PRINTED IN GREAT BRITAIN BY R. & R. CLARK, LIMITED, EDINBURGH

MEMOIRS OF THE ROYAL METEOROLOGICAL SOCIETY, Vol. III. No. 26.

A THEORY OF UPPER-ATMOSPHERIC OZONE 1

BV

S. CHAPMAN, M.A., D.Sc., F.R.S.

[Manuscript received November 26, 1929.]

INTRODUCTION.

1. The object of this paper is to develop a quantitative theory of the equilibrium and changes of ozone and atomic oxygen in the upper atmosphere.

The existence of the ozone, and many facts regarding its distribution and changes, are now well established 2, 3. McLennan's identification of the green auroral line 4, shown in the spectra both of polar and non-polar auroræ, as due to atomic oxygen, proves that oxygen is present in the atomic state at heights of 100 km. and above during polar auroral displays, and, in non-polar regions, at all times, in varying measure and at a height

which is as yet unknown.

No theoretical discussion of the presence and changes of these gases in the atmosphere appears to have been attempted hitherto. The production of the ozone has been alternatively attributed to solar corpuscular radiation, possibly associated with auroræ and magnetic storms, or to ultra-violet radiation; recently the latter view has fallen into disfavour, because ozone is least abundant at the end of the summer, and most abundant at the end of the winter. One of the main results of this paper is the proof (on the basis of certain assumptions which are considered reasonable) that such an annual variation of ozone is quite compatible with the production of ozone solely by ultra-violet radiation. Hence the latter view cannot at present be rejected. But neither, on the other hand, can it be accepted definitely as yet; the present theory neglects certain factors, partly because their magnitude is quite uncertain: but they may possibly be dominant factors in the ozone changes and, if so, the theory would need substantial modification. Fortunately the theory makes certain predictions (cf. §§ 26, 27) capable of being tested by observation and experiment, so that further light on the points in doubt may be hoped for.

The discussion involves the consideration of the amount of atomic oxygen at the level of maximum ozone density. In another paper 5 I hope to deal with the question of the proportion of ozone and atomic oxygen at greater heights, showing that atomic oxygen probably becomes an important constituent beyond 100 km. This result is of obvious interest

¹ A brief account of this paper was given at the Paris Conference on Ozone held in

May 1929.

2, 3 For references to the now extensive literature on atmospheric ozone, cf. (x) C. Relationships (International Research Council), 1929, p. 49; and (2) G. M. B. Dobson, D. N. Harrison, and J. Lawrence, Proc. R. Soc. A., 122, 1929, p. 456.

4 J. C. McLennan, Bakerian Lecture, Proc. R. Soc., A., 120, 1928, p. 327, and

references there cited.

⁵ Since communicated to the *Philosophical Magasine*, London, together with a further paper containing a discussion of another theory which has been proposed to account for the

in connection with the green light of the polar and non-polar auroræ; it may also have an important bearing on the state of ionisation of the outer atmosphere.

THE FACTS CONCERNING ATMOSPHERIC OZONE.

2. The main known facts regarding atmospheric ozone are as follows:

(a) The average amount of ozone in the atmosphere at the equator is equivalent to a layer of pure ozone, at normal temperature and pressure, about 2 mm. thick; it increases with latitude to nearly 3 mm. in Europe.

(b) There is an annual variation in the amount of ozone. The maximum occurs in spring and the minimum in autumn in each hemisphere. Thus the variation changes sign in crossing the equator; the range of the variation on either side of the mean increases from zero at the equator to about 0.5 mm. at Lerwick.

(c) In medium and higher latitudes there are irregular day-to-day variations at any station; these are closely associated with the weather conditions at the time, and particularly with the temperature of the troposphere, and the pressure at 10 to 15 km. height. In low latitudes the amount of ozone is nearly constant from day to day.

(d) Preliminary measurements by Chalonge at Paris suggested that there is about 0.7 mm. more ozone in this latitude by night than by day, but later measurements do not confirm this. There appears to be no perceptible daily variation of the ozone.

(e) The ozone is situated at an average height of about 40 or 45 km.; this height is approximately the same when the ozone is abundant as when it is deficient.

2a. The day-to-day variations seem to indicate that in European latitudes there is considerable transport of air from place to place, even in the stratosphere at heights of 45 km.; and that the motions there are associated with those occurring in the troposphere.

A very small systematic component of this motion of the upper air might suffice to bring about the slow annual variation of ozone. There appears unfortunately to be no direct way of testing whether or not the annual variation actually is produced in this way. It may prove easier to settle the point by examining other possible hypotheses. In the following discussion the bodily transport of ozonised air is completely left out of account, partly because at present it cannot be estimated quantitatively, and also in order to see whether a consistent explanation of the facts about atmospheric ozone can be arrived at without assuming such motion.

THE FORMATION OF ATMOSPHERIC OZONE.

3. The formation of atmospheric ozone requires the dissociation of oxygen molecules O₂ into oxygen atoms O, and the attachment of the latter to other O₂ molecules. The dissociation of O₂ may be brought about either by ultra-violet solar radiation, in the band 1300-1850 Å, or by corpuscular radiation. The atmosphere is probably subjected to radiations of both kinds. The ultra-violet radiation will fall almost exclusively on the day hemisphere. The aurora polaris is almost certainly produced by solar corpuscles, which are guided towards the polar regions by the earth's magnetic field, and must therefore be electrically charged. It is not unlikely that neutral solar corpuscles also impinge on the earth; if so, they will fall on the day hemisphere, like the ultra-violet radiation.

The relative importance of these various causes of ozone cannot yet be ascertained in any simple way. The intensity of the corpuscular radiation is quite unknown, while that of the ultra-violet radiation can only be more or less plausibly conjectured.

The greater ozone content in high latitudes than in low, and, in high latitudes, in spring than in autumn (corresponding to a large increase in ozone during the winter, when these latitudes receive but little ultra-violet radiation), has led several writers to conclude that corpuscular radiation, rather than ultra-violet, must be the chief source of atmospheric ozone: and that the principal rôle of ultra-violet radiation, which is most abundant during the summer half year, is to reduce the amount of ozone. But, as will be shown, it is possible to reconcile the above facts with the hypothesis that ultra-violet radiation is the sole or main source of ozone; and there is at least one reason for regarding this view as more probable than the other. For according to Fabry the radiation in the band 1300-1850 Å would be principally absorbed approximately at the same level, about 45 km., as that at which the ozone is observed to be abundant. The auroral corpuscular radiation, on the other hand, does not descend below about 90 km., and

no particles are known which are so penetrating as to get down to 45 km.

and be there absorbed. Ozone formed at 90 km. would descend to 45

km. only very slowly, whether by convective mixing or by steady fall under

gravity—in the latter case the time of descent would be reckoned in years. The height of the ozone layer is thus slightly favourable to the ultraviolet theory of its formation, and it appears worth while to find whether, and under what conditions, ultra-violet radiation alone is capable of accounting for the observed facts about ozone, leaving corpuscular radiation, and bodily transport of ozonised air, entirely out of account, without necessarily suggesting that they are unimportant. It may be possible to test whether the conditions imposed in the present theory are fulfilled; if not, it will definitely indicate that one, at least, of the neglected factors is of importance. The theory is found also to lead to certain predictions which can be tested by further observations on atmospheric ozone.

THE DIFFUSION OF OZONE.

4. Taking the ozone content to be 3 mm. (at normal temperature and pressure), the number of O_3 molecules per sq. cm. column of atmosphere is 8.10^{18} . If the ozone is uniformly distributed throughout the atmosphere above 40 km., there is in this region one O_3 molecule per 1500 O_2 molecules, whereas if it is similarly distributed above 50 km. the ratio is about 1 to 400. Thus even at these heights the O_2 molecules far outnumber those of O_3 , while at lower levels the disproportion is much greater.

The ozone layer may extend upwards throughout the atmosphere from about 40 km., but it is known that in the lower atmosphere there is a relatively small proportion of ozone. The maximum density of O_3 seems to occur at about 40 km. The decrease in the ozone density below this level requires explanation, for if the atmosphere were uniformly mixed the ozone concentration should be uniform, and the actual density should increase downwards in proportion to the total density of the atmosphere. Twisted meteor trails give clear indication of convection and mixing in the upper atmosphere, but the rate at which the ozone would be transferred

⁶ McLennan, J. C., Ruedy, R., and Krotkov, V. (Ottawa, Trans. R. Soc. Canada, 22, 1928, p. 300) state the contrary, apparently by an oversight in regard to the unit in which the ozone content is usually expressed.

downwards from the level at which it is newly produced cannot be calculated at present. It seems likely that mixing will be less effective just below the layer of maximum ozone density than elsewhere, because this is a region where the actual (and not merely the potential) temperature is increasing upwards, so that the air there is more than usually stable. But even were there no convective mixing, the ozone should descend steadily, owing to its excess weight as compared with nitrogen and oxygen; the rate of such descent can be estimated.

It is sufficient to take the coefficient of diffusion D for O2 in air to be the same as that of O₀ in nitrogen, namely, 0·17 at normal temperature and pressure. At a height where the total air density is a times that at ground level, D = 0.17/a. A correction factor roughly equal to T/273 is also needed (T being the absolute temperature at the given level), but this can be ignored since only the order of magnitude of D is here required. The coefficient of mobility is 7 D/kT, or, taking T=300, it is $4.10^{12}/a$. The excess force of gravity on an O_3 molecule in air is approximately 3.10^{-20} dyne, so that the downward velocity v of the ozone will be $10^{-7}/a$ cm. sec. $^{-1}$. At 40 km. a is about 1/300, and $v = 3 \cdot 10^{-5}$ cm. sec. $^{-1}$, or about 3 cm. per day.8 Above or below this level, v is greater or less in inverse proportion to the density; the rate of transfer of Oa molecules across any horizontal surface is equal to the product of v into the number of O₃ molecules per c.c., and it is therefore the same at all levels so long as the concentration of ozone is uniform, while if the concentration increases (or decreases) upwards, the rate of transfer alters proportionately. At 100 km. v is about 50 metres per day; these values of v show how long a time would be required for O₃ formed at auroral levels to sink to 40 km. level owing solely to gravity.

If the ozone be uniform in concentration above 40 km., the rate of descent, at any level in this region, is about 3. 108 O₃ molecules per sq. cm. per sec.; if the same amount of ozone were spread uniformly above 30 km., the corresponding number would be about 107.

The lower limit of the ozone layer will naturally be somewhat indefinite. owing to diffusion or mixing. In the boundary layer, where the O₈ concentration is decreasing downwards, the O3 will be steadily sinking owing to gravity, as in the upper layers, and there will be an additional downward flow due to the concentration gradient. At the top of the boundary layer, as has just been seen, the number of molecules per sq. cm. entering the layer per sec. is about 3. 108; at lower levels the number due to gravity fall will progressively decrease, so that between any two levels more molecules enter from above than flow out from below. Thus O₈ molecules must in this region be continuously transformed into something not ozone, by reactions between themselves or, more probably, with other atmospheric gases. The total rate of disappearance in the whole boundary layer is equal to the number entering from above, i.e. about 3. 108. This is a very small number; the loss per day would be about 2. 1018, or about 4. 1016 per half year—a number quite inappreciable compared with the actual decrease in the ozone content at Lerwick from spring to autumn, namely, about 2.1018. The loss of ozone at the base of the layer in which it is formed therefore seems negligible in comparison

⁷ Where k is Boltzmann's constant $1.37 \cdot 10^{-16}$.

⁸ Y. Rocard, *Paris, Comptes Rendus Acad. Sci.* 188, 1929, p. 1336, estimates the velocity of descent of ozone in a nitrogen atmosphere, at 50 km., as 20 metres per day, and concludes that this obviously has no influence on the distribution of the ozone. While concurring in the conclusion, I believe the above method of estimating v to be the correct one.

even with the slow annual variation of ozone, and still more so in comparison with the large changes, over Europe, from day to day. The loss at the lower boundary might, however, be greater than has here been calculated, if ozone is carried downwards by convective mixing of the air as well as by steady diffusive fall subject to gravity.

THE DISSOCIATION OF OZONE BY ULTRA-VIOLET RADIATION.

5. It is known that ozone is decomposed by radiation in the (Hartley) band 2300-2900 Å.; the quantum of energy in this region (at 2500 Å., say) is about $7.8 \cdot 10^{-12}$ erg. If one such quantum is required to dissociate one O_3 molecule (presumably into O_2 and O) the dissociation energy is about 110,000 calories per gm. mol

The amount of solar radiation received in this band, at the outside of the atmosphere, is unknown; it cannot be measured because almost all of it is absorbed at a high level, nor can it be estimated, at present, from the theory of the sun's radiation. If the sun were a complete radiator, at the temperature 6000° K, the amount of energy received at the earth at the equator at noon would be about 3.7.104 ergs. cm. -2 sec. -1, or about 5. 1015 quanta, sufficing, if completely absorbed by O2 molecules, and if each quantum absorbed decomposes one ozone molecule, to dissociate 5. 1015 per cm.2 sec. This is far greater than the rate of destruction of O₃ molecules at the base of the layer, as estimated in §4; moreover, if it continued for 1600 seconds, or about half an hour, unchecked by any compensating process, all the 8. 10¹⁸ O₃ molecules per cm.² would disappear. Since this does not happen, either the photo-electric efficiency of the process must be extremely small (that is, only a very small proportion of the quanta absorbed are effective in dissociating ozone molecules). or some restoring process must go on, and the most obvious is the reformation of O₃ molecules by union between O atoms and O₃ molecules.

As has just been stated, it is not possible to conclude that the number of O₃ molecules dissociated per cm.² sec. actually is 5.10¹⁵, because it is uncertain whether the sun radiates as a black body in this region, and because the proportion of quanta effective for dissociation is unknown; but the region is sufficiently near the limit up to which the sun's radiation is measurable, for the extrapolation to be not very unsafe. It is therefore likely that the actual rate of dissociation of O₃ is not much, if any, greater than 5.10¹⁵, and also perhaps not very much less.

THE RATE OF FORMATION OF OXYGEN ATOMS.

6. The dissociation of O₃ molecules produces oxygen atoms at a rate which has been estimated as probably of the order 5.10¹⁵ per cm.² sec. It is likely that oxygen atoms are formed also from oxygen molecules O₂, since the latter are known to be dissociated by radiation in the band 1300-1800 Å. The energy of the quantum at 1800 Å is 11.10⁻¹¹ erg, and proportionately greater at 1300 Å. The amount of radiation received at the earth from the sun in this band is far more uncertain than in the case of the Hartley band, since it is fully absorbed and much further from the limit of measurement of the sun's spectrum. If the sun radiated in this region like a black body at 6000° K, the energy received would be about 700 ergs/cm.² sec. at the equator at noon; the corresponding number of quanta is about 6.10¹³. If each quantum dissociates one O₂ molecule (corresponding to a dissociation energy of about 160,000 calories per gm.

mol., or about 9 volts) the number of O atoms formed per cm.² sec. would be 1.2.10¹⁴—much smaller than the number formed by dissociation of O₃. Actually the number of O atoms formed from O₂ is very uncertain. The somewhat smaller value 1.6.10¹⁸ per cm.² sec. may be kept in mind as indicating the possible order of magnitude, in order not to over-estimate the rate of production of O.

The O atoms formed by dissociation of O_2 may be different from one another, and from those formed from O_3 ; they may be ionised or excited, and unequally ready to attach themselves to an O_2 molecule to form ozone. A complete theory would have to take account of such differences, but at present the necessary knowledge is lacking. It is therefore sufficient to suppose that of the whole number of O atoms present at any time, certain fractions take part, each second, in the reactions

 $O + O = O_2$

 $O + O_2 = O_3,$

reaction (c), and thirdly by the reaction

(c) $O + O_3 = 2 O_2$. In the average over any sufficiently long time, O atoms of each kind

In the average over any sufficiently long time, O atoms of each kind produced must disappear in numbers equal to those formed; and the same applies to the O₈ molecules.

THE REACTIONS IN WHICH OZONE DISAPPEARS.

7. It will be supposed that ozone is produced solely by the reaction (b), but that it may disappear in at least three ways; firstly by the converse process of dissociation

which occurs (§ 5) through absorption of radiation in the Hartley band, and possibly also spontaneously, or by reason merely of collisions with other molecules in the course of their "thermal" motions; secondly by the

(e) 2 O₃ = 3 O₂.

The latter is generally supposed to be the mode of purely thermal decomposition of ozone, but this view has recently been contested by Riesenfeld and his collaborators, o who assert that it also decomposes

monomolecularly, presumably according to the formula (d).

According to their experiments, made between 85° and 95° C, the decomposition occurs according to the equation

$$\frac{dc}{dt} = -k_1c - k_2c^2,$$

where c denotes the ozone concentration in molecules per litre, and the coefficients of monomolecular and bimolecular reaction, k_1 and k_2 , depend on temperature: and have the values

$$k_1 = 2.5$$
. 10^{-3} min.⁻¹; $k_2 = 4.1$ litre mol.⁻¹ min.⁻¹,

at 95° C., increasing with the temperature by respectively 2.10⁻³ and 2.5 per 10°, over the range 80° to 100° C. The bimolecular constant k_2 is independent of the partial pressure of admixed O_2 , or argon, but is increased by the presence of N_2 and, still more, of CO_2 , the values at 95° C. in the presence of a considerable excess of N_2 and CO_2 being respectively about

8 See the discussion given by C. N. Hinshelwood in "Kinetics of Gas Reactions." 10 E. H. Riesenfeld and W. Bohnholtzer, Zs. physik. Chemie, 130, 1927, p. 241 E. H. Riesenfeld and H. J. Schumacher, ibid. 138, 1928, p. 268. 5 and 7. The monomolecular constant, on the other hand, they consider to be independent of the presence of any of these gases.

At the very low pressures existing in the layer of atmospheric ozone, where c is of the order 2.10^{-8} or less, the bimolecular decomposition would be quite negligible compared with the monomolecular, if at the temperature T of the layer the ratio of the magnitudes of k_1 and k_2 is similar to that given by Riesenfeld for 95° C. The value of T is not known accurately, but is unlikely to be less than about 30° C., and may be 100° C. or even more. Riesenfeld's experiments give but little indication of the probable value of k_1 at 30° C., but perhaps suggest 10⁻⁴ as the order of magnitude. This would correspond to a reduction of ozone in the ratio 10 to 1 in about 120 days, which would be insensible in the course of a single day and night, but would affect the annual ozone

If, however, T is of the order 100° C., the observed constancy of the ozone during the day and night seems incompatible with Riesenfeld's value of k_1 , which would imply a reduction in the ratio 8 to 1 in the course of 12 hours. Should observation confirm that T is of this order, I should regard it as a disproof of Riesenfeld's value of k_1 , or rather as an indication that his k_1 does not correspond to a real homogeneous gas reaction. He himself states that part of k_1 is due to wall reactions in his vessel, though he considers the major part to depend on a real homogeneous gas reaction. The difficulties of laboratory experiments on the thermal decomposition of ozone, and the discrepancies (which he discusses) between his results and those of other workers to whom he refers, make it unsafe to rely on the experimental values of k_1 and k_2 at present. It is, however, desirable to bear in mind the possibility of a slow thermal decomposition, whether bimolecular or monomolecular, of upper-atmospheric ozone, in connection with the annual and 11-year variations, though it is unlikely that it affects the daily variation.

THE BIMOLECULAR THERMAL DECOMPOSITION OF OZONE.

8. Only a very small fraction of the collisions between pairs of O₂ molecules appear to bring about the reaction (e) at ordinary temperatures; for the reaction to occur, it seems to be necessary that the colliding molecules shall jointly possess, relative to axes moving with their mass centre, an amount of energy E which, reckoned in calories per gm. mol., is about 23,000; this, called the energy of activation, is far in excess of the normal molecular energy at 300° or 400° K, the approximate temperature of the atmospheric ozone layer (the normal energy is about 3 RT or 1800 cal/gm. mol. at 300° K). The fraction of collisions in which the molecules possess this energy E, when the gas is in thermal equilibrium at temperature T, is approximately $e^{-E/RT}$, or, when $T=300^{\circ}$, about 10^{-17} . At this temperature the total number of collisions between pairs of O₃ molecules is about $10^{-10}n_3^2$ per cm.³ sec., where n_3 denotes the number of O_3 molecules per cc. Hence the number of O_3 collisions which cause reversion to O_2 is about $10^{-27}n_3^2$ per cm.³ sec. The total number of such collisions per sq. cm. column of atmosphere can be calculated approximately by assuming that n_3 varies as $e^{-z/\hbar}$, where z denotes height above the base of the ozone layer, and h is a length of the order 10 km. or 106 cm. Then $\int n_3^2 dz$ throughout the layer is $\frac{1}{2} h(n_3)_0^2$, where $(n_3)_0$ denotes the value of n_8 at the base of the layer (z=0). If this level is at height 40 km. above the ground, $(n_3)_0$ is about 10^{18} . Thus the total

number of the reactions (f) will be about 105 per cm.2 sec. This is quite insignificant compared with even the loss of ozone at the base of the layer (§ 4). It would take 1014 seconds, or more than 106 years, for all the O3 molecules to disappear by this means, at this constant rate. It would therefore seem that purely thermal bimolecular decomposition of ozone can play no significant part in the balance of processes which determine its amount and its variations.

Even if the ozone layer is at 400° K instead of 300° K, the same conclusion holds good; in this case $e^{-E/RT}$ is about $10^{-12.5}$ or 3.10^{-18} , and the number of effective collisions between Oa molecules is about 3. 10⁻²³n₈² per cm³. sec. The time required for all the ozone to disappear by this means, at this constant rate, would be more than thirty years.

Riesenfeld's value of k_2 , about 6 litre/mol. min. at 95° C., is equivalent to $3 \cdot 10^{-22} n_3^2$ effective collisions per cm³. sec., or about ten times as many as here estimated for the higher temperature of 400° K or 123° C.; the discrepancy therefore amounts to more than a factor of 10, and if Riesenfeld's value is correct, the bimolecular thermal decomposition would require consideration in connection with the 11-year ozone variation if $T=400^{\circ}$, but probably not if $T=300^{\circ}$; in either case it would be without appreciable influence on the diurnal and annual variations.

TWO-BODY AND THREE-BODY REACTIONS.

9. In a reaction between a number of molecules and atoms, which during a collision combine or redistribute themselves, momentum and energy are conserved; if radiation is absorbed or emitted, this must be reckoned in the equation of energy, but its momentum is negligible compared with that of atoms or molecules at ordinary temperatures. When two or more such particles are involved both before and after the reaction, the conservation of energy and momentum can be fulfilled in a variety of ways, but not so when two particles unite to form a single molecule, as in the reactions (a) and (b); in this case the velocity of the final molecule is definitely determined by those of the reacting particles, according to the principle of momentum. If radiation is emitted, this is usually of definite wave-length and energy, and, together with the kinetic energy of the final molecule, does not in general equal the initial energy of the two original particles. Consequently it is believed that in such cases the reaction will not in general occur when the two particles collide, unless some third body is adjacent which can supply or carry off the balance of energy, enabling both momentum and energy to be conserved in the reaction, though not otherwise affecting the combination. That is to say, reactions of the type (a) and (b) result only from three-body collisions, while those of type (c) or (e) do not require the intervention of a third body, because after the reaction there is more than one particle. Possibly every collision of the type (c) may induce the reaction, though on the other hand, as in (e), energy of activation may be needed: at present the facts appear not to be known.

In the reaction (d), or in the dissociation of O₂, i.e.,

$$O_2 = O + O,$$

produced by absorption of radiation, the energy absorbed is partly used in separating the two parts of the original molecule, while some may appear as excess kinetic energy of the products of dissociation. Such excess kinetic energy rapidly becomes distributed among the other gas molecules, and goes to raise the temperature. The products of dissociation (O, or O and Oa) may be excited or ionised, and may radiate energy (of longer wave-length than the original) in returning to their normal state, or in recombining. This energy may be absorbed by the gas and further raise the temperature. If all the dissociated particles recombine, the gas is left in its original form except that its temperature has been raised by the absorption of radiant energy and its conversion mainly into molecular kinetic energy. It is thus that the relatively high temperature of the ozone layer is explained.

THE COEFFICIENTS OF REACTION.

10. Let n_1 , n_2 , n_3 denote the number of O, O_2 , and O_3 atoms or molecules respectively per cc. At 300° K (the temperature adopted as that of the ozone layer, in the subsequent calculations, which can, however, easily be modified should T prove to have a higher value) the number of collisions per cc. per second between particles O_a , O_b (where a and b may be any of the numbers 1, 2, 3) will be approximately 10⁻¹⁰n_an_b; the factor 10⁻¹⁰ is roughly sufficient in all cases, though really the factor should be a little larger or smaller in proportion to the square of the mean diameter of the particles, and therefore in a descending scale for the collisions O3, O3; O, O2; O2, O; O2, O; O, O. Of these collisions only a fraction are, in general, effective in producing a reaction. The number of these effective collisions per cc. per sec. will be denoted by $k_{ab}n_an_b$ in the case of the two-body reactions (c), (e), and by $k_{ab}nn_an_b$ in the case of the three-body reactions (a), (b), where n will denote the number of molecules of every kind present per cc. Thus we shall be concerned with coefficients k_{11} , k_{12} ,

 k_{18} , k_{38} in the four reactions (a), (b), (c), (e).

In a gas at equilibrium at 300° K, k_{38} is taken to be of order 10⁻²⁷, or about 10⁻²³ in a gas at 400° K. Possibly during the daytime, when the ozone layer is absorbing solar radiation, k_{33} may have a greater value, because part of the radiant energy absorbed by O_2 or O_3 , and afterwards transformed into thermal kinetic energy, may at some stage in the course of transformation be shared by O₃ molecules. This might occur when O₃ was the "third body" involved in collisions of the type (a), (b); in these the amounts of energy involved, 160,000 or 110,000 cal./gm. mol. respectively, are about seven and five times the energy of activation (23,000 cal./gm. mol.) required for the reaction (e); but the chance of the third body being O3 is very small, less than I in 4000. Moreover even those O3 molecules which thus become activated are likely to lose their excess energy before meeting another O3 molecule, because on the average they meet 4000 molecules of other kinds between each collision with another O3 molecule. Hence the number of reactions (e) which occur by day, owing to activation brought about in this way, is likely to be only 10⁻⁶ or 10⁻⁷ times the total number of reactions of the type (a) and (b). They may be of significance for the 11-year ozone variation, but scarcely for the annual and daily

The values of the coefficients k_{11} , k_{12} , k_{13} appear to be quite unknown

To avoid the constant insertion of the factors n associated with k_{11} and k_{12} , we shall write

$$K_{11} \equiv k_{11}n, K_{12} = k_{12}n.$$

THE CHEMICAL EQUILIBRIUM IN THE DENSEST PART OF THE OZONE LAYER.

11. In considering the effect of these various processes which influence the formation and disappearance of ozone, it is convenient to ignore, for the present, the large variation of density of the air and its constituents, with respect to height, and to deal with the actions in the lower, denser parts of the ozone layer. It will therefore be imagined, for the time being, that the ozone is all contained in a layer of air of uniform density, 10 km. thick, containing the same amount of nitrogen, oxygen, and ozone as the actual extended layer. Then n, n_3 , n_2 will be of the order 4.10¹⁶, 8.10¹², and 10¹⁶ respectively, taking the base of the ozone layer to be at the level 40 or 45 km. The dissociation of O2 and O3 by absorption of radiation will be regarded as uniformly distributed throughout the 10 km. layer; N_2 and N_3 will denote the number of O_2 and O_3 molecules respectively dissociated per cc. per sec. in this layer. At the equator at midday their order of magnitude may be about 8. 106 and 5. 109, and less at other places and times; but these values, and especially that of N_2 , are rather uncertain

(§§ 5, 6). During the day the equations of rate of change of n_1 , n_2 , n_3 , the day the equations of rate of change of n_1 , n_2 , n_3 , the day the equations of rate of change of n_1 , n_2 , n_3 , the day the equations of rate of change of n_1 , n_2 , n_3 , the day the equations of rate of change of n_1 , n_2 , n_3 , the equation of n_1 , n_2 , n_3 , n_3 , n_4 , n_4 , n_5 as follows:

(1)
$$\frac{dn_1}{dt} = 2N_2 + N_3 - n_1(2K_{11}n_1 + K_{12}n_2 + k_{13}n_3).$$

(2)
$$\frac{dn_2}{dt} = N_3 - N_2 - K_{12}n_1n_2 + K_{11}n_1^2 + 3k_{33}n_3^2 + 2k_{13}n_1n_3.$$

(3)
$$\frac{dn_8}{dt} = -N_3 + K_{12}n_1n_2 - 2k_{33}n_3^2 - k_{13}n_1n_3.$$

These equations apply also during the night if the terms N_2 , N_3 are omitted.

12. In (2), (3) the terms $k_{33}n_3^2$ will be omitted as negligible (cf. § 8). Since the average values of n_1 , n_2 , n_3 over any long period of time are constant, the average values of their rates of change are zero, and therefore the same is true also of the right-hand sides of (1), (2), (3). Hence, denoting mean values by brackets, the equations (3), (2), (1) lead to the results:

$$\{N_3\} = \{K_{12}n_1n_2 - k_{13}n_1n_3\},\,$$

(5)
$$\{N_3\} - \{N_2\} = \{K_{12}n_1n_2 - K_{11}n_1^2 - 2k_{13}n_1n_3\},$$

(6)
$$2\{N_2\} + \{N_3\} = \{2K_{11}n_1^2 + K_{12}n_1n_2 + k_{13}n_1n_3\};$$

hence also, by (4), (5),

(7)
$$\{N_2\} = \{K_{11}n_1^2 + k_{13}n_1n_3\}.$$

Since the N's, n's, and k's are essentially positive, (4) implies that $\{K_{12}n_1n_2\}$ exceeds $\{k_{13}n_1n_3\}$, and that the former is not less than $\{N_3\}$; (7) implies that $\{K_{11}n_1^2\}$ and $\{k_{18}n_1n_8\}$ are at most of the order $\{N_2\}$, and therefore very small compared with $\{K_{12}n_1n_2\}$, since $\{N_3\}$ so much exceeds $\{N_2\}$. In other words, the number of O atoms that attach themselves to O2 molecules to form O3 is far greater than the number that unite with one another, and with O₂, to form O₂ molecules; the ratio of the two classes of reactions, O_3 -forming and O_2 -forming, is at least as great as $\{N_3\}/\{N_2\}$, and does not exceed $\{N_2+N_3\}/\{N_2\}$, i.e.,

$$I + \{N_3\}/\{N_2\} > \{K_{12}n_1n_2\}/\{K_{11}n_1^2 + k_{13}n_1n_3\} > \{N_3\}/\{N_2\}.$$

In so far as the changes in $\{N_2\}$ and $\{N_3\}$ are due merely to the varying presentation of the earth toward the sun, throughout the day and through the varying seasons of the year, the ratio N_3/N_2 remains constant, so that $\{N_3\}/\{N_2\} = N_3/N_2$ at any epoch; according to the tentative estimates already indicated, this ratio is about 600.

13. It is an observed fact that n_3 is nearly constant throughout the day and night, and even its annual range is not large in comparison with total amount. Hence approximately $\{K_{12}n_1n_2\} = K_{12}n_2\{n_1\}$, $\{k_{13}n_1n_3\} = k_{13}\{n_3\}\{n_1\}$, and therefore at all times $K_{12}n_2\{k_{13}n_3\}$ is of order 600. Thus at any hour of the day or night $K_{12}n_1n_2$ is about 600 times as large as $k_{13}n_1n_3$, and so the latter can be neglected, to a first approximation, in (1), (2), (3).

The daily variation of n_3 is known to be small, but its actual value has not been determined. It will be supposed that it does not exceed 10 per cent of $\{n_3\}$, that is, the range is less than 8.1011. A variation of this magnitude, occurring in half a day (4.32. 104 secs.) would correspond to a maximum value of about 3.10^7 for dn_3/dt . This upper limit is small compared with the maximum (noon) value of $\{N_3\}$ at all save very high latitudes. Hence at noon, and indeed throughout the day except within a few minutes of sunrise or sunset, when N_3 is reduced to the order of magnitude 3.10⁷, N_3 in (3) must be nearly balanced by the term $K_{12}n_1n_2$, so that $n_1 = N_3/K_{12}n_2$. During the hours of sunlight N_3 will vary approximately as $\cos (\pi t/t_0)$, where t_0 denotes the duration of sunlight, and t denotes time, measured in the same units, measured backwards or forwards from noon; hence n, must vary in the same way, except near sunrise and sunset. That is, it has its maximum near noon, with relatively low values at sunrise and sunset. During the night, when N_2 and N_3 are zero, n_1 decreases steadily (cf. 1). The whole daily variation of n_1 is therefore simple, and as follows: it rises from dawn (or shortly after sunrise) till about noon, and then sinks towards sunset, and continues to decrease during the night. Its mean value is therefore of the same order of magnitude as, but rather smaller than, the noon value (its maximum); i.e., $\{n_1\}$ is about $\frac{1}{2}\langle n_1\rangle_{\max}$. Since $\{K_{12}n_1n_2\} > 600$ $\{K_{11}n_1^2\} > 600$ $K_{11}\{n_1^2\}$ it follows— n_1 being positive—that $K_{12}n_2 > 600$ $K_{11}\{n_1\}$; thus $K_{12}n_2$ is at least about 300 K_{11} $(n_1)_{\max}$, and the term $K_{11}n_1^2$ in (1), as well as $k_{18}n_1n_3$, can be neglected in comparison with $K_{12}n_1n_2$.

14. Adding (1) and (3), we get (accurately, save for the neglect of $k_{33}n_3^2$) to decrease during the night. Its mean value is therefore of the same

(8)
$$\frac{1}{2}d\frac{(n_1+n_2)}{dt} = N_2 - K_{11}n_1^2 - k_{12}n_1n_2.$$

Hence, integrating between any two instants of time, and denoting the intervening change in n_1 or n_3 by $[n_1]$, $[n_3]$, we have

$$[n_1] = -[n_3] + 2[N_2 dt - 2](K_{11}n_1^2 + k_{18}n_1n_8)dt.$$

Let the earlier instant be that at which n_1 attains its daily minimum; then $[n_1]$ is essentially positive, rising to a maximum equal to its daily range, and decreasing again to zero 24 hours later.

According to our previous estimate of the whole daily range of n_2 , we have $[n_3] \leq 8.10^{11}$, while the maximum value of $2 \int N_2 dt$, taking the integral throughout the whole day, is of order 2.4.32.104.9.106 or 8.1011. Since the last term in (9) is essentially negative, the extreme change in n_1 throughout 24 hours cannot exceed the sum of the maximum values of the

first two terms, viz., 8. $10^{11} + 8$. 10^{11} or 1.6. 10^{12} . Because n_1 has its maximum value near noon, and falls to a small fraction of this maximum near sunset, decreasing throughout the night, it follows that the whole range in n_1 is equal, in order of magnitude, to the noon maximum value, which is therefore, at most, of order $1.6.10^{12}$, or about one-fifth the value of n_8 . Thus the number of O atoms is always small compared with the number of O3 molecules (in the main ozone layer).

It has been seen that throughout the hours of daylight, except near sunrise and sunset, $n_1 = N_3/K_{12}n_2$ approximately; $K_{12}n_2$ is nearly constant, and likewise the ratio N_3/n_1 which it nearly equals; both N_3 and n_1 have their maximum values at or close to noon, and the upper limit just found for n_1 enables a lower limit to be placed upon $K_{12}n_{2}$, i.e.,

$$K_{12}n_2 \geqslant (N_3)_{\text{max.}}/1.6.10^{12};$$

if $(N_2)_{\text{max}}$, at the equator, has a magnitude of the order suggested in § 11, i.e., 5.109, it follows that

(9a)
$$K_{12}n_2 \geqslant 3. \text{ io}^{-3}, K_{12} \geqslant 3. \text{ io}^{-19},$$

since n_2 is of order 10¹⁶. Further, since $K_{12} = k_{12}n$, and n is of order 4. 10¹⁶, it follows that $k_{12} \ge 3 \cdot 10^{-35}$.

THE DAILY VARIATION OF ATOMIC OXYGEN.

15. After dark, (1) is approximately equivalent to

$$\frac{dn_1}{dt} = -K_{12}n_2n_1,$$

whence it follows that

$$n_1 \propto \exp(-K_{12}n_2t).$$

It follows that after nightfall n_1 decays in the ratio 10 to 1 in each interval 1/4343 $K_{12}n_2$; since $K_{12}n_2 \ge 3$. 10⁻³ (according to the estimate of N_3 given in § 5), this interval is less than 800 seconds or about 14 minutes. Thus in less than half an hour n_1 is only 1°/0 of its sunset value, that is, practically all the O atoms left at sunset have attached themselves 11 to O_2 to form O2.

The variation of n_1 during the day is approximately given by

(12)
$$n_1 = \frac{(N_3)_{\text{max.}}}{K_{12}n_2} \cos \frac{\pi t}{t_0},$$

or more accurately, from (1), neglecting the small terms N_2 and $-(2K_{11}n_1^2)$ $+k_{13}n_1n_3$,

(13)
$$n_1 = A \exp(-K_{12}n_2t)$$

$$+\frac{(N_3)_{\max}}{(K_{12}n_2)^2+(\pi/t_0)^2}\bigg[K_{12}n_2\,\cos\frac{\pi t}{t_0}+\frac{\pi}{t_0}\Big\{\sin\frac{\pi t}{t_0}+\exp.(-K_{12}n_2t)\Big\}\bigg],$$

where A is an arbitrary constant; its magnitude, which proves to be

11 This result applies only to the lower, denser, part of the ozone layer; at higher levels K_{12} decreases in proportion to the atmospheric density, so that the rate of attachment of oxygen atoms to oxygen molecules, which depends on $K_{12}n_2$, decreases upwards approximately as the square of the density; hence at sufficiently high levels the oxygen atoms disappear only slowly during the night. If the present theory had been inconsistent with this conclusion it would stand condemned, for the spectrum of the non-polar aurora plainly inaicates that atomic oxygen is present at some level in the atmosphere throughout the night.

A THEORY OF UPPER-ATMOSPHERIC OZONE

negligibly small, is found from the condition that the sunset value of n_1 sinks exponentially during the night to the sunrise value, according to (11). Since $K_{12}n_2 > 3.10^{-3}$, while π/t_0 is of order 7.10⁻⁵, (13) is very nearly

THE DAILY VARIATION OF THE OZONE CONTENT.

16. To obtain the daily variation of n_0 from (3), by substituting for n_1 , it is necessary, in the term $K_{12}n_1n_2$, where n_1 is multiplied by the relatively large factor $K_{12}n_2$, to use the form (13) for n_1 , and not the approximation (12). The principal term on the right of (3) proves to be

$$-rac{\pi(N_3)_{ ext{max}}}{K_{12}n_2t_0}\cosrac{\pi t}{t_0},$$

and this leads to the approximate solution

(14)
$$n_8 = \text{constant} - \frac{(N_9)_{\text{max}}}{K_{12}n_2} \cos \frac{\pi t}{t_0}$$

or

$$(15) n_1 + n_3 = \text{constant.}$$

Here various small terms in (3) are neglected, which are unimportant as regards the daily variation of n_3 , but which determine its mean value and its seasonal variation (see § 17 et seq.). The approximate equation $n_1 + n_3 = \text{constant}$ is deducible directly by adding (1) and (3), when it appears that the daily variation of $n_1 + n_3$ is governed only by the small rate of change expressed by $2(N_2 - K_{11}n_1^2 - k_{13}n_1n_3)$, which is far less than the rates of change of n_1 and n_3 separately, according to (12) and (14).

It is now possible to give more precision to the conclusions of $\S\S$ 13, 14, in which, from the assumption that the daily range of n_3 did not exceed 8. 10¹¹, that is 10°/ $_{\circ}$ of its mean value, an upper limit for n_{1} , and a lower limit for $K_{12}n_{22}$ were deduced. The subsequent proof of the approximate constancy of $n_1 + n_3$, together with the almost zero night value of n_1 , indicates that the maximum value of n_1 is nearly equal to the range of n_3 , and therefore on the assumption here made, to 8. 1011; the corresponding and therefore on the assumption here made, to 8.10⁻²; the corresponding lower limit of $K_{12}n_2$, if $N_3 = 5.10^9$ as here tentatively estimated, is 6.10^{-3} . These values of $(n_1)_{\max}$ and $K_{12}n_2$ will henceforward be used, but it should be clearly understood that $(n_1)_{\max}$ must really be determined by careful observations of the daily variation of n_3 , while $K_{12}n_2$ is uncertain not only on account of n_1 , but also on account of N_3 . It is probable, however, that the respectively upper and lower *limits* to n_1 and $K_{12}n_2$ are correct as regards order of magnitude.

THE MEAN VALUE OF THE OZONE CONTENT, AND ITS SEASONAL VARIATION.

17. According to the previous discussion the regular daily variation of the ozone content, though too small to have been observed as yet, depends on a daylight dissociation the effects of which are almost completely annulled soon after sunset. The mean equilibrium value of the ozone content, and its seasonal variation, are not primarily dependent on the terms N_8 and $K_{12}n_1n_2$ in (3) which express this dissociation and recombination, but rather on the smaller terms in the equations (1-3), which, though negligible as regards the daily variation, have slowly cumulative The following discussion is based on the equation

$$d\frac{(n_1+n_3)}{dt}=2(N_2-K_{11}n_1^2-k_{13}n_1n_3)$$

obtained by adding together (1) and (3); this equation is strictly accurate, on the basis of the physical assumptions underlying the present theory, except that the term $k_{33}n_3^2$ (and possibly also a term k_3n_3), representing the spontaneous thermal decomposition of ozone, is neglected, on grounds already indicated (§ 8). It may be noted that N_3 does not appear explicitly in the equation, nor n_2 ; n_2 undergoes a small daily variation which affects (1) and (3) separately by amounts comparable with the terms $K_{11}n_1^2$ and $k_{12}n_1n_3$, but which do not influence the combined equation (1)+(3).

Let the above equation be integrated over a period of 24 hours from any hour of the day to the same hour of the next day. The integral of the left-hand side will equal the change in $n_1 + n_3$ during the 24 hours; this will be denoted by $\delta(n_1 + n_3)$ so that

$$\delta(n_1 + n_3) = 2 \int_0^{24} (N_2 - K_{11}n_1^2 - k_{13}n_1n_3) dt.$$

It is convenient to take the initial hour as that of midnight or oh., because then (and indeed throughout the whole night save for a short time after sunset) $n_1 = 0$ to a high degree of approximation, and therefore $\delta(n_1 + n_2)$ $=\delta n_3^{-1}$, where n_3^{-1} denotes the midnight value of n_3 . Hence

(16)
$$\delta n_3^{1} = 2 \int_{0}^{24} (N_2 - K_{11} n_1^{2} - k_{13} n_1 n_3) dt.$$

In evaluating the right-hand side of (16), quantities of a lower order than those retained may be neglected; in particular, since $n_1 + n_2$ is very nearly constant throughout the day and night, and therefore equal to the midnight value $0 + n_3^{-1}$ or n_3^{-1} , we may replace n_3 in (16) by $n_3^{-1} - n_1$, giving

$$\delta n_3^{\ 1} = 2 \int N_2 dt - (K_{11} - k_{13}) \int n_1^{\ 2} dt - k_{13} n_3^{\ 1} \int n_1 dt.$$

In this equation N_2 is zero at night, while n_1 is so small that the night contribution to the integrals in (17) may be neglected. Thus the integration will be confined to the day hours, during which $N_2 = (N_2)_{\text{max}} \cos (\pi t/t_0)$, while n₁ is given with sufficient accuracy by (12), in terms of time reckoned from midday (t=0) backwards to sunrise $(t=-\frac{1}{2}t_0)$ or forward to sunset $(t=\frac{1}{2}t_0)$, t_0 denoting the duration of sunlight. Inserting these values in (17), and performing the integration from sunrise to sunset,

(18)
$$\delta n_3^{-1} = \frac{4t_0}{\pi} (N_2)_{\text{max.}} - \frac{1}{2}t_0 (K_{11} - k_{13}) \frac{(N_3)^2_{\text{max.}}}{(K_{12}n_2)^2} - \frac{2t_0}{\pi} k_{13} n_3^{-1} \frac{(N_3)_{\text{max.}}}{K_{12}n_2}.$$

The graph of n_8 throughout the year consists of a main wave with maximum in spring and minimum in autumn, on which, according to the present theory, there is superposed a small daily fluctuation, not yet definitely determined. In considering the seasonal variation we wish to ignore this small fluctuation, and consider the form of the main wave; this is conveniently done by finding the slope of the nearly identical curve drawn smoothly through the points on the actual curve corresponding to a particular hour on each day. This hour is here taken to be midnight, and the slope of the smoothed curve is taken to be given with sufficient accuracy by treating twenty-four hours as a small interval, and dividing

δn₃¹ by this interval. For the present purpose it is convenient to measure epoch in the year by the time \(\tau \) elapsed from (say) the vernal equinox, reckoned at the rate of 2m per year. In this unit twenty-four hours is equal to $2\pi/365$, which will be regarded as an infinitesimal, $\delta\tau$. On dividing δn_3^{-1} by $\delta \tau$ the result will be regarded as the slope dn_3^{-1}/dt of the smooth curve. Thus

$$(19) \qquad \frac{dn_3^{\ 1}}{d\tau} = \frac{365t_0}{\pi^2} \left[2(N_2)_{\text{max}} - \frac{1}{4}\pi (K_{11} - k_{19}) \frac{(N_3)^2_{\text{max}}}{(K_{12}n_2)^2} - k_{13}n_3 \frac{1(N_3)_{\text{max}}}{(K_{12}n_2)} \right]$$

On the right of this equation, t_0 , $(N_2)_{\rm max}$ and $(N_3)_{\rm max}$ are functions of τ . The unit of time in which t_0 is expressed must agree with that in which N_2 , N_3 , and K, k are reckoned; the values hitherto quoted are based on the second as the unit.

18. The daily maximum values of N_2 and N_3 , denoted by $(N_2)_{\text{max}}$, and (N₈)_{max}, occur at noon, and vary throughout the year according to the epoch 7, because of the varying presentation of the earth towards the sun. So long as the intrinsic character of the sun's radiation remains constant (as will be supposed for the present), the ratio N_2/N_3 remains constant, and we may write

(20)
$$(N_2)_{\text{max}} = A_2 F(\tau), (N_3)_{\text{max}} = A_3 F(\tau),$$

where the function $F(\tau)$ is the same for both, and may be chosen so that its mean value is unity. Thus A_2 , A_3 denote the mean values of $(N_2)_{\text{max}}$. and $(N_8)_{\text{max}}$.

The duration of sunlight, t_0 , also varies throughout the year, being

least in winter and greatest in summer; let

(21)
$$f(\tau) \equiv (t_0/t_0)F(\tau),$$

where te denotes the mean or equinoctial duration of sunlight, namely, twelve hours or 4.32. 104 seconds. Then (19) may be written as

$$(22) \qquad \frac{dn_3^1}{d\tau} = \frac{365t_e}{\pi^2} \left[2A_2 f(\tau) - \frac{1}{4}\pi (K_{11} - k_{13}) \frac{A_3^2 f(\tau) F(\tau)}{(K_{12} n_2)^2} - k_{13} n_3^1 \frac{A_3 f(\tau)}{K_{12} n_2} \right].$$

19. In connection with this equation it may be noted that the O, O₃ reaction (c) is essential to the existence of an equilibrium value of ozone, so long as the thermal decomposition of ozone is negligible, as has been supposed. If the O, O_3 reaction did not occur, that is, if $k_{13} = 0$, (22) would contain n_3^{-1} only in $dn_3^{-1}/d\tau$, and the addition of a constant to n_3^{-1} would not affect the equation. The seasonal variation would be independent of the total amount of ozone present, just as is the case with regard to the daily variation, according to the preceding theory. 12 The determination of the mean value of n_8^1 would absolutely require the consideration of the thermal decomposition.

20. Further, it may be shown that, according to (22), n_3 cannot have a regular seasonal variation unless K_{11} and k_{13} are unequal. For, if $K_{11} = k_{13}$ (22) reduces to

(23)
$$\frac{dn_3^1}{d\tau} = B(n_{30} - n_3^1)f(\tau) \qquad (K_{11} = k_{13})$$

where

(24)
$$B = \frac{365t_e}{\pi^2} \quad \frac{k_{13}A_3}{K_{12}n_2}, \quad n_{30} = \frac{2K_{12}n_2A_2}{k_{13}A_3}$$

12 Assuming in both cases, that the ozone content was sufficient to ensure practically complete absorption of the radiation in the Hartley band.

The solution of (23) is

(25) $n_3^1 = n_{30} + Ce^{-B\phi(\tau)},$

where

(26)
$$\phi(\tau) = \int_0^{\tau} f(\tau) d\tau,$$

and C is an arbitrary constant. Now $f(\tau)$ is essentially positive, though periodic in τ with the period 2π ; hence $\phi(\tau)$ is positive and increases continually, though not uniformly, with τ . If we write

(27)
$$\lambda = (1/2\pi B) \int_{0}^{2\pi i} f(\tau) d\tau,$$

then

(28)
$$B\phi(\tau) = \lambda \tau + X(\tau),$$

where $X(\tau)$ is a function periodic in τ , with the period 2π and with zero values at $\tau = 0$, 2π , 4π , . . . and mean value zero. Hence

$$(29) e^{-B\phi(\tau)} = e^{-\lambda\tau} \cdot e^{-X(\tau)},$$

where the second factor is periodic while the first steadily decreases. In (25) the second term represents the annual variation of n_3^1 , which according to (29) must decrease from year to year; that is, $K_{11} = k_{13}$ is incompatible with a permanent annual variation of n_3^1 , on the basis of the various assumptions made in deriving (22). On this basis, if $K_{11} = k_{13}$, the only permanent state is one in which the resultant production and destruction of ozone throughout each day just balance one another at all seasons of the year. While n_3^1 would not vary seasonally, the noon value of n_3 , equal to $n_3^1 - (n_1)_{\max}$, would have a summer minimum and winter maximum, but of range so small as not to be observable with the present instrumental accuracy; this does not correspond with observation.

21. When $K_{11} \neq k_{13}$, the equation (22), which may conveniently be written in the form

$$\frac{dn_3^{\ 1}}{d\tau} = \{B(n_{30} - n_3^{\ 1}) - B^1 F(\tau)\} f(\tau),$$

has the solution

(30)
$$n_3^{1} = n_{30} + Ce^{-B\phi(\tau)} - B^{1}e^{-B\phi(\tau)}[e^{B\phi(\tau)}f(\tau)F(\tau)d\tau],$$

where

(31)
$$B^{1} = \frac{\pi}{4} \frac{BA_{3}}{K_{12}n_{2}} \left(\frac{K_{11}}{k_{13}} - 1 \right).$$

As in the previous paragraph, it follows that $Ce^{-B\phi(\tau)}$ tends to zero, and this term can be omitted in considering the permanent annual variation of n_3^1 , which is included in the last term of (30). To calculate this term, when $f(\tau)$ and $F(\tau)$ are known, λ and $X(\tau)$ must first be determined: in the general case $f(\tau)$ $F(\tau)$ exp. $X(\tau)$ must then be expanded as a Fourier's series. The integration of the product of this series into exp. λ τ can then be performed, and yields exp. λ τ multiplied by a second Fourier's series; the factor exp. λ τ cancels out with the factor exp. $(-\lambda \tau)$ included in $e^{-B\phi(\tau)}$ outside the integral sign in (30), so that the whole last term is obtained as a period function of τ , the mean value of which is not necessarily zero. Alternatively a numerical calculation, in which the integration is extended over intervals from zero up to one period of τ , will

yield the result in a numerical form which in some cases may be more convenient than the analytical form.

22. Neither of these methods will be followed here; probably all that is warranted at the present stage of the observations is to calculate the sign and magnitude of the annual variation at fairly low latitudes, where the annual range is small, and the variation may be approximately represented by the first periodic term in the Fourier's series for n_3 . Thus we consider a latitude in which it is sufficiently accurate to write

$$(32) F(\tau) = 1 + a \sin \tau,$$

(33)
$$f(\tau) = (t_0/t_e)F(\tau) = 1 + \beta \sin \tau,$$

where

$$(34) 1>\beta>a>0,$$

and a, β are small enough for their products and powers to be neglected in comparison with unity; (32) represents a seasonal variation of N_2 and N_3 , in which these pass through their mean values at the vernal and autumnal equinoxes $(\tau = 0, \tau = \pi)$, and through their maxima and minima at midsummer $(\tau = \frac{1}{2}\pi)$ and midwinter $(\tau = \frac{3}{2}\pi)$; β is greater than α because t_0/t_e is of the form $1 + \gamma \sin \tau (\gamma > 0)$ in low latitudes, so that, to the first order in α and γ , the mean value of $f(\tau)$, like that of $F(\tau)$, is unity, and $\beta = \alpha + \gamma > \alpha$.

23. It is readily verified that the solution, neglecting powers and products of α and β , is

(35)
$$n_3^1 = n_{30} - \frac{B^1}{B} - \frac{B^1 a}{1 + B^2} (B \sin \tau - \cos \tau);$$

it may be noted that, to this degree of approximation, β does not appear in the result.

The observed annual variation of n_2 is roughly of the form

(36)
$$n_3^1 = (n_3^1)_0 + (n_3^1)_1 \cos \tau,$$

where $(n_3^{-1})_1$ is positive; corresponding to maximum n_3^{-1} at the vernal equinox. In order that (35) may approximately agree with (36), four conditions must be satisfied, as follows.

(a) The $\sin \tau$ term in (35) must be small compared with the $\cos \tau$ term, that is, B must be a small number. If so, (35) reduces approximately to

$$n_2^1 = n_{20} - (B^1/B) + B^1 a \cos \tau.$$

(b) The coefficient of $\cos \tau$ in (35) or (37) must be positive, that is, $B^1 > 0$, or, by (31),

$$K_{11} > k_{13}$$

(c) The constant term in (35) must be positive, i.e.,

$$(39) n_{30} > B^1/B.$$

(d) The constant term in (35) must exceed the coefficient of the $\cos \tau$ term, i.e.,

$$(40) n_{80} - B^1/B > B^1 a.$$

24. Before considering these conditions numerically, it is convenient to sum up here the main results of the discussion of §§ 11-23. The daily

variation of n_1 and n_3 was first considered, and it was concluded that, very approximately,

 $(41) n_1 = N_3 / K_{12} n_2$

throughout the day, except near sunrise and sunset. Thus at noon, when n_1 attains its maximum,

 $(n_1)_{\text{max.}} = (N_3)_{\text{max.}} / K_{12} n_2.$

Further, $n_1 + n_3$ was found to be very nearly constant throughout the day and night; since n_1 is practically zero at night, $(n_1)_{max}$ is approximately equal to the daily range in n_3 . Thus

(43) daily range in
$$n_8 = \langle N_3 \rangle_{\text{max}} / K_{12} n_2$$
,
$$= A_8 F(\tau) / K_{12} n_2$$
,

by (20).

Next, by considering the annual variation of n_3 , it was concluded that, for the maximum of n_3 to occur in spring and the minimum in autumn,

$$B\left(=\frac{365t_e}{\pi^2}\frac{k_{13}A_3}{K_{12}n_2}\right)$$

must be small; and that the annual mean value of n_3 , i.e. $(n_3^{-1})_0$, and the semi-range in its value, are as follows:

(45)
$$(n_8^1)_0 = n_{80} - \frac{B^1}{B} = \left(\frac{730 l_e A_2}{\pi^2} - B^1\right)/B,$$

$$(a_3^{1})_1 = B^{1}a$$

a being a known number (>1) depending on the latitude. Thus by (46) we can deduce B^1 from the observed value of $(n_3^1)_1$. Then (45), written in the alternative form

(47)
$$A_2 = \frac{\pi^2}{730 t_e} \{ B^1 + (n_3^1)_0 B \},$$

enables upper and lower limits to be placed on A_2 , since 0 < B < 1. Moreover since B must actually be small, A_2 is determined within rather narrow

limits, and if B is known, A_2 is definitely fixed.

If B can be estimated from the observations of the annual variation, $k_{13}A_3/K_{12}n_2$ becomes known. If also the daily range of n_3 can be determined at any epoch τ in the year (so that $F(\tau)$ is known), (43) gives the value of $A_3/K_{12}n_2$; in conjunction with the value of B_1 this determines k_{13} . Further, this knowledge then enables the value of K_{11} to be inferred from the value of B^1 . Thus the observation of the daily range and the annual variation of n_3 would determine the values of

$$A_2$$
, k_{13} , K_{11} , $A_3/K_{12}n_2$,

where, in the last quantity, n_2 may be considered known. The present theory does not enable the separate values of A_3 and K_{12} to be inferred, though if A_3 is estimated, as in § 5, K_{12} is then determined.

25. These considerations will now be applied numerically to the observations of n_3 for southern England; a may be taken as about $\frac{1}{3}$, and $(n_3^1)_0$, $(n_3^1)_1$ as $8 \cdot 10^{12}$ and $2 \cdot 10^{12}$. By (46), $B^1 = 6 \cdot 10^{12}$, whence, by (47),

$$A_2 = 1.9 \cdot 10^6 + 2.5 \cdot 10^6 B$$
,

so that A_2 cannot much exceed 2.106 since B is small. This is rather smaller than the very tentative estimate given in § 6, but it is of interest to

find that that estimate is of the same order of magnitude as the value here deduced. This value suggests either that in the region 1300-1800 Å the sun's radiation is only about one-fifth as intense as that of a black body at 6000°, or else that only about one quantum in five dissociates a molecule of O_a.

In order to make further progress, it is necessary to form estimates of B and the daily range of n_3 , which will be denoted by $[n_3]$. By (43)

and (44).

$$k_{18} = \frac{\pi^2 F(\tau)}{365 t_e} \frac{B}{[n_8]} = 6.3 \cdot 10^{-7} \frac{B}{[n_8]},$$

if we write $F(\tau)=1$. If $B=\frac{1}{10}$, and $[n_3]=\frac{1}{10}.8\cdot 10^{12}$, as assumed in §§ 13, 14, we find $k_{13}=8.10^{-20}$; the value is greater or less than this according as B exceeds or is less than the proportionate daily range of n_3 . There is no reason to suppose this is equal to B, but the value 8.10^{-20} obtained on this assumption seems not unreasonable as regards order of magnitude, and it satisfies the inequality $K_{12}n_2 > 300k_{13}n_3$ of § 13, taking $K_{12}n_2$ to be at least 6.10^{-3} , as found in § 16 (these involve the estimate 5.10^9 for A_3 , and the ratio $A_8/A_2=2500$, taking $A_2=2.10^6$, according to § 25).

Taking $B^1 = 6.10^{12}$, $B = \frac{1}{10}$, $[n_3] = 8.10^{11}$, $k_{13} = 8.10^{-20}$, the value of K_{13} is found to be about 8.10^{-18} . These values are merely illustrative; the ozone observations are at present not accurate enough to warrant definite conclusions as to $[n_3]$ and B, and, consequently, as to k_{13} and K_{11} .

26. The predicted annual variation of n_3 , which depends on B^1a , is zero at the equator, where a = 0, and is reversed in southern latitudes, in

accordance with observation.

In high latitudes, where a approaches 1, the preceding analysis becomes inadequate; it is no longer possible to ignore powers of a above the first, and either further terms in the Fourier's series must be considered, or (30) must be evaluated by quadratures. The higher harmonics must become of considerable importance when a = 1, corresponding to a station on the arctic circle; for according to (36) $dn_2^{-1}/d\tau$ is greatest at midwinter, when A_2 and A_3 just sink to zero; but (22) shows that $dn_3^{1}/d\tau$ must be zero when A_2 and A_3 vanish, and therefore (36) cannot be true in such a latitude, if the present theory is true. One of the most definite tests of the theory will be the observation (by the ultra-violet absorption of moonlight) of the ozone in the arctic circle during the period of continual darkness; according to the theory the ozone should be constant during this time, and the large increase from autumn to spring must occur during the prior and subsequent periods of decreasing and increasing daylight which are separated by the time of continual darkness. If this is not verified, it will prove that some important factor concerned in the equilibrium and variations of ozone has been left out of this discussion.

THE VARIATION WITH LATITUDE OF THE ANNUAL MEAN OZONE CONTENT.

27. The variation of the annual mean ozone content $(n_3^{-1})_0$ with latitude will next be considered: it is given by (45) as

$$n_{30} - B^{1}/B$$
,

where, by (24), (31)

$$n_{30} = \frac{2K_{12}A_2}{k_{13}A_3}, \quad \frac{B^1}{B} = \frac{\pi}{4} \frac{A_8}{K_{12}n_2} \left(\frac{K_{11}}{k_{13}} - 1\right).$$

By (43) the second term in B^1/B is of the same order as the daily range of n_2 , and therefore inappreciable; hence it is sufficient to write

$$\frac{B^1}{B} = \frac{\pi}{4} \frac{K_{11}}{K_{12}} \frac{A_3}{k_{18} n_2}.$$

Both A_2 and A_3 vary with the latitude ϕ proportionately to $\cos \phi$, their ratio, which is an intrinsic property of the solar spectrum, being therefore independent of latitude. Thus n_{30} will vary only through the factor $2K_{12}k_{13}$, which is independent of the temperature, but proportional (through K_{12}) to the density of the air in the ozone layer. The ratio K_{11}/K_{12} in B^1/B is independent of the latitude, while the factor $A_3/k_{13}n_2$ varies as $\cos \phi$ divided by the atmospheric density (possibly also with a factor depending slightly on temperature, through k_{12}).

factor depending slightly on temperature, through k_{13}).

It is not known how the height and density of the ozone layer vary with latitude. If the height is determined by the level of maximum absorption of the sun's ultra-violet radiation, it should be least at the equator; the increase in height at latitude ϕ should be $-H \log_e \cos \phi$, where H is the height of the "homogeneous" atmosphere. At latitude 60°, taking H as 8 km., this is about 5·5 km. The density of the air at the level of maximum absorption of radiation varies as $\cos \phi$.

If the density of the ozone layer varied in this way, n_{30} would be proportional to $\cos \phi$, while B^1/B would be independent of ϕ , so that $(n_3^{-1})_0$ would decrease with latitude. This is not in accordance with observation. The change would, moreover, be a large one; $(n_3^{-1})_0$ is of order $8 \cdot 10^{12}$ at latitude 60°, while B^1 , according to our previous tentative estimates for southern England, is about $6 \cdot 10^{12}$, so that B^1/B , B being small, is large compared with $6 \cdot 10^{12}$ or $8 \cdot 10^{12}$; hence also n_{30} , which equals $B^1/B + (n_3^{-1})_0$, is large compared with $(n_3^{-1})_0$. Thus $(n_3^{-1})_0$, according to (45), is the difference between two quantities which at $\phi = 60^{\circ}$ are much larger than itself; if one of these is independent of ϕ , while the other varies as $\cos \phi$, the ozone content at the equator should be of order $2B^1/B$, and therefore much greater than is observed.

The present theory can therefore be further tested by determining the variation of density of the ozone layer with latitude, by making careful observation of its height at different latitudes. The observed decrease of $(n_2^{-1})_0$ towards the equator can be reconciled with (45) only if the density decreases with latitude more slowly than as $\cos \phi$. Suppose, for example, that the density varied as $\cos^s \phi$. Then n_{30} would vary as $\cos^s \phi$, and B^1/B as $\cos^{1-s} \phi$; if $s=\frac{1}{2}$, n_{30} and B^1/B would both decrease with latitude in the same ratio, and $(n_3^{-1})_0$ would vary in the like ratio. To explain the observed increase of $(n_3^{-1})_0$ with latitude, it is necessary to suppose that s is slightly less than $\frac{1}{2}$, so that B^1/B decreases more slowly with latitude than n_{30} .

THE DEPENDENCE OF THE OZONE CONTENT ON SOLAR CHANGES,

28. The effect of intrinsic day-to-day changes in the sun's ultra-violet radiation will next be considered. Suppose on a particular day that N_2 and N_3 are in excess of their normal values at that epoch in the year. The principal effect during the day will be a reduction in the ozone content by extra dissociation due to N_3 ; the reduction will be greatest

at the equator. But even if N_8 is increased by 50 per cent, the increase in n_1 will be less than 5.10¹¹ at noon, and still smaller nearer sunset, at the time to which the day observations of ozone refer; hence the (equal) decrease in n_8 will not be easily measurable. During the following night the O atoms will revert mainly to ozone, and the net change for the day will be given by (18), with the appropriate abnormal values of N_2 and N_3 inserted. If N_2 and N_3 increase proportionately, the middle term of (18), containing N_3^2 , will have the largest increase, and since this term is negative $(K_{11} > k_{18})$ it follows that δn_8^1 will not be increased in proportion to N_2 and N_3 ; since n_3^1 is in any case very small, as it corresponds to the slow seasonal variation, the change in n_8^1 following the day of abnormal radiation is likely to be insensible.

It is probable that the quiet-day diurnal magnetic variation (S_q) varies in proportion to some component of the sun's ultra-violet radiation; if so, then according to the above theory there should be an inverse correlation between the range of S_q , and the day value of n_3 ; there should be no appreciable correlation between S_q and the night value (n_3^{-1}) of the ozone. The correlation between S_q and n_3 is not likely to be detectable in the European ozone data, the day-to-day changes in which are probably determined mainly by horizontal convection of ozone, associated with weather changes; the correlation, if it exists, should be best shown by the equatorial ozone data, but will almost certainly be small.

29. It is well known that S_q increases by 50 per cent or more from sunspot minimum to sunspot maximum, and this is probably due to a similar variation of intensity of ultra-violet radiation. It cannot safely be assumed that N_2 and N_3 vary in a constant ratio; the change is likely to lessen with increasing wave-length, since in the visible spectrum there is little or no sunspot variation. Thus N_2 may vary more than N_3 with sunspot epoch; the extreme case to consider is that in which N_3 is constant, and N_2 is proportional to $I-\theta$ cos τ , where τ now denotes sunspot epoch, measured from minimum, at the rate 2π per eleven years; then the equation of change is the same as (19), except that 365 must be replaced by II × 365, and N_3 is constant; also t_0 will be treated as constant, seasonal effects being supposed eliminated by considering annual means of n_3 . The solution is

(48)
$$n_3^{1} = n_{80} - \frac{B^1}{B} - \frac{11 \times 365 t_0}{\pi^2} 2A_2 \theta \frac{11B\cos \tau + \sin \tau}{1 + (11B)^2}.$$

The constant terms are unchanged. The coefficient of the last factor in the variable term is $7 \cdot 10^{13} \theta$, which is larger than $n_{30} - B^1/B$ unless θ is about $\frac{1}{10}$. The phase of the variable term depends on the value of B; if $B = \frac{1}{10}$, as was tentatively supposed in § 24, n_3^{-1} is definitely out of phase with N_2 by about 45°; if B is much less than $\frac{1}{10}$, the phase difference increases to 90°. If B is as large as $\frac{1}{3}$, which is rather too great to be consistent with the seasonal variation, then n_3^{-1} will vary nearly in parallel with N_2 , having its maximum near sunspot maximum. Fowle 18 states that such a variation occurs at certain northern stations, but that the data for Montezuma, in Chile, do not show it. According to Dobson there is little indication of a sunspot relationship, but such evidence as exists favours an inverse relationship. The latter would be difficult to account for by the present theory.

If N_3 , instead of being constant, also varies, the above results must be modified. If N_2 and N_3 vary in the same ratio, the analysis of § 24

¹³ Fowle, F. E., Washington, D.C. Smithsonian Misc. Coll. 81, 1929.

becomes applicable, except that (i) t_0 is to be treated as constant, so that $f(\tau)$ and $F(\tau)$, or a and β , are identical, (ii) a sin τ must be replaced by $-\theta \cos \tau$. Hence (35) is still valid, if B^1 , B are replaced by 11 B^1 , 11 B, a by θ , cos τ by $-\sin \tau$, and $\sin \tau$ by $-\cos \tau$, *i.e.*,

(49)
$$n_3^{1} = (n_3^{1})_0 - \frac{IIB^{1}\theta}{I + (IIB)^2} (\sin \tau - IIB \cos \tau).$$

Here again we meet the serious difficulty that unless θ is very small there should be a large sunspot variation of n_3^1 ; the phase will depend on the value of II B. The latter can scarcely exceed 3, and if this is its value, the amplitude of the sunspot variation is at least $3.3 \ B^1 \theta$, or $2.10^{13} \theta$. Unless θ is 0.1 or less, which is perhaps smaller than would be expected, the sunspot variation, according to the present theory, should be easily measurable.

The thermal decomposition of ozone has been ignored in this discussion of the sunspot variation; it must tend to reduce, and alter the phase of, the variations that would otherwise occur. So far as present indications go, it would seem to be too small to affect appreciably even the 11-year ozone variation, but when the present observational uncertainties regarding the latter are removed, further light may be thrown on the purely thermal decomposition. At present it is scarcely worth while to discuss the non-linear differential equation which is obtained in place of (19) when the bimolecular decomposition of ozone is considered.

It has been assumed that nitrogen plays no part in determining the equilibrium concentration of ozone. It seems not unlikely that the reactions $O+N_2=N_2O$, $O_3+N_2=O_2+N_2O$ may occur to some extent, but, if so, there is probably some counterbalancing dissociation of N_2O ; the consideration of these processes would greatly complicate the discussion, and there is still less basis to go upon in their case than in that of the processes actually dealt with.

PRINCIPAL SYMBOLS.

```
n<sub>1</sub>, n<sub>2</sub>, n<sub>8</sub>, n-$ 10: numbers of O, O<sub>2</sub>, O<sub>3</sub>, and air atoms or molecules per cc., at or near the level of maximum ozone density.
n<sub>3</sub><sup>1</sup>-$ 17: midnight value of n<sub>3</sub>.
(n<sub>3</sub><sup>1</sup>)<sub>0</sub>-$ 24: annual mean value of n<sub>3</sub><sup>1</sup>.
δn<sub>3</sub><sup>1</sup>-$ 17: change of n<sub>3</sub><sup>1</sup> from one midnight to the next.
N<sub>2</sub>, N<sub>3</sub>-$ 11: the number per cc. of O<sub>2</sub> and O<sub>3</sub> molecules dissociated per sec. at or near the level of maximum ozone density.
k<sub>10</sub>, k<sub>12</sub>, k<sub>13</sub>, k<sub>33</sub>-$ 10: coefficients of recombination.
K<sub>11</sub>=k<sub>11</sub>n; K<sub>12</sub>=k<sub>12</sub>n-$ 10.
t-$ 13: time measured in seconds backwards or forwards from noon.
t<sub>0</sub>-$ 13: duration of sunlight, in seconds, on any day.
t<sub>e</sub>-$ 18: annual mean value of t<sub>0</sub>, that is, 12 hours or 43,200 seconds.
τ-$ 17: time elapsed from the vernal equinox, measured at the rate 2π per year.
A<sub>2</sub>, A<sub>3</sub>-$ 18: annual mean values of N<sub>2</sub>, N<sub>3</sub> at noon.
F(τ)-$ 18: ratio of N<sub>2</sub> or N<sub>3</sub> at noon at the epoch τ in the year, to their annual mean values A<sub>2</sub>, A<sub>3</sub>.
f(τ)-$ 18 (21).
B, n<sub>30</sub>-$ 20 (24).
B<sup>1</sup>-$ 21 (31).
a, β-$ 22, (32), (33).
```

SUMMARY

The main part of the paper consists of a discussion of the daily and annual variations of the ozone content of the atmosphere in any latitude up to about 50°. The ozone is treated as if it were uniformly spread through a layer of air 10 km. thick, having the same density as the air at the level of maximum ozone density. Convection and diffusion of ozone are neglected. The thermal decomposition of ozone (20g = 30g) is discussed, and estimated to be negligible, except possibly in connection with an eleven-year (sunspot) variation of ozone. The ozone is supposed formed and decomposed in the 10 km. layer; formation is attributed ultimately to dissociation of O2 by ultra-violet radiation (1300-1800 Å); the ozone is supposed decomposed by longer-wave radiation (2300-2000 Å); the intensities of radiation in these bands are supposed to be not greatly different from those that would occur in the spectrum of a black body at 6000°; the photo-electric efficiency of the radiations is supposed not to be very low. Then, by day, the dissociation of ozone would seriously reduce its amount, were it not compensated by rapid re-formation $(O + O_2 = O_3)$. The fact that the daily variation of ozone is inconspicuous is used to estimate a lower limit for the rate of this recombination.

In so far as dissociation $(O_3 = O + O_2)$ and re-formation $(O + O_2 = O_3)$ balance one another, they have no ultimate effect on the amount of ozone; but new O atoms are formed by dissociation of O_2 , and this tends to increase the amount of ozone. This rate of increase is supposed held in check by reactions which cause the reversion of some of the O (formed from O_2 and O_3) and O_3 to O_2 , by the reactions $2O = O_2$, $O + O_3 = 2O_2$. These reactions occur mainly by day; most of the O atoms then present have been formed from O_3 . It is shown that the varying rates of these reactions can explain the observed annual variation of ozone, provided

that the coefficients of reaction have suitable values.