On the Time Required for the Establishment of a Stationary Amount of Oxygen in the Atmospheres of Planets Containing Water Vapor

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Abstract

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On the Time Required for the Establishment of a Stationary Amount of Oxygen in the Atmospheres of Planets Containing Water Vapor

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In paper (1) the amount of water vapor decomposing under the action of solar radiation under present-day conditions in the Earth' s atmosphere at an altitude of 70–80 km was calculated. The hydrogen formed as a result of such a decomposition process diffuses into higher layers, whence its dissipation occurs, while the oxygen released in the process of photodecomposition enters the atmosphere in an amount, in order of magnitude, equal to 10^9 cm$^{-2} \cdot$ sec^{-1}.

The magnitude of the rate of entry of free oxygen into the atmosphere in the process of photodissociation of water is determined by the amount of molecular oxygen present in the atmosphere, since it screens water vapor from intense photodecomposition. If O_2 were completely absent from the atmosphere, the rate of photodecomposition would be of the order of 10^{12} cm$^{-2} \cdot$ sec^{-1}; at the present time the content of O_2 in the atmosphere is such that equality is ensured between the amount of O_2 entering the atmosphere through the photodecomposition of water and the amount consumed in the oxidation of the surface (about $1.5 \cdot 10^9$ cm$^{-2} \cdot$ sec^{-1}, according to geological estimates (2)).

Of course, at the present time, in the presence of a highly developed biosphere, one cannot consider the oxygen balance of the Earth' s atmosphere while confining oneself to processes occurring in the inorganic world; obviously, the rates of the processes of oxygen release and absorption in the biosphere many times exceed the corresponding rates in the processes of photodecomposition of water vapor and oxidation of the Earth' s surface. But one may pose the question: was it possible for an appreciable amount of free oxygen to accumulate in the Earth' s atmosphere before the emergence of organic life as a result of the photodecomposition of water vapor? The answer to this question can be obtained only by estimating the time required for the accumulation of a specified amount of oxygen in the Earth' s atmosphere through the process of photodecomposition of H_2O, with losses to surface oxidation present. Such an estimate is made in the present paper.

Of course, it is very difficult to imagine the conditions that preceded the emergence of organic life on Earth. We shall assume that the intensity and spectral composition of solar radiation were the same as under present-day conditions, and that from an altitude of 15 km to an altitude of 80 km the atmosphere is isothermal with a scale height H equal to $6 \cdot 10^5$ cm (the latter approximately corresponds to the present-day value of the temperature of the 15–80 km layer in the absence of the ozone maximum and with the same mean molecular weight of air). We shall assume that, as at the present time, the atmospheric gases are completely mixed up to an altitude of 80 km, and that water vapor at altitudes from 15 km and above constitutes $2 \cdot 10^{-5}$ of the total amount of gas by volume (^{3}). We shall choose the altitude of 15 km as the initial level $z = 0$, and the values of all concentrations referring to this level will be denoted by the subscript 0.

The values of the near-surface concentrations of all components of the atmosphere, with the exception of water vapor, are obtained by multiplying n_{i0} by e^2 (the height scale below 15 km is taken to be $7.5 \cdot 10^5$ cm). The total near-surface concentration of particles of atmospheric air n is taken to be $2.7 \cdot 10^{19}$ cm^{-3}.

In an oxygen-free atmosphere of a planet containing water vapor, shielded by nothing from the action of solar radiation, the number of acts of photodissociation of H_2O

$$\int\limits_0^\infty I(z) n_1(z) \sigma_1 dz = I_0 \int\limits_0^\infty n_1(z) \sigma_1 e^{-\sigma_1 n_1(z) H} dz \simeq I_0 \tag{1}$$

is approximately equal to I_0, the intensity of the incident radiation in the interval 1860–1430 Å, expressed in photons per square centimeter per second (provided that $e^{-\delta_1 n_1(z) H} \ll 1$).

At a distance of $150 \cdot 10^6$ km from the Sun, the value of I_0 is about 10^{12} cm$^{-2} \cdot$ sec^{-1}. The height at which photodissociation occurs most intensely is $z_{\max} \simeq 45$ km. The amount of O_2 entering the atmosphere in this process is $5 \cdot 10^{11}$ cm$^{-2} \cdot$ sec^{-1}. As a result of the accumulation of O_2 in the atmosphere, part of the solar energy from the interval 1860–1430 Å is spent on the photodissociation of O_2 molecules, and the process of water photodissociation, and consequently the rate of oxygen supply to the atmosphere, slows down; the height of the effective layer where photodissociation mainly occurs increases.

From the point of view of absorption by molecular oxygen, the interval 1860-1430 Å may be divided into two parts: interval a, 1860–1760 Å, which contains the Schumann-Runge bands (^{4}), where the mean absorption cross section σ_2 of O_2 may be estimated as 10^{-20} cm^2 (the corresponding value for water vapor in this interval is $\sigma_1 = 0.5 \cdot 10^{-18}$); $I_{0a} = 8 \cdot 10^{11}$ cm^{-2}sec^{-1}. Interval b, 1760–1430 Å, is the Schumann-Runge continuum, where $\sigma_2 = 2 \cdot 10^{-17}$ cm^2, $\sigma_1 = 4 \cdot 10^{-18}$, $I_{0b} = 5 \cdot 10^{11}$ cm$^{-2} \cdot$ sec^{-1}.

For the intensity of radiation penetrating to height z in the atmosphere, we have

$$I(z) = I_0 e^{-[\sigma_1 n_1(z) + \sigma_2 n_2(z,\tau)]H}. \tag{1a}$$

Here $n_1(z)$ is the concentration of water-vapor particles; $n_2(z,\tau)$ is the concentration of molecular oxygen; τ is the time measured from the moment when n_2 was equal to zero. It follows from (1) that absorption in oxygen will become appreciable when n_2 reaches a value of the order of $\frac{\sigma_1}{\sigma_2} n_1$. For interval b this will occur at $n_2 \simeq 0.2n_1$, and in interval a only at $n_2 \simeq 50n_1$. At a rate of entry of O_2 into the atmosphere equal to $5 \cdot 10^{11}$ cm$^{-2} \cdot$ sec^{-1}, the concentration of O_2 in the atmosphere becomes comparable with the concentration of water vapor at a height of 15 km in a time

$$t = \frac{2 \cdot 10^{-5} \cdot 2.7 \cdot 10^{19} \cdot 8 \cdot 10^5}{6 \cdot 10^{11}} \simeq 30 \text{ years},$$

i.e., interval b practically instantaneously ceases to play a role in the photodissociation of H_2O, since it is absorbed by molecular oxygen already at a negligibly small concentration of it in the atmosphere ($2 \cdot 10^{-5}$ of the total amount of gas). Therefore the problem of the relaxation time in the atmosphere of the present amount of O_2 may be solved by taking into account only interval a.

At each moment of time τ, per 1 cm^2 there occur

$$N(\tau) = \int\limits_0^\infty \sigma_1 n_1(z) I(z,\tau)\, dz \tag{2}$$

photodissociations of H_2O. The rate of oxidation of the Earth’ s surface is

$$V = Ae^2 n_{20}(\tau),$$

where A is a constant depending on the properties of the surface. The number of O_2 molecules that have entered the atmosphere during time t is

$$X(t) = \frac{1}{2}\int_0^t N(\tau)\, d\tau - e^2 \int_0^t An_{20}(\tau)\, d\tau. \tag{3}$$

The quantity X can be expressed in terms of $n_{20}(t)$:

$$X(t) = He^2 n_{20}(t). \tag{4}$$

After substituting (1) into (2) and integrating, we obtain

$$N(\tau) = \frac{I_0}{1 + \sigma_2 n_{20}(\tau)/\sigma_1 n_{10}}. \tag{5}$$

After substituting (4) and (5) into (3) and solving the resulting equation, we have the following expression for determining t for a given $n_{20}(t)$:

$$\frac{t}{T} = -\frac{1}{2C}\ln\left[1 - C\frac{n_{20}}{n_{10}} - \frac{\sigma_2}{\sigma_1}C\left(\frac{n_{20}}{n_{10}}\right)^2\right] + \frac{B}{2C}\ln\frac{1 + 2B\frac{\sigma_2}{\sigma_1}\frac{n_{20}}{n_{10}} - B^2\left(1 + \frac{2\sigma_2}{\sigma_1}\frac{n_{20}}{n_{10}}\right)}{1 - 2B\frac{\sigma_2}{\sigma_1}\frac{n_{20}}{n_{10}} - B^2\left(1 + \frac{2\sigma_2}{\sigma_1}\frac{n_{20}}{n_{10}}\right)}. \tag{6}$$

Here

$$T = \frac{2e^2 H n_{10}}{I_0}, \qquad C = \frac{2e^2 A n_{10}}{I_0}, \qquad B = \frac{1}{\sqrt{1 + 4\sigma_2/C\sigma_1}}.$$

As $A \to 0$ (absence of oxidation),

$$\frac{t}{T} \to \frac{n_{20}}{n_{10}} + \frac{\sigma_2}{2\sigma_1}\left(\frac{n_{20}}{n_{10}}\right)^2. \tag{7}$$

Table 1 gives the results of calculating the time required for the accumulation of a specified amount of O_2, as a percentage of the total amount of gas in the atmosphere, for two different values of the rate constant for surface oxidation.

Table 1

$A = 3.3 \cdot 10^{-10}$	$A = 3.3 \cdot 10^{-10}$	$A = 3.3 \cdot 10^{-10}$	$A = 3.3 \cdot 10^{-10}$	$A = 3.3 \cdot 10^{-9}$	$A = 3.3 \cdot 10^{-9}$	$A = 3.3 \cdot 10^{-9}$	$A = 3.3 \cdot 10^{-9}$
$\frac{n_{20}}{n_{10}}$	O_2, %	$\frac{t}{T}$	t, years	$\frac{n_{20}}{n_{10}}$	O_2, %	$\frac{t}{T}$	t, years
10^2	0.2	200	$6 \cdot 10^3$	10^2	0.2	200	$6 \cdot 10^3$
10^3	2	$1.1 \cdot 10^4$	$3.3 \cdot 10^5$	10^3	2	$1.1 \cdot 10^4$	$3.3 \cdot 10^5$
$0.5 \cdot 10^4$	10	$2.9 \cdot 10^5$	$8.7 \cdot 10^6$	$1.5 \cdot 10^3$	3	$2.5 \cdot 10^4$	$7.5 \cdot 10^5$
$0.6 \cdot 10^4$	12	$4.4 \cdot 10^5$	$1.3 \cdot 10^7$	$2 \cdot 10^3$	4	$5.05 \cdot 10^4$	$1.5 \cdot 10^6$
$0.7 \cdot 10^4$	14	$6.25 \cdot 10^5$	$1.9 \cdot 10^7$	$3 \cdot 10^3$	6	$1.6 \cdot 10^5$	$4.8 \cdot 10^6$
$0.8 \cdot 10^4$	16	$9 \cdot 10^5$	$2.7 \cdot 10^7$	$3.5 \cdot 10^3$	7	$5 \cdot 10^5$	$1.5 \cdot 10^7$
$0.9 \cdot 10^4$	18	$1.33 \cdot 10^6$	$4 \cdot 10^7$	$3.55 \cdot 10^3$	7.1		
10^4	20	$2 \cdot 10^6$	$6 \cdot 10^7$				

$A = 3.3 \cdot 10^{-10}$	$A = 3.3 \cdot 10^{-10}$	$A = 3.3 \cdot 10^{-10}$	$A = 3.3 \cdot 10^{-10}$	$A = 3.3 \cdot 10^{-9}$	$A = 3.3 \cdot 10^{-9}$	$A = 3.3 \cdot 10^{-9}$	$A = 3.3 \cdot 10^{-9}$
$1.1 \cdot 10^4$	22	$4.5 \cdot 10^6$	$13.5 \cdot 10^7$				
$1.12 \cdot 10^4$	22.4						

surface. The value of the constant $A = 3.3 \cdot 10^{-10}$ corresponds to the oxidation rate calculated in (2). If, in the period preceding the emergence of life on Earth, there existed no stronger processes for absorbing free O_2 from the atmosphere, then in a time of about 60 million years the amount of oxygen accumulated in the atmosphere owing to the interaction of water vapor with solar radiation would reach a value close to the present-day content of O_2. If, however, the oxidation rate was an order of magnitude greater than the average, then the amount of accumulated oxygen was about 7% of the total amount of gas. As we see, the time required for the establishment of a content of free oxygen close to the stationary amount is small compared with the age of the planet. Therefore there are grounds to suppose that the emergence of living matter on Earth occurred already in the presence of a certain definite amount of free oxygen in the atmosphere.

In connection with the suggestion that the process of photodissociation of $\mathrm{CO_2}$ (5) may once have played a role in the oxygen balance of the terrestrial atmosphere, let us estimate the relative intensity of this process. We shall assume (which is an obvious overestimate) the relative concentration of $\mathrm{CO_2}$ particles up to an altitude of 120 km to be equal to $3 \cdot 10^{-4}$ of the total amount of gas. The photodissociation threshold of $\mathrm{CO_2}$ is $\lambda_0 = 1690$ Å; the maximum absorption cross section σ_3, equal to $4 \cdot 10^{-19}$ cm^2, lies near 1500 Å. With the present content of $\mathrm{O_2}$ in the atmosphere (6), the most intense photodissociation of $\mathrm{CO_2}$ should occur at an altitude of about 115 km, since in deeper layers the Schumann-Runge continuum is strongly weakened by absorption by $\mathrm{O_2}$. The total gas density at an altitude of 115 km is about 10^{-11} g/cm^3, $\mu = 24$. The concentration of $\mathrm{CO_2}$ particles at an altitude of 115 km, under our assumption of complete mixing up to this altitude, is $n_{30} \approx 7.5 \cdot 10^7$ cm^{-3}. The total number of $\mathrm{CO_2}$ photodissociations occurring above the 115 km level, according to formula (1), is

$$I_0 \left[1 - e^{-\sigma_3 n_{30} H}\right] \approx I_0 \sigma_3 n_{30} H = 10^7 \text{ cm}^{-2} \cdot \text{s}^{-1},$$

i.e., much less than the number of $\mathrm{H_2O}$ photodissociations. Such an inequality was, of course, maintained at any content of molecular oxygen in the terrestrial atmosphere, since it is due to the fact that the photodissociation threshold of

CO_2 lies within the Schumann–Runge continuum, whereas water vapor decomposes owing to radiation in the interval 1860–1760 Å, where the much weaker Schumann–Runge bands in the absorption spectrum of O_2 occur.

Main Geophysical Observatory
named after A. I. Voeikov

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Note: Figure translations are in progress. See original paper for figures.