THE PHOTO-CHEMISTRY OF SOME MINOR CONSTITUENTS OF THE EARTH'S ATMOSPHERE
(CO₂, CO, CH₄, N₂O)

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Summary

Carbon dioxide and carbon monoxide: The rate of photo-dissociation of CO_2 is appreciable only in the region above about 100 km. If local equilibrium prevails the carbon would occur mainly as the monoxide in this region, and as the dioxide below. However, oxidation may proceed so slowly that the life of a CO molecule is long compared with the characteristic time associated with atmospheric mixing effects. In this case the CO resulting from photo-dissociation would not be confined to above the 100 km level, but would extend much lower; its total abundance could scarcely be great enough to produce the observed absorption lines. It is estimated that the various forms of combustion taking place on the Earth would provide the CO content of the atmosphere within perhaps four years or even less.

Methane: Dissociation of CH_4 in the upper atmosphere is brought about mainly by collision processes. These prevent the existence of appreciable CH_4 above the 100 km level and probably keep the concentration low even down to 70 km. The yield to date from oil wells and coal mines appears to be less than the amount of the gas now in the atmosphere. Seepage from fuel beds, and the anaerobic decay of vegetable matter, are the only obvious naturally occurring sources of significance. As far as can be judged at least ten years (and probably much longer) is required for the production of the atmospheric abundance.

Nitrous oxide: Information on the necessary rate of formation of N_2O is obtained by calculating the photo-dissociation rate. One hypothesis is that soil micro-organisms produce the gas, but it appears that the yield would only be sufficient if N_2O were a major end-product of denitrification. Many of the homogeneous gas reactions suggested by earlier workers must be rejected, since there is an inadequate supply of the requisite parent particles. The only acceptable parent particles seem to be those arising directly or indirectly from the photo-dissociation of O_2 in the Herzberg continuum. Various reactions involving O, O_3 and N_2 are discussed. Though they are very slow they might nevertheless give rise to sufficient N_2O.

1. *Introduction.*—The photo-chemistry of atmospheric oxygen has been studied by many scientists (**1**), and though much detailed work remains to be done, the researches of Chapman and others have led to a general understanding of the factors involved in the formation of the ozone layer and of the atomic region. While the desirability of a similar study of nitrogen has long been realized, comparatively little has yet been achieved because of some special difficulties that arise and because of lack of certain basic data; and as nitrogen is obviously the next most important gas to investigate there has been a neglect of the other constituents—though Meinel's discovery (**2**) of the hydroxyl bands in the spectrum of the airglow recently stimulated Bates and Nicolet (**3**) to carry out an exploratory survey of the photo-chemistry of water vapour. The object

of the present paper is to remedy this omission partially by investigating the position regarding carbon dioxide, carbon monoxide, methane and nitrous oxide. Originally the research was directed at obtaining information on the altitude distribution of the polyatomic molecules (which is of importance in connection with studies of the thermo-balance in the upper atmosphere). During the course of it the existence of several interesting cycles was realized, and these are also discussed.

2. *Model atmosphere.*—Table I gives the current estimates of the particle concentrations, $n(M)$, and temperatures, T, at various altitudes, z, up to 130 km (3). They are significantly different from those accepted at the time of the main work on the O–O_2–O_3 equilibrium. Since this equilibrium is of importance in the study of the minor constituents it had therefore to be re-investigated. The processes involved have been discussed fully by earlier writers (1), so that we need only indicate them briefly, and record the assumptions made in calculating the rates at which they occur.

TABLE I
Structure of Atmosphere

Altitude z (km)	Particle Concentration $n(M)$ (cm^{-3})	Temperature T (deg. K)
130	$1 \cdot 2 \times 10^{12}$	450
120	$2 \cdot 7 \times 10^{12}$	360
110	$7 \cdot 4 \times 10^{12}$	305
100	$2 \cdot 3 \times 10^{13}$	270
90	$8 \cdot 7 \times 10^{13}$	245
80	$3 \cdot 9 \times 10^{14}$	215
70	$2 \cdot 5 \times 10^{15}$	190
60	$8 \cdot 2 \times 10^{15}$	275
50	$2 \cdot 3 \times 10^{16}$	290
40	$6 \cdot 8 \times 10^{16}$	250
30	$3 \cdot 9 \times 10^{17}$	225
20	$2 \cdot 0 \times 10^{18}$	220
10	$8 \cdot 8 \times 10^{18}$	220
0	$2 \cdot 6 \times 10^{19}$	285

Photo-dissociation of molecular oxygen is produced by the absorption of solar radiation in the strong Schumann–Runge continuum beginning at $\lambda\,1759$:

$$O_2 + h\nu \rightarrow O(^3P) + O(^1D), \tag{1}$$
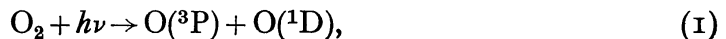
and in the weak Herzberg continuum beginning at $\lambda\,2421$:

$$O_2 + h\nu \rightarrow 2O(^3P). \tag{2}$$

In the presence of a third body the atoms thus liberated may recombine

$$O + O + M \rightarrow O_2 + M, \tag{3}$$

or they may unite with oxygen molecules

$$O + O_2 + M \rightarrow O_3 + M, \tag{4}$$

forming ozone. This substance may be destroyed by the collision process

$$O + O_3 \rightarrow 2O_2, \tag{5}$$

and by photo-dissociation in the strong Hartley continuum beginning about $\lambda\,3500$:

$$O_3 + h\nu \rightarrow O_2 + O(^1D), \tag{6}$$

and in the weak Chappuis continuum beginning about $\lambda 8000$:

$$O_3 + h\nu \to O_2 + O(^3P). \tag{7}$$

Following the usage of other authors the reciprocals of the life-times of oxygen and ozone molecules towards photo-dissociation by (1) and (2), and by (5) and (6), will be denoted by J_2 and J_3, and the rate coefficients associated with (3), (4) and (5) by k_1, k_2 and k_3 respectively.

The intensity of the incident radiation down to $\lambda 2200$ has been determined by means of rocket-borne instruments {*cf.* Durant (**4**)}, and in the spectral region of interest beyond it probably approximates to that which would ensue if the Sun were a 5000 deg. K black body {*cf.* Nicolet (**5**), Greenstein (**6**)}. Since the relevant absorption cross-sections are also known * the values of J_2 and J_3 at various optical depths can hence be computed. The position regarding the rate coefficients is much less satisfactory. For reasons discussed elsewhere (**3**) it was tentatively assumed that in ordinary air

$$k_1 = 5 \times 10^{-34} T^{1/2} \, \text{cm}^6/\text{sec}, \tag{8}$$

$$k_2 = 5 \times 10^{-36} T^{1/2} \, \text{cm}^6/\text{sec}, \tag{9}$$

where T, as usual, is the temperature; and that the relative efficiencies of O_2, N_2 and O as third bodies are as $1.0 : 0.6 : 0.1$ approximately {Penndorf (**8**)}. Since Eucken and Patat (**9**) have measured the ratio of k_2 to k_3 this latter is then also determined.

At altitudes down to about 70 km it is usually supposed that the concentrations $n(O_2)$ and $n(O)$ are controlled by processes (1), (2) and (3), so that

$$J_2 n(O_2) = k_1 n(O)^2 n(X), \tag{10}$$

where $n(X)$ is the *effective* number of third bodies found by weighting O_2, N_2 and O in the manner indicated above. In addition, if $n(M)$ is the total particle concentration (given in Table I) then

$$n(O_2) + n(N_2) + n(O) = n(M), \tag{11}$$

and since the relative abundance of oxygen and nitrogen is presumably the same as at ground level,

$$n(O) + 2n(O_2) = 0.53 n(N_2). \tag{12}$$

These equations are somewhat troublesome. They were solved by commencing at the 130 km level (which is at essentially zero optical depth) and proceeding downwards to the 80 km level in altitude intervals so narrow that the attenuation in each is small {*cf.* Penndorf (**8**)}. The labour involved was however scarcely justified, since eqn. (10) over-simplifies the situation. Atomic hydrogen and certain radicals, which are present in the upper atmosphere, catalyse the formation of molecular oxygen. Bates and Nicolet (**3**) have investigated the extent to which this is likely to influence the equilibrium. They found that the effect may be significant below 85 km, and gave crude estimates of $n(O)$ and $n(O_3)$ down to the 65 km level. These were adopted, as there are insufficient basic data to improve upon them. At low altitudes catalysis becomes unimportant and (2), (4), (5), (6) and (7) are the dominant reactions. In principle the equilibrium

* Reference (**3**) lists the principal original papers on the subject and discusses the extrapolation of some of the experimental results. Its recommendations were followed, except that in the case of the Herzberg continuum the absorption cross-section curve obtained by Buisson, Jausseran and Rouard (**7**) was adopted.
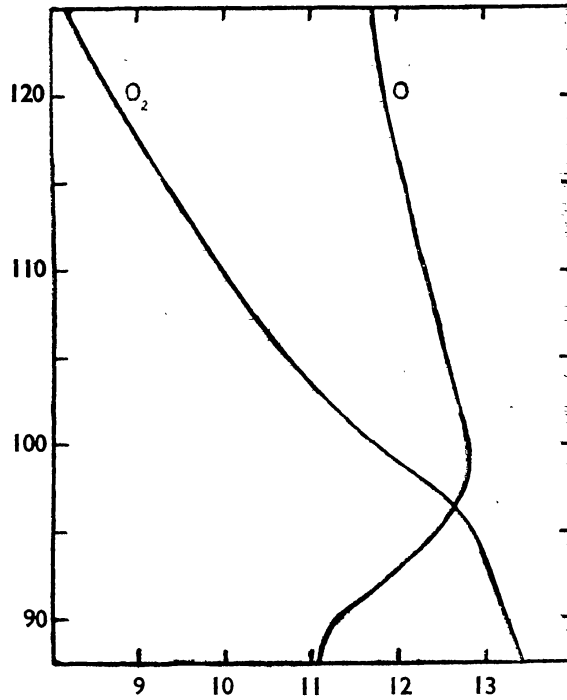
Fig. 1.—*Distribution of n(O) and n(O$_2$). (Day equilibrium.*)*

Ordinates : Altitude in kilometres.
Abscissae : Log$_{10}$ (particle concentration).

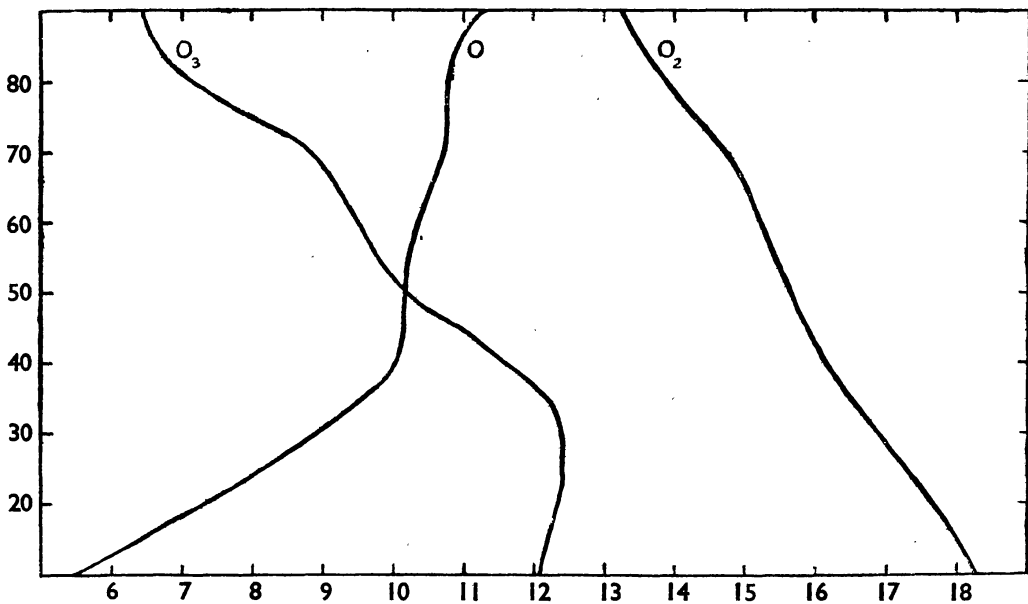Fig. 2.—*Distribution of n(O) and n(O$_2$) and n(O$_3$). (Day equilibrium.)*

Ordinates : Altitude in kilometres.
Abscissae : Log$_{10}$ (particle concentration).

* In the region covered by Fig. 1, n(O$_3$) is too small to be of interest. (It should be noted that the moderate rate of fall-off shown in Fig. 2 does not continue to greater altitudes, it becomes much more rapid at the O$_2$–O transition layer.)

can be determined using theory alone, but various difficulties enter and the full calculations were carried out only near the 50 km level. For altitudes up to 40 km it was judged best to accept the measurements on $n(O_3)$ {Fabry [7]} and to deduce $n(O)$ from them by means of the relation

$$n(O) = n(O_3)\{J_3/k_2 n(O_2) n(M)\} \tag{13}$$

with

$$n(O_2) = 0 \cdot 21 n(M) \tag{14}$$

{*cf.* [3]}. As has already been mentioned k_2 is not known reliably. It is possible that steric hindrance is not as severe as assumed {*cf.* Bamford [10]}, so that the use of (13) may cause $n(O)$ to be overestimated.

The distributions in the different regions were finally combined together as shown in Figs. 1 and 2. It may perhaps be mentioned that the main changes in the slopes of the $n(O)$ and $n(O_3)$ curves are due to the fact that the coefficient k_3 is extremely sensitive to the temperature. While such qualitative features are likely to be real the general accuracy of the results is unfortunately very poor.

Some of the reactions of interest involve atomic hydrogen, hydroxyl and perhydroxyl. Estimates of $n(H)$, $n(OH)$ and $n(HO_2)$ are available from the work of Bates and Nicolet [3].

3. *Carbon dioxide and carbon monoxide.*—The fractional volume concentration of carbon dioxide is not the same all over the Earth's surface, even apart from purely local effects {*cf.* Rankama and Sahama [11]}. However, for present purposes it may with sufficient accuracy be taken as constant and equal to 3×10^{-4} {Paneth [12]}. In the altitude range concerned diffusive separation is unimportant.

In 1949 Migeotte [13], then working at Columbus, Ohio, announced that certain lines in the $4 \cdot 7 \mu$ region of the solar spectrum are due to atmospheric carbon monoxide. Later in Switzerland he and Neven [14] succeeded in confirming this. Adel [15], in Flagstaff, Arizona, failed to detect the lines, but as they appear in a spectrum recently obtained by Shaw, Chapman, Howard and Oxholm [16] (also working at Columbus, Ohio), their reality is not in doubt. The lines observed are members of the fundamental vibrational band. Matheson, and Penner and Weber [17] have carried out laboratory measurements on them. The former found the Lorentz half-breadth in air at atmospheric pressure to be $0 \cdot 10$ cm^{-1}, and the latter found the associated Einstein spontaneous transition coefficient to be 33/sec. Combining these data with equivalent widths obtained from the published spectrograms (in particular from those of Shaw and his collaborators, as they include some weak lines attributed to the isotopic molecule $C^{13}O$ which probably lie on the linear part of the curve of growth), it is estimated that there is about $0 \cdot 2$ atm-cm of carbon monoxide in the atmosphere. The figure is of necessity rather crude—an error by a factor of perhaps 3 either way is possible. Much more reliable determinations have recently been made by Migeotte and Neven*, who on two different days obtained about $0 \cdot 4$ atm-cm and $0 \cdot 1$ atm-cm at the Jungfraujoch (showing that the abundance is variable). The lower value (which is presumably the least affected by any local contamination) will be tentatively adopted; it corresponds approximately to a fractional volume concentration of 1×10^{-7} or to 3×10^{18} CO molecules/cm^2 column.

* We wish to thank Dr Migeotte for informing us of the results prior to their publication.

The photo-chemistry of the two gases is clearly closely related. Radiation to the short wave-length side of $\lambda 1690$ dissociates carbon dioxide into carbon monoxide and excited (^{1}D) atomic oxygen

$$CO_2 + h\nu \rightarrow CO + O(^1D). \tag{15}$$

The cross-section for the process has been measured by Wilkinson and Johnston (**18**). Using their results, taking the Sun as usual to be a 5 000 deg. K black body (*cf.* Section 2) and averaging over day and night, it may be shown that in the region just above the 100 km level $\tau(CO_2)$ the life-time of a CO_2 molecule towards photo-dissociation through (15) is about 5×10^6 sec. Owing to absorption in the Schumann–Runge continuum of molecular oxygen the intensity of the active radiation falls off rapidly below this level. Consequently $\tau(CO_2)$ becomes extremely long, being very many years even at 95 km, and essentially infinite at 90 km.

Carbon dioxide may be re-formed through

$$CO + O + M \rightarrow CO_2 + M. \tag{16}$$

This process has been studied by Groth (**19**) and by Jackson (**20**), who find that the probability that it occurs in a normal three-body collision is some 100 times less than the probability of (4), which itself is small. If the estimate given in (9) is correct, then the rate coefficient for (16) would only be $5 \times 10^{-38} T^{1/2}$ cm^6/sec. As is well known (*cf.* **21**), the oxidation of carbon monoxide is accelerated by the presence of moisture. This is generally attributed to the reactions

$$CO + OH \rightarrow CO_2 + H, \tag{17}$$

$$CO + HO_2 \rightarrow CO_2 + OH. \tag{18}$$

These must also be taken into account in the upper atmosphere. The rate coefficients may be expressed in the form

$$k = \eta P \exp(-E/RT), \tag{19}$$

where R is the gas constant (1·987 cal/deg-mole), η is the collision frequency for unit concentrations, P is the steric hindrance factor and E is the activation energy. Unless there is evidence to the contrary it is usual in order-of-magnitude calculations to take the product ηP to be about $1 \cdot 5 \times 10^{-11} T^{1/2}$ cm^6/sec or rather less (*cf.* **22**). At the temperatures prevailing in the upper atmospheric region of interest the rate coefficients depend critically on the activation energy. Unfortunately the values appropriate to (17) and (18) do not appear to have been determined. To explore the situation two alternative arbitrary assumptions were made: (*a*) that for both reactions E is zero, (*b*) that for both it is 5 kcal. Calculations were then carried out on $\tau(CO)$, the mean life-time of a CO molecule towards oxidation by (16), (17) and (18) in the model atmosphere already described. In spite of the uncertainties some general conclusions can be reached.

Even with the highest possible rate coefficients it is found that $\tau(CO)$ is of the order of centuries near the 110 km level and is longer at greater altitudes. Life-times so extended have of course little real meaning. Below 100 km however $\tau(CO)$ may be moderate: at the 90, 80 and 70 km levels assumption (*a*) gives it

to be about 10^5, 10^3 and 10 sec and assumption (*b*) gives it to be about 10^9, 10^8 and 10^7 sec respectively.   Thus

$$\tau(CO_2) \ll \tau(CO) \text{ for } z > 110 \text{ km} \tag{20}$$

and
$$\tau(CO_2) \gg \tau(CO) \text{ for } z < 90 \text{ km}. \tag{21}$$

In equilibrium

$$n(CO)/n(CO_2) = \tau(CO)/\tau(CO_2), \tag{22}$$

and therefore the carbon would be almost entirely in the dioxide form below the 90 km level and in the monoxide* form above the 110 km level.   The altitude of the transition level is difficult to estimate precisely but it is certainly very close to 100 km.   For reasons which will be apparent later the significance to be attached to the derived relative abundances does not justify giving them in full.   To demonstrate their trend it is sufficient to mention that at 130 km (where (16) is the only oxidation process of importance) the calculated value of $n(CO)/n(CO_2)$ is 10^6 approximately.

. It is natural to enquire at this stage whether the photo-dissociation would give rise to enough carbon monoxide to account for the observed infra-red absorption lines.   At first it might be thought obvious that this is utterly impossible ; for the fractional volume concentration of carbon dioxide in the lower atmosphere is 3×10^{-4}, and the total particle concentration and local scale-height at 100 km are $2 \cdot 3 \times 10^{13}$/cm^3 and 10 km respectively.   Hence there would only be about 7×10^{15} CO molecules/cm^2 column above the transition level, which is much too small a number.   However, such an argument is faulty, in that it assumes that equilibrium conditions prevail.   This assumption is only justified if $\tau(CO_2)$ and $\tau(CO)$ are short compared with a characteristic atmospheric parameter, $\tau(M)$, which is a measure of the time required for winds and diffusion to produce mixing.   The value of $\tau(M)$ is unfortunately unknown, but it must be considerable in view of the stabilizing effect of the positive temperature gradient of the atmosphere in the region of the transition layer.   As has already been noted, $\tau(CO_2)$ is about 5×10^6 sec at altitudes above 100 km.   This is not unduly long, so that, in general, the degree of dissociation may well be high (though perhaps not as high as simple equilibrium calculations would indicate).   At altitudes below 100 km, $\tau(CO)$ is the life-time of importance. Its value is here mainly controlled by processes (17) and (18).   Or, referring to the figures already given, it can be that if the activation energy E is zero then $\tau(CO)$ would be quite short.   In this case the mean concentration of carbon monoxide would be kept low by oxidation.   However, if, as is more probable, E is 5 kcal or above, the position would be quite different, since $\tau(CO)$ would be several months or more even at 70 km.   Consequently the equilibrium calculations would be unlikely to be correct.   Instead of carbon monoxide being mainly confined to the region above the transition level it would also be prevalent in the region below, for any reaching there would remain for a very long time before becoming oxidized.   In extreme circumstances the altitude at which photo-dissociation ceases would not be apparent from the carbon monoxide distribution curve, which would closely follow that of the main atmospheric gases down to perhaps 70 km or even lower.   The total abundance resulting from photo-dissociation cannot be calculated until $\tau(CO)$ and $\tau(M)$ are known.   Though the departure from chemical equilibrium may well be very pronounced, the associated

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* Further breakdown of the carbon oxides is unlikely to occur to any marked extent, since CO (like the isoelectronic N$_2$) is difficult to photo-dissociate {*cf.* Gaydon (23)}.

increase in the abundance is unlikely to be sufficient to explain the spectroscopic observations; for this would only be possible if the monoxide were as prevalent as the dioxide down to the 30 or 40 km level. A measurement of the altitude of the region in which the CO lines are formed would be of considerable interest.

It must not be forgotten that carbon monoxide is a major by-product of modern civilization. Vast quantities are vented into the atmosphere both by internal combustion engines and by solid-fuel furnaces.

The first source is the easier to assess quantitatively. Petrol consists of about 85 parts of carbon to 15 parts of other elements (**24**). The annual consumption of it is about $1 \cdot 5 \times 10^{14}$ g. From an analysis of the exhaust gases of motor vehicles given by Dunstan (**25**) it appears that as much as 40 per cent of the carbon is emitted as the monoxide. Hence the amount of carbon monoxide released into the atmosphere is approximately $1 \cdot 2 \times 10^{14}$ g/year. Since the surface area of the Earth is $5 \cdot 1 \times 10^{18}$ cm^2, and the mass of a CO molecule is $4 \cdot 7 \times 10^{-23}$ g, this is equivalent to a mean of 5×10^{17} CO molecules/cm^2/year. Diesel engines give but a minor contribution, as they are highly efficient and as the quantity of heavy oil used is relatively small.

Coal is by far the most important solid fuel. Its composition varies widely. The carbon content may be as low as 60 per cent in lignites and as high as 95 per cent in anthracites (**26**). On an average it may be taken to be perhaps 80 per cent. The amount of coal used in a year is about $1 \cdot 7 \times 10^{15}$ g. Unfortunately it is difficult to obtain representative data on the proportion of carbon monoxide in the combustion products, as this is critically affected by the conditions under which burning takes place. Thus Hurley and Sparks (**27**) have analysed the flue gases from boiler furnaces and find that the CO/CO_2 ratio ranges from $0 \cdot 005$ to $0 \cdot 20$, depending on such factors as the air draft. Fuel engineers of course try to keep the ratio as low as possible in the interests of thermal efficiency. When it equals $0 \cdot 02$ the heat loss is only 1 per cent (**26**), which suggests that little effort would be made to ensure a more complete combustion (especially as the use of too much excess air also causes losses). Forest and prairie fires are estimated by Kalle (*cf.* **11**) to add as much carbon dioxide to the atmosphere as does the burning of coal, but no information is available on the carbon monoxide. From the figures given above it would seem not unreasonable to suppose that the mean value of the CO/CO_2 ratio for all forms of non-explosive combustion is at least $0 \cdot 01$ and is probably rather more. On this assumption the contribution to the production rate (averaged over the Earth) is 3×10^{17} CO molecules/cm^2/year or greater.

Volcanic emanations contain some carbon monoxide, but from data given by Rankama and Sahama (**11**) it is at once apparent that the quantity released in this way is small.

Summation of the sources mentioned gives that the total production rate is at least some 8×10^{17} CO molecules/cm^2/year, which is sufficient to provide the estimated carbon monoxide content of the atmosphere within four years or less. Unless some destruction process occurs on the ground itself or at low altitudes, such a production rate must be of importance in determining the equilibrium abundance. For comparison it may be mentioned that the action of solar radiation on the upper atmosphere would yield fewer than 1×10^{16} CO molecules/cm^2/year even if the fractional volume concentration of carbon dioxide in the region concerned were kept as high as one-fifth of what it would be if photo-dissociation did not occur.

Combustion processes certainly lead to considerable localized contamination: for example, while the presumed global average of the fractional volume concentration of carbon monoxide is 1×10^{-7}, it appears from measurements made by various investigators that the value in busy streets is frequently 1×10^{-4}, that in cities 5×10^{-6} and that in urban areas 2×10^{-7} or less (28).* Clearly winds would ensure a widespread dispersal of the contamination even if the mean life of the CO molecules (which has yet to be discussed) should prove to be only a few days. In spite of its remoteness the Bernese Oberland (where Migeotte and Neven conducted their experiments) would be affected. On the other hand, the fact that the combustion occurring in the northern hemisphere is far greater than that occurring in the southern hemisphere might conceivably cause carbon monoxide to be more abundant in the former than in the latter. Thus the meridional circulation of the atmosphere (30) is not such as to facilitate the transfer of contamination from one hemisphere to the other; and in any case even a steady breeze having a N.–S. component of 20 km/hour would take about a month to travel 90° of latitude. It would be interesting in this connection to have data on the amount of carbon monoxide above some southern observatory (say in New Zealand).

The carbon monoxide molecules resulting from combustion apparently cannot have a life exceeding four years (*v. supra*). It would appear therefore that oxidation processes occurring in the upper atmosphere can be ignored. Thus the particle concentration at the 50 km level is more than 10^3 times smaller than that at ground level. Hence if a molecule were normally to reach the 50 km level within the time stated it would follow that a molecule at this level would normally take only a day to fall to ground level, which seems unlikely.

It is difficult to reach any final conclusion about the rate of oxidation of carbon monoxide in the dense lower atmosphere. For a process might restrict $\tau(CO)$ to less than four years and yet be so slow as to have escaped detection in the laboratory. Some relevant information is however available.

The reaction between carbon monoxide and molecular oxygen is exothermic, but it can probably be dismissed, since Mellor (31) reports that Berthelot could find no evidence for its occurrence when he exposed dry and moist mixtures of the two gases to sunlight for seven years. As can readily be verified from the estimated rate coefficient of (16), and the concentrations given in Fig. 2, atomic oxygen cannot cause appreciable loss. Ozone also is a very inefficient oxidizer of carbon monoxide. Zatsiorskii, Kondrateev and Solnishkova (32) find that the activation energy of

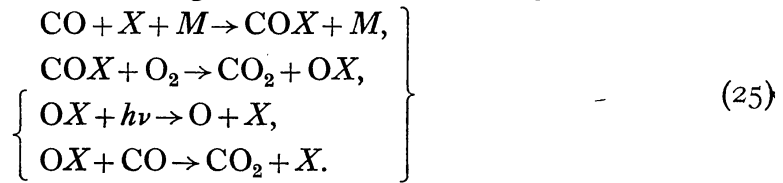$$O_3 + CO \rightarrow O_2 + CO_2 \tag{23}$$

is about 20 kcal. On substituting in (19) it can hence be seen that the process is unimportant. A prohibitively high activation energy appears indeed to be characteristic of the reaction with many oxygen compounds. For example, that associated with

$$NO_2 + CO \rightarrow NO + CO_2 \tag{24}$$

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* Abnormally high concentrations of carbon dioxide of course also occur but the departure from the mean is less pronounced. Thus Haldane (29) states the fractional volume concentration in the air of London is about $6 \cdot 5 \times 10^{-4}$ which is little over twice the global average of 3×10^{-4}. Judging from the ratio of the excess CO to excess CO_2 in town air it would seem unlikely that we have overestimated the rate of production of carbon monoxide.

In view of the spectroscopic estimates, the figure for urban areas is surprisingly small.

is thought to be 28 kcal {Brown and Crist (33)}.   However, the atmosphere may contain minute traces of some highly active substances and it is not easy to exclude the possibility of one of them oxidizing carbon monoxide through a chain such as

$$\left.\begin{array}{r} CO + X + M \to COX + M, \\ COX + O_2 \to CO_2 + OX, \\ \left\{\begin{array}{l} OX + h\nu \to O + X, \\ OX + CO \to CO_2 + X. \end{array}\right. \end{array}\right\} \qquad (25)$$

Quite a moderate collision efficiency would suffice even if the abundance of the catalyst at low levels were only 10^{-12} times that of all other constituents.

Reactions on the surface of the Earth may also occur.   (i) Carbon monoxide unites readily with haemoglobin.   The process is however reversible and in fact very little of the gas is oxidized in the body tissues.   Clark, Stannard and Fenn (34) have recently investigated the effect.   From their results it may easily be demonstrated that the global average of the rate of oxidation is negligible.   (ii) Plants are affected by the presence of carbon monoxide (35) which may therefore be undergoing destruction by them (though the chlorophyll reaction may also be reversible).   Quantitative data appear to be lacking.   But noting that the life-time of a CO_2 molecule towards assimilation is about ten years {cf. Rankama and Sahama (11)} it would seem rather improbable (though not impossible) that the corresponding life-time of a CO molecule is four years or less.   (iii) As has long been known, carbon monoxide in contact with soil is rapidly oxidized by various micro-organisms, in particular B. oligocarbophilus (36).   The effect has been investigated by a number of workers but it is difficult to make quantitative deductions from their results.   Most of the experiments consisted of introducing an air–carbon monoxide mixture into a flask containing some form of organic matter and studying how its composition changed with time.   Usually there was little change during an initial period, but after one or two weeks (during which the micro-organisms presumably multiplied) oxidation began, and after another one or two weeks was complete.   The interpretation of all such laboratory studies is of course complicated by the fact that both the carbon monoxide content of the air used and the surface to volume ratio of the apparatus had values far in excess of those typical of the lower atmosphere.   Nevertheless it is clear from them that B. oligocarbophilus is a very powerful agency for the destruction of carbon monoxide.   Some suggestive field observations have also been reported.   Thus after an extensive fire in an anthracite mine Jones and Scott (37) carried out periodic analysis of the gases in some sealed galleries of volume 2×10^{11} cm^3. They found that the carbon monoxide disappeared within 20 days and attributed this to the oxidizing action of micro-organisms.

From the foregoing discussion it is apparent that the mechanism responsible for the removal of carbon monoxide from the air near ground level cannot yet be identified with certainty; and that only a lower limit can be given to the rate of the process concerned.   In the circumstances no final decision can be reached as to the extent to which combustion influences the equilibrium.   But so much of the gas is produced in this way that considerable quantities must get carried into the stratosphere in spite of the possible rapid destruction near ground level. Bearing in mind that the yield from the photo-dissociation of carbon dioxide is relatively very small, it would seem likely that combustion is the main source of the carbon monoxide observed spectroscopically.

4. *Methane.*—The only hydrocarbon so far detected in the Earth's atmosphere is methane.* Migeotte (**40**) identified some of its characteristic lines in the $3\cdot4\mu$ region of a solar spectrogram taken in Columbus, Ohio, and later (**41**) identified further lines in the $7\cdot7\mu$ region of a spectrogram obtained by Adel in Flagstaff, Arizona. The discovery was confirmed by McMath, Mohler and Goldberg (**42**) working in Pontiac, Michigan, on the $2\cdot0\mu$ region. Later measurements at the same observatory (**43**) give the abundance as $1\cdot2$ atm-cm or $3\cdot2 \times 10^{19}$ CH_4 molecules/cm² column.

Photo-dissociation of methane,

$$CH_4 + h\nu \rightarrow CH_3 + H, \tag{26}$$

begins about $\lambda 1450$, and reaches its peak between $\lambda 1300$ and $\lambda 1200$. The absorption cross-sections in the region up to $\lambda 1365$ have been determined by Wilkinson and Johnston (**18**). Those in the region beyond are relatively unimportant because of the fall-off in the intensity of the solar emission. They were estimated with sufficient accuracy by extrapolation using as a guide crude data provided by the work of Duncan and Howe (**44**). On carrying out the usual computations the rate of (26) at zero optical depth was found to be only about 4×10^{-7}/sec per CH_4 molecule. It will be seen later that photo-dissociation is not the major disruptive process.

Recombination of methyl radicals and hydrogen atoms requires the presence of a third body

$$CH_3 + H + X \rightarrow CH_4 + X \tag{27}$$

{Steacie (**45**)} and consequently is very slow at the low gas densities prevailing in the upper atmosphere. Indeed a collision between a methyl radical and a hydrogen atom is more likely to lead to further break-down through

$$CH_3 + H \rightarrow CH_2 + H_2. \tag{28}$$

For this is a two-body process and its activation energy is probably less than 5 kcal {Gorin, Kauzmann, Walter and Eyring (**46**)}. Moreover the methyl radicals are destroyed by numerous other collision reactions {*cf.* (**45**)} which convert them finally to carbon monoxide or carbon dioxide. Amongst the primary processes likely to be important is

$$CH_3 + O_2 \rightarrow CH_2O + OH. \tag{29}$$

Van Tiggelen (**47**) has given evidence for supposing that this proceeds very rapidly (the estimated activation energy being only some $1\cdot5$ kcal). It is apparent therefore that the removal of a single hydrogen atom from a methane molecule leads to the essentially permanent destruction of that molecule. The concentration of methane at any particular altitude is thus not determined by the local equilibrium between dissociation and recombination, but rather by that between dissociation and atmospheric mixing effects. As a result the distribution of the gas cannot be calculated at present. But some general information on it may be obtained from the consideration of $\tau(CH_4)$, the mean life-time of methane molecules at various levels.

In addition to the direct photo action (already discussed) $\tau(CH_4)$ is influenced by several collision processes. Methane reacts rather slowly with atomic oxygen,

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* The suggestion that ethylene is present {Sutherland and Callendar (**38**)} is not supported by the recent observations of Shaw and Claassen (**39**) in Columbus, Ohio, which were sufficiently sensitive to have revealed much less than $0\cdot01$ atm-cm of the gas.

atomic hydrogen and hydroxyl. Thus the activation energy of the more probable of

$$CH_4 + O \rightarrow CH_2 + H_2O \tag{30}$$

and

$$CH_4 + O \rightarrow CH_2O + H_2 \tag{31}$$

is about 8 kcal {Steacie and Parlee (**48**)}; that of

$$CH_4 + H \rightarrow CH_3 + H_2 \tag{32}$$

is about 11 kcal {Geib and Steacie (**49**)}; and that of

$$CH_4 + OH \rightarrow CH_3 + H_2O \tag{33}$$

is also about 8 kcal {van Tiggelen (**47**)}. However, Geib and Harteck (**50**) find that when perhydroxyl radicals are present methane is rapidly oxidized even at temperatures below 100 deg. K, so that with these there must be a reaction with a very low activation energy (probably not exceeding 2 kcal).

The activation energies indicated were substituted in (19) to obtain crude estimates of the rate coefficients. These estimates were used in the compilation of Table II, which gives the approximate values of $\tau(CH_4)$ at various altitudes, and records which of the reactants is the most important.

TABLE II

*Oxidation of Methane by Collision Processes**

Altitude (km)	Principal Reactant	$\tau(CH_4)$ (sec)
120	O	10^2
100	O	10^3
90	O, HO$_2$	10^5
80	HO$_2$	10^5
70	HO$_2$	10^4

* In the region below 70 km the calculated values of $\tau(CH_4)$ are too unreliable to be worth giving. One major source of error is the uncertainty in the perhydroxyl concentration (3). This concentration probably decreases at altitudes much less than 70 km so that $\tau(CH_4)$ increases. However, because of the rise in temperature the atomic oxygen reaction again becomes important and between 60 km and 50 km it limits $\tau(CH_4)$ to perhaps 10^5–10^6 sec.

Clearly methane must be almost completely absent from the region above the 100 km level, since $\tau(CH_4)$ is there very short. Remembering that a thermo-incline hinders mixing, it seems probable indeed that oxidation keeps its abundance low, down to at least near the temperature minimum at 70 km. Little can be said about the equilibrium in the thermo-decline immediately below, but it should be noted that there is likely to be a significant loss of methane between the 60 km and 50 km levels where the temperature is a maximum. Owing to the nature of the reaction products the destruction of CH$_4$ molecules at such moderate altitudes may be a very significant factor in the chemistry of the upper atmosphere.

In view of the immense amount of fuel won from the Earth's crust during the past century it is natural to enquire if the methane now in the atmosphere could have escaped from oil wells and coal mines and thus be of comparatively recent origin.* The following figures are of relevance.

* We wish to thank Mr P. Kerr of the Institute of Petroleum, London, and Mr F. S. Hartwell of the Safety in Mines Research and Testing Establishment, Sheffield, for helpful correspondence on this topic.

Volume of atmospheric methane

($v.$ *supra*) $= 6 \times 10^{18}$ cm^3 (34)

$\left\{\begin{array}{l} \text{Amount of crude oil raised to date} \\ \text{Average volume of methane associated} \\ \quad \text{with one barrel of crude oil} \\ \text{Volume of methane associated with} \\ \quad \text{total crude oil raised} \end{array}\right.$

Amount of crude oil raised to date $= 6 \times 10^{10}$ barrels   (35)

Average volume of methane associated
with one barrel of crude oil $= 7 \times 10^7$ cm^3 (36)

Volume of methane associated with
total crude oil raised $= 4 \times 10^{18}$ cm^3 (37)

Amount of coal raised to date $= 1 \times 10^{11}$ tons   (38)

Average volume of methane associated
with one ton of coal $= 5 \times 10^6$ cm^3 (39)

Volume of methane associated with
total coal raised $= 5 \times 10^{17}$ cm^3 (40)

The main uncertainty clearly lies in the assumed quantitative relations between the methane and the crude oil and coal. Those quoted are based on information given in the standard treatise of Bone and Himus (26). Confirmation of relationship (36) was obtained from published statistical data on the production of natural gas (which is of course mainly methane) and crude oil {*cf.* Thorp (28)}. High accuracy is not required, since the methane released by oil-field operations is normally not deliberately vented into the atmosphere because of the risk of an explosion. Some is pumped back underground (to increase the oil output); some is used for local power generation; the remainder is either piped away from the field for general industrial or household purposes, or (in undeveloped countries where this is not practicable) is simply burnt in flares. Consequently the volume of methane which has actually escaped must be much less than 4×10^{18} cm^3. As almost all the methane released in mining operations passes into the atmosphere relationship (39) is rather critical. Fortunately most authorities seem to make much the same estimate as do Bone and Himus. Thus by averaging the methane content of the upcast air of 500 pits Hinsley (51) deduces that the annual discharge of the gas from British collieries is some 2×10^{15} cm^3, which corresponds to 1×10^7 cm^3/ton *; and this is consistent with the generally accepted ventilation requirement {*cf.* Statham (52)}. To be sure, many of the mines described in the literature are much richer in methane; for example, in the Lancashire coalfield some have yields of about 1×10^8 cm^3/ton {Fraser (53)} and in the N. Staffordshire coalfield some have yields of almost 2×10^8 cm^3/ton {Jones (54)}. But such cases are reported because of the exceptional fire-damp hazard and should not be taken as representative.

The conclusion would hence appear to be that though the quantity of methane which has escaped from oil wells and coal mines is vast it is nevertheless probably smaller than the amount now in the atmosphere.

There are only two obvious naturally occurring sources of methane: seepage from fuel beds and vegetable matter decaying under anaerobic conditions. No direct quantitative information on the yield could be found but a limit to it can at least be set.

* Since this was written we have received an almost identical (but slightly smaller) estimate from Mr G. H. Watson of the National Coal Board, London, who also informs us that the figure for continental Europe is about the same, and that for America is probably less.

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Assimilation deprives the atmosphere of about 4×10^{20} C-atoms/cm²/year {*cf.* Rankama and Sahama (11)}. The gain of CH_4 molecules must certainly be far less: that it should be more than 0·01 times as much is indeed scarcely credible. Consequently the time required to produce the observed $3·2 \times 10^{19}$ CH_4 molecules/cm² column must be quite long—probably well in excess of ten years. Far too little is known about the loss processes in the lower atmosphere to make a discussion of them profitable at present, but it may be remarked that methane (like carbon monoxide) is oxidized by certain chemically active substances and by various micro-organisms (36).

Slobad and Krogh (55) have carried out some mass spectrographic analyses of the air near ground level. They found the fractional volume of hydrocarbons to be 5×10^{-8} to 1×10^{-7}, which is some 40 to 20 times smaller than the fractional volume concentration methane would have if it were uniformly distributed through the atmosphere.* The natural inference is that the gas is largely confined to a layer at moderate or high altitudes. Migeotte (56), too, claims that the absorption lines are formed in a region where the temperature is 236 deg. K. This temperature is encountered at only four levels (*cf.* Table I). Only the two lower, one at about 8 km and another at about 35 km, need be considered, since any methane formed near the two upper would not have a sufficiently prolonged existence (*v. supra*), and since in any case if it were confined to a layer near these upper levels its fractional volume concentration would have to be improbably high in order to provide the observed total content in a vertical column.

Opposing evidence on the altitude distribution has recently been presented by Goldberg (57), who considers that it is essentially the same as that of the main atmospheric constituents. He reached this conclusion from a study of curves of growth of the absorption lines obtained at Mt. Wilson, California, and Lake Angelus, Michigan, and from a comparison of the total abundance of methane over these two stations (which are at altitudes of 1·7 km and 0·3 km respectively). In addition he pointed out that the true temperature of the methane is appreciably higher than the effective temperature obtained from the spectroscopic measurements, and on applying the necessary correction deduced a value only slightly lower than that at ground level. This disposes of one of the original arguments for a methane layer at moderate or high altitude. But the positive evidence on the methane distribution is hardly final, since the curve of growth test is not yet very sensitive and since (as Goldberg himself realized) the comparison of abundances test involves the implicit assumption that the methane content of the air depends only on the altitude and not on the geographical position.† There is clearly a grievous conflict with the measurements of Slobad and Krogh. A check on these is urgently required. As data up to 25 km would be useful, the facilities offered by balloon flights should be exploited. The altitude of the centre of mass of the methane is of considerable interest, since it determines the fractional volume concentration in the mesosphere, and hence the importance of the gas as a source of hydrogen (3).

* In view of possibility of the escape of hydrocarbons from oil fields it is interesting to note that the air analysed included samples from different parts of Texas. It is desirable that the investigations be extended to cover tropical regions (where anaerobic decay is particularly important).

† To emphasize the importance of this assumption it may be noted that there is only a 20 per cent difference in the observed abundances over Lake Angelus and over Mt. Wilson. Methane production by decay would be greater near the former station than near the latter—though whether it is appreciable in either is uncertain.

A layer such as that apparently indicated by the results of Slobad and Krogh would scarcely be anticipated. It is of course conceivable that the main production takes place in the tropics and that the methane is carried rapidly to the stratosphere by the rising air currents there prevalent {*cf.* Rossby (**30**)}; furthermore, the lower atmosphere is probably being depleted of methane (for example, through destruction on the Earth's surface caused by micro-organisms). But if the characteristic time parameter associated with the gas is ten years or more, as estimated, it would be expected that mixing effects would be sufficient to keep the distribution fairly uniform. Goldberg's results are thus favoured.

5. *Nitrous oxide.*—The first evidence for the presence of nitrous oxide in the atmosphere was obtained by Adel (**58**) from observations on the $7 \cdot 6 \mu$ region of the solar spectrum. Confirmatory evidence has since been obtained by other infra-red spectroscopists (**59**), and the abundance has been estimated to be $0 \cdot 8$ atm-cm or 2×10^{19} molecules/cm² column. The location has not yet been properly determined. However, if the nitrous oxide were mainly confined to a 10 km thick layer * the mean concentration would be as much as 2×10^{13}/cm³; and since the total particle concentration at an altitude of 70 km is only $2 \cdot 5 \times 10^{15}$/cm³ it would seem most unlikely that any such layer could lie so high. More definite evidence will be reported later.

The long wave-length limits of the nitrous oxide continua are rather ill-defined, but it appears that a very weak absorption begins at about $\lambda 3070$ and that the main absorption begins at about $\lambda 2400$ or slightly above. The products of dissociation have not yet been identified with certainty but there is little doubt that in the low-energy region the process taking place is

$$N_2O + h\nu \rightarrow N_2 + O(^3P \text{ or } ^1D), \tag{41}$$
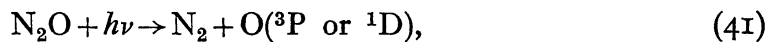
and there is considerable support for the view that that in the high-energy region is

$$N_2O + h\nu \rightarrow NO + N(^4S) \tag{42}$$

{*cf.* Bamford (**10**), Gaydon (**23**)}. Dutta, and Romand and Mayence (**60**), have determined the absorption cross-sections to the short wave-length side of $\lambda 2700$. Their results are in harmony. Unfortunately quantitative measurements have not been made in the remaining spectral region of interest. A qualitative study has however been carried out by Sponer and Bonner (**61**), who find that the absorption diminishes as the wave-length is increased up to about $\lambda 2820$, and that it then rises to a broad maximum near $\lambda 2900$. The variation does not appear to be very pronounced between $\lambda 2800$ and the limit at $\lambda 3070$; and from an estimate given by Sponer and Bonner the cross-section in this region appears to be of order 1×10^{-23} cm². Sufficient data are thus available to calculate the approximate photo-dissociation rate at various altitudes. The values obtained are displayed in Table III. Those at very low levels may be considerably in error because of uncertainty regarding the extent of the attenuation of the incoming solar radiation.

The destruction of nitrous oxide by collision processes is relatively unimportant. Thus

$$N_2O + O \rightarrow N_2 + O_2 \tag{43}$$

and $$N_2O + O \rightarrow 2NO \tag{44}$$

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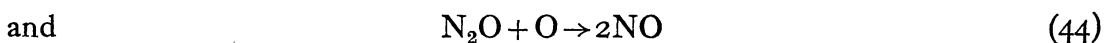
* 10 km is of course the approximate scale height in the lower and middle atmosphere.

can be neglected, since the activation energy of both exceeds 13 kcal {Henrique, Duncan and Noyes (**62**)}; and the experiments of Willey and Rideal (**63**) on the chemical action of active nitrogen on various substances indicate that

$$N_2O + N \rightarrow N_2 + NO \qquad (45)$$

is also slow.

As it is by no means obvious that there is any upper atmospheric reaction capable of yielding the replenishment necessary to maintain the observed abundance, it is worth examining whether the nitrous oxide could originate on, or near, the surface of the Earth.

TABLE III

Photo-dissociation Rate of Nitrous Oxide

Altitude (km)	Rate (/N_2O molecule/sec)		
	Process (41)	Process (42)	Total
$\geqslant 100$	$4 \cdot 5 \times 10^{-8}$	$2 \cdot 0 \times 10^{-6}$	$2 \cdot 0 \times 10^{-6}$
80	$4 \cdot 5 \times 10^{-8}$	$1 \cdot 5 \times 10^{-6}$	$1 \cdot 5 \times 10^{-6}$
60	$4 \cdot 5 \times 10^{-8}$	$1 \cdot 0 \times 10^{-6}$	$1 \cdot 0 \times 10^{-6}$
50	$4 \cdot 0 \times 10^{-8}$	$8 \cdot 0 \times 10^{-7}$	$8 \cdot 5 \times 10^{-7}$
40	$2 \cdot 5 \times 10^{-8}$	$5 \cdot 5 \times 10^{-7}$	$6 \cdot 0 \times 10^{-7}$
30	$1 \cdot 0 \times 10^{-8}$	$2 \cdot 5 \times 10^{-7}$	$2 \cdot 5 \times 10^{-7}$
20	$4 \cdot 5 \times 10^{-9}$	$1 \cdot 0 \times 10^{-8}$	$1 \cdot 5 \times 10^{-8}$
10	$3 \cdot 0 \times 10^{-9}$	3×10^{-12}	$3 \cdot 0 \times 10^{-9}$
0	$2 \cdot 5 \times 10^{-9}$	$\sim 10^{-21}$	$2 \cdot 5 \times 10^{-9}$

The gas is known to be produced by a variety of widely distributed micro-organisms (**36**), and Adel (**64**) advocates the view that these are responsible for its presence in the atmosphere. Proper quantitative data to test the hypothesis are lacking. Bearing in mind other loss processes {such as the leaking of nitrates into the subsoil or into the drainage water (**65**)}, it is reasonable to assume however that the rate of formation of nitrous oxide by soil micro-organisms is less than the rate of fixation of nitrogen over the land which, according to Hutchinson (**66**), averages only some 2×10^{17} to 1×10^{18} N_2 molecules/cm²/year.* The reliability of this figure is difficult to assess.† As would be expected, it is much less than the rate of assimilation of carbon (*cf.* Section 4): but the difference is not so great as to suggest that it is a gross underestimate. A yield of perhaps 5×10^{17} N_2O molecules/cm²/year would thus seem the maximum possible; and a much smaller yield would seem more probable. If this is correct, then 40 years or more would be required to produce the amount of nitrous oxide indicated by the spectroscopic observations. It will be noted that 5×10^{17} N_2O molecules/cm²/year is equivalent to a production rate of 3×10^4 N_2O molecules/cm³/sec distributed over an altitude range of 6 km, which is of the same order as the calculated destruction rate in the troposphere (*cf.* Table III). Thus if the upper limit to the estimated possible yield from them is approached, micro-organisms might well be the source of the nitrous oxide. Research is required to determine if indeed the gas is not merely an important intermediary, but is a major end-product of denitrification (as is necessary). It would be surprising if this should prove to be the case.

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* It may be remarked that lightning discharges give only a minor contribution to the fixation rate and moreover lead mainly to compounds other than nitrous oxide. As may easily be verified, they are therefore unimportant in the present connection.

† In a discussion of the nitrogen cycle in agriculture Russell (**65**) quotes rates which are more than an order of magnitude higher; but how representative these are he does not indicate,

Nitrous oxide seems to occur in the air near ground level.   The mass spectroscopic measurements of Slobad and Krogh (**55**) indicate that its fractional volume concentration there is about 5×10^{-7}, which is not significantly different from the mean (1×10^{-6}) deduced from the total amount in a vertical column.   Confirmatory evidence for its presence was obtained by Gebbie *et al.* (**67**) during the course of some work on the atmospheric transmission in the infra-red.   It has been argued (**64**) that this strongly favours the suggestion that the nitrous oxide originates in the soil.   But as will be seen, homogeneous gas reactions may also provide a source at low levels.
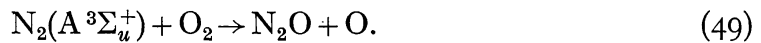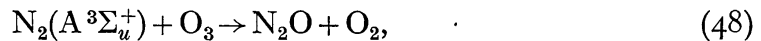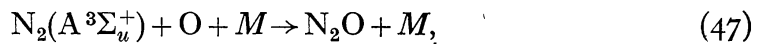
The various possibilities can easily be listed.   In examining them it must be remembered that in general the parent particles concerned must themselves be appearing at a rate at least equal to the rate at which they are reacting; and this in turn must be at least equal to the rate of photo-dissociation of the nitrous oxide.   Many of the mechanisms which have been discussed by earlier workers fail to satisfy the requirement.

Bamford (**10**) has suggested that N_2O may be formed from O^+ ions in some unspecified way, Nicolet (**68**) that it may be formed from O^- ions through associative detachment

$$O^- + N_2 \rightarrow N_2O + e \tag{46}$$

(though this is endothermic).   Both suggestions are unacceptable, since the rate of production of neither ion {*cf.* Bates and Massey (**69**)} even approaches the necessary value.

Amongst Bamford's other proposals is that metastable nitrogen molecules $N_2(A\,^3\Sigma_u^+)$ may be involved.   The reactions envisaged are presumably

$$N_2(A\,^3\Sigma_u^+) + O + M \rightarrow N_2O + M, \tag{47}$$

$$N_2(A\,^3\Sigma_u^+) + O_3 \rightarrow N_2O + O_2, \tag{48}$$

$$N_2(A\,^3\Sigma_u^+) + O_2 \rightarrow N_2O + O. \tag{49}$$

These are not at all attractive.   Under upper atmospheric conditions the formation of $N_2(A\,^3\Sigma_u^+)$ is difficult.   The rate of direct excitation by solar radiation is utterly negligible.   In connection with the theory of the airglow much abortive effort has been directed to finding a plausible collision process.   The only ones which provide sufficient energy appear to be the three-body association of nitrogen atoms through

$$N + N + M \rightarrow N_2(A\,^3\Sigma_u^+) + M \tag{50}$$

or

$$N + N + N_2 \rightarrow N_2 + N_2(A\,^3\Sigma_u^+). \tag{51}$$
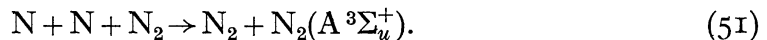
Even if the rate coefficients of these are high (which is unlikely in view of the electronic transition incurred), there remains the necessity of providing an adequate source of nitrogen atoms.   Photo-dissociation of molecular nitrogen seems to be the sole possibility.   Laboratory experiments prove that this does not occur readily {*cf.* (**70**)}; and reference to the figures given above shows that it should actually be taking place in the upper atmosphere at a rate which is comparable with the rate of photo-dissociation of molecular oxygen.   There can therefore be little doubt * that the supply of atomic nitrogen (and so of metastable nitrogen molecules) is quite insufficient.   Moreover the attenuation of the incoming

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* The fact that some of the nitrogen atoms may be regenerated through (42) does not appreciably weaken the argument, since only a small fraction of them would follow the reaction path leading to nitrous oxide.

radiation is such that any supply there is would be well above the probable location of the nitrous oxide layer. It may also be urged that (48) is unimportant in this region. Again, the concentration, $n(N_2A\,^3\Sigma_u^+)$, is unlikely to exceed $1 \times 10^5/cm^3$ (*cf.* Appendix). On taking * $n(O)$ to be $1 \times 10^{13}/cm^3$ and $n(M)$ to be $3 \times 10^{13}/cm^3$ at the 100 km level, it can be seen that in order that (47) should yield the required 4×10^7 N_2O molecules/cm³/sec its rate coefficient would have to be some 10^{-24} cm⁶/sec, which is of course impossible. In the case of (49) this alternative approach is also useful. For since $n(O_2)$ does not exceed $5 \times 10^{12}/cm^3$ a rate coefficient of at least 10^{-10} cm³/sec would be needed. Similarly

$$N + N + O_2 \rightarrow N_2O + O \tag{52}$$

is most unpromising, as the rate coefficient would have to be more than 10^{-31} cm⁶/sec even if $n(N)$ were $1 \times 10^{12}/cm^3$. Though these last two rate coefficients do not imply collision cross-sections exceeding gas kinetic values, they are improbably large. It is to be noted in this connection that the formation of nitrous oxide from active nitrogen and molecular oxygen does not appear to have been reported {*cf.* (**71**)}.

No process involving metastable oxygen molecules, $O_2(a\,^1\Delta_g$ or $b\,^1\Sigma_g^+)$, is at all plausible. For example,

$$O_2(a\,^1\Delta_g \text{ or } b\,^1\Sigma_g^+) + N_2 \rightarrow N_2O + O \tag{53}$$
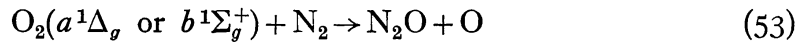
is strongly endothermic, so that it can be dismissed without detailed consideration.

The low heat of formation of N_2O also prevents most oxides from interacting with molecular nitrogen. To be sure

$$HO_2 + N_2 \rightarrow N_2O + \dot{O}H \tag{54}$$

may be almost thermochemically neutral {*cf.* Bodenstein, Schenk and Kornfeld (**72**) and Gaydon (**23**)}. However, its rate is probably slow, since the influence of molecular nitrogen on the hydrogen–oxygen reaction seems to be merely that of an inert gas {Gibson and Hinshelwood (**73**)}. Furthermore it may be shown from the work of Bates and Nicolet (**3**) that the perhydroxyl radicals in the upper atmosphere are not replenished sufficiently rapidly.

The main processes thus far discussed (that is, processes involving positive or negative ions, metastable molecules or oxides) all fail, in that the supply of the parent particles is inadequate to balance the loss that would be incurred in producing the nitrous oxide at as great a rate as it is being destroyed. This rate is indeed so great that it was clear from the onset that the only mechanism likely to give sufficient parent particles is the photo-dissociation of molecular oxygen. The reactions following such photo-dissociation would have been considered earlier, but that it was judged important to demonstrate the need for invoking them as conclusively as possible by first disposing of the alternatives that had been proposed.

The altitude distribution of the rate of photo-dissociation of molecular oxygen was obtained in the course of the calculations outlined earlier. It is characterized by two maxima, one due to the Schumann–Runge continuum and another due to the Herzberg continuum, located at altitudes of approximately 100 km and 30 km respectively. The yield of oxygen atoms in the first is some $1 \times 10^7/cm^3$/sec; that in the second is some $5 \times 10^7/cm^3$/sec. When the particular reactions which might lead to the formation of nitrous oxide are described it

* Rather high values of the concentrations are deliberately chosen.

will be apparent that they could not occur to a sufficient extent at the altitude of the Schumann–Runge maximum. For this and other reasons attention will be confined to the Herzberg maximum.

In the region near 30 km the atomic oxygen initially formed reacts rapidly to give ozone, from which it is rapidly re-liberated by further photo-dissociation (*cf.* Section 2). As a result the supply of either substance is sufficient to meet the nitrous oxide requirement. With even normal oxygen atoms and ozone molecules there is the possibility of

$$O + N_2 + M \rightarrow N_2O + M \tag{55}$$

and

$$O_3 + N_2 \rightarrow N_2O + O_2. \tag{56}$$

These processes certainly do not occur readily {*cf.* Bamford (**10**)}, but as the concentrations of the reactants are considerable it does not follow that they are unimportant. In addition both types of particle will make collisions while still retaining some of their energy of formation. The $O(^1D)$ atoms* provided by (6), and the activated O_3^* molecules provided by (4), may yield N_2O by reactions which take the same course as (55) and (56) and will be referred to as (55') and (56') respectively.

Just above ground level the temperature is approximately 285 deg. K, $n(N_2)$ is $2 \times 10^{19}/cm^3$; $n(O_2)$ is $5 \times 10^{18}/cm^3$; $n(O_3)$ is perhaps some $5 \times 10^{11}/cm^3$ and $n(O)$ is perhaps of order $1 \times 10^4/cm^3$: further O_3^* molecules and $O(^1D)$ atoms are being formed at rates of about $2 \times 10^8/cm^3/sec$ and $4 \times 10^7/cm^3/sec$ respectively. Thus there would be a yield of say 5×10^4 N_2O molecules/cm^3/sec† provided either

(i) the rate coefficient of (55) is 1×10^{-38} cm^6/sec;

(ii) the rate coefficient of (56) is 5×10^{-27} cm^6/sec;

(iii) there is a 1 in 1×10^3 chance that an $O(^1D)$ atom interacts through (55') before deactivation (as would be the case if, for example, the rate coefficient of (55') were 1×10^{-36} cm^6/sec and that associated with deactivation were 2×10^{-14} cm^3/sec); or

(iv) there is a 1 in 4×10^3 chance that an O_3^* molecule interacts through (56') before deactivation (as would be the case if, for example, the rate coefficient of (56') were 6×10^{-14} cm^3/sec and that associated with deactivation were 1×10^{-10} cm^3/sec).

It is difficult to determine whether any one of these requirements is actually met. The following comments are however offered.

If (55) leads to normal $X\,^1\Sigma$ N_2O molecules the rate coefficient would scarcely be expected to be great as 1×10^{-38} cm^6/sec, since a reversal of electron spin would be involved and since the activation energy would probably be appreciable {*cf.* Stearn and Eyring (**75**)}. However, a final decision cannot yet be reached theoretically. Laboratory investigations, too, provide but inconclusive evidence on the matter. The most significant experiments are those carried out by Leighton and Steiner (**76**), who passed mixtures of molecular nitrogen and oxygen through a cell illuminated by radiation in the Schumann–Runge continuum so that oxygen atoms (half of them in the ^1D state) were freed and

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* There does not appear to be an adequate source of $O(^1S)$ atoms {*cf.* Bates and Seaton (**74**)}.

† This is greater than the rate of photo-dissociation of molecular oxygen at ground level, but no difficulty arises, since the time scale is such that mixing with the air at higher levels ensures an ample supply of *odd* oxygen atoms and since moreover (41) tends to replace those lost.

reactions involving them could proceed. In one run the $n(N_2)/n(O_2)$ ratio was as high as 10^3; no nitrous oxide could be detected and apparently only ozone was formed. However, on referring to the detailed results it will be seen that it cannot be inferred with complete certainty that condition (i) is not satisfied.

There appears no reason to suppose that the rate coefficient for (56) could not be 5×10^{-27} cm³/sec: for such a rate coefficient would be possible even with an activation energy of 20 kcal; and, as it would allow an ozone molecule to have a life of several months in nitrogen at room temperature and atmospheric pressure, the process would not have been detected during any of the laboratory investigations.
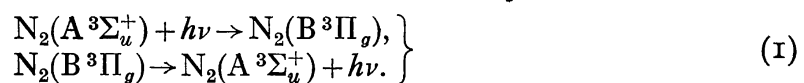
Conditions (iii) and (iv) also do not appear to be excluded by the published experimental data. Neither is particularly severe. Thus judging from the potential energy curve along which an $O(^1D)$ atom and an $N_2(X\,^1\Sigma_g^+)$ molecule approach each other {*cf.* Stearn and Eyring (**75**)} (55′) should not be abnormally slow; since (56′) involves an O_3^* molecule its activation energy might well be small, as is implied by the suggested rate coefficient; and the assumptions regarding the deactivation of $O(^1D)$ and O_3^* are not unreasonable.

As the high activation energy makes the rate of (56) extremely sensitive to the temperature the yield of nitrous oxide from it must decrease through the troposphere. In view of the increase in the photo-dissociation rate (*cf.* Table III) it would clearly lead to a low-lying bank. Examination of the other processes shows that with them also the greatest equilibrium concentration would occur near ground level. However, the fall-off with altitude would be comparatively slow. Consequently (42) would give rise to a considerable number of *odd* nitrogen atoms. Now in the lower mesosphere their re-association is hindered by the rapid oxidation occurring {Bates (**77**)}. There is therefore the possibility that (55), (55′) or (56′) would lead to an unacceptable accumulation of nitric and higher oxides if they were as effective as required. With (56) no such difficulty arises.

APPENDIX

The concentration of $N_2(A\,^3\Sigma_u^+)$ molecules in the upper atmosphere

Illuminated metastable nitrogen molecules readily absorb and re-emit through the First Positive band system

$$\left.\begin{array}{l} N_2(A\,^3\Sigma_u^+) + h\nu \to N_2(B\,^3\Pi_g), \\ N_2(B\,^3\Pi_g) \to N_2(A\,^3\Sigma_u^+) + h\nu. \end{array}\right\} \tag{1}$$

Resonance scattering at twilight should therefore provide a sensitive means of detecting their presence in the upper atmosphere. To investigate the effect it is necessary first to determine the transition probability. This can be done by standard quantal methods.

The oscillator strength is given by the formula

$$f = (1/3Ra_0^2\lambda)D, \tag{2}$$

where R is Rydberg's constant, a_0 is the radius of the first Bohr orbit, λ is the wave-length of the radiation concerned and D is

$$\left| \int X(\sigma_g 2p \mid \mathbf{r})\mathbf{r}X^*(\pi_u 2p \mid \mathbf{r})\,d\tau \right|^2 \tag{3}$$

with $X(\sigma_g 2p | \mathbf{r})$ and $X(\pi_u 2p | \mathbf{r})$ the normalized wave functions of the active electron in the $A\,^3\Sigma_u^+$ and $B\,^3\Pi_g$ states respectively and $\mathbf{r}$ its position vector (*cf.* Mulliken (**78**)}. On the crude LCAO approximation

$$X(\sigma_g 2p) = N_0(\psi_0{}^a - \psi_0{}^b), \tag{4}$$

$$X(\pi_u 2p) = N_1(\psi_1{}^a + \psi_1{}^b), \tag{5}$$

where N_0 and N_1 are normalizing factors, a and b denote the atom on which the orbital is based, and

$$\psi_0 = f(r)\cos\theta, \tag{6}$$

$$\psi_1 = f(r)\sin\theta \begin{cases} \cos\phi \\ \sin\phi. \end{cases} \tag{7}$$

Representing $f(r)$ by the function

$$(\gamma^5/\pi)^{1/2} r \exp(-\gamma r) \tag{8}$$

and substituting in (3) it can be shown that when the internuclear distance is Ra_0 then

$$D = T^2/(1 - S_0)(1 + S_1), \tag{9}$$

where

$$T = \frac{\alpha^5 R}{240}\left\{5A_4 - 6A_2 + A_0\right\}, \tag{10}$$

$$S_0 = \frac{\alpha^5}{120}\left\{5A_4 - 18A_2 + 5A_0\right\}, \tag{11}$$

$$S_1 = 2T/R, \tag{12}$$

$$\alpha = \gamma R, \tag{13}$$

and

$$A_n = \int_1^\infty \exp(-\alpha x)x^n \, dx. \tag{14}$$

Spectroscopic measurements show that R is approximately $2\cdot4a_0$ {*cf.* Herzberg (**79**)}. As usual α is poorly determined: a value of about 4 is indicated by the self-consistent field wave functions of Brown, Bartlett and Dunn (**80**) and a value of about 5 by Slater's rules (which, though crude, have proved remarkably successful in molecular calculations). On carrying out the necessary computation it was found that D is either $0\cdot068$ or $0\cdot026$, depending on whether the smaller or larger α is used. Adopting the mean, $0\cdot05$, and taking the wave-length to be $6\,000$ A (*v. infra*), it can be seen from (2) that the oscillator strength is of order 2×10^{-3}. The corresponding Einstein coefficient A is 2×10^5/sec.

If the effect of vibration in producing energy spread is neglected, then the photon emission due to (1) is

$$P = s\Omega A \exp(-hc/\lambda kT)/N_2(A\,^3\Sigma_u^+) \text{ molecule/sec.} \tag{15}$$

where s is the ratio of the statistical weight of upper state to that of the lower (2), Ω is the dilution ($5\cdot4 \times 10^{-6}$) and T is the temperature ($6\,000$ deg. K) of the solar radiation, k is Boltzmann's constant, and the other symbols are as already defined (**81**). Numerical substitution yields

$$P = 4 \times 10^{-2}/N_2(A\,^3\Sigma_u^+) \text{ molecule/sec.} \tag{16}$$

Montgomery and Nicholls (**82**) have recently evaluated the nuclear overlap integrals associated with the individual bands. The intensity distribution through the system can thus be deduced (**81**). This need not be given in detail.

9

It is sufficient to mention that approximate calculations indicate that $\lambda\lambda$ 6705, 6624, 6545 and 6468 of the $v' - v'' = 3$ sequence should be prominent, the photon emission in each being at least 0·05 times the total. Now resonance scattering of the First Positive system at twilight has never been observed.* If the photon emission in any of the bands mentioned were as great as $2 \times 10^2/cm^3/sec$ it could scarcely have escaped detection. From the estimated efficiency of the scattering process it is hence apparent that the concentration of metastable nitrogen molecules does not exceed $10^5/cm^3$. The assumed upper limit to the twilight intensity of the First Positive bands is considered to be conservative. A precise spectroscopic determination of this limit would be very useful in that it would enable a more severe restriction to be placed on the concentration of metastable molecules.

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* It is to be noted that Elvey (83) has withdrawn the claim that λ 6560 (which might be a blend of several of the First Positive bands) is enhanced during twilight.

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