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The aeronomic problem of oxygen dissociation

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ABSTRACT

The vertical distribution of molecular oxygen above 100 km, obtained from recent rocket data, cannot be explained by photo-chemical equilibrium.

An aeronomic study of departures from photo-equilibrium conditions in the lower thermosphere shows that atmospheric mixing or diffusion must be operative. It is concluded that the process of diffusion contributes increasingly to molecular oxygen concentrations at greater heights. By considering a diffusive equilibrium, it is found that new information can be obtained for various aeronomic processes.

1. INTRODUCTION

It has been shown by NICOLET and MANGE (1952, 1954) that the problem of oxygen dissociation above 100 km does not depend on photo-equilibrium conditions, but on atmospheric processes such as molecular diffusion and mixing.

Using incomplete observational data they have discussed the conditions for departure from photochemical equilibrium. Recently, NICOLET (1954a) has considered the atmospheric motions which are necessary to maintain mixing effects in a vertical distribution of molecular oxygen.

Consistent rocket data on the total content of molecular oxygen have been obtained very recently by BYRAM, CHUBB, and FRIEDMAN (1954). They are particularly useful in checking the atmospheric behaviour as far as the dissociation of oxygen is concerned. Thus, this question is considered in this paper.

2. VERTICAL DISTRIBUTIONS

Above 110 km, the atmospheric behaviour is well represented by the equation

$$p/p_0 = (H/H_0)^{-1/\beta} \tag{1}$$

in which p denotes the pressure, H the scale height, and β the constant gradient of the scale height.

According to HAVENS, KOLL, and LAGOW (1952), we can adopt, at 120 km, $p_0 = 3{\cdot}5 \times 10^{-5}$ mm of Hg, $H_0 = 10$ km and $\beta = 0{\cdot}2$.

In the aeronomic problem (NICOLET and BOSSY, 1949), the atmospheric concentration will be given by the equation

$$n/n_0 = (H/H_0)^{-(1+\beta)/\beta} \tag{2}$$

in which n denotes the concentration of the principal constituent.

When we consider a minor constituent such as O_2 in an atmosphere consisting of atomic oxygen and molecular nitrogen, it is possible to consider *a priori* a vertical distribution of this molecule according to various laws. Therefore, we can write the following equation

$$n(O_2)/n_0(O_2) = (H/H_0)^{-X(1+\beta)/\beta} \tag{3}$$

in which X is a parameter determining a certain distribution. It is evident that $X = 1$ means a vertical distribution of O_2 following the atmospheric distribution. When $X = 1{\cdot}28$, molecular oxygen is distributed with height according to a diffusive equilibrium, for it is easy to show that

$$X = [\beta + m(O_2)/m(M)]/1 + \beta \tag{4}$$

is satisfied under this condition.

When $X = 2{\cdot}92$, equation (3) describes molecular oxygen which is in photochemical equilibrium at altitudes where the optical depth is negligible. In other words, the photochemical equilibrium equation is

$$n(O_2) = k_1 n(M) n^2(O)/J_2 \tag{5}$$

in which $k_1 n(M)$ is the recombination coefficient depending on three-body collisions with the atmospheric particle M, and J_2 is the photodissociation rate coefficient which is constant. Since $k_1 \propto T^{1/2} \propto H^{1/2}$ and $n(M)n^2(O) \propto H^{17{\cdot}5}$, the exponent leads to 2·92 for the value of X.

Any intermediate value between $X = 1$ and $X = 1{\cdot}28$ in equation (3) represents a vertical distribution of O_2 between mixing and diffusive equilibrium, and any value between $X = 1{\cdot}28$ and $X = 3$ a distribution corresponding to unstable conditions between diffusive equilibrium and photo-equilibrium.

3. CALCULATED CONCENTRATIONS

Rocket data published by BYRAM, CHUBB, and FRIEDMAN (1954) give the total number of molecules versus height, namely values of the order 6×10^{-3} atmo-cm (N.T.P.) at 108 km, 3×10^{-3} at 112 km and 10^{-3} at 118 km. These values indicate a slow decrease with height of the concentration above 110 km.

According to equation (3), the concentration will be given by

$$n(O_2) = \frac{X(1+\beta) - \beta}{H} \int_z^\infty n(O_2)\,dz \tag{6}$$

if the observations are represented by

$$\int_z^\infty n(O_2)\,dz = \frac{n(O_2)H}{X(1+\beta) - \beta} \tag{7}$$

Adopting $3{\cdot}5 \times 10^{-3}$ atmo-cm at 110 km, the observational data are accounted for by a value of $X = 1{\cdot}28$. Fig. 1 shows the vertical distribution versus height of the total number of O_2 molecules compared with the total number of atmospheric molecules if there is no dissociation.* With such a distribution the rocket data are followed with a precision of ±15%. In other words the observational points are inside of the two dashed curves corresponding to $(3{\cdot}5 \pm 0{\cdot}5)\ 10^{-3}$ atmo-cm at 110 km.

Therefore, the vertical distribution of O_2 is obtained from (6) using $X = 1{\cdot}28$.

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* These data do not agree exactly with those published by the Rocket Panel (1952). However, following Naval Research Laboratory data closely, there is only a difference in height of between 1 and 2 km.

4. DEPARTURE FROM PHOTO-EQUILIBRIUM CONDITIONS

Considering that $n(O_2) < n(O)$ and that the differential equation representing photochemical conditions for oxygen is

$$\frac{dn(O_2)}{dt} = n(O_2)J_2 - k_1 n(M)n^2(O) \tag{8}$$

we may write the approximate solution as follows

$$n(O_2) = n_{t=0}(O_2)e^{-J_2 t} + \frac{k_1 n(M)n^2(O)}{J_2}[1 - e^{-J_2 t}] \tag{9}$$

From observational results $n_{t=0}(O_2)$ must be, at least, the concentrations obtained by diffusive equilibrium. They are greater than the photochemical values. Therefore, the times which it is important to consider are given by the exponential factor $J_2 t$. Since $J_2 = 1{\cdot}56 \times 10^{-6}$ sec^{-1} at zero optical depth (NICOLET and MANGE, 1954), the decrease of $n(O_2)$ as a function of time is very slow. As may be seen from Fig. 2, 5 days (of 12 hours duration) are required to reduce the concentration to 70% of its initial value. Furthermore, 35 days are needed to reach 10% of the diffusive equilibrium value. On the other hand, it also requires 35 days to reach the photochemical value (90%) and we are dealing with aeronomic conditions corresponding to departures from photoequilibrium conditions.

Using the numerical values indicated in Section 2 and $k_1 = 5 \times 10^{-34}T^{1/2}$ (BATES and NICOLET, 1950), equation (3) with $X = 3$ provides the photochemical values of $n(O_2)$. At 108 km, the concentration is $1{\cdot}5 \times 10^{11}$ cm^{-3} while the value adopted from rocket data is of the order of $1{\cdot}5 \times 10^{11}$ cm^{-3} at 110 km. Therefore, we may choose 110 km as a sufficiently good approximation for an initial level to compare all the possible vertical distributions of O_2.

The results are given in Fig. 3 in which the full curves show vertical distributions of O_2 according to mixing, diffusion and photochemical equilibrium. Dotted curves represent intermediate states between diffusion and photo-equilibrium conditions. Since the photochemical values are negligible (10^4 times less at 170 km) compared with the observational values, it is important to determine the magnitude of diffusive transport effects.

5. UPWARD DIFFUSION OF MOLECULAR OXYGEN

If the loss of oxygen molecules by photodissociation is not more than 10% per day, the increase of concentration by diffusive transport is very large.

Considering that the velocity of diffusion of a minor constituent is given by the following equation (CHAPMAN and COWLING, 1939)

$$w(O_2) = -\frac{D}{H}\left[\frac{1}{n(O_2)}\frac{\partial n(O_2)}{\partial z} - \frac{1}{H}\left(\beta + \frac{m(O_2)}{m(M)}\right)\right] \tag{10}$$

in which D is the ordinary diffusion coefficient, we can calculate the velocities of diffusion using various values of X.

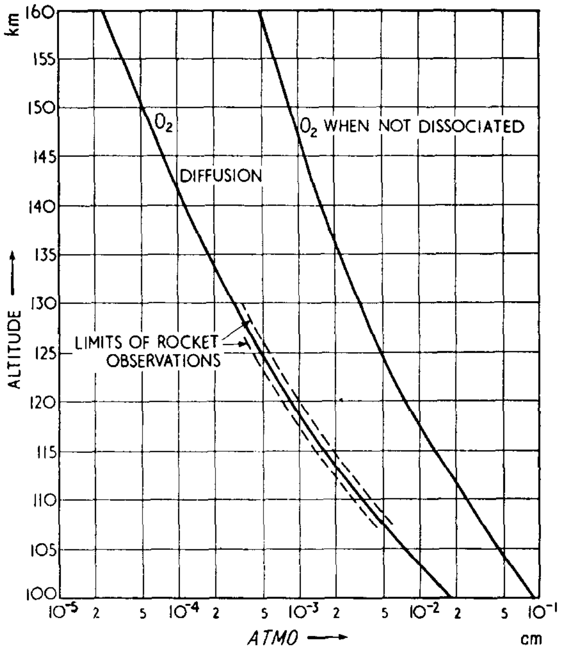

Fig. 1. Total number of O_2 molecules versus height. One atmo-cm equals $2 \cdot 7 \times 10^{19}$ molecules. The vertical distribution of undissociated O_2 molecules corresponds to the atmospheric distribution in a mixed atmosphere; the diffusive equilibrium distribution is based on an absolute value at 110 km given by rocket observations.

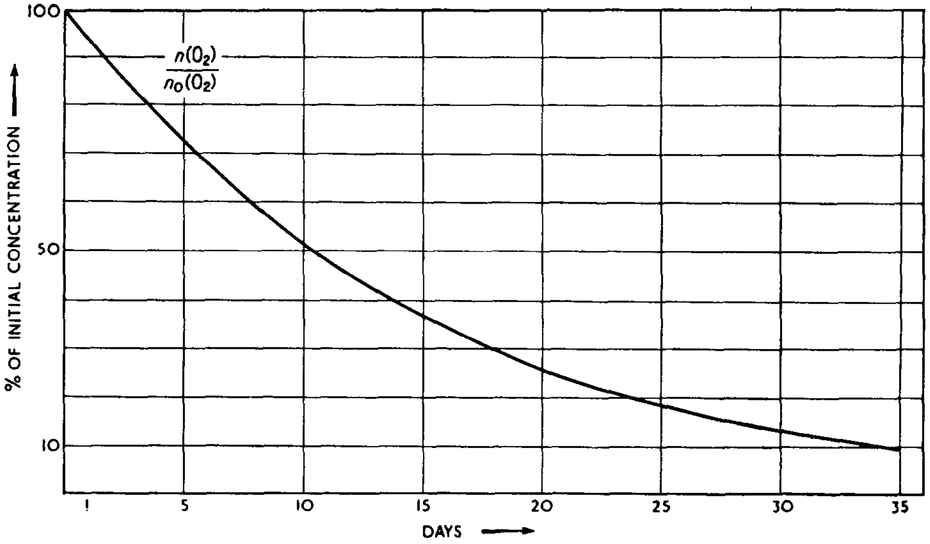

Fig. 2. Variation of O_2 concentration that is larger than a photo-chemical equilibrium value when solar photodissociation is acting. The number of days (12 hours duration) corresponds to a dissociation effect associated with a 4500°K radiation temperature.

Starting with $X = 3$ (photochemical equilibrium) we see in Fig. 3 that the upward transport velocities increase with height. At 160 km, for example, the O_2 concentration has increased more than 10 times in less than 3 hours.

In other words, when the time required to reach photoequilibrium is several days, the time to reach diffusive equilibrium is only a matter of hours or a few days. Since it is not the purpose of this paper to attempt to discuss the entire problem of diffusion of O_2, the numerical values will not be considered further. However, it can be pointed out that the molecular oxygen concentration must decrease with height following a diffusive equilibrium if atmospheric mixing is not involved. In other words, the values obtained from a diffusive equilibrium correspond to minimum values. Since mixing due to atmospheric motions (vertical winds) must exist, it is possible that the vertical distribution of O_2 follows that of the atmosphere. It appears that this would not lead to a regular distribution. However, in their analysis of other rocket data, more difficult to interpret, NICOLET and MANGE (1954) have found that there is a possibility of strong mixing. In any case, the actual concentration of O_2 will be given by an intermediate distribution between mixing (maximum value) and diffusion (minimum value). At 200 km, for example, the concentration of O_2 is 10^7 cm^{-3}, but can reach 10^8 cm^{-3}. This problem will be discussed in a forthcoming paper.

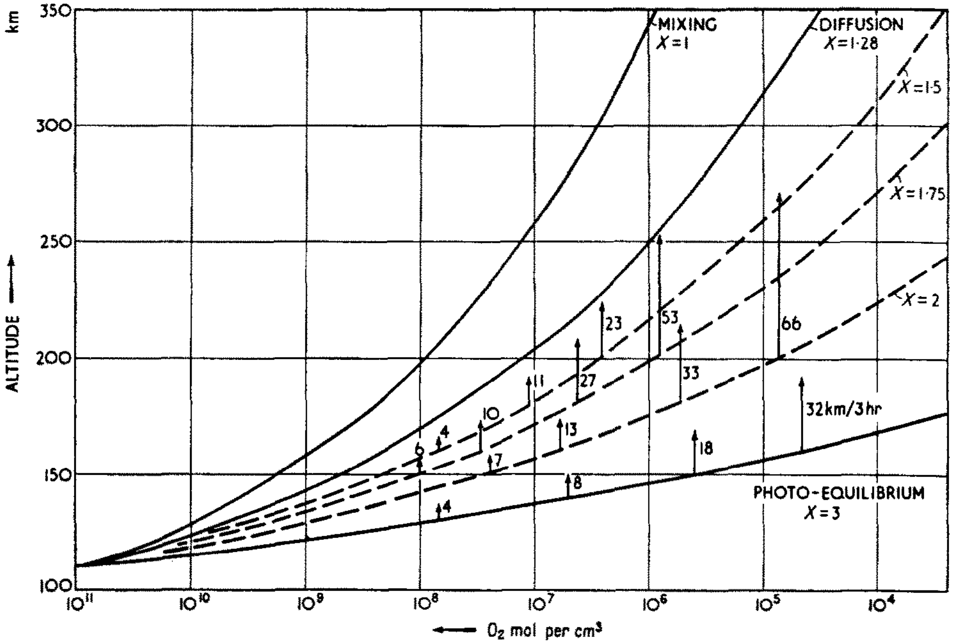

Fig. 3. Vertical distribution of molecular oxygen from 110 km to 350 km following mixing, diffusive and photochemical equilibriums. The effect of vertical velocities due to the diffusion process is shown by arrows indicating an upward motion of O_2 molecules during an average time of 3 hours.

6. THE TRANSITION REGION BELOW 110 KM

The percentage dissociation of O_2 can be obtained if an atmospheric model based on pressures obtained from rocket data is assumed. In this paper, the value of the pressure at 120 km published by HAVENS, KOLL, and LAGOW (1952) is used with a linearly varying scale height of gradient $\beta = 0{\cdot}2$. Above 110 km this model, which does not differ appreciably from the Rocket Panel (1952) model, leads to correct values for the concentrations. However, when the percentage dissociation of O_2 is computed, the result is very sensitive to the assumed model.

If we compare the number of molecules per cm^3 (see Table 1) obtained from the Rocket Panel Model and from our model for an atmosphere without dissociation, it is evident that the differences can be neglected.

Table 1. *Concentrations of molecules in an undissociated atmosphere*

Altitude (*km*)	*Rocket Panel*	*Nicolet*
100	$1{\cdot}80 \times 10^{13}$	$1{\cdot}70 \times 10^{13}$
110	$4{\cdot}32 \times 10^{12}$	$3{\cdot}92 \times 10^{12}$
115	$2{\cdot}18 \times 10^{12}$	$1{\cdot}94 \times 10^{12}$
120	$1{\cdot}18 \times 10^{12}$	$1{\cdot}03 \times 10^{12}$
125	$6{\cdot}67 \times 10^{11}$	$5{\cdot}74 \times 10^{11}$
130	$3{\cdot}97 \times 10^{11}$	$3{\cdot}39 \times 10^{11}$

However, when the percentage of dissociation is computed from the formula

$$\% = [1 - n(O_2)/0{\cdot}2n(M)]100 \qquad (11)$$

it is found that the value obtained is very sensitive to small variations in $n(O_2)$ and $n(M)$. For this reason, it is very difficult to determine the aeronomic conditions below 110 km where the percentage of dissociation is less than 70 or 80%, while it is easy to follow the dissociation above 120 km. In diffusive equilibrium we have the results shown in Table 2. These results are of the same order as the observational results obtained by BYRAM, CHUBB, and FRIEDMAN (1954) between 120 and 130 km.

Table 2. *Percentage of oxygen dissociation above* 120 *km in diffusive equilibrium*

Altitude (*km*)	*Percentage*	*Altitude*	*Percentage*
120	85	145	90·5
125	86	150	91·5
130	87·5	155	92·0
135	89	160	92·5
140	89·5	170	93·5

This procedure cannot be used below 110 km. In this region, $n(O_2)$ becomes of the same order as $n(O)$, while solution (9) of equation (8) is only valid when $n(O) > n(O_2)$. Furthermore, the photochemical equilibrium value of $n(O_2)$ is not very different from its diffusive equilibrium value so that it is difficult to follow theoretically the vertical distribution of O_2 and O at lower heights. Finally, the photo-equilibrium value is dependent on the increasing optical depth in terms of the total number of O_2 molecules. Using the equation of photochemical equilibrium (equation (8) in which $dn(O_2)/dt = 0$)

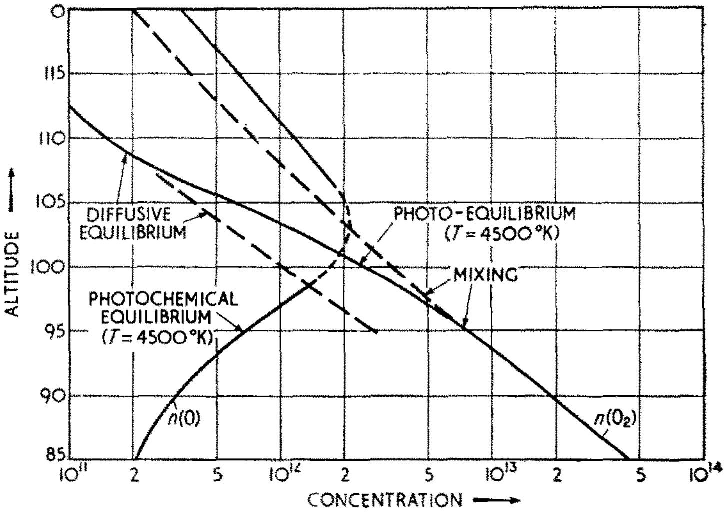

Fig. 4. Vertical distribution of molecular and atomic oxygen in the transition region when the photochemical equlibrium depends on a 4500°K radiation temperature.

$$n(O_2)J_2 = k_1 n(M) n^2(O)$$

and the numerical values of J_2 given by NICOLET and MANGE (1954), it is easy to see that the transition region must be between 95 and 105 km.* In Fig. 4, the curve of $n(O)$ below 108 km represents an equilibrium distribution showing that the maximum of the concentration of atomic oxygen is of the order of 2×10^{12} cm^{-3}.

However, considering a specific level, such as 97 km, where $n(O) < n(O_2)$, it is easy to see that the time, τ_{Rec}, of recombination defined by

$$\tau_{Rec}(O) = 1/k_1 n(M) n(O)$$

is still longer than one month. For this reason, all the indicated concentrations below 100 km are minimum values. Atmospheric motions may act during one month to enhance the atomic oxygen concentration increasingly in the downward

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(*) The parameter of temperature is 4500°K.

direction. If a concentration of 2×10^{12} atoms is reached at 97 km, the time of recombination is still one month. This result means that the percentage of dissociation of O_2 equals 20%.

As an example, let us consider a concentration of oxygen atoms of the order of 2×10^{12} cm^{-3} between 85 and 95 km, namely a percentage of dissociation from 2% to 13%. The time of recombination increases from 85 km to 95 km, by steps of 2·5 km, from 4 to 6, 9, 14, and 20 days. These results demonstrate that concentrations of atomic oxygen do exist which are larger than those given by photochemical equilibrium.

Therefore, even if the entire process in the transition region depends primarily on the photochemical action, the exact vertical distribution of atomic oxygen, nevertheless, is subject to atmospheric motions.

7. CONCLUSIONS

Since molecular oxygen has a vertical distribution above 110 km which is completely different from a photo-equilibrium distribution, many aeronomic processes must be studied in another form.

The presence of O_2^+ bands which was found by NICOLET (1948) in the auroral spectrum and recognized afterwards in their spectra by VEGARD (1950), PETRIE and SMALL (1952) and GARTLEIN and SHERMAN (1952) are not limited in altitude by the O_2 content but by the process of excitation.

An excitation process of the oxygen green line in the airglow (NICOLET, 1954b) can be identified with a dissociative recombination process $O_2^+ + e \rightarrow O + O$ following a charge transfer process like $O^+ + O_2 \rightarrow O_2^+ + O$. If such a mechanism may be operative in the aurora (SEATON, 1954), it is not limited only to the lower regions, and consequently may depend on the variation of the electron concentration.

It was formerly postulated that the rapid decrease of O_2 with altitude was an objection against the origin of the *E*-layer by ionization of O_2. In fact, the problem of the formation of the *E*-layer depends on the number of solar photons emitted in the ultraviolet region 1030–910A and in the x-ray region. According to recent rocket measurements (BYRAM, CHUBB, and FRIEDMAN, 1953), the number of x-ray photons appears to be larger than the number of ultraviolet photons and, therefore, the origin of the *E*-layer should be due to x-rays. Nevertheless, the presence of O_2 at high altitudes must have an important effect in Region *F*, in that it can explain the charge transfer needed by BATES and MASSEY'S (1947) hypothesis for the recombination.

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