiated in the airglow is almost certainly stored during the day as a result of dissociation and, to a much smaller extent, ionization. The presence in strength of the forbidden lines of atomic oxygen shows that some, at least, of the radiation must come from altitudes so high that collision deactivation of the upper metastable states involved is not serious. Many attempts were made to determine the height of the emitting layers from ground observations of various kinds, but with indifferent success. Some results have been obtained in the last few years by the use of rocket-borne detectors, which indicate that the oxygen green line is emitted most strongly from a layer about 30 km thick, centred round a height of 100 km—close to the transition level between atomic and molecular oxygen. The sodium lines were found to be emitted at a slightly lower level, at 85 km. The red oxygen line exhibits a very different behaviour to the green, so far as daily and seasonal variations are concerned, and there is evidence that it is emitted mainly at a much greater altitude.

The nature of the reactions which give rise to atoms and molecules has been the subject of much speculation.

Hydroxyl Bands

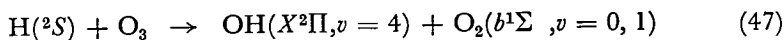
The most striking example of co-ordination of theory and experiment in the chemistry of the upper atmosphere is afforded by the infra-red hydroxyl band emissions. To explain the strongest airglow emission, Herzberg⁵³ and Bates and Nicolet²⁶ independently suggested that atomic hydrogen plays a catalytic role through the reactions:



Although rare constituents are involved, it is possible that the reactions are so fast that the rate of production of excited hydroxyl is great enough. One point in favour of this explanation is that there is insufficient energy available to raise the hydroxyl to a vibrational level with the vibrational quantum number $v > 9$, and it is a conspicuous feature of the bands in the airglow that none arises from states with $v > 9$.

Spectroscopic studies by McKinley, Garvin and Boudart⁵⁴ of the $\text{H} + \text{O}_3$ diffusion flame have shown that the bands were emitted almost exactly as predicted. Recently, quantitative spectroscopy of the emission from the reaction has shown that the relative populations of the vibrational levels of OH in the laboratory flame and the night sky are very similar.⁵⁵

It is also found that the rate of production of OH in the 4th vibrational level is much higher than any other. This is attributed to the reaction



This process was proposed because the 0-0 and 1-1 bands of the $O_2(b^1\Sigma_g^+) \rightarrow O_2(X^3\Sigma_g^-)$ system (the atmospheric system) have been observed in the H-O₃ atomic flame.⁵⁶ It seems quite possible that this process may contribute significantly to the Kaplan-Meinel (0-1) band of the atmospheric system, which is the only radiation attributable to $O_2(b^1\Sigma_g^+)$ observed in the night sky. An attractive feature of this hypothesis is that it explains why no atmospheric bands arising from large initial vibrational quantum numbers have been observed, and why there appears to be a correlation between the airglow intensities of the OH bands and the Kaplan-Meinel band.⁵⁷ Thus, the laboratory studies not only confirm the hypothesis advanced for the appearance of the hydroxyl bands, but also provide a new and previously unsuspected mechanism for one of the night sky emissions.

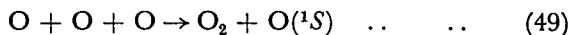
Krasovskii⁵² has suggested that the excited hydroxyl molecules responsible for the airglow emission are produced by a reaction between atomic hydrogen and vibrationally excited molecular oxygen. This proposal is extremely difficult to test. However, Bates and Moisevitch^{57a} have criticized it on theoretical grounds, and an experimental study^{57b} of the hydroxyl band emissions from a reacting mixture of H and O₂ has yielded results contradictory to Krasovskii's proposal. Hence, the most generally accepted origin of the hydroxyl emissions remains the reaction of atomic hydrogen with ozone.

Atomic Oxygen Lines

In the visible spectrum of the airglow, the brightest feature is the green line of atomic oxygen, which arises from the transition

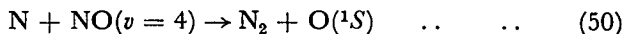


Chapman⁵⁸ suggested that the source of the excitation energy for the upper state of the green line is the energy of recombination of oxygen atoms in the three-body reaction:



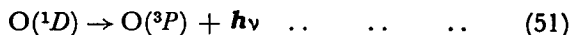
Even if the chance of excitation at each three-body collision is quite small, this seems to be a likely source of sufficient excited atoms.

An alternative to this reaction has recently been suggested.⁵⁹ It is

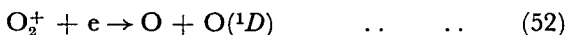


This does not seem to be a probable alternative, since it requires the appearance of nitric oxide bands in the night sky spectrum, and none are found. Although no other process seems likely, it would be very desirable to confirm the existence, and measure the rate, of the termolecular atom recombination process.

Another prominent feature of the airglow spectrum is the red oxygen line, which arises from the transition



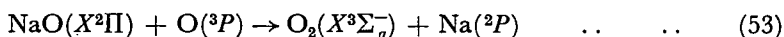
Since the excited atom which produces this emission is the product of the green line emission, one would expect the two lines to be emitted together at the same altitude. This is not the case. The red lines are emitted from altitudes much above the layer at 100 km where the green lines originate. The absence of the red emission at 100 km has been shown⁶⁰ to be due to collisional deactivation of the excited atoms. The emission from high altitudes (where collisional deactivation is unimportant) is thought⁶¹ to arise from the reaction



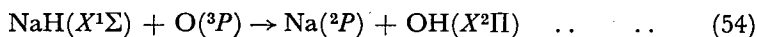
which occurs above 100 km.

The Sodium-D Lines

The presence of the sodium-D lines is remarkable in itself, apart from any question of the reactions which are responsible for them. Chapman³⁷ suggested that the reaction which leads to excitation involves NaO:

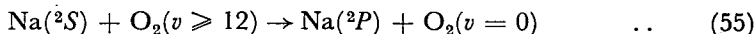


There is doubt, however, whether this reaction is exothermic. The dissociation energy of NaO would need to be less than 3.0 eV, and the estimate by Bawn and Evans³⁸ gives 3.1 eV. Bates and Nicolet²⁶ have suggested that one should consider NaH rather than NaO, allowance being made for the fact that there is atomic hydrogen present, through the decomposition of water vapour (*see* p. 10). The reaction would then become:



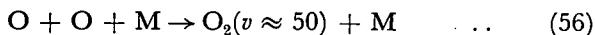
This would certainly be exothermic, but it is difficult to decide whether it is rapid enough, there being no way of determining the concentration of NaH in the atmosphere.

Still another process has been proposed,⁵² whereby free sodium is excited by collisions with vibrationally excited oxygen.

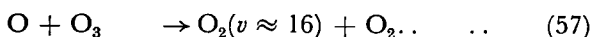


Electronic excitation by transfer of energy from vibrationally excited molecules is normally most unlikely, but there are reasons for believing it may occur in this case. The principal virtue of this process is that it explains the observation that the sodium emission in the airglow appears to originate in a region where the sodium is predominantly free, as well as the emission of sodium-D lines from sodium ejected into the atmosphere at altitudes where the sodium does not react chemically with the atmosphere.⁶³

The vibrationally excited oxygen required is presumed to arise from the reactions^{64,65}



and



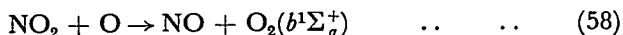
A difficulty with this mechanism for the sodium airglow is that deactivation of vibrationally excited oxygen by oxygen atoms may be so fast as to make the steady-state concentration of excited oxygen too low.

Oxygen Bands

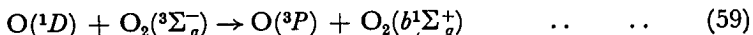
Molecular oxygen bands can arise from the three-body recombination of normal oxygen atoms. Such recombination need not produce O_2 molecules in the ground $^3\Sigma_g^-$ state exclusively, but it can also form molecules in the $a^1\Delta_g$, $b^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states, all of which dissociate into normal atoms along attractive potential energy curves. These are the upper states of the infra-red atmospheric, the Kaplan–Meinel atmospheric, and the Herzberg bands of O_2 , so that these systems would be expected to appear in the airglow. The last two certainly do, but the infra-red bands fall in a wavelength region not yet studied. On the other hand, estimates of the intensities suggest that the proposed source could provide far more intense bands than are naturally observed. These estimates are based on the assumption that the chances of forming molecules in the ground state, or any one of the three excited states, are comparable. Some inhibiting factor, as yet unknown, may cause the ground state to be strongly favoured and so reduce the band intensities.

Bates has suggested that reactions with atomic oxygen may deactivate the excited molecules before they can radiate.⁶⁶

In addition to atom recombination, several other processes might be possible sources of the Kaplan–Meinel ($b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$) atmospheric band. One of these has been mentioned above, the reaction of H and O_3 . Others are^{60,66}



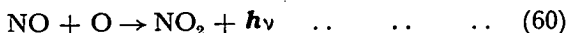
and



Only the reaction of H and O_3 has been confirmed experimentally.

Other Airglow Emissions

A rather strong continuous emission is observed in the airglow. It is most intense near 5300 Å, and is emitted mainly between 85 and 110 km. Its origin is uncertain, although a possibility is^{24,26}



Recent results obtained in the U.S.S.R. indicate that the continuum may be more intense than previously realized.

A line at 5199 Å attributed to atomic nitrogen is observed in the twilight glow and during the early part of the night.¹⁷ The excited nitrogen may arise from dissociative recombination of molecular nitrogen ions.¹⁸

A line of atomic hydrogen at 6562.8 Å has recently been discovered by Prokudina⁶⁹ in the airglow. It has been attributed to fluorescent scattering of solar Lyman-β radiation by interplanetary atomic hydrogen.⁷

Artificial Luminescence in the Night Sky

Ejection of chemicals from rockets into the upper atmosphere is a promising technique for the study of chemical reactions under conditions which cannot easily be duplicated in the laboratory. Except for certain molecular-beam experiments, the study of reactions in the laboratory at pressures below 10^{-4} mm in the absence of wall effects is a practical impossibility, as the mean free path approaches 1 m at this pressure. The pressure is 10^{-4} mm a few kilometres above 100 km (see Table I), and there are no walls whatsoever. There are some difficulties with this technique, however. First of all, the observer is 100 km or so away from the reaction he is studying. This makes it difficult to follow the course of the reaction. A simple solution is to study luminescent reactions, the course of which can be easily observed from the ground. Another difficulty is that the composition of the atmosphere at these altitudes is not completely known, especially as regards minor constituents such as H or N. This is unfortunate, since many of these minor constituents are so reactive that they must be taken into account.

The experiments to date have been aimed at the identification of atmospheric constituents by their luminescent reactions with ejected chemicals. In the first such experiment, atomic oxygen was detected⁷ by reaction with nitric oxide near 100 km (see p. 5). The luminescence from the reaction faded more quickly than expected, indicating a reaction of nitric oxide with some minor atmospheric constituent, probably atomic nitrogen. If this could be confirmed, and the rate constant measured, the fading of the glow could be used to determine the atomic nitrogen concentration. In another experiment, atomic nitrogen was sought by its reaction with ethylene to produce CN band emissions.⁷¹ Unfortunately, the light produced was too weak to permit a complete spectral analysis, which is necessary because atomic oxygen also reacts with ethylene to produce light. As a result, only qualitative evidence for the presence of atomic nitrogen was obtained.

It may be anticipated that further experiments of this kind will be performed as more knowledge is gained about the upper atmosphere. For example, the supposed origin of the hydroxyl bands from the reaction of atomic hydrogen and ozone could be checked by the release of hydrogen or ozone into the atmosphere at the appropriate altitudes. A quantitative experiment of this kind might permit determination of the atomic hydrogen concentration.

An unexpected result of putting chemicals into the atmosphere has been the appearance of luminescent reactions of unknown origin. Sodium vapour ejected at night reacts with the atmosphere⁶³ to yield sodium-D lines at 65, 100 and 140 km. The reactions responsible for the luminescence are not known, although collisions with vibrationally excited oxygen or electronically excited nitrogen have been suggested for the emissions at 100 and 140 km. Another mysterious luminosity is produced⁷² by the explosion of grenades at altitudes over 100 km. The reactions responsible are not known. Such a variety of products are produced by the explosion that identification of the species which produce the luminescence is very difficult.

CHEMISTRY OF EXTRA-TERRESTRIAL ATMOSPHERES

As on earth, photodecomposition and photo-ionization in the atmospheres of the other planets will yield a variety of free radicals and ions. These species will react with one another, absorb and emit light, to produce phenomena as complex and interesting as observed in our own atmosphere. We shall discuss the atmospheres, and some phenomena attributable to their chemical properties, for Venus, Mars and Jupiter. As space technology progresses, the upper atmospheres of these planets assume greater importance.

Venus

Venus is completely covered by clouds which are believed to be about 30 km high.⁷³ Only the atmosphere above the clouds is accessible to observation in the visible and infra-red region of the spectrum (radio waves appear to penetrate the cloud layer). The atmosphere above the clouds has been found to consist mostly of carbon dioxide, the observed amount being 1000 m-atm. All attempts to find water vapour in the Cytherean atmosphere failed until recently,⁷⁴ when spectroscopic observations from a balloon floating above the terrestrial water vapour confirmed its presence. The amount of water on Venus above the clouds is estimated as the equivalent of 19 microns of liquid water, which is about four times as much as in the terrestrial stratosphere. It can be presumed that there is much more water below the cloud surface. For all other gases, only upper limits can be given,⁷⁵ such as 100 cm-atm of CO, 20 cm-atm of CH₄ and 4 cm-atm of NH₃. Thus, the known composition of the Cytherean atmosphere is principally CO₂, with traces of water vapour. It is likely that inert gases such as N₂ and Ar are present. The summary of various spectral observations which follows shows that a number of other species exist in the atmosphere, whose nature is as yet unknown.

Recent observations by Sinton and Strong⁷⁶ have shown the existence of an absorption band in the atmosphere at 11.2 μ . The molecule responsible for this band is unknown. On some occasions, the CO₂ bands normally observed in this spectral region disappeared completely, indicating that an unknown absorbing material was above the carbon dioxide. It was suggested that the origin of both the unidentified band and the grey material above the CO₂ was polymerized carbon suboxide.

Other unidentified absorptions have been found in the violet and near ultraviolet region by Kozyrev.⁷⁷ He reports two distinct features of the Cytherean spectrum: (i) a continuous absorption, beginning near 4500 Å and growing very intense in the violet end of the spectrum, and (ii) absorption bands at 4372 Å and 4120 Å. Recent observations by Heydon, Kiess and Kiess,⁷⁸ working with a higher dispersion than Kozyrev, have confirmed the existence of the continuous absorption, but not the bands. Thus, either the bands observed by Kozyrev are transient in nature, or as Kuiper has suggested,⁷⁹ arise from the terrestrial atmosphere. Support for the former view is that Kozyrev⁸⁰ failed to observe the bands in the spectra of Mars and Jupiter, whereas he presumably would have if they were of terrestrial origin.

The continuous absorption, which gives the planet a yellow tint, is very difficult to account for. Rayleigh scattering by the atmosphere can account for part of it. If scattering from clouds of ice crystals (or other material) is added to the Rayleigh scattering, the absorption may be explained. Otherwise, the absorption could result from coloured chemical compounds, either in the clouds, or in the atmosphere. Kuiper has suggested⁷⁹ that the clouds are composed of yellow carbon suboxide polymer. Urey and Brewer⁸¹ have suggested that brown carbonaceous compounds are dissolved in the droplets of the clouds, or alternatively, that ions of CO^+ or CO_2^+ in the upper atmosphere absorb light. Kiess and co-workers⁷⁸ have advanced the notion that nitrogen dioxide is responsible for the absorption. It is difficult to eliminate entirely any of these possibilities, although, as will be seen below, the presence of carbon suboxide or nitrogen dioxide does not seem likely on purely chemical grounds.

The band absorptions observed by Kozyrev, if real, do not seem to correspond to absorptions by any neutral molecule which one might think to be common on Venus. However, there is a correspondence⁸¹ between the observed absorption bands and emission bands of N_2^+ and CO^+ . According to physical evidence presented by Urey and Brewer⁸¹ CO^+ is more likely than N_2^+ .

Not only is light absorbed by various species in the Cytherean atmosphere, but light is also emitted. The so-called ashen light of Venus is the faint emission of light by the atmosphere on the dark side of the planet. The ashen light has been analysed spectroscopically by Kozyrev⁸² and by Newkirk,⁸³ with the result that a number of band emissions were found. Kozyrev suggested that some of them were emitted by N_2^+ . Unfortunately, Newkirk could not confirm the existence of these bands. However, the two observers agree on the existence of strong emissions near 4415 Å and 4435 Å. The former is estimated to be eighty times more intense than the green oxygen line in the terrestrial airglow. Neither of the two bands appears to arise from hitherto observed emissions of N_2^+ , CO , CO^+ and CO_2^+ . The band at 4435 Å corresponds roughly to the Goldstein-Kaplan bands of N_2 at 4446.2 Å, 4438.8 Å and 4432.3 Å. The band at 4415 Å corresponds very approximately to both the second positive band of N_2 at 4416.7 Å, and one of the maxima of the carbon monoxide flame bands at 4413 Å. Certain identification of the emitting molecules must await more accurate measurements. The bands observed by Newkirk seem to be superimposed upon a continuum beginning near 4500 Å and growing brighter towards the blue. Speculatively, this emission could arise from the carbon monoxide flame bands or flame continuum. The appearance of the carbon monoxide flame bands in the Cytherean airglow might be anticipated from the fact that these bands arise from excited CO_2 formed by the three-body reaction of CO with oxygen atoms.⁸⁴ Since photodissociation of CO_2 to CO and O must take place in the upper atmosphere of Venus, the recombination of CO and O must continually occur, with the accompanying emission of light. In addition to the flame bands, one might also expect emission of the CO flame continuum from the bimolecular reaction of CO and O

in high temperature regions of the upper atmosphere.⁸⁵ How intense these emissions might be cannot be stated, since the oxidation of CO may occur mainly by reaction with OH. Also, the luminous efficiencies are unknown.

The composition of the clouds has long been a subject for speculation. One of the most important properties of the clouds is the extent to which they polarize sunlight reflected from them. Lyot⁸⁶ measured the polarization, and sought materials which would yield similar results. The best reproduction of the Cytherean polarization was observed from a cloud of water droplets. Lyot concluded from this that the clouds were composed of transparent liquid droplets, probably water. Recent measurements by Kuiper⁷⁹ of polarization of infra-red light from Venus did not seem to support this conclusion, and it was suggested that the clouds were composed of yellow carbon suboxide polymer rather than of water. However, water has now been observed in the atmosphere in amounts exceeding that in our own stratosphere. This eliminates the carbon suboxide hypothesis, since carbon suboxide and water react rapidly with one another to form malonic acid.⁸⁷ It therefore seems not unlikely that the clouds are water. No other substance has been suggested which fits the available evidence so well.⁸⁸

It is clear that an expanded knowledge of the photochemistry of carbon dioxide-water mixtures would be of help in understanding the phenomena discussed above, as well as in predicting things not now observable. For example, it is certain that CO₂ will be dissociated to form C, CO and O, and that H₂O will be dissociated to yield H and OH in the upper atmosphere of Venus. The amount of sunlight incident on Venus is roughly twice that incident on Earth, so that considerable dissociation may be expected. The reactions of the dissociation products among themselves will yield a host of other compounds, such as O₂, O₃ and H₂, and possibly HCO. Knowledge of the chemical kinetics of these reactions would allow one to estimate the abundance and altitude distribution of these compounds.

Mars

The only atmospheric absorption bands certainly identified in the spectrum of Mars are those of CO₂. However, the amount of CO₂ found in this way is insufficient to account for the total pressure of gas found by light scattering, and the remainder of the gas is thought to be nitrogen. The polar caps are believed to be ice, so that traces of water vapour are present. The probable composition of the Martian atmosphere is as follows:⁷³

| <i>Component</i> | <i>Volume per cent</i> |
|------------------|------------------------|
| CO ₂ | 2.2 |
| N ₂ | 93.8 |
| Ar | 4.0 |
| H ₂ O | trace |
| O ₂ | <.1 |

A considerable chemical similarity between the Martian and Cytherean atmosphere is evident. Both have CO_2 , traces of water, and no observable amounts of oxygen. The photochemistry of the atmospheres should be similar.

Perhaps it is not surprising to find that the Martian atmosphere exhibits a continuous absorption much like that observed for Venus. The practical effect of this absorption is the disappearance of surface details of the planet when it is viewed in blue light. For this reason, the effect has been called the blue haze, or violet layer of Mars. The simplest explanation of the haze is that it consists of a cloud of ice crystals.⁸⁹ However, the haze clears away occasionally, very rapidly, and uniformly, and always when the earth is between Mars and the Sun. This suggests that the haze results from some effect of charged particles from the Sun on the Martian atmosphere, since the magnetic field of the earth can be expected to shield Mars from solar particles at opposition. Urey and Brewer^{81,90} have suggested that the solar particles produce absorbing molecules or ions in the upper atmosphere, either directly or by secondary radiations produced locally, and that these molecules or ions cause the blue haze. Possibly, ions such as CO^+ , CO_2^+ or N_2^+ could be responsible. Still another suggestion for a chemical origin of the blue haze has been made by Kiess *et al.*⁹¹ on the basis of high-dispersion spectral measurements of Mars in the violet region of the spectrum. The continuous absorption appears to begin near 4200 Å, and superimposed on it are what appear to be a number of ill-defined absorption bands. The general appearance of the spectrum is quite similar to that of NO_2 so that its presence on Mars is indicated. Kiess *et al.* have also suggested that many of the other observed features of Mars—the polar caps, seasonal colour changes and so on—can be attributed to NO_2 . If NO_2 is present, its infra-red bands should be observed. A band at 3.43 μ attributed by Sinton⁹² to Martian vegetation, corresponds to an NO_2 band.

However, the weak band at 10 μ was not observed by Sinton and Strong.⁹³ Furthermore, NO_2 at low pressures is decomposed quite efficiently⁹⁴ by light of wavelengths shorter than 3660 Å, so that the presence of appreciable amounts of it is difficult to understand, as well as implying the presence of NO and O_2 , which have never been detected. Evidently, the nature of the blue haze of Mars is still an open question.

Jupiter

The atmosphere of Jupiter consists principally of hydrogen and helium, with small amounts of ammonia and methane. The latter compounds will be decomposed by sunlight in the upper Jovian atmosphere to yield a variety of radicals and ions. Several phenomena observed on Jupiter may have their origin in photochemical processes in the atmosphere. Periodic changes in brightness of the planet associated with changes in solar activity may be due to changes in the amounts of radicals and ions in the atmosphere.⁸¹ The colours of Jupiter have been ascribed to frozen free radicals trapped in frozen ammonia or methane crystals.⁹⁵ A continuous absorption in the violet, similar to that previously discussed for Venus and Mars, is observed for Jupiter.⁹⁶ As

before, the origin of this absorption may be from scattering of light by the atmosphere and clouds, or from absorbing molecules and ions in the atmosphere, or (most probably) from a combination of the two. Radio emissions from Jupiter at 18 Mc/s appear to be emitted in beams, rather than isotropically.⁹⁷ A plausible explanation of this is that the emission is from storms below the ionosphere, and that the ionosphere restricts the radiation escaping to space to a beam. The angular width of the beam suggests that the ion density of the Jovian ionosphere is quite similar to that of Earth. This is surprising, since Jupiter receives only a fraction of the solar radiation received by the earth. Perhaps some easily ionized molecule is abundant in the Jovian atmosphere.

The photochemistry of the Earth's upper atmosphere is a fascinating, but complex, subject. With the expanded use of rockets as vehicles to convey instruments to high altitudes, and to carry out experiments as explained above, there will be a rapid accumulation of data which will help to clarify many issues. There will always be the need, however, for reliable quantitative information on the rates of reactions which are unusual, so far as the chemist is concerned, and occur strictly in the gas phase.

Photochemical phenomena in the atmospheres of the nearer planets are of growing importance and interest. At present there is insufficient observational material on which to build any significant theoretical interpretation but in the next few years we expect much more information to be gathered by observation from balloons, from satellites with space-stabilized instrument platforms and eventually from space vehicles penetrating to the near neighbourhood of the planets in question.

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