

A Self-Consistent Treatment of the Oxygen Dissociation Region in the Upper Atmosphere*

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A self-consistent theory is suggested for the determination of the distribution of atomic and molecular oxygen and the temperature in the region 100–140 km of the atmosphere. It is assumed that solar radiation is responsible for the photodissociation of the oxygen molecules, and that the recombination of the atoms by two-body radiative processes is more important than that by three-body collisions (as justified from theoretical considerations). From the postulated conditions for the steady state, namely, for any given volume, (a) the average time rate of dissociations equals that of recombinations, and (b) the average time rate at which radiation energy is absorbed in dissociation processes equals that at which radiation energy is emitted in recombination processes, together with an appropriate form of the barometric equation, it is possible to obtain the concentrations of the molecular and the atomic oxygen and the temperature, all as functions of height, provided the temperature and its gradient are given at one height.

Calculations have been carried out for three sets of these boundary values at 100 km, namely, (i) $T=300^\circ\text{K}$, $dT/dx=10^\circ/\text{km}$, (ii) $T=300^\circ\text{K}$, $dT/dx=5^\circ/\text{km}$, and (iii) $T=270^\circ\text{K}$, $dT/dx=5^\circ/\text{km}$. In all these cases, dissociation begins between the heights 90 and 100 km and is not complete until around 150 km. The total gas pressure for various heights above 100 km calculated for case (iii) above agrees quite well with the data obtained from V-2 rocket flights.

In the appendices, three-body recombinations are discussed. The cross section for a three-body recombination process is defined, and its relation with the cross section of its inverse two-body excitation process is obtained on statistical mechanical arguments. Also, the relation between the absorption coefficient for a photodissociation process and the cross section of its inverse radiative recombination process is obtained.

I. INTRODUCTION

IN the upper atmosphere, the atoms and molecules are ionized or dissociated on the absorption of solar radiation of the proper frequencies, and the resulting ions or atoms recombine either in their respective inverse processes, namely, a two-body radiative recombination, or in three-body collisions. The degree of ionization or dissociation of a given atomic or molecular species at any given height depends on the following factors: the intensity of the radiation involved, the density of the gas, the temperature of the gas at that height, and such atomic or molecular quantities as the radiation absorption coefficient and the cross sections for the recombination collisions. The problem of investigating the region in which oxygen is dissociated into atoms has been studied by Wulf and Deming,¹ Majumdar,² Rakshit,³ and Penndorf,⁴ after the original suggestion of Chapman.⁵ While these authors differ in details in the assumptions in their theories, their results depend essentially on an assumption made concerning the total number of oxygen molecules in a column of unit cross section above any given height, which is just the quantity to be calculated from their theories. Thus their results are arbitrary in the sense that they have already been assumed in their calculations.

This question of self-consistency and other assumptions in their theories are discussed in Appendix 7. The purpose of the present work is to show that in principle a self-consistent theory can be formulated, in which the temperature and the concentrations of the atoms and molecules of oxygen can all be obtained as functions of the height from a knowledge of the temperature and its gradient at a certain height. The theory is illustrated by an actual calculation in which the most reasonable assumptions are made concerning the processes involved in the region of the atmosphere under consideration. The result obtained differs considerably from those of the previous authors.

To avoid discontinuity in the discussion and the presentation of the theory and the result, we have relegated to the appendices the derivations of equations and some of the arguments and calculations in the theory.

II. GENERAL FORMULATION OF THE PROBLEM

In studying the variation of the temperature and the degree of dissociation of the oxygen molecules as functions of height in the upper atmosphere, it must be assumed that the time τ_{dis} required to reach dissociative equilibrium is small compared with the time τ_{dif} required to establish diffusive equilibrium and also with the average time interval between winds. That $\tau_{dis} \ll \tau_{dif}$ is necessary for the existence of a transition region in which oxygen passes from the molecular into the dissociated state is obvious, for otherwise the atoms and molecules will be separated by diffusion in the gravitational field. Calculations (Appendix 3) show that for oxygen, τ_{dis} is of the order of days, while, on the other hand, τ_{dif} is of the order of years for the pressure

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¹ O. R. Wulf and L. S. Deming, *Terr. Mag.* **41**, 299 (1936); **43**, 283 (1938).

² R. C. Majumdar, *Indian J. Phys.* **12**, 75 (1938).

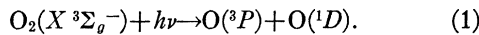
³ H. Rakshit, *Indian J. Phys.* **21**, 57 (1947).

⁴ R. Penndorf, *J. Geo. Res.* **54**, 7 (1949); *Phys. Rev.* **77**, 561 (1950).

⁵ S. Chapman, *Phil. Mag.* **10**, 367 (1930).

existing at the height 100 km. The situation as to the existence and the frequency of winds at these heights is a more obscure one. As there is still a lack of direct evidence either for or against the existence of winds at such heights, we shall ignore them in the present work, since the assumption of winds of sufficient frequency and strength to churn up this region of the atmosphere would render meaningless the very problem of finding the degree of dissociation and temperature as a function of the height.

We shall then consider the following idealized model of the atmosphere. In certain regions, the most important physical processes taking place are assumed to be the dissociation of the oxygen molecules by solar radiation, and the recombination of the oxygen atoms into molecules. Other constituents, such as nitrogen, will not be considered except in so far as they contribute to the total pressure of the atmosphere. For the dissociation process, it seems quite certain that the most important absorption process leading to dissociation is the absorption in the Schumann-Runge continuum beyond 1750Å. We write this process as



We shall denote by σ_ν the absorption cross section (in cm^2) for this process. The cross section σ_ν is defined below. Let $\rho_\nu(\infty)$ be the solar radiation energy density per unit frequency range at the "top" of the atmosphere. On account of the absorption by the molecules lying above x , the density at the height x is given by

$$\rho_\nu(x) = \rho_\nu(\infty) \exp[-\sigma_\nu N_2(x)], \quad (2)$$

where

$$N_2(x) = \int_x^\infty n_2(x) dx, \quad (3)$$

$n_2(x)$ being the number density of oxygen molecules and $N_2(x)$ the number of oxygen molecules in a column of unit cross section above the height x . The number of oxygen molecules dissociated per unit volume per second at the height x is

$$n_2(x) \int_{\nu_0}^\infty [\sigma_\nu c \rho_\nu(x) / h\nu] d\nu$$

where ν_0 is the threshold frequency of the process (1). This statement defines σ_ν . It will be shown later that most of the oxygen atoms are in the 3P state. Let us denote the coefficient of recombination by B so that the number of recombinations per unit volume per second is $n_P^2 B$, where n_P is the number density of atoms in the 3P state. B is in general a function of temperature and hence of height. The condition for a steady state is

$$n_2 \int_{\nu_0}^\infty [\sigma_\nu c \rho_\nu(\infty) \exp(-\sigma_\nu N_2) / h\nu] d\nu = B n_P^2(x). \quad (4)$$

Let P be the total pressure, and n the number

density of nitrogen molecules. One has

$$dP = -[(2n_2 + n_P)M + nM_N]g dx, \quad (5)$$

and

$$P = (n_2 + n_P + n)kT, \quad (6)$$

where M , M_N are the atomic weight of oxygen and the molecular weight of nitrogen, respectively. Thus there are four unknown functions n_2 , n_P , n , and T which are related by Eqs. (4) and (5) plus (6).

To get rid of the nitrogen in the theory, Rakshit³ and Penndorf⁴ assume that the proportion of nitrogen to oxygen (atomic plus molecular) remains the same at 4:1 at all heights concerned in the problem. This assumption presupposes the constant mixing of the atmosphere by winds. If this is so, the time intervals between winds must be short compared with the time τ_{diff} required to establish diffusive separation and long compared with the time τ_{dis} required to establish dissociative equilibrium. Furthermore, their assumption that at any height

$$nM_N : (n_2 + \frac{1}{2}n_P)2M = 4:1 \quad (7)$$

also implies that the atomic and molecular oxygen do not redistribute themselves. This is equivalent to assuming an atmosphere separated by transparent partitions into parallel layers. Instead of assuming (7) we shall assume that above ~ 100 km the nitrogen is in diffusive equilibrium with the oxygen (but we shall *not* assume that molecular and atomic oxygen are in diffusive equilibrium with each other). Then one can work with the partial pressure p of oxygen alone so that (5) and (6) become

$$dp = -(2n_2 + n_P)Mg dx, \quad (8)$$

$$p = (n_2 + n_P)kT, \quad (9)$$

which give the differential equation

$$\frac{d}{dx}[(n_2 + n_P)T] = -\frac{Mg}{k}(2n_2 + n_P). \quad (10)$$

As there are still three unknown functions $n_2(x)$, $n_P(x)$, $T(x)$ given by Eqs. (4) and (10),^{5a} a certain temperature distribution $T(x)$ is assumed in all the above-mentioned investigations. On doing this, and eliminating n_P in (10) by means of (4), one obtains a nonlinear differential equation of the second order for N_2

$$F\left(\frac{d^2 N_2}{dx^2}, \frac{dN_2}{dx}, N_2, T, \frac{dT}{dx}, x\right) = 0, \quad (11)$$

where F is a known function of the various arguments, and depends on N_2 through integrals of the form of that on the left-hand side of (4). This equation is to be solved subject to the boundary conditions that at a sufficiently low altitude x_0 where the degree of dissociation is probably extremely small, $-N_2'(x_0)$ may be

^{5a} Or a similar equation obtained by assuming (7) in (5) and (6).

given a value estimated from another source of information, and at a sufficiently great height, N_2 is small, i.e.,

$$-N_2'(x_0) = n_2(x_0) \text{ given, } N_2(\infty) = 0. \quad (11a)$$

In principle, on the assumption of a certain $T(x)$, a definite recombination mechanism and the proportion (7) or an alternative as mentioned above, the problem is reduced to the solution of Eq. (11) subject to the above boundary conditions. The important point is that the n_2, N_2 are thereby completely determined, and any further assumption about any one of these quantities is not only unnecessary but is in fact inconsistent with the problem.

An actual calculation, however, in this manner will entail extremely laborious computations, on account of the complicated form of Eq. (11) and of the nature of the boundary conditions. On integrating the equation numerically upward from x_0 one knows the initial slope $N_2'(x_0)$ but not the function $N_2(x_0)$, so that it is necessary to perform the integration for various values of $N_2(x_0)$ until the solution vanishes monotonically as $x \rightarrow \infty$.

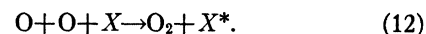
In the present paper the authors suggest an alternative self-consistent treatment of the problem in which no assumption above $T(x)$ is made, but instead another physical assumption is made for the steady state. The advantages of this theory are the following: (1) the temperature $T(x)$ determined by the steady state is given by the theory itself without its being assumed on empirical grounds; (2) the form of the differential equation for T and of the boundary conditions on T and dT/dx enables the problem to be solved with much less numerical work than is the case in the treatment discussed above.

III. PROPOSED SELF-CONSISTENT THEORY

We shall show that all the functions $n_P(x), n_2(x), T(x)$ can be obtained as functions of the height x , if, in addition to Eqs. (4) and (10), we postulate that in the region of the atmosphere under consideration, the amount of energy absorbed from solar radiation in the process (1) per unit volume per second be equal to the energy radiated by the recombination processes. The heat loss due to conduction has been neglected as a simplifying assumption, which may be justified, since the rate of loss of heat in any layer by conduction depends on the pressure and on d^2T/dx^2 , both of which are small. In the following, we shall illustrate our theory by carrying out some numerical calculations on the basis of some assumed recombination processes. It is to be emphasized that while the exact numerical result depends on these assumptions, the principle of the method is more general and may be applied to future calculations when further empirical information becomes available.

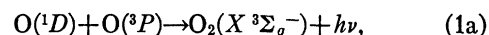
Consider now the processes that lead to the recombination of the oxygen atoms. Wulf and Deming,¹ and

recently Penndorf⁴ work with the assumption that two oxygen atoms recombine in a three-body collision,



In Appendix 5, arguments will be given to show that for the pressures prevalent at and above the height of 100 km, three-body collisions of the type (12) are much less important than two-body radiative recombinations. As no direct experimental data on this point are available and as quantitative theoretical calculations are difficult, we shall base our assumption of two-body recombination on our discussions in Appendix 5. The calculations of Majumdar² and Rakshit³ are also based on the assumption of two-body recombinations.

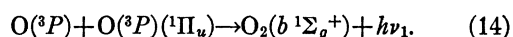
Of the two-body radiative recombinations, there is first the inverse process of (1), namely,



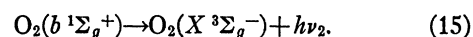
whose cross section β_v is defined in Eq. (16) below. The 1D state of O has a transition probability $A_D \cong 10^{-2} \text{ sec}^{-1}$ for the magnetic dipole transition to the 3P state, emitting the red auroral lines



In view of the short lifetime of $O(^1D)$, we have to consider collisions between two 3P atoms. In Appendix 6, we give some arguments that make it plausible to assume that the most important recombination process probably involves a dipole transition, such as



We shall denote by β_v' the cross section of such a process. The $O_2(b^1\Sigma_g^+)$ will make a subsequent transition to the normal state of the molecule on emitting the "atmospheric bands"



Although this detailed assumption is by no means certain, it seems to have some support in the identification by Meinel⁶ and Kaplan⁷ of the atmospheric band (0,1) of oxygen in the infrared region of the spectrum of the night sky.^{7a}

Let the number density of oxygen atoms in the 1D state be denoted by n_D . The time rates of change of the concentrations are given by^{7b}

⁶ A. B. Meinel, Trans. Am. Geophys. Union 31, 21 (1950).

⁷ J. Kaplan, Phys. Rev. 78, 82 (1950).

^{7a} The recent discovery of the OH vibration-rotational bands in the night sky spectrum by A. B. Meinel, Astrophys. J. 111, 555; 112, 121 (1950) suggests the reactions $O + OH \rightarrow O_2 + H$, $O + O_2 + X \rightarrow O_3 + X^*$, $H + O_2 \rightarrow OH + O_2$ as the effective processes for the recombination of the atomic oxygen into molecules. In the present work, we have not considered these processes, since it is not certain that the OH bands come from the same regions of the atmosphere (above 100 km) considered in our problem. Our theory may be applied to these processes when more information becomes available.

^{7b} We have neglected the removal of the 1D state of the oxygen atoms by collisions of the second kind on the following consideration. The cross section of a collision in which the energy of $O(^1D)$ is transferred to the electronic energy of another atom or

$$dn_2/dt = -n_2 \int_{\nu_0}^{\infty} (\sigma_v c \rho_v(x)/h\nu) d\nu + n_P^2 \int_0^{\infty} \beta_v' v F(v) dv + n_P n_D \int_0^{\infty} \beta_v v F(v) dv, \quad (16)$$

$$dn_D/dt = n_2 \int_{\nu_0}^{\infty} (\sigma_v c \rho_v(x)/h\nu) d\nu - n_D A_D - n_P n_D \int_0^{\infty} \beta_v v F(v) dv, \quad (17)$$

$$dn_P/dt = n_2 \int_{\nu_0}^{\infty} (\sigma_v c \rho_v(x)/h\nu) d\nu + n_D A_D - n_P n_D \int_0^{\infty} \beta_v v F(v) dv - 2n_P^2 \int_0^{\infty} \beta_v' v F(v) dv, \quad (18)$$

where $F(v)$ is the velocity distribution function of the atoms with respect to the relative velocity v , and β_v the cross section of (1a). It is seen that unless one ignores the frequent process (13), it is necessary to include such a process as (14) in order to have any steady state expressed by the vanishing of the time rates of change of the concentrations in (16), (17), and (18).

Consider Eq. (17). The transition probability A_D is 10^{-2} per sec. From the calculations later on in this work (Appendix 4), one finds, for $n_P = 10^{12}/\text{cm}^3$

$$n_P \int_0^{\infty} \beta_v v F(v) dv \cong 10^{-7}/\text{sec}. \quad (19)$$

Hence $O(^1D)$ disappears mostly through the transition (13), and for the steady state, Eq. (17) gives

$$n_2 \int_{\nu_0}^{\infty} (\sigma_v c \rho_v(x)/h\nu) d\nu \cong n_D A_D.$$

Equation (18) then gives, for the steady state,

$$n_D A_D \cong n_P^2 \int_0^{\infty} \beta_v' v F(v) dv. \quad (20)$$

Finally consider Eq. (16). The relative importance of the last two terms depends on n_P , n_D , β_v , and β_v' . β_v can be calculated from the observed σ_v by means of the principle of detailed balancing (Appendix 1). β_v' for such a process as (14) is not known either experimentally or theoretically, but as (14) is assumed to be

molecule is small except when there is very close resonance. The cross sections of processes in which the electronic excitation is transferred to the translational vibrational and rotational energy of the colliding atom or molecule are very small. If these are $\sim 10^{-4}$ times the gas kinetic cross section then the probability of 1D being de-excited by particles of concentration $10^{12}/\text{cm}^3$ is only $10^{-3}/\text{sec}$.

an allowed dipole transition, β_v' will be of the same general order of magnitude as β_v . As $n_D/n_P \ll 1$, we may write Eq. (16) for the steady state in the form

$$n_2 \int_{\nu_0}^{\infty} (\sigma_v c \rho_v(x)/h\nu) d\nu = n_P^2 \int_0^{\infty} \beta_v' v F(v) dv. \quad (21)$$

This is recognized as being Eq. (4).

We shall assume another condition for the steady state, namely, that in any given volume of the atmosphere, the energy absorbed from the solar radiation be equal to the radiations emitted by the radiative processes. The energy absorbed in the process (1) is $h\nu$. The energy emitted in the processes (13), (14), (15) is $h(\nu_{\text{red}} + \nu_1^0 + \nu_2^0) + \frac{1}{2}mv^2$, where ν_1^0 , ν_2^0 are the threshold frequencies in (14) and (15), and $\frac{1}{2}mv^2$ is the kinetic energy of the $O(^3P)$ atoms in the center-of-mass coordinate system. Let χ be the dissociation energy of $O_2(X^3\Sigma_g^-)$ into $O(^1D) + O(^3P)$ so that $\chi = h(\nu_{\text{red}} + \nu_1^0 + \nu_2^0) = h\nu_0$. Furthermore, let $\chi_1 = h\nu_1^0$. The condition for energy balance is then

$$n_2 \int_{\nu_0}^{\infty} \sigma_v c \rho_v(x) d\nu = n_P^2 \left[\int_0^{\infty} (\chi_1 + \frac{1}{2}mv^2) \beta_v' v F(v) dv + (\chi - \chi_1) \int_0^{\infty} \beta_v' v F(v) dv \right]. \quad (22)$$

To obtain the barometric equation, we shall assume that the nitrogen exists in the molecular state in the region of the atmosphere under consideration, and that its distribution is independent of the oxygen except that at any height x all the component gases have the same gas kinetic temperature. We then have Eq. (10). Equations (21), (22), and (10) are the three basic equations in the theory.

IV. DETAILED CALCULATIONS

We shall now seek the explicit forms of the three basic equations (21), (22), and (10). For this purpose, it is necessary to know the absorption coefficient σ_v and the recombination cross section β_v' in (21) and (22). The coefficient σ_v is known both experimentally and theoretically from the work of Ladenburg *et al.*,⁸ and of Stueckelberg.⁹ The cross section β_v' is not known, but its relation with the corresponding absorption coefficient σ_v' of the inverse process of (14) can be found by means of the principle of detailed balancing. To avoid the discontinuity of our presentation here, we have given this calculation in Appendix 1. It is shown in Appendix

⁸ Ladenburg, Van Voorhis, and Boyce, *Phys. Rev.* **40**, 1018 (1932); R. Ladenburg and C. C. Van Voorhis, *Phys. Rev.* **43**, 315 (1933).

⁹ E. C. G. Stueckelberg, *Phys. Rev.* **42**, 518 (1932); **44**, 234 (1933). There is a misprint in the second article. The expression $N_j = N \exp[j(j+1)B_0/kT]$ should read

$$N_j f_2(T) = N \exp[-j(j+1)B_0/kT],$$

where $f_2(T)$ is given by Eq. (38).

2 that on writing $\sigma_{\nu}' = K' \nu f_1(\nu)$, $\sigma_{\nu} = K \nu f(\nu)$, Eqs. (21) and (22) become

$$n_2 \int_{\nu_0}^{\infty} f(\nu) \rho_{\nu}(x) d\nu = A n P^2 \int_{\nu_0}^{\infty} \nu^3 f_1(\nu) \exp(-h\nu/kT) d\nu, \quad (23)$$

$$n_2 \int_{\nu_0}^{\infty} \nu f(\nu) \rho_{\nu}(x) d\nu = A n P^2 \left[\int_{\nu_0}^{\infty} \nu^4 f_1(\nu) \exp(-h\nu/kT) d\nu + (\chi - \chi_1) h^{-1} \int_{\nu_0}^{\infty} \nu^3 f_1(\nu) \exp(-h\nu/kT) d\nu \right], \quad (24)$$

where

$$A = \frac{16r_0^2 h^2 K' G_2 \pi^3}{c^3 K G_1' (M k T)^{3/2}} \exp \frac{\chi_1}{kT}, \quad (25)$$

the various quantities being defined in Appendix 2.

$$\frac{\int_{\nu_0}^{\infty} \nu^3 f(\nu) \exp[-\sigma_2 N_2 - h\nu/k\theta] d\nu}{\int_{\nu_0}^{\infty} \nu^4 f(\nu) \exp[-\sigma_2 N_2 - h\nu/k\theta] d\nu} = \frac{\int_{\nu_0}^{\infty} \nu^3 f_1(\nu) \exp(-h\nu/kT) d\nu}{\int_{\nu_0}^{\infty} \nu^4 f_1(\nu) \exp(-h\nu/kT) d\nu + (\chi - \chi_1) h^{-1} \int_{\nu_0}^{\infty} \nu^3 f_1(\nu) \exp(-h\nu/kT) d\nu} \quad (27)$$

It is seen that the solution of Eq. (27) is of the form

$$N_2 = N_2(T). \quad (28)$$

To obtain this solution, we evaluate the integrals on the left-hand side of (27) by using the empirical absorption coefficient $\sigma_{\nu} = K \nu f(\nu)$. On account of the very rapid decrease of both factors $\exp(-\sigma_{\nu} N_2)$ and $\exp(-h\nu/k\theta)$ with increase in frequency beyond the threshold ν_0 , the most important contribution to the integrals comes from the immediate neighborhood of ν_0 . The measurements of Ladenburg *et al.* do not cover this region (from $\nu = 1.71 \times 10^{15}$ to 1.81×10^{15} per sec). For this region, a theoretical curve for σ_{ν} has been calculated on the basis of the work of Stuekelberg with constants so chosen that the theoretical curve fits the observed data beyond $\nu = 1.8 \times 10^{15}$ sec⁻¹. In the absence of any direct experimental data, this procedure seems to be the most reasonable one. We find

$$\sigma_{\nu_0} = 0.68 \times 10^{-18} \text{ cm}^2, \quad (d\sigma_{\nu}/d\nu)_{\nu_0} = 1.12 \times 10^{-32} \text{ cm}^2 \text{ sec}.$$

For very large values of $N_2 (> 2 \times 10^{19}/\text{cm}^2)$, practically all the contributions to the integrals come from a narrow frequency range $\Delta\nu$ near ν_0 , and in this case the expansion

$$\sigma_{\nu} = \sigma_{\nu_0} + (d\sigma_{\nu}/d\nu)_{\nu_0} (\nu - \nu_0) \quad (29)$$

will be sufficient. For smaller $N_2 (\sim 10^{19}/\text{cm}^2)$, the contributions will come from a larger frequency region $\Delta\nu$. In this case, instead of adding another term to the expansion (29), we approximate the σ_{ν} by (29) with a greater slope. For still smaller values of $N_2 (\sim 10^{18}/\text{cm}^2)$, we represent the σ_{ν} curve by a triangle so that the integrations can be carried out analytically.

To evaluate the integrals on the right-hand side of

The radiation energy density ρ_{ν} is given by (2) in which $\rho_{\nu}(\infty)$ at the top of the atmosphere will be assumed to be that of a blackbody of temperature $\theta (\cong 6000^\circ\text{K})$ diluted by the factor W representing the solid angle subtended by the sun divided by 4π , namely, $W = 5.4 \times 10^{-6}$. The calculations as carried out in this manner will be valid for the case in which the sun is at the zenith all the time. Since the dissociation and recombination processes are slow processes, the average radiation available over day and night may perhaps be better represented by $W/4$.

For the ultraviolet region beyond 1750Å, the spectral distribution may be replaced by Wien's law so that

$$\rho_{\nu}(x) = \frac{1}{4} W 8\pi h \nu^3 c^{-3} \exp(-h\nu/k\theta) \exp[-\sigma_{\nu} N_2(x)]. \quad (26)$$

From Eqs. (23) and (24), one obtains

(27), one needs the absorption coefficient $\sigma_{\nu}' = K' \nu f_1(\nu)$ which is not known. It is seen, however, that on account of the very rapid decrease of the factor $\exp(-h\nu/kT)$ with increase of frequency beyond the threshold ν_1^0 , all the contribution to the integrals comes only from a small range of frequency beyond ν_1^0 . Hence we may

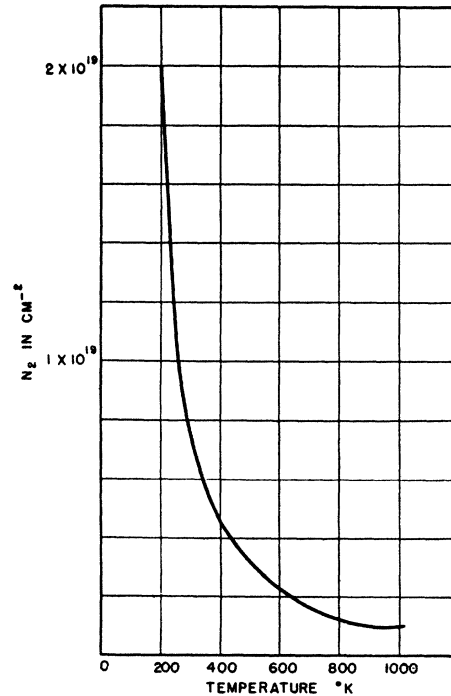


FIG. 1. Theoretical values from Eq. (27) of the total number $N_2[x(T)]$ of oxygen molecules in a column of unit cross section above the height $x(T)$, as a function of T .

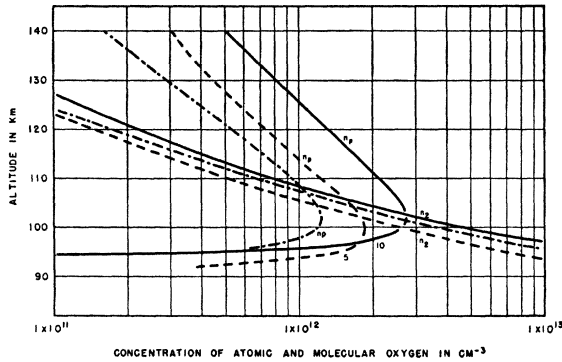


FIG. 2. Calculated number densities n_P and n_2 of atomic and molecular oxygen, respectively, as functions of height. (i) $T=300^\circ\text{K}$, $dT/dx=10^\circ/\text{km}$: solid curves. (ii) $T=300^\circ\text{K}$, $dT/dx=5^\circ/\text{km}$: dashes. (iii) $T=270^\circ\text{K}$, $dT/dx=5^\circ/\text{km}$: dots and dashes.

expand

$$\sigma_v' = \sigma_v'(\nu_1^0) + C(\nu - \nu_1^0) \quad (29a)$$

and it is necessary only to assume that C has a value of the same order as the corresponding coefficient in (29). On carrying out these calculations, we obtain the solution (28) which is shown in Fig. 1. For large $N_2 (> 2 \times 10^{19}/\text{cm}^2)$, (28) approaches the form

$$N_2 \approx \frac{1}{(d\sigma_v/d\nu)_{\nu_0}} \left[\frac{h}{kT} - \frac{h}{k\theta} + \frac{2}{\nu_1^0} - \frac{2}{\nu_0} \right] \\ \approx 3.98 \times 10^{21} \left(\frac{1}{T} - \frac{1}{\theta} \right) / \text{cm}^2. \quad (28a)$$

For smaller $N_2 (\sim 10^{18}/\text{cm}^2)$, (28a) gives too high a value for N_2 and Fig. 1 must be employed.

It can be shown that Eq. (28a) represents a condition of detailed balance in which the number of dissociations in the vicinity ν_0 equals the number of recombinations

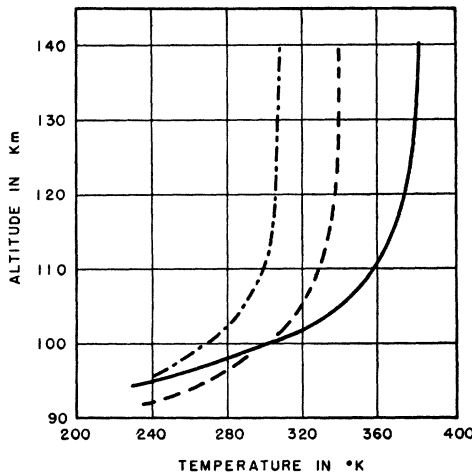


FIG. 3. Calculated temperatures as functions of height. (i) $T=300^\circ\text{K}$, $dT/dx=10^\circ/\text{km}$: solid curve. (ii) $T=300^\circ\text{K}$, $dT/dx=5^\circ/\text{km}$: dashes. (iii) $T=270^\circ\text{K}$, $dT/dx=5^\circ/\text{km}$: dots and dashes.

in the vicinity of ν_0^0 . Thus for large values of N_2 (or equivalently for low values of T) there almost prevails detailed balance. However, for small values of N_2 (or large values of T) the mechanism assumed does *not* require detailed balance.

From the numerical solution of (27) as shown in Fig. 1, one obtains, in view of (3), an expression for the concentration of oxygen molecules

$$n_2 = -(dN_2/dT)(dT/dx) \equiv P(T)dT/dx. \quad (30)$$

Thus n_2 depends on the height x through $T(x)$ and $dT(x)/dx$.

To obtain the concentration of oxygen atoms n_P , we insert (28) and (30) in (23). Now, to evaluate the integral on the right-hand side of (23), it is necessary to make a stronger assumption concerning σ_v' than before, namely, that σ_v' is about the same as σ_v in the immediate neighborhood of their respective thresholds. On this assumption, one obtains for n_P

$$n_P = Q(T)(dT/dx)^{1/2}, \quad (31)$$

where $Q(T)$ is a somewhat complicated but known function of T . n_P depends on the height x through $T(x)$ and $dT(x)/dx$.

On putting (30) and (31) into Eq. (10), which can be written in the form

$$\frac{d^2T}{dx^2} = -\frac{2}{T} \frac{dT}{dx} \left\{ \frac{Mg}{k} + \frac{1}{n_P + 2n_2} \frac{dT}{dx} \left[n_2 + n_P \right. \right. \\ \left. \left. + T \frac{\partial}{\partial T} (n_P + n_2) \right] \right\}, \quad (32)$$

one obtains a differential equation of the second order for T . Equation (32) can be solved if two boundary values, such as T and dT/dx , are known at a certain height in the region for which the condition of the atmosphere is mainly governed by the processes of dissociation and recombination assumed in the theory. Equations (30) and (31) then give the concentrations n_2 and n_P as functions of the height. Thus it is seen that on the assumptions of the two conditions for the steady state, the temperature is automatically determined by the reaction processes themselves, together with the distributions of the atomic and molecular oxygen. It is in this sense that the present work is free from the additional assumptions that have been found necessary by the other investigators.¹⁻⁴

V. NUMERICAL RESULTS AND DISCUSSION

To solve Eq. (32), we need the temperature and its gradient at a certain height. The empirical results available at present give quite different values for the temperature and its gradient. Thus the data from the V-2 rocket flights give an approximate value of 270°K for the temperature at 100 km,¹⁰ whereas the data from

¹⁰ Best, Havens, and LaGow, *Phys. Rev.* **71**, 915 (1947); R. E. Newall, Jr., *Trans. Am. Geophys. Union* **31**, 25 (1950).

radio wave reflection measurements indicate a value 300°K.¹¹ It does not seem possible to say which of these values is more reliable, since the former temperature is derived from a pressure curve whose individual readings can be in error by as much as a factor 2, while the latter temperature is derived with the use of cross sections for the collisions between electrons and molecules which may not be accurate. In any case one must also allow for differences arising from difference in latitude and in season in the different measurements. Hence we have solved Eq. (32) by numerical integration for a few values for the temperature and its gradient at 100 km. In the figures the results are plotted for three cases, namely, at 100 km, (i) the temperature T is 300°K and its gradient $dT/dx=10^\circ/\text{km}$, (ii) $T=300^\circ\text{K}$, $dT/dx=5^\circ/\text{km}$, (iii) $T=270^\circ\text{K}$, $dT/dx=5^\circ/\text{km}$. Figure 2 gives the number densities n_2 and n_P , Fig. 3 gives the temperature, and Fig. 4 gives the percentage of dissociation, all as functions of the height, for these three cases.

From Fig. 3 it is seen that the temperature increases with the height, approaching asymptotically a constant value depending on the values of T and dT/dx at 100 km. But in these very high regions, the result of the present calculation is no longer valid, as processes other than the photodissociation and recombination of oxygen become effective. Thus one may understand any deviation in the observed temperature variation with height from the behavior shown in Fig. 3.

From Fig. 2 it is seen that in each case the distribution of atomic oxygen with height shows a maximum as expected. In case (i), the maximum n_P is $2.7 \times 10^{12}/\text{cc}$ and lies at 102 km. In case (ii), the maximum n_P is $1.86 \times 10^{12}/\text{cc}$ and lies at 99 km. In case (iii), the maximum n_P is $1.22 \times 10^{12}/\text{cc}$ and lies at 102 km.

Figure 4 shows that, in all three cases, the degree of dissociation increases rather slowly with height and dissociation is not complete until a height of about 150 km is reached. This result is to be compared with those of Rakshit³ and Penndorf,⁴ who find that the dissociation is practically completed within a layer about 15 km thick.^{11a}

All the results represented in Figs. 1, 2, 3, and 4, have been obtained from the two conditions for the steady state, the barometric equation, and the values of T and dT/dx at one given height. As no assumption whatsoever has been made about any of the various number densities, it must be regarded as a satisfactory feature of the theory that the concentration of molecular oxygen at 100 km at least comes out to be quite close to the empirical values, as shown below. To test the results of theory, we shall compare our calculated results with the V-2 rocket data¹⁰ which give the total gas pressure of the atmosphere for all heights up to about 130 km. To make this comparison, the partial

¹¹ D. F. Martyn and O. O. Pulley, Proc. Roy. Soc. (London) A154, 455 (1936).

^{11a} See the discussion of the results of these authors in Appendix 7.

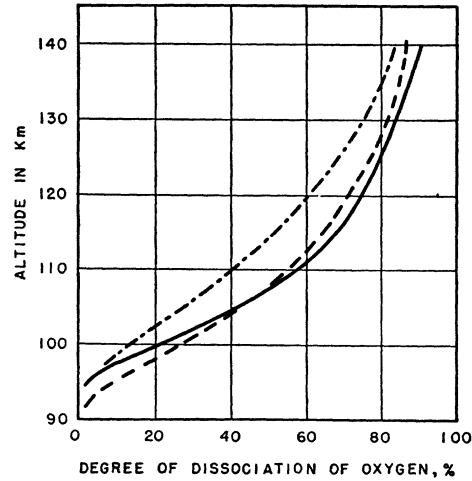


FIG. 4. Calculated degree of dissociation of oxygen as function of height. (i) $T=300^\circ\text{K}$, $dT/dx=10^\circ/\text{km}$: solid curve. (ii) $T=300^\circ\text{K}$, $dT/dx=5^\circ/\text{km}$: dashes. (iii) $T=270^\circ\text{K}$, $dT/dx=5^\circ/\text{km}$: dots and dashes.

pressures of atomic and molecular oxygen are calculated for each of the three sets of boundary conditions above

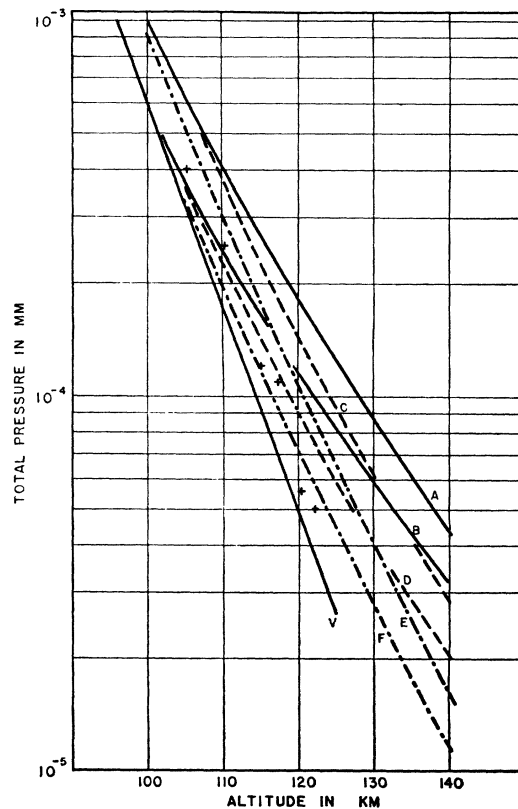


FIG. 5. Total pressure of the atmosphere in mm of Hg as function of height. (i) $T=300^\circ\text{K}$, $dT/dx=10^\circ/\text{km}$: solid curves A, B. (ii) $T=300^\circ\text{K}$, $dT/dx=5^\circ/\text{km}$: dashes C, D. (iii) $T=270^\circ\text{K}$, $dT/dx=5^\circ/\text{km}$: dots and dashes E, F. A, C, E curves: concentration of nitrogen at 100 km so chosen as to give the total pressure at 100 km indicated by the radio wave data. B, D, F curves: concentration of nitrogen at 100 km so chosen as to give the total pressure at 100 km indicated by the V-2 rocket data.

and added to the partial pressure of nitrogen to obtain the total pressure. For case (i), two curves (solid lines) have been calculated and shown in Fig. 5 corresponding to two different assumed values for the partial pressure of nitrogen at 100 km. In one curve (*A* in Fig. 5) the number density of nitrogen molecules is taken to be 2.54×10^{13} per cc so that the total particle density is that indicated by the radio wave reflection data.¹² In the other curve *B*, the number density of nitrogen molecules at 100 km is taken to be 1.4×10^{13} per cc so that the total particle density at that height agrees with the total pressure given by the V-2 rocket data. In each of these two cases, the partial pressures of nitrogen at other heights are calculated by means of the differential barometric equation with the temperature at various heights taken from Fig. 3. It is readily found that the concentration ratio of nitrogen to oxygen at 100 km comes out to be 4.2 and 2.2 for curves *A* and *B*, respectively.

In an entirely similar manner, two curves *C*, *D* (dotted in Fig. 5) are calculated for the case (ii) $T = 300^\circ\text{K}$ and $dT/dx = 5^\circ/\text{km}$ at 100 km. The ratio of nitrogen to oxygen at 100 km then comes out to be 8.1 and 4.9 for the curves *C* and *D*, respectively. For the case (iii) $T = 270^\circ\text{K}$, $dT/dx = 5^\circ/\text{km}$ at 100 km, two curves *E* and *F* (dot and dash in Fig. 5) are obtained for which the ratio of nitrogen to oxygen at 100 km is 6.5 and 3.9, respectively.

In Fig. 5 the total pressure as measured in V-2 flights is given by the crosses and the curve *V*. From the way in which the theoretical curves are calculated, it is clear that we must compare curves *B*, *D*, *F* with the empirical data. It is then seen that curve *F* agrees very well with the V-2 data. It is also noteworthy that the nitrogen-oxygen ratio comes out to be very close to the value usually assumed. Considering the fact that both the atomic and the molecular oxygen concentrations and the temperature all come out from the two conditions for the steady state and the barometric equation without any further assumption other than the values of T and dT/dx at one given height, one may regard the theory as satisfactory in a qualitative way, since it does give correctly the essential features such as the total pressure, the rising temperature and dissociation with height, and the nitrogen-oxygen ratio. It must be emphasized, however, that in view of the uncertainties in the detailed processes assumed for the recombination of the oxygen atoms, no significance should be claimed for the above-mentioned agreement. The main purpose of the present work is rather to show that a completely self-consistent treatment can be formulated which is free from the other assumptions of the previous investigators, and that this treatment can give reasonable results compared with the empirical data.^{12a}

¹² See S. K. Mitra, *The Upper Atmosphere* (The Royal Asiatic Soc. of Bengal, Calcutta, 1948).

^{12a} It might be mentioned that if occasional winds occur at

The authors wish to thank Professor H. M. Foley for his interest and discussions on this work, and Miss Lorraine Ourom for carrying out most of the numerical calculations.

APPENDIX 1. RELATION BETWEEN ABSORPTION COEFFICIENT AND RECOMBINATIONS CROSS SECTION

Let $\sigma(P, j, q, \nu; p, P')$ be the cross section for the process (1) in which a molecule having the total linear momentum P , the rotational quantum number j , and the vibrational quantum number q , absorbs a photon of frequency ν and dissociates into two atoms having a momentum p with respect to each other and a momentum P' for their center of mass. Let $\rho_\nu d\nu$ be the radiation energy density in the frequency range between ν and $\nu + d\nu$, and $n_2(P, j, q)$ be the number of such molecules per unit volume. Then the number of this type of dissociation per unit volume per second is

$$n_2(P, j, q)\sigma(P, j, q, \nu; p, P')(c\rho_\nu/h\nu)d\nu. \quad (33)$$

Let $n_D(P_D)dP_D$, $n_P(P_P)dP_P$ be the number of atoms per unit volume in the 1D and 3P states having momenta between P_D and $P_D + dP_D$, and between P_P and $P_P + dP_P$, respectively. We define the cross section $\beta(p, P'; P, j, q, \nu)$ by stating that the following expression

$$n_D(P_D)n_P(P_P)\beta(p, P'; P, j, q, \nu)[1 + c^3\rho_\nu/8\pi h\nu^3]v \quad (34)$$

represents the number of radiative recombinations per unit volume per second which are the inverse of process (1). In these recombinations two atoms of relative momentum p and total momentum P' recombine by a radiative transition to form a molecule whose state is described by P, j, q . For convenience, we shall write σ for $\sigma(P, j, q, \nu; p, P')$ and β for $\beta(p, P'; P, j, q, \nu)$. We let v represent the relative velocity of the atoms.

β can be determined in terms of σ by means of the principle of detailed balancing. For this purpose, let us assume the system to be in thermodynamical equilibrium so that $n_D(P_D)$, $n_P(P_P)$, $n_2(P, j, q)$ obey the Boltzmann statistics and $\rho_\nu d\nu$ is the energy density for black body radiation, all distributions being characterized by the same temperature T . The principle of detailed balancing states that

$$n_2(P, j, q)\sigma c\rho_\nu d\nu/h\nu = n_P(P_P)n_D(P_D)\beta[1 + c^3\rho_\nu/8\pi h\nu^3]v. \quad (35)$$

Now one has

$$n_2(P, j, q) = \frac{4\pi(2j+1)n_2e^{\chi/kT}}{h^3f_1(T, 2M)f_2(T)f_3(T)} \exp\left(-\frac{P^2}{4MkT}\right) \times \exp\left(-\frac{j(j+1)h^2}{4\pi^2r_0^2MkT}\right) \exp\left(-\frac{qh\omega}{kT}\right)P^2dP, \quad (36)$$

and

$$n_P(P_P)n_D(P_D) = \frac{16\pi^2n_Dn_P}{h^3f_1\left(T, \frac{M}{2}\right)f_1(T, 2M)} \exp\left(-\frac{P'^2}{4MhT}\right) \times \exp\left(-\frac{P^2}{MkT}\right)P'^2dP'p^2dp, \quad (37)$$

where χ is the energy of dissociation (including the zero-point energy), r_0 the equilibrium distance between the atoms, ω the vibrational frequency of the molecule, and M the mass of the oxygen atom. $f_1(T)$, $f_2(T)$, $f_3(T)$ are the partition functions respectively of translational, rotational, and vibrational motion

intervals larger than the time to establish dissociative equilibrium but short enough to disturb the diffusive equilibrium between the molecular oxygen and nitrogen, the result of the present work will still be largely valid. The effect will be to raise the level of molecular oxygen, or, equivalently, to give molecular oxygen a somewhat lighter mass. The principal result would be that the rate of change with height of the various calculated quantities would decrease somewhat. The authors are indebted to Professor C. H. Townes for pointing this out.

and are given by

$$\begin{aligned} f_1(T, M) &= (2\pi M k T)^{3/2} / h^3, \\ f_2(T) &= 4\pi^2 M r_0^2 k T / h^2, \\ f_3(T) &= e^{\chi/kT} (1 - e^{-h\omega/kT}). \end{aligned} \quad (38)$$

Also one has

$$\rho_p = 8\pi h \nu^2 c^{-3} (e^{h\nu/kT} - 1)^{-1}. \quad (39)$$

The conservation of momentum before and after collision gives

$$P = P'. \quad (40)$$

The conservation of energy gives

$$h\nu + \frac{P^2}{4M} + \frac{j(j+1)h^2}{4\pi^2 M r_0^2} + qh\omega = \frac{P'^2}{4M} + \frac{\beta^2}{M} + \chi. \quad (41)$$

The relation between the concentrations of atoms and molecules at equilibrium is given by the reaction isochore, namely,

$$\frac{n_P n_D}{n_2} = \frac{2G_1}{G_2} \frac{f_1(T, 2M) f_1(T, M/2)}{f_1(T, 2M) f_2(T) f_3(T)}, \quad (42)$$

where G_2 is the electronic and nuclear degeneracy of the molecule, G_1 is the statistical weight of the atoms, and the "symmetry factor" 2 represents an additional degeneracy arising from the fact that the nuclei of the atoms are identical.

Substitution of (36) through (42) into (35) gives^{12b}

$$\beta = 4(2j+1)(G_2/G_1)(h^2\nu^2/M^2c^2v^2)\sigma. \quad (43)$$

The ratio of β to σ is thus independent of temperature, as it should be, since β and σ are atomic properties. The ratio of β to σ could also have been obtained from quantum mechanics using Dirac's transition probabilities. The ratio of β to σ is then simply proportional to the ratio of the density of atomic states to that of molecular states.^{12c}

Actually we are more interested in finding β' , the recombination coefficient for the process (14), rather than β , since most of the atoms recombine by this process. Defining σ' as the detailed cross section for the inverse process of (14), we have

$$\beta' = 4(2j+1)(G_2'/G_1')(h\nu/Mc)^2\sigma' \quad (43a)$$

where G_1' is the statistical weight of the two atoms in the 3P state, which is different from G_2' .

APPENDIX 2. EQUATIONS FOR THE STEADY STATE IN THE DETAILED MODEL

In Eq. (21) and (22), for simplicity, we have neglected to indicate the dependence on the rotational and vibrational states of the molecule. We can rewrite them to include the dependence by using σ and β' defined above. Equations (21) and (22) become

$$\sum_{P, j, q} \int_{\nu_0}^{\infty} n_2(P, j, q) (\sigma c \rho_p / h\nu) d\nu = \sum_{P', p} n_P(P_P) n_P(\bar{P}_P) \beta' v (1 + c^2 \rho_p / 8\pi h \nu^2), \quad (44)$$

and

$$\sum_{P, j, q} \int_{\nu_0}^{\infty} n_2(P, j, q) \sigma c \rho_p d\nu = \sum_{P', p} n_P(P_P) n_P(\bar{P}_P) h \nu \beta' v (1 + c^2 \rho_p / 8\pi h \nu^2). \quad (45)$$

Here $n_P(P_P) n_P(\bar{P}_P)$ is to be replaced by a distribution given in terms of the relative momentum p of the recombining atoms and the momentum P' of their center of mass. The frequency ν and the relative velocity v are related by the law of conservation of energy.

The values of j in (44) should be restricted to even integers, since the nuclei of the oxygen atoms are identical and have zero spin. However, in our case where the rotational levels are highly

^{12b} Compare this relation with the corresponding formula for the cross sections of photo-ionization of an atom and the inverse radiative recombination between the ion and the electron, given by E. A. Milne, *Phil. Mag.* 47, 209 (1924).

^{12c} The authors are indebted to Dr. A. Bohr for this observation.

excited so that sums over j are replaced by integrals, the effect of using only even values of j cancels out, excepting in the case of the reaction isochore, where the effect has already been taken into account by the symmetry factor 2. Hence we shall not explicitly use the restriction.

At temperatures which are believed to exist in the 100 km region, we may assume that the molecules are in their lowest vibrational state of the lowest electronic state. Since χ is of the order of 7 volts, whereas the rotational energy is of the order 0.02 volt, we shall regard ν_0 as a constant given by $h\nu_0 = \chi$. This is in agreement with the observation that the Schumann-Runge continuum starts quite sharply at the wavelength 1751 Å.

We shall now make use of the result of Stueckelberg for σ . The expression Γ_{kW} in Stueckelberg's paper⁹ is, in our notation

$$\Gamma_{kW} = (2j+1)\sigma c \rho_p d\nu / h\nu,$$

and

$$\sigma_p = \sum_j \frac{(2j+1)}{f_2(T)} \sigma \exp \left[\frac{j(j+1)h^2}{4\pi^2 M r_0^2 k T} \right] = \frac{64\pi^{7/2}}{3c} \frac{M}{2h^2 \gamma a} \mathfrak{M}^2(r_1) v f(\nu), \quad (46)$$

where γ , a , and $\mathfrak{M}(r_1)$ are constants which Stueckelberg determines from the empirical results of Ladenburg *et al.* The function $f(\nu)$ can be calculated from the data given by Stueckelberg.⁹ It should be noted that σ_p is independent of the temperature as it should be, since it is a molecular property.

Since we wish to find β' , it is seen from (43a) that we must know σ' . The cross section σ' has not been measured or calculated. We shall make the reasonable assumption that σ_p' has a form similar to that for σ_p . Thus we write

$$\sigma_p' = \sum_j \frac{(2j+1)}{f_2(T)} \sigma' \exp \left[\frac{j(j+1)h^2}{4\pi^2 M r_0^2 k T} \right] \equiv K' v f_1(\nu). \quad (46a)$$

On using the laws of conservation of energy and momentum, Eqs. (43a), (46), and (46a), and neglecting the induced emission in (44) and (45) which is very small, one finally obtains the equations for the steady state in the form (21) and (22) in the paper. It is seen that even though one starts with a different value for the rotational temperature from the translational temperature, only the translational temperature appears in Eqs. (21) and (22). The rotational temperature has dropped out on account of the averaging process in (46).

APPENDIX 3. TIME REQUIRED TO REACH DISSOCIATIVE STEADY STATE

To find the time required to reach the dissociative steady state when an atmosphere initially consisting of molecular oxygen at constant temperature throughout is illuminated by sunlight, it is necessary to integrate Eq. (18) from the time sunlight is turned on to the time at which $dn_P/dt = 0$. However, this time is infinite. Hence we shall find instead the time required to reach 10 percent of the final dissociation, say, and multiply this time by 10. This time will represent a sort of relaxation time giving the order of magnitude for the time required to reach the dissociative steady state.

On neglecting the recombinations Eq. (18) becomes

$$dn_P/dt = An_2, \quad (47)$$

where the coefficient A is given, in view of (18), (26), and (46), by

$$A = \frac{1}{4} W (8\pi/c^2) \int_{\nu_0}^{\infty} v^2 f(\nu) \exp[-\sigma_p N_2 - h\nu/k\theta] d\nu. \quad (48)$$

If the region which is considered is at 100 km, where N_2 is large, only that part of the integrand which is near ν_0 contributes. Hence near ν_0 we write $\sigma_p = \sigma_{\nu_0} + (d\sigma_p/d\nu)_{\nu_0}(\nu - \nu_0)$ in the integrand and find

$$A = (2\pi/c^2) W K \exp(-K\nu_0 f' N_2 - h\nu_0/k\theta) \times \int_{\nu_0}^{\infty} v^2 f(\nu) \exp[-\{K(\nu_0 f' + f) N_2 + h/k\theta\}(\nu - \nu_0)] d\nu, \quad (49)$$

where $f = f(\nu_0)$ and $f' = f'(\nu_0)$. Since the exponential factor in the integrand decreases very rapidly with increasing ν , we may write

the integral as

$$v_0^3 \int [K(v_0 v' + f) N_2 + h/k\theta]^{-1}.$$

A is a function of the time and altitude through the variable $N_2(x)$. As only orders of magnitude are being estimated, we shall simplify the calculation by giving $N_2(x)$ a constant value in time, which will represent the average value. According to Fig. 1, the value of $N_2(x)$ at 100 km for the case $T=300^\circ\text{K}$ at 100 km in the dissociative steady state is $\approx 7 \times 10^{18}$. With this value, one gets for the time for dissociation steady state about 10 days. Even if this estimate is too small by a factor 10, this time is still shorter than the time required for the establishment of diffusive equilibrium, which is of the order of years for this height.¹²

APPENDIX 4. THE RADIATIVE RECOMBINATION COEFFICIENT

Having found β , one can calculate the recombination coefficient for two oxygen atoms, one of which is in the 1D state and the other in the 3P state. It is given by

$$B = \int_0^\infty \beta_n v F(v) dv = 2.19 \times 10^{-22} T \text{ cm}^3/\text{sec}. \quad (50)$$

For $T=300^\circ\text{K}$, we have $B=6.56 \times 10^{-20} \text{ cm}^3/\text{sec}$. This can be compared with the result given by Nicolet¹³ for two oxygen atoms approaching each other along the level giving the Herzberg bands, namely, $B=7.6 \times 10^{-20} \text{ cm}^3/\text{sec}$.

It can be shown that, under the assumption about σ_n' made earlier, the recombination coefficient for two oxygen atoms, both in the 3P state, is

$$B' = \int_0^\infty \beta_n' v F(v) dv = (G_1/G_1') (v_1^0/v_0)^2 B \approx \frac{1}{2} B.$$

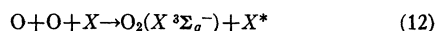
With these recombination coefficients, since $n_D \ll n_P$, it can be seen that the number of recombinations per sec of type (1a) is much less than that for the process (14), i.e.,

$$n_P n_D B \ll n_P^2 B'.$$

Hence our assumption that (14) is a more important process than (1a) for the formation of molecules is justified.

APPENDIX 5. CROSS SECTIONS FOR THREE-BODY RECOMBINATION COLLISIONS

We wish to investigate the relative importance of three-body recombination collisions of the type (12)

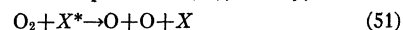


and two-body radiative recombination collisions of the type (14). The coefficient of a two-body radiative collision can be calculated from the absorption coefficient of the inverse process, as shown in Appendix 1. We shall obtain below a similar relation between the coefficients of the 3-body process (12) and of its inverse 2-body process. Before doing that, we shall make an estimate of a three-body collision coefficient on the basis of the classical kinetic theory.

Consider the process (12), in which the particles are represented by spheres of radius a moving with an average velocity v . Simple considerations show that the number of three-body collisions (a particle X collides with a system of two O atoms when they are within a distance $2a$ of each other) per unit volume per second is $2\pi v a^3 [\text{O}]^2 [X]$, where the brackets indicate number densities. If one takes $a=1.5 \times 10^{-8}$ cm, then, at temperatures of a few hundred degrees absolute, the coefficient $C=2\pi v a^3$ of three-body collisions in this sense is $1.5 \times 10^{-33} \text{ cm}^6/\text{sec}$. This must now be multiplied by the ratio of statistical weights of the molecular state $^3\Sigma_g^-$ of O_2 and the atomic state ($^3P+^3P$), namely, $3/81$. Thus if every 3-body collision, according to this classical model, leads to the formation of O_2 , the coefficient C is $5 \times 10^{-35} \text{ cm}^6/\text{sec}$. This rather optimistic estimate is about 10^2 times smaller than

the values deduced from experiments on gases other than oxygen.¹⁴

We shall now make a more detailed study of three-body collisions. Consider the inverse process of (12), namely,



which is a two-body collision. The cross section for the three-body collision (12) can then be obtained in terms of the two-body collision cross section of (51) by means of the principle of detailed balancing. We shall examine all the possible two-body processes (51). Since the three-body collision cross section will be proportional to the two-body collision cross section, only that two-body process which is the most probable need be considered.

The particles which exist in the region of the upper atmosphere in which we are interested are electrons, oxygen atoms, oxygen molecules, and nitrogen molecules. It is possible to disregard the electrons as an important third body, since the maximum electron density is of the order of $10^6/\text{cm}^3$ and is very much smaller than the densities of oxygen atoms, molecules, and nitrogen molecules, namely, $10^{11}/\text{cm}^3$, $10^{12}/\text{cm}^3$, and $10^{13}/\text{cm}^3$, respectively. We shall hence only consider two-body collisions (51) in which the third body X is an atom or a molecule.

Consider now the dissociation of a diatomic molecule in (51). There are two cases possible: (a) the molecule may jump from a vibrational state of the normal electronic state to a vibrational state in the continuum of the same electronic state, or (b) it may jump from a vibrational state of the normal electronic state to an excited repulsive electronic state. In the case (a), the third body may supply this energy of vibrational excitation from its kinetic energy of translational motion, or from its electronic energy, and if the third body is a molecule, from its vibrational energy. Now the probabilities of such processes are very small,¹⁵ and we may consider only the case (b). This process of the transfer of the electronic energy of one particle to the electronic energy of a molecular is similar to the one in which two atoms exchange excitation energy upon collision. The calculation of Stueckelberg indicates that the probability of such a transfer can be quite large in certain cases.¹⁶ Hence we shall assume that the most important process (51) is a collision in which X transfers its energy of electronic excitation to an oxygen molecule.

We shall now define a "cross section" for the three-body collision (12). Let the electronic states of the two atoms arising from (51) be denoted by a and b , their number densities by n_a and n_b , respectively. Let the number density of oxygen molecules having momentum P , rotational quantum number j , and vibrational quantum number q be denoted by $n_2(P, j, q)$. Let $\sigma_2(P, j, q, P_x^*; P', p, P_x)$ be the cross section for a collision in which an oxygen molecule in the state P, j, q is dissociated by an electronically excited third body of momentum P_x^* and the number density $n_x^*(P_x^*)$. The number of collisions (51) per unit volume per second is then

$$\sigma_2 u^* n_2(P, j, q) n_x^*(P_x^*), \quad (52)$$

where u^* is the relative velocity of the oxygen molecule and the excited X^* .

Let the number density of atoms in the state a and having a momentum between P_a and $P_a + dP_a$ be denoted by $n_a(P_a) dP_a$. The number density of atoms in state b will be denoted similarly. Let $n_x(P_x)$ be the number density of unexcited X having a momentum P_x . The number of three-body recombinations (12) per unit volume per second is given by the following expression, which defines the "cross section" σ_3 for the three-body process (12):

$$n_a(P_a) n_b(P_b) v \sigma_3(P', p, P_x; P, j, q, P_x^*) n_x(P_x), \quad (53)$$

where v is the relative velocity of the oxygen atoms with respect to each other. Thus, the cross section σ_3 is of the dimension area \times volume, so that it can be interpreted as the cross section per unit concentration of the third body X .

¹⁴ E. Rabinowitch, *Trans. Faraday Soc.* **33**, 283 (1937).

¹⁵ N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1949), Chapter XII.

¹⁶ Reference 15, Chapter VIII.

¹³ M. Nicolet, *Mem. inst. roy. meteorologique de Belgique*, No. 19 (1943).

The statement of detailed balance is

$$\sigma_2 u^* n_2(P, j, q) n_x^*(P_x^*) = n_a(P_a) n_b(P_b) \sigma_3 n_x(P_x), \quad (54)$$

where the number densities are given by the Boltzmann theorem, all quantities being characterized by the same temperature. The $n_2(P, j, q)$ and $n_a(P_a) n_b(P_b)$ are given by expressions similar to (36) and (37). Also, we have

$$n_x(P_x) = \frac{4\pi G_x n_{xt}}{h^3 f_1(T, M_x) f_\epsilon} \exp\left(-\frac{\epsilon + P_x^2/2M_x}{kT}\right) P_x^2 dP_x, \quad (55)$$

$$n_x^*(P_x^*) = \frac{4\pi G_x^* n_{xt}}{h^3 f_1(T, M_x) f_\epsilon} \exp\left(-\frac{\epsilon^* + P_x^{*2}/2M_x}{kT}\right) P_x^{*2} dP_x^*, \quad (55a)$$

where n_{xt} is the total number of the third body X per unit volume, M_x the atomic or molecular weight of X , ϵ and ϵ^* are the electronic energies of the normal and the excited states, respectively, G_x and G_x^* their statistical weights, and f_ϵ is the partition function of the electronic states, of X . We shall replace the momenta P and P_x^* and P' and P_x by the relative momentum of the third body with respect to the molecule P_r , P_r^* and the total momentum P_t , P_t^* of the whole system, the unstarred and starred referring to values before and after collision, respectively. The conservation of momentum and energy gives

$$P_t = P_t^*$$

and

$$\begin{aligned} \frac{P_t^{*2}}{2(2M+M_x)} + \frac{P_r^{*2}}{2\mu} + \frac{j(j+1)h^2}{4\pi^2 M r_0^2} + qh\omega \\ = \frac{P_t^2}{2M} + \frac{P_r^2}{2\mu} + \frac{P_t'^2}{2(2M+M_x)} + (\epsilon - \epsilon^*) + \chi, \end{aligned}$$

where

$$\mu = 2MM_x/(2M+M_x).$$

Substitution of all of these into (54) and the use of the reaction isochore similar to (42) lead to the relation

$$G_x^* G_2 (2j+1) u^* \sigma_2 d u^* = \pi G_x G_1 (M/h)^3 \sigma_3 u^2 d u v^2, \quad (56)$$

where u is the relative velocity of the third body with respect to the center of mass of the pair of atoms after collision, and G_1 and G_2 are the statistical weights of the oxygen atoms and molecules, respectively. It is seen that the ratio of σ_3 to σ_2 is independent of the temperature, as it should be, since the cross sections are atomic and molecular properties.

The relation (56) is quite general. We shall now assume that only exchange of electronic energy plays a part, so that no translational energy is transferred, i.e., $u = u^*$. Furthermore, since σ_2 is greatest at resonance, we may set $\chi = \epsilon^* - \epsilon$. We shall assume that the molecule is in its normal vibrational state, and that the kinetic energy of the dissociated atoms comes from the rotational energy of the molecule. On replacing the discrete rotational states by a continuum, and using the relation between the velocities u , u^* , v given above, the relation (56) simplifies to

$$\sigma_3 = 2\pi h r_0^3 (u G_2 G_x^*/M v^2 G_1 G_x) \sigma_2. \quad (57)$$

It is easy to see that σ_3 is of dimension length to the fifth power.

The total number Q_3 of three-body recombination collisions per unit volume per second is obtained by integrating (53) over all velocities v and u . As σ_2 has been assumed to depend only on the exchange of electronic energy, it will be an insensitive function of the velocities. Hence, we have

$$Q_3 = 2\pi h r_0^3 (G_2 G_x^*/M G_1 G_x) \langle u \rangle_{\text{av}} \langle 1/v \rangle_{\text{av}} n_x n_a n_b. \quad (58)$$

The average value of $1/v$ is obtained from the Boltzmann distribution in velocity for the reduced mass of the oxygen molecule, and $\langle u \rangle_{\text{av}}$ is obtained for the reduced mass μ defined previously. The factor G_x^*/G_x is of the order unity. Hence the total number of three-body recombinations per unit volume per second is given by

$$Q_3 = 10^{-20} \sigma_2 n_a n_b n_x = C n_a n_b n_x, \quad (59)$$

where C is the three-body recombination coefficient. To estimate the value of C , one needs the two-body collision cross section σ_2 .

Now σ_2 is in general smaller than, or of the order of, the gas kinetic cross section, but for some cases may be considerably larger at resonance. For lack of both theoretical and experimental information for the system $O_2 + X^*$ in (51), we shall take for σ_2 the gas kinetic value 10^{-16} cm² and obtain

$$C = 10^{-36} \text{ cm}^6/\text{sec}.$$

To estimate the relative importance of two-body and three-body collisions at the height of about 100 km, we shall take for n_x the value 10^{13} /cm³ which is of the order of the total number density of gas molecules at that height. For the two-body radiative recombination, we have, from Appendix 4, the value $B' = 10^{-20}$. Hence the ratio of two- to three-body recombinations at this height is given by

$$Q_2/Q_3 = (B' n_a n_b)/(C n_a n_b n_x) = 10^3. \quad (60)$$

For greater heights and hence smaller n_x , three-body recombinations will be still less important.

This and the simple estimate made at the beginning of this appendix lead us to assume two-body recombinations in our calculations.

It might be mentioned that Fowler uses a similar three-body treatment in his discussion of electron capture by an ion.¹⁷

APPENDIX 6. RADIATIVE RECOMBINATIONS BETWEEN TWO OXYGEN ATOMS

To investigate the relative importance of the possible radiative recombinations between two $O(^3P)$ atoms, we first note that the following types of states can arise from two such atoms: $^1\Sigma_g^+$, $^1\Sigma_u^-$, $^1\Pi_g$, $^1\Pi_u$, $^1\Delta_g$, $^3\Sigma_u^+$, $^3\Sigma_g^-$, $^3\Pi_u$, $^3\Pi_g$, $^3\Delta_u$, $^5\Sigma_g^+$, $^5\Sigma_u^-$, $^5\Pi_g$, $^5\Pi_u$, $^5\Delta_g$. Of these, $X^3\Sigma_g^-$ is the normal state. Three other states have been identified from the analysis of the spectrum, namely, $b^1\Sigma_g^+$, $a^1\Delta_g$, $A^3\Sigma_u^+$. The other states have not yet been located.

We shall investigate the nature of the process or processes that contributes most to the recombination of the atoms on the basis of the following arguments. It is generally believed that the source of energy of radiation emitted in the night sky is the recombination of oxygen atoms into molecules, although the exact mechanisms whereby the various lines and bands in the spectrum are excited are not known with definiteness. Since the intensity of the night sky radiation is found to change only inappreciably during the whole night, it follows that not more than a small fraction, say perhaps 1/100, of the oxygen atoms present at sunset can have disappeared during the night, i.e.,

$$10 \cdot 60^2 n_P^2 \int_0^\infty \beta_{v'} v F(v) dv \leq \frac{1}{100} n_P.$$

For the height where n_P is $\sim 10^{12}$ /cm³, this gives for the recombination coefficient the order of magnitude $\leq 3 \times 10^{-19}$ cm³/sec. This value can be compared with the value calculated in Appendix 4 for the recombination process (1a) which involves an allowed dipole transition. Thus it seems most probable that the process or processes contributing most to the recombination of the oxygen atoms involve allowed dipole transition.

There are two possibilities for such recombinations: (1) two $O(^3P)$ atoms approaching each other in a state which combines by dipole transition to form the normal state $X^3\Sigma_g^-$, and (2) two $O(^3P)$ atoms approaching each other in a state which combines to form a stable excited state by dipole transitions. Reference to the list of possible states formed from two $O(^3P)$ atoms given above shows that the only state that combines with $X^3\Sigma_g^-$ by dipole transitions is the $^3\Pi_u$ -state. This state has not been found, but either it must be strongly repulsive, or the potential energy curve has a weak minimum at large nuclear separation, for otherwise absorption bands from the ground state would have been found. In either case, the transition probabilities to the lower vibrational states of $X^3\Sigma_g^-$ will be small on account of the Franck-Condon principle. Transition probabilities to highly

¹⁷ R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, London, 1936), Sec. 17.6.

excited vibrational states of $X^3\Sigma_g^-$ will also be small, since at large nuclear separations the matrix element of the dipole moment of the system will be small.

Passing on to the case (2), it is seen that two $O(^2P)$ atoms approaching each other in the state $^1\Pi_u$ will be in a position to make a dipole transition to the state $b^1\Sigma_g^+$. The potential curve of $^1\Pi_u$ is not known, but it is not impossible that it has a weak minimum or is weakly repulsive in such a way that the turning point (where the horizontal line representing the kinetic energy of the approaching atoms intersects the potential curve) lies vertically above the neighborhood of the minimum of the $b^1\Sigma_g^+$ curve. In these cases, the transition probabilities will be of the order estimated above.

The resulting molecule in the state $b^1\Sigma_g^+$ can go down to the normal state $X^3\Sigma_g^-$ either on emitting the so-called atmospheric bands with transition probabilities of the order 0.1 per second, or in a collision of the second kind with another atom or molecule. The cross section for the transfer of energy of electronic excitation of one particle to the kinetic energy of a heavy particle (atom or molecule) is very small. As the collision frequency in a gas of number density $10^{12}/\text{cm}^3$ is of the order 20 per second, the radiative transition mentioned above may be more important than the de-excitation by collisions of the second kind with atoms or molecules. The identification of the atmospheric bands in the infrared spectrum of the night sky^{6,7} seems to lend some weight to this suggested mechanism.

APPENDIX 7. DISCUSSIONS OF THE WORK OF PENNDORF AND OF RAKSHIT

A. We shall first examine Penndorf's work.⁴ Penndorf starts with an atmosphere having an assumed temperature distribution $T(h)$ and total pressure distribution $P(h)$ before dissociation by solar radiation takes place. On assuming the proportion given by (7), the total oxygen concentration $[O_2]_t$ before dissociation is calculated by means of the relation,

$$P(h) = ([N_2]_t + [O_2]_t)kT. \quad (61)$$

Let A^* be the number of quanta of solar radiation absorbed in a thickness s per unit cross section per second at the height h , and $J_{\lambda\lambda}$ be the number of quanta in the solar radiation per 10A interval crossing unit area per second at the height h . Let $k_{\lambda\lambda}''$ be the absorption coefficient ($k_{\lambda\lambda}'' = \sigma_{\nu}$ of the present paper) and let the subscript G denote the steady state. Then†

$$A^* = \int J_{\lambda\lambda} [1 - \exp(-sk_{\lambda\lambda}''[O_2]_G)] d\lambda, \quad (P-21)$$

and for the upper regions where $sk_{\lambda\lambda}''[O_2]_G \ll 1$,

$$A^* = s[O_2]_G \int J_{\lambda\lambda} k_{\lambda\lambda}'' d\lambda. \quad (P-22)$$

For either (P-21) or (P-22), one has

$$A^* = f_1 [O_2]_G s, \quad (P-23, 24)$$

which defines f_1 as the probability per second of a molecule at the height h absorbing a dissociating photon from the solar radiation. The steady state is given by

$$f_1 [O_2]_G = k[M]_G [O]_G^2, \quad (P-18)$$

where k is the recombination coefficient for three-body processes. For the upper regions where the dissociation is almost complete, Eq. (P-18) is replaced by (P-19), which is obtained from (P-18) by setting $[O]_G$ equal to $2[O_2]_G$.

(1) It is seen from Table IV of Penndorf's paper‡ that the assumption

$$[O_2]_G + \frac{1}{2}[O]_G = [O_2]_t \quad (P-9)$$

has been made. This implies that the oxygen atoms and molecules do not readjust themselves after dissociation has taken place. This is equivalent to assuming an atmosphere which is separated

into parallel layers by transparent partitions before the solar radiation is "turned on." As a consequence of assumption (P-9), there results an inconsistency. The total pressure $P(h)$ with which the calculation is started is that given by (61). After dissociation has taken place, the total pressure is given by

$$P(h) = ([N_2]_t + [O_2]_G + [O]_G)kT,$$

which in view of (P-9) becomes

$$P(h) = ([N_2]_t + [O_2]_t + \frac{1}{2}[O]_G)kT, \quad (62)$$

which is obviously different from that given by (61) except where there is no dissociation. To illustrate this, let us consider the height 130 km. From the assumed $T=330^\circ\text{K}$ and $P=0.00011$ mb and the relations (7) and (61), Penndorf obtains $[O_2]_t = 3.92 \times 10^{11}/\text{cc}$, and $[N_2]_t = 1.78 \times 10^{12}/\text{cc}$, as shown in Table II. Now, according to Table IV, which has been calculated on the basis of Table II, the oxygen is almost completely dissociated so that $[O]_G = 7.84 \times 10^{11}/\text{cc}$; but this would have led to a total pressure of 1.17×0.00011 mb, contradicting the original assumed value. The difficulty emphasized here is not so much with the factor 1.17 as with the intrinsic impossibility of obtaining $[O_2]_t$ or $[O]_G$ from (62) on any assumed $T(h)$ and $P(h)$ without the use of Eq. (11).

(2) Consider now the central part of the calculation in Penndorf's paper. The procedure of the calculation is described as follows: "The calculations started at 130 km, where the amount of $[O_2]_G$ is found to be small, and formula (22) was used. . . . Having computed A^* by numerical integration, f_1 was obtained by (23). Thereupon, the amount of oxygen atoms or molecules in the equilibrium state was computed by either (18) or (19). Since $[O_2]_G$ resulting from formula (19) enters the basic equation for the absorption (20), the correct value had to be found by testing until the value used in the exponent equaled the result of (19)."

Now Eq. (P-18) or (P-19), together with the assumption (P-9), gives only one equation containing two unknowns $[O_2]_G$ and f_1 . The quoted paragraph above seems to have stated that f_1 is obtained from (P-21) and (P-23) (or P-22 and P-24); but Eq. (21) or (P-22) is not an additional equation for f_1 and $[O_2]_G$ in the sense that it can be combined with (P-18) or (P-19) to give f_1 and $[O_2]_G$, since A^* is not known from any other relation than Eq. (P-21) or (P-22) itself. Thus, it is not clear how $[O_2]_G$ and f_1 could have been obtained from essentially a single equation—namely, (P-18) or (P-19). In fact it is not clear how A^* could have been obtained by "numerical integration" at all, since $J_{\lambda\lambda}$ at the height h depends on $\int_{\lambda}^{\infty} [O_2]_G dh$ according to Eq. (2), and to find $[O_2]_G$ at all heights is exactly the central part of the problem.

On trying to reconstruct Penndorf's procedure, it seems that the only reasonable way the calculation could have been started is as follows. At 130 km, $J_{\lambda\lambda}$ was assumed to have the value of the solar radiation unattenuated by absorption by the overlying layers. With this $J_{\lambda\lambda}$ at 130 km, f_1 was calculated for this height from (P-23), and with this f_1 , $[O_2]_G$ was calculated from (P-19). This $[O_2]_G$ was then inserted into (P-22) to give A^* for a layer of 1 km thick, and the reduction in $J_{\lambda\lambda}$ therein, so that $J_{\lambda\lambda}$ for the next layer below could be calculated.

If this is the actual procedure adopted by Penndorf, then the following objection may be raised. On the technical side, since $J_{\lambda\lambda}$ depends exponentially on the total number $N_2 = \int_{\lambda}^{\infty} [O_2]_G dh$ of the existing molecules above h , the calculated result will depend very strongly on the assumption made about N_2 . The assumption that $J_{\lambda\lambda}$ at 130 km has the full, or any other, value of the solar radiation implies that $k_{\lambda\lambda}'' N_2 \ll 1$, and this in turn implies that the oxygen is highly dissociated at and above 130 km; but this is exactly what is to be calculated from the theory and must not be assumed in the calculation. In principle, the objection is that the problem is already completely determined by Eq. (11) and the boundary conditions (11a) and will be inconsistent with any further assumption about N_2 . It is the failure to recognize this that has led to this and the other difficulty with the total pressure discussed above.

† For convenience we follow Penndorf's notations in this Appendix and denote by (P-18) Eq. (18) in his paper, etc.

‡ There are many misprints in the exponents under $[O_2]_G$ in Table IV

(3) Another debatable point in Penndorf's work is the assumption that the oxygen atoms recombine in three-body processes. The relative importance of two-body and three-body processes has been discussed in Appendix 5 above. It may perhaps be mentioned here that since no provision is made for the emission of radiation in Penndorf's theory, the oxygen will keep on transforming solar radiation into the kinetic energy of the atoms and molecules, with a consequent continual rise in the temperature of the atmosphere; for at the low pressure and low values of the d^2T/dh^2 in this part of the atmosphere, the loss of heat by conduction is very slow.

(4) The result given in Table VII for the time of "half-recombination" in the absence of solar radiations does not seem right. One certainly expects the time taken for "half-recombination" to be shorter the greater the value of the coefficient of recombination k_1 . The reverse, however, is shown in Table VII.

B. Consider now Rakshit's work.³ As Rakshit's work is a refinement of, and supersedes, the earlier work of Majumdar,² it will be sufficient to confine our discussions to Rakshit's paper.

(1) Rakshit also assumes a given temperature distribution $T(h)$ and the proportion (7). From $T(h)$ and the total pressure P at 80 km, the total pressure and the partial pressure p of oxygen before dissociation are calculated for other heights. Here, as in Penndorf's work, the assumption (P-9) is also made, with the same consequent difficulty with the pressure. Thus at 115 km, the assumed $T=300^\circ\text{K}$ and $P=1.50\times 10^{-4}$ mm of mercury lead to the partial pressure p of oxygen $p=3.00\times 10^{-5}$ mm as given in Table II. On the other hand, from Table III, one finds for the partial pressure p_d after dissociation the value 5.4×10^{-5} mm, contradicting the original total pressure assumed.

(2) Rakshit calculates the total number N_2 of oxygen molecules in a column of unit cross section above the height h by means of the relation $N_2=pNH$, where p is the partial pressure of oxygen

before dissociation, H the height of the homogeneous atmosphere for O_2 , and N the number of molecules of a gas per cc at standard temperature and pressure. It is not clear how H has been obtained, but the use of the partial pressure of oxygen molecules before dissociation instead of that of the existing molecules is obviously unjustified. Thus, Rakshit's calculation is open to the same objections discussed in A, (1) and (2), above.

(3) Rakshit assumes that the recombination process is simply the reverse of the dissociation process—namely, (1a). The distribution of oxygen atoms in the 3P and 1D states is assumed to be given by the Boltzmann theorem. Now for $T=300^\circ\text{K}$, the Boltzmann factor is $\exp(-77)$ so that the concentration of 1D atoms will be extremely small and the dissociation process becomes practically unidirectional. For this reason, recombinations involving two 3P atoms, even though very improbable, have to be considered. Failure to consider these would lead to too high an estimate for the degree of dissociation.

That the calculated values for the degree of dissociation x are not too high is due to an error in the calculation. The ratio $n_A'n_B/n_{AB}$ should have been $4Nx^2 \exp(-E/kT)/(1-x)$ instead of the expression $Nx^2/(1-x)$ given by Rakshit, since $n_A' = n_B \exp(-E/kT)$ and hence $n_A' \ll n_B$. E is the energy difference between the 1D and the 3P states of oxygen. When this correction is made, Eqs. (12), (14), and (15) in Rakshit's paper should all be multiplied by the factor $\frac{1}{2} \exp(E/kT) \cong \frac{1}{2} \exp(77)$ on the right-hand side. It is seen that Rakshit's theory, when correctly calculated, would have led to too high values for x for all heights.

(4) The relation between the absorption coefficient ψ_ν ($\psi_\nu = \sigma_\nu$ in the present paper) and the recombination cross section β_ν of the reverse process as obtained by Rakshit depends on the temperature of the gas. This cannot be correct, the correct relation being (43) given in Appendix 1 above.

On the Dispersion of Resistivity and Dielectric Constant of Some Semiconductors at Audiofrequencies

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Semiconducting $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$, prepared in different ways, has been investigated. It appeared that the ac resistivity and the apparent dielectric constant of the material show a dispersion which can be explained satisfactorily with the help of a simple model of the solid: there should be well-conducting grains separated by layers of lower conductivity. Dispersion formulas are given. There is good agreement between experiment and theory.

I. INTRODUCTION

MEASUREMENTS by Blechstein¹ in 1938 showed that certain manganese ferrites have an astonishingly high apparent dielectric constant. Brockman, Dowling, and Steneck² also found such high dielectric constants in ferromagnetic cores made of ferrites which had been developed in this laboratory.³ This property was, in fact, essential in the theory for the dimensional

resonance effects in these cores investigated by these authors.

In order to obtain more quantitative information about the behavior of the ferrites, precise impedance measurements were carried out with disks and rods of several compositions. In the present paper the measurements at room temperature and a phenomenological theory of the impedance of NiZn ferrite and its dispersion are given.

II. EXPERIMENTAL DETAILS

A new alternating current bridge constructed and already described by Köhler and Koops⁴ was used. The

* This paper has been written by Dr. J. Volger of this laboratory from observations and calculations left by the late Ir. Koops (deceased October 22, 1950).

¹ E. Blechstein, *Physik. Z.* **39**, 212 (1938).

² Brockman, Dowling, and Steneck, *Phys. Rev.* **77**, 85 (1950).

³ J. L. Snoek, *New Developments in Ferromagnetic Materials* (Elsevier Company, New York, 1947).

⁴ J. W. L. Köhler and C. G. Koops, *Philips Research Repts.* **1**, 419 (1946).