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

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(Received May 5, 1952)

In a previous paper a self-consistent model was set up for the dissociation of oxygen in the upper atmosphere under the assumption of number balance and radiative energy balance and a form of the barometric equation. In the present paper a similar model is used, but the requirement of radiative energy balance is dropped and a temperature distribution is assumed. The resulting calculations indicate that for this model the dissociation region is much narrower than in the previous model and that it occurs at lower altitudes.

I. INTRODUCTION

IN a previous paper[1] it was shown that it was possible to set up a self-consistent scheme for calculating the oxygen dissociation ratio under the following assumptions:

1. The principal dissociation process is

$$O_2(X^3\Sigma_g^-)+h\nu \underset{\sigma_\nu}{\longrightarrow} O(^3P)+O(^1D), \quad (1)$$

where $h\nu$ is the energy of the quantum of radiation absorbed from the sunlight.

2. The principal recombination processes are two-body recombination processes in which two oxygen atoms recombine to form an oxygen molecule, the excess energy being in the form of radiation. An example of such a process is

$$O(^3P)+O(^3P) \underset{\beta_{v'}}{\longrightarrow} O_2(b^1\Sigma_g^+)+h\nu_1 \longrightarrow O_2(X^3\Sigma_g^-)+h\nu, \quad (2)$$

where β_v' denotes the recombination cross section.

3. Dissociative equilibrium exists so that the rate of dissociation equals the rate of recombination at any altitude.

4. The rate of energy absorbed in process (1) equals the rate of emission of energy in process (2).

5. The time required to establish dissociative equilibrium is less than that required to establish diffusive equilibrium between the oxygen atoms and molecules.

6. There is diffusive equilibrium between the nitrogen and oxygen of the atmosphere.

There are, in addition, various assumptions of a less fundamental and a less controversial nature. They were used in reference 1 and will be used again in the present paper. They will be brought up as needed.

The reasons for making the above assumptions are discussed in detail in reference 1. With the above assumptions it was shown possible to set up a system of three equations from which it was possible to solve for the three fundamental unknowns: the temperature T, the number density of atoms n_p, and the number density of oxygen molecules n_2, all as functions of altitude x, provided certain boundary conditions were given. These boundary conditions were taken as the temperature and temperature gradient at some altitude x_0 within the region where dissociation takes place. The most striking feature of the resulting calculation was that the dissociation region was quite large in contrast to the results of previous workers who found that the region was quite narrow.[2-7]

It was emphasized in reference 1 that the numerical results must not be taken too seriously because it is not known how valid the assumptions 1–6 are, nor how accurately the cross sections σ_ν and β_v' that were used represented the experimental results. In particular, β_v' had to be assumed since no theoretical or experimental work had been done to determine this cross section. The principal result of reference 1 was to show that a self-consistent method could be set up with the assumptions 1–6, so that, if in the future assumptions 1–6 can be shown valid and better values of the cross sections are available, the method indicated in reference 1 can be used. It should be noted that the assumptions made were self-consistent; that is, it was not necessary to assume a distribution of n_2, one of the quantities to be calculated. It was shown that the work of some of the previous workers was not self-consistent in this sense.[8]

Of the various assumptions perhaps the most controversial is assumption 4. This assumption, that of radiative energy balance is perhaps not valid because energy processes other than (1) or (2) may occur, e.g., heat conduction. The object of the present work is to carry out a self-consistent treatment of the problem without making assumption 4. Having given up assumption 4, it will no longer be possible to calculate all three

* The research reported in this publication has been sponsored by the Geophysics Research Division of the Air Force Cambridge Research Center, Air Research and Development Command under Contract AF-19 (122) 463.

[1] H. E. Moses and T. Y. Wu, Phys. Rev. **83**, 109 (1951).

[2] S. K. Mitra, *The Upper Atmosphere* (The Royal Asiatic Society of Bengal, Calcutta, 1948).

[3] O. R. Wulf and L. S. Deming, Terr. Magn. Atmos. Elect. **41**, 299 (1936).

[4] O. R. Wulf and L. S. Deming, Terr. Magn. Atmos. Elect. **43**, 283 (1938).

[5] R. C. Majumdar, Indian J. Phys. **12**, 75 (1938).

[6] H. Rakshit, Indian J. Phys. **21**, 57 (1947).

[7] R. Penndorf, J. Geophys. Research **54**, 7 (1949); Phys. Rev. **77**, 561 (1950).

[8] See reference 1, Appendix 7.

quantities T, n_2, n_p as functions of altitude, as was done in reference 1, for we shall have too few equations. Instead, we shall take the temperature T as given and calculate n_2 and n_p as functions of the altitude under appropriate boundary conditions. This dropping of assumption 4, while having the disadvantage of compelling us to assume a value of T, has the advantage of making the resulting theory applicable over a larger range of altitudes. This is true because assumption 4 can be true only in regions where processes (1) and (2) are principal processes leading to conversion of radiation to heat, whereas the treatment of the present paper will be true at any altitude, provided the atmospheric density is sufficiently low to permit one to assume two-body recombinations.[9]

It is to be emphasized that in this paper, as in reference 1, the numerical calculations should not be taken too seriously. The numerical calculations are undertaken essentially to show the nature of the solution of the problem.

II. THE BASIC EQUATIONS

We shall now write the basic equations in some generality and later include our assumptions. The first of these equations is the number balance equation, in which the number of dissociations per unit volume per second equals the number of recombinations per second. Let us consider the dissociation processes. It is generally agreed that the principal dissociation process is process (1), in which the oxygen molecule is dissociated from the normal electronic bound state to the dissociated state in the Runge-Schumann continuum on the absorption of radiation with a wavelength smaller than 1750A. The cross section for this process has been studied experimentally[10,11] and theoretically.[12] Denoting, as above, this cross section by σ_ν we have, for the number of dissociations per unit volume per second at any altitude x,

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

where $\rho_\nu(x)$ is the radiation density per unit frequency available at the altitude x, $n_2(x)$ is the number density of oxygen molecules at the altitude x, and ν_0 is the threshold frequency corresponding to the wavelength 1750A.

Now on account of the attenuation of light by the oxygen molecules above the altitude x, we have

$$\rho_\nu(x)=\rho_\nu(\infty)\exp[-\sigma_\nu N_2(x)], \qquad N_2(x)=\int_x^{\infty}n_2(x)dx, \tag{3}$$

where $\rho_\nu(\infty)$ represents the radiation density available at the "top" of the atmosphere. Then one can write:

$$\text{No. dissociations/sec}=n_2(x)I(N_2), \tag{4}$$

$$I(N_2)=\int(c/h\nu)\sigma_\nu\rho_\nu(\infty)\exp(-\sigma_\nu N_2)d\nu. \tag{5}$$

The number of recombinations per unit volume per second can be written as $n_p^2(x)B'(T)$, where $n_p(x)$ is the number density of oxygen atoms at altitude x; $B'(T)$ is the recombination coefficient, which depends on the specific recombination assumed; and T is the temperature at the altitude x. The recombination coefficient depends upon the temperature through the average relative velocities of the atoms which is obtained by using the Boltzmann distribution characterized by a temperature T. Hence, the equation of number balance is

$$n_2(x)I(N_2(x))=n_p^2B'(T). \tag{6}$$

The barometric equation is

$$dP/dx=-g(Mn_p+2Mn_2+M_Nn_N),$$

where P is the pressure at altitude x and g is the gravitational constant, namely,

$$P=(n_p+n_2+n_N)kT, \tag{7}$$

where M is the mass of the oxygen atom, n_N is the number density of nitrogen molecules, and M_N is the mass of the nitrogen molecule. Hence, the barometric equation is

$$-(d/dx)[(n_p+n_2+n_N)kT]=(Mn_p+2Mn_2+M_Nn_N)g. \tag{8}$$

Equations (6) and (8) are the basic equations of our theory. It should be noted that these equations are quite general and are largely independent of the model. In these equations we shall assume T and n_N as given functions of x. The unknown functions that we wish to solve for are n_1 and n_2.

III. DETAILED MODEL

We shall work with the model in which the radiation from the sun is that due to a blackbody of temperature 6000°K. This assumption specifies $\rho_\nu(\infty)$. A more controversial assumption is that which determines n_N as a function of the altitude x. Most of the previous workers assume that the ratio of nitrogen to oxygen $n_N/(n_2+2n_p)$ has a constant value, namely 4, the value of the ratio at the surface of the earth. This assumption requires that winds of sufficient frequency and strength occur so as to disturb diffusive equilibrium. If such winds occurred, they would most likely also disturb the distribution of oxygen atoms and molecules so that the problem of finding the dissociation ratio would be meaningless. We therefore take the opposite point of view, namely, that diffusive equilibrium predominates between oxygen and nitrogen (assumption 6). This

[9] See concluding paragraph of the present paper.
[10] Ladenburg, Van Voorhis, and Boyce, Phys. Rev. **40**, 1018 (1932).
[11] R. Ladenburg and C. C. Van Voorhis, Phys. Rev. **43**, 315 (1933).
[12] E. C. G. Stueckelberg, Phys. Rev. **42**, 518 (1932); **44**, 234 (1933).

assumption means that oxygen and nitrogen are distributed independently of each other. With this assumption we have

$$(d/dx)[n_N kT] = -M_N n_N g, \tag{9}$$

and Eq. (8) becomes

$$(d/dx)[(n_p+n_2)kT] = -[Mn_p+2Mn_2]g, \tag{8a}$$

and all reference to the distribution of nitrogen in the barometric equation (8a) disappears.

The most controversial assumption is that which deals with the recombination process. Some of the previous workers[3,4,7] assume that recombination is a three-body process; that is, the energy released by the recombination of the two oxygen atoms is given to a third body when the three bodies collide. Schematically,

$$O+O+M \rightarrow O_2+M^*, \tag{10}$$

where M is the third body and the asterisk represents the third body in a state that is excited either internally or in the sense that it has greater translational energy.

Others[5,6] prefer to think of the recombination as being a two-body radiative process in which the excess energy is emitted in the form of radiation

$$O+O \rightarrow O_2+h\nu. \tag{11}$$

For simplicity and in order to minimize the difference between the model of our present paper and that of reference 1, we assume in the present calculation two-body recombinations.

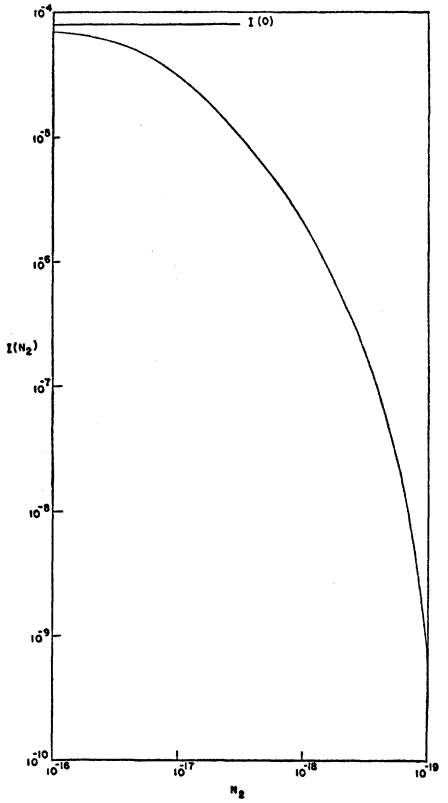

FIG. 1. Dissociation probability as function of N_2.

If one assumes a two-body process, it can be shown[1] that this process goes so slowly that virtually all the oxygen atoms in the state ^1D which result in dissociation, Eq. (1), will have had time to drop to the ^3P state by emission of the forbidden red line

$$O(^1D) \rightarrow O(^3P)+h\nu_{\text{red}}, \tag{12}$$

so that virtually all the atoms are in the ^3P state; hence, the notation n_p for the atomic number density. Then the most probable recombination process, assuming two-body recombinations, is one typified by the equation

$$O(^3P)+O(^3P)(^1\pi_u) \rightarrow O_2(b^1\Sigma_g^+)+h\nu, \tag{13}$$

and the rate of recombination is

$$n_p^2 \int_{v=0}^{\infty} v\beta_v' f_T(v)dv,$$

where v is the relative velocity of the two atoms, β_v' is the recombination cross section of process (13), and $f_T(v)$ is the Boltzmann distribution in the relative velocity v. Unfortunately, the cross section β_v' for process (13) is not known, but one can estimate it by assuming that within a statistical weight factor and a factor arising from a different threshold frequency it is much the same as the known cross section β_v for the process inverse to process (2), namely,

$$O(^3P)+O(^1D) \rightarrow O(X^3\Sigma_g^-)+h\nu. \tag{2a}$$

Hence, we can evaluate

$$B'(T) = \int_0^{\infty} v\beta_v' f_T(v)dv$$

of Eq. (6).

As a further assumption, we take $T=T_0+\alpha(x-x_0)$, to be the temperature at the altitude $x=x_0$ and α being the gradient of the temperature. In point of fact it is sufficient to take $T=T_0=$const. because it turns out that the numerical results are independent of α if α is sufficiently small ($\alpha<10°$/km, say). This point will be discussed more fully shortly. However, we shall take α arbitrary, since the equations are not essentially more complicated for this case.

IV. THE BASIC EQUATIONS AND THE METHOD OF SOLUTION

The basic equations for the calculations are the number balance Eq. (6) and the barometric equation (8a) which for $T=T_0+\alpha(x-x_0)$ has the following form:

$$d(n_2+n_p)/dx = -T^{-1}\{\alpha(n_2+n_p)+(Mg/k)(n_p+2n_2)\}. \tag{8b}$$

$I(N_2)$ and $B'(T)$ have been calculated and are given

graphically as functions of their arguments in Figs. 1 and 2.

To solve Eqs. (6) and (8b) it is convenient to introduce the total number density

$$f(x)=n_2(x)+n_1(x). \tag{14}$$

From Eqs. (14) and (6) one obtains

$$n_2=\tfrac{1}{4}\{-[I(N_2)/B(T)]^{\frac{1}{2}}+[I(N_2)/B(T)+4f]^{\frac{1}{2}}\}^2, \tag{15}$$

$$n_p=\frac{-1+[1+4fB(T)/I(N_2)]^{\frac{1}{2}}}{2B(T)/I(N_2)}, \tag{16}$$

and (8b) can be written either as

$$df(x)/dx=-T^{-1}\{(Mgk^{-1}+\alpha)f(x)+Mgk^{-1}n_2(x)\} \tag{17}$$

or

$$df(x)/dx=-T^{-1}\{(2Mgk^{-1}+\alpha)f(x)-Mgk^{-1}n_p(x)\}. \tag{18}$$

It is convenient to consider Eqs. (17) and (15) as the differential equation for $f(x)$ when $n_2(x)$ is small and Eqs. (18) and (16) as the differential equation for $f(x)$ when $n_p(x)$ is small, though both sets of equations are, of course, the same. Of course, we use $\int_x^\infty n_2(x)=N_2$ in either case.

At low altitudes where N_2 is large and n_p is small so that to a very good approximation $f(x)\cong n_2(x)$, Eq. (18) becomes the ordinary barometric equation for $n_2(x)$. Similarly, at high altitudes where $f(x)\cong n_p(x)$, Eq. (17) shows that $n_p(x)$ obeys the ordinary barometric equation.

Thus, for low altitudes $n_2(x)$ obeys the ordinary barometric equation, whereas for high altitudes $n_p(x)$ obeys the ordinary barometric equation, while in the intermediate region neither does, and $n_p(x)$ and $n_2(x)$ influence each other greatly; consequently $n_2(x)$ falls much more rapidly than predicted by the ordinary barometric equation.

Equations (17) and (15) or, equivalently (18) and (16) were solved by the following scheme. One prescribes $n_2(x_0)$ and takes for $N_2(x_0)$ the result predicted by the ordinary barometric equation, just to have some starting value for $N_2(x_0)$.

On carrying a numerical integration of Eqs. (17) or (18) one gets distribution $n_p(x)$, $n_2(x)$, $N_2(x)$ based on the choice of $N_2(x_0)$. The curve for $N_2(x)$ does not approach 0 as $x\to\infty$. Instead, one gets a curve which approaches a constant $N_{2\min}$.

In order to get a better value of $N_2(x_0)$ one takes the old value of $N_2(x_0)$ and subtracts $N_{2\min}$. Using the new value of $N_2(x_0)$, one repeats the calculation. Again one finds a curve for $N_2(x)$ similar to the one above, except $N_{2\min}$ is much smaller (of course, one wishes it to be 0). One takes still a third value of $N_2(x_0)$ which consists of the second value of $N_2(x_0)$ minus the second value of $N_{2\min}$, and the integration is repeated. Eventually, one gets a value of $N_{2\min}$ which is so small and occurs at such a large value of x that at the region at which dissociation becomes important and below, the results are no longer sensitive to $N_{2\min}$. At this point the iteration procedure stops. In the calculations carried out, 6 iterations were required.

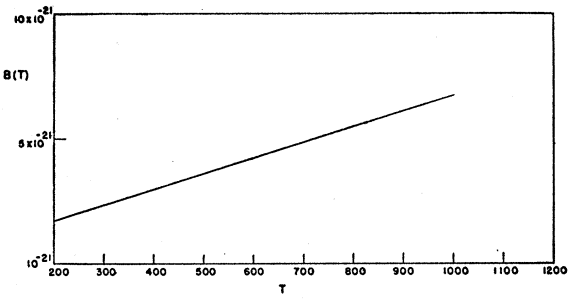

FIG. 2. Recombination cross section as function of temperature.

The final result is the following: At low altitudes the curves for $n_2(x)$ with and without dissociation agree if the curves are fitted at some point x_0' (which may be less than x_0) where there is virtually no dissociation.

For low enough altitudes the curves for $N_2(x)$ with and without dissociation will also agree because the most important contribution to $N_2(x)$ at low altitudes (well below x_0') in either case comes from the value of $n_2(x)$ within a few kilometers of x, since $n_2(x)$ in both cases is relatively very small for x at any distance from the altitude being considered.

The important feature of the present work is that, aside from assigning a boundary value n_2 at $x=x_0$, no *a priori* assumption is made on the distribution of $n_2(x)$ or equivalently on the function $N_2(x)$. These distributions are obtained from the basic equations. In all of the previous work on the oxygen dissociation problem (except in reference 1) such *a priori* assumptions are made, as pointed out in Appendix 7 of reference 1.

V. RESULTS OF NUMERICAL CALCULATIONS

Three cases were calculated numerically. In all three cases n_2 at $x-x_0$ was taken as $10^{14}/\text{cm}^3$. (If O_2 is assumed to constitute 1/5 of the atmosphere, x_0 would correspond to 85 km.) This choice is not special, though it may seem so, since $n_2(x)$, $n_p(x)$ depend only on the difference $x-x_0$. The three different cases correspond to different choices of the temperature function $T=T_0+\alpha(x-x_0)$. In the first case T_0 was taken as 195°, and α was taken as 5°/km. In the second case $T_0=200°\text{K}$, $\alpha=0$.

In the third case $T_0=300°\text{K}$, $\alpha=0$. Comparison of results for the first and second cases gave essentially the same results, indicating that small temperature gradients do not affect the results greatly. This consequence is due to the small size of the region in which dissociation is important, so that if the temperature has not too large a gradient, the temperature is essentially constant in the region.

Since the first and second cases agree so closely, we have given graphs only of the second and third cases.

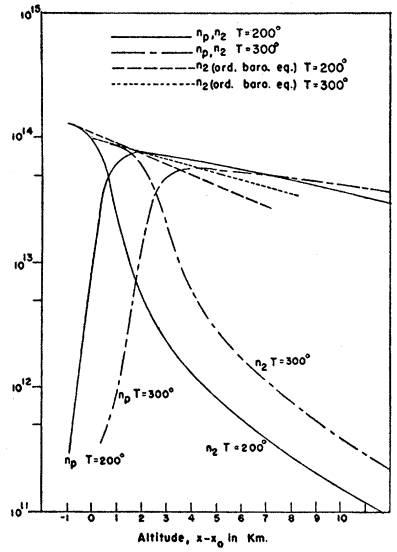

FIG. 3. Atomic and molecular density of oxygen as a function of altitude.

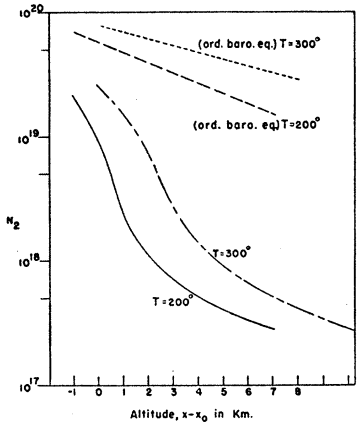

FIG. 4. N_2 as a function of altitude.

Figures 3 and 4 represent the results for the calculations.

As is seen in both cases, the dissociation takes place in a very narrow region of the order of a kilometer near the altitude at which $n_2=10^{14}$ (hence, the choice $n_2(x_0)=10^{14}$). The effect of the higher temperature is to spread out the region of dissociation and raise the altitude of this region. N_2 is much larger for the higher temperature, the reason being that $n_2(x)$ decreases more slowly with the higher temperature.

Also indicated on the graphs are the results when the ordinary barometric equation without dissociation is used for n_2, $n_2=n_{20}'\exp[-(2Mg/kT)(x-x_0')]$, where n_{20}' and x_0' are chosen so that they coincide with the value obtained for $n_2(x)$, at sufficiently low altitudes. It is clear that in the region of dissociation and above that $n_2(x)$, $N_2(x)$ deviate considerably from the values obtained from the ordinary barometric equations. Hence, the use of the ordinary barometric equation by some workers to give values of $n_2(x)$, $N_2(x)$ is obviously incorrect.

VI. OTHER DISSOCIATION MODELS

Comparison of our present results with those of reference 1 show considerable differences. First of all, in reference 1 the region of dissociation is at the altitude for which $n_2=10^{12}$. Secondly, the dissociation is much broader, of the order 15 km. Thirdly, N_2 is much larger than the value obtained using the ordinary barometric equation, whereas in the present case it is smaller. The principal reasons for these differences is that we have dropped the energy balance requirement, assumption 4, and perhaps more important, we have used different boundary conditions. In the present paper we have required explicitly that $N_2(x)\to 0$ as $x\to\infty$. In reference 1 we could not apply this condition explicitly because the theory of that paper was not valid at great altitudes, since the energy balance condition could not be satisfied as such altitudes. It was necessary in the theory of reference 1 that processes occurred such that $n_2(x)$ did not decrease too rapidly at high altitudes, but the discussion of such processes was outside the theory.[13]

The results of the present model are more satisfactory than those of reference 1 in that $N_2(x)\to 0$ for $x\to\infty$ as required. However, this does not necessarily mean that the model of reference 1 is incorrect (although the numerical results seem untenable), since with more accurate cross sections the model of reference 1 might give more similar results, and, in particular, lead to smaller values of N_2.

One result of the present calculations is that the dissociation region occurs where the atmospheric density is so great that it is conceivable that three-body collisions are important as a recombination process. It is possible within the framework of the present paper, to assume three-body recombinations instead of the assumption 2 for two-body recombinations. Such a model would require more secondary assumptions, such as the efficiencies of various possible third bodies and their distributions. A calculation, similar to the present one but on the assumption of three-body recombination, is being carried out and will be reported separately.

[13] If in the model of reference 1 one had taken as boundary conditions $n(x)\to 0$ as $x\to\infty$ and had given a value of n_2 at some altitude x_0, one would have found that the temperatures calculated from the model would be of the order of a thousand degrees. This result suggests that in order to obtain more reasonable temperatures one should take into account in the energy balance equations ways of conserving energy other than by the radiation processes of (1) and (2), in particular through heat conduction.