

Dissociation of Oxygen in the Upper Atmosphere

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The molecular oxygen content of the upper atmosphere between 110 and 130 km was determined by measuring the transmission of solar radiation in a narrow wavelength band from 1425 to 1500 Å. The radiation was detected by means of an ultraviolet photon counter flown in an Aerobee rocket. At 130 km the concentration of O₂ was 10¹⁰ per cc. On the basis of the Rocket Panel density scale, 12 percent of the atmospheric oxygen was still undissociated.

MOLECULAR oxygen in the earth's upper atmosphere is dissociated by the action of solar ultraviolet light in the Schumann-Runge continuum below 1750 Å. The degree of dissociation varies sharply with altitude and depends primarily on the solar intensity. For a 6000°K solar spectrum, theory¹ predicts a transition region about 10 kilometers thick, centered at a height of about 95 km, and essentially complete dissociation in E-layer. If the photospheric temperature is lower the rate of dissociation decreases and atmospheric mixing and diffusion begin to play an important role. Nicolet and Mange² have shown that the O₂ distribution may depart completely from photochemical equilibrium above 110 km if the solar temperature is as low as 4500°K.

It is possible to determine the partial pressure of O₂ independently of O and N₂ from a measurement of transmission of ultraviolet radiation in the spectral region near 1450 Å at the maximum of the O₂ continuum. In this portion of the spectrum O₂ absorbs

strongly and all other major atmospheric constituents are almost completely transparent. To perform the measurement in the upper atmosphere, a photon counter sensitive only to wavelengths near 1450 Å was exposed from a rocket to the direct rays of the sun. The response of the detector at any particular altitude compared to the response at peak altitude was interpretable in terms of the intervening amount of atmospheric O₂.

INSTRUMENTATION

The first attempt at this type of measurement was made in a V-2 rocket experiment³ in 1949. Although the data gave an indication of the rapid disappearance of O₂ above 100 km, the quantitative evaluation of O₂ concentration *versus* altitude was complicated by the fact that the detector exhibited a weak response to wavelengths longer than 1600 Å. For the present experiments this difficulty was eliminated by the development of a photon counter which had high sensitivity between 1425 and 1500 Å, but was essentially dead to light outside this band. The importance of the restriction on long wavelength sensitivity is apparent when the source of radiation resembles a blackbody with its maximum in the visible. If the effective sun temperature is 4500°K, the number of quanta between 1400 and 1500 Å which enter the earth's atmosphere is about 2.9×10^{10} quanta cm⁻² sec⁻¹ as compared to 4.6×10^{12} quanta cm⁻² sec⁻¹ between 1500 and 2000 Å. A satisfactory detector was made by filling a photon counter tube with a mixture of 43 mm NO, 640 mm He and 0.5 mm xylene. The window, which was mounted in the side of the tube, was a synthetic sapphire disk, 6 mm in diameter and 0.5 mm thick. The response of the tube is illustrated by the spectral sensitivity curve of Fig. 1 and may be attributed entirely to the photoionization of xylene. Longer wavelength response is suppressed by the capture of photoelectrons near the cathode by NO to form negative ions. The principle of operation of this type of tube is described in detail in a paper to be published.⁴

Calibration of the detector was carried out in the following manner. The response of the photon counter

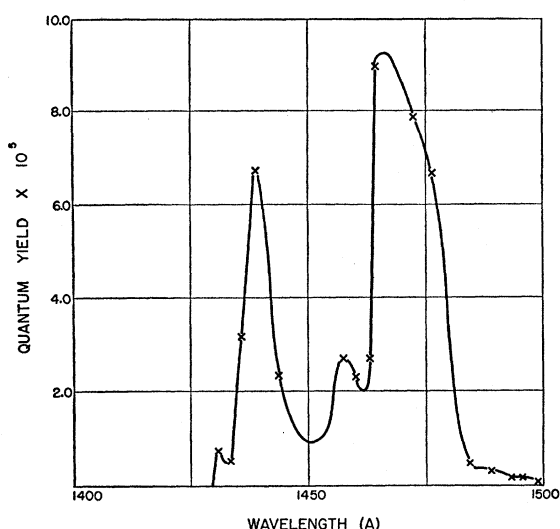


FIG. 1. Spectral sensitivity of photon counter filled with mixture of nitric oxide, helium, and xylene. Short-wavelength limit is characteristic of sapphire window. Long-wavelength limit is photoionization threshold of xylene.

¹ R. Penndorf, *J. Geophys. Research* **54**, 7 (1949).

² M. Nicolet and P. Mange, *J. Geophys. Research* **59**, 1 (1954).

³ Friedman, Lichtman, and Byram, *Phys. Rev.* **83**, 1025 (1951).

⁴ T. A. Chubb and H. Friedman, *Rev. Sci. Instr.* (to be published).

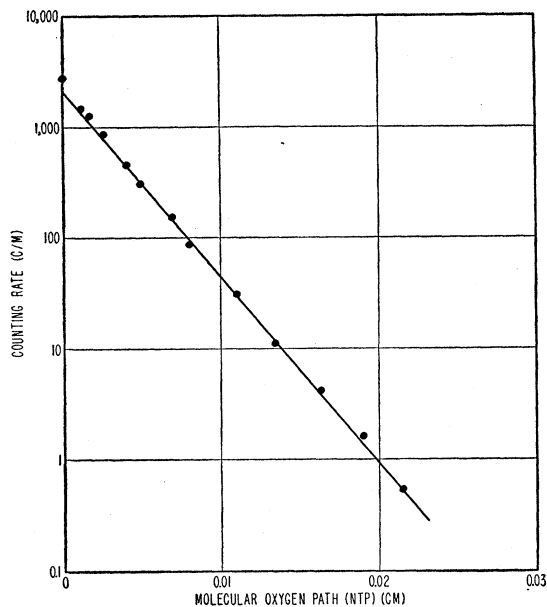


FIG. 2. Counting rate *versus* path length of light in molecular oxygen. Because of the broad maximum in the molecular oxygen continuum and the comparatively narrow band response of the photon counter, the semilog plot is almost a straight line with a slope of 386 cm^{-1} (base e).

to the light of a hydrogen discharge was obtained by means of a vacuum ultraviolet monochromator. The output of the monochromator was in turn measured by means of a photomultiplier, the front surface of which was coated with a fluorescent film of sodium salicylate. Finally, the multiplier and fluorescent film combination was calibrated by means of a standard Hg lamp at 2537 Å. The fluorescent quantum efficiency of the salicylate was assumed to be independent of wavelength in accord with the measurements of Johnson *et al.*⁵ and of Watanabe *et al.*⁶

To test the narrow band characteristic of the tube, it was exposed to the light of a corona discharge in hydrogen through an absorption column of air. By taking advantage of the fact that the intensity of the corona lamp could be varied over three decades without altering its spectral distribution, it was possible to measure the effective absorption coefficient of air over almost 4 decades. The results of this calibration are shown in Fig. 2 and support the conclusion that the entire response was confined to a narrow spectral region near the maximum of the O_2 absorption band. Each photon counter prepared for flight was checked similarly shortly before installation in the missile. The effective O_2 absorption coefficient determined in this way was used in calculating the amount of O_2 at high altitude from the rocket measurements.

The experiment was repeated in three Aerobee

⁵ Johnson, Watanabe, and Tousey, *J. Opt. Soc. Am.* **41**, 702 (1951).

⁶ Watanabe, Inn, and Zelikoff, *J. Chem. Phys.* **20**, 1969 (1952).

rockets which reached altitudes of 125, 106, and 130 km. The data of the two lower altitude flights are less complete, but appear to confirm the results of the last missile, on which the computations reported here are primarily based. The oxygen-measuring photon counter was one of a group of six counters of diverse types flown in the missile. Counting rates were continuously recorded throughout flight in the following manner. The pulse output of each counter drove its own thyratron ratemeter which delivered a signal to one channel of a 15-channel telemetering transmitter. As the rocket spun about its axis, each detector was in turn exposed to the direct rays of the sun. The angle between the sun and the normal to the counter window was measured by means of aspect calibrated photocells. The timed responses of the photon counters and aspect photocells together with radar tracking data (aided by a radar beacon transmitter in the rocket) furnished the raw data from which the oxygen distribution was derived.

EXPERIMENTAL RESULTS

The corrected counting rate *vs* altitude curve for the 1425–1500 Å photon counter is shown in Fig. 3. These data were obtained by recording the peak counting rate on each rocket roll. The counting rate was corrected for losses due to counter dead-time. Next, an aspect correction was made to adjust for the angle between the sun and the normal to the counter window. The correction was determined from laboratory measurements of count rate *versus* aspect angle made by exposing similar counters to an ultraviolet lamp. At the peak, the dead-time correction amounted to 30 percent of the corrected count. During ascent to within one kilometer of peak, the rocket was very stable and the maximum aspect correction was 20 percent of the cor-

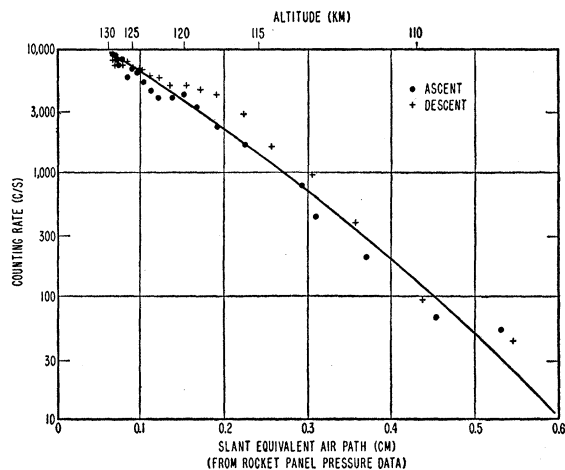


FIG. 3. Observed counting rate during flight of N.R.L. Aerobee 16 *versus* slant equivalent air path. In drawing the smooth curve greater weight was given to the ascent data since the required aspect corrections were smaller than for the descending portion of the flight.

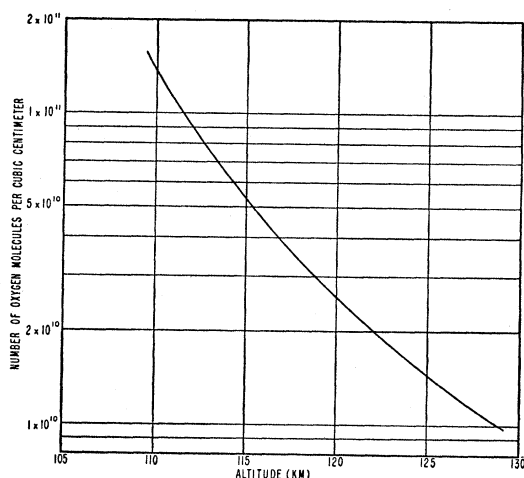


FIG. 4. Concentration of oxygen molecules *versus* altitude, computed from experimental data of Fig. 3.

rected count. On descent, the maximum aspect correction reached a value of 38 percent.

From the smooth curve drawn in Fig. 3, the number of O_2 molecules per cc was computed as a function of altitude and the result is shown in Fig. 4. An O_2 absorption coefficient of 386 cm^{-1} was used in calculating these results in accordance with the absorption measurements of Fig. 2. Figure 5 shows the total overhead vertical path of molecular oxygen reduced to NTP assuming that $0.43 \times 10^{-3} \text{ cm-atmos}$ of O_2 still remained above the missile at 130 km. This residual O_2 corresponded to an extrapolation of the count rate curve of Fig. 3 to a zero air path value of 16 500 counts/sec. Figure 6 shows the "percent dissociation of oxygen" as a function of altitude as computed from the amount of molecular oxygen shown in Fig. 4. Percent dissociation is expressed as,

$$\text{percent dissociation} = 1 - \frac{\rho(O_2)}{0.23\rho(\text{air})}, \quad (1)$$

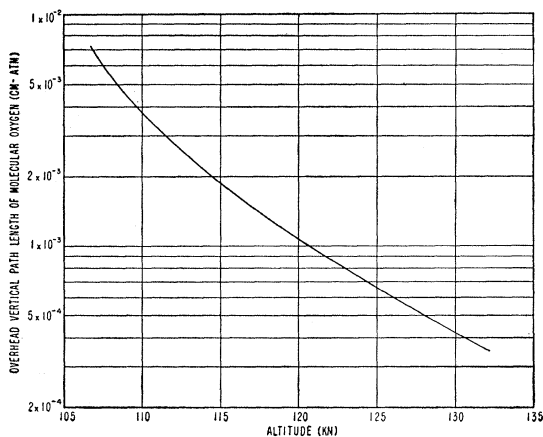


FIG. 5. Residual overhead O_2 path length *versus* altitude.

where $\rho(O_2)$ is the measured density of molecular oxygen and $\rho(\text{Air})$ is the assumed ambient density of air. In Fig. 6 Curve *A* is the "percent dissociation" based on ambient densities given by the Rocket Panel⁷; Curve *B* is the percent dissociation assuming $\frac{1}{3}$ Rocket Panel densities. The actual ambient densities above 100 km during the flight of Aerobee 16 were measured by air absorption of 44–60 Å x-rays and were found to be less than 0.4 Rocket Panel densities and probably no more than 0.3 Rocket Panel values.

DISCUSSION

The rocket measurements show the existence of much larger quantities of molecular oxygen above 125 km than would be expected from a simple photochemical equilibrium. Since the time of diffusion becomes short compared to the time of dissociation above 125 km, an appreciable amount of O_2 will diffuse to the height

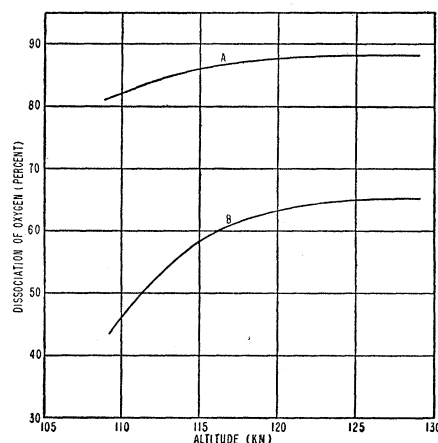


FIG. 6. Percent dissociation of atmospheric oxygen *versus* altitude. Curve *A* is based on air density published in Rocket Panel Report (see reference 7). Curve *B* is based on densities only one-third of the Rocket Panel values.

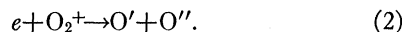
of F_2 region. Preliminary results of the present rocket measurements were used to support the theory² that the distribution of O_2 above 110 km is controlled by diffusive separation and turbulent mixing. At 170 km, Nicolet⁸ computed an expected O_2 content at least 10^4 times as great as the photochemical values. The diffuseness of the transition region from O_2 to O is consistent with the comparatively weak solar intensity deduced from the photon counter measurements. In Aerobee 16, detectors which were sensitive in the spectral ranges 1230–1350 Å and 1425–1500 Å indicated photospheric radiation equivalent to blackbody emission at 3900°K and 4000°K respectively. This is in contrast to apparent solar temperatures of 5000°K at 2000 Å⁹ and 6000°K in the visible spectrum.

⁷ Rocket Panel, Phys. Rev. **88**, 1027 (1952).

⁸ M. Nicolet, J. Atm. and Terrest. Phys. **5**, 132 (1954).

⁹ Johnson, Purcell, Tousey, and Wilson, Astrophys. J. **117**, 238 (1953).

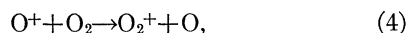
The presence of O₂ at *F*-layer altitudes should have a profound effect on the rate of electron recombination as suggested by Bates and Massey.¹⁰ Since atomic oxygen ions can be converted to molecular ions in collisions with neutral oxygen molecules, the molecular ions can then recombine with electrons by dissociative recombination,



The recombination coefficient for this process may be as large as 10⁻⁷ cm³ sec⁻¹. By contrast, in the absence of molecular oxygen, electron recombination proceeds by radiative recombination,



for which the recombination coefficient is of the order of 10⁻¹² cm³ sec⁻¹. Since the conversion of atomic to molecular ions,



¹⁰ D. R. Bates and H. S. W. Massey, Proc. Roy. Soc. (London) **A192**, 1 (1947).

can take place by either charge exchange or by ion-atom interchange, a large reaction cross section is expected. According to Bates,¹¹ the rate coefficient for ion-atom interchange may be as high as 10⁻¹⁰ cm³ sec⁻¹. The high-altitude O₂ concentrations indicated by the rocket experiment and the theoretical cross section for exchange ionization are sufficient to explain the recombination coefficients of 10⁻¹⁰ to 10⁻⁹ observed in *F*₂ region.¹² The manner in which the recombination coefficient decreases from *E* region to *F*₂ region depends on the partial pressure of O₂. The expected rate of decrease is sufficient to account for the production of a major portion of *F*₂ region by the same source of ionization that is responsible for *F*₁.^{12,13}

¹¹ D. R. Bates, Proc. Phys. Soc. (London) (to be published).

¹² Havens, Friedman, and Hulburt, Report of the Conference on the Physics of the Ionosphere, The Physical Society, London (1954).

¹³ N. Bradbury, Terrestrial Magnetism and Atm. Elec. **43**, 55 (1938).

Theory of Electron Penetration*

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The theory of electron penetration in an infinite medium under the combined influence of scattering and slowing down is developed to the point of numerical application. Sample calculations of energy dissipation *versus* distance from the source are compared with experiments by Frantz, by Clark, Brar, and Marinelli, and by Loevinger. The agreement is good provided that relativistic scattering cross sections are used. The energy loss is treated in the continuous slowing down approximation; the resulting error is appreciable only at extreme penetrations.

1. INTRODUCTION

THIS paper considers the following problem: A source of electrons with kinetic energy T_0 is embedded in a material. As the electrons move away from the source they lose energy and change direction. We want to determine the energy dissipated by the electrons at various locations in the material. A knowledge of the distribution of energy dissipation implies a knowledge of the spectral and directional distributions also, but this additional information need not be described explicitly.

Phenomenological work on this problem has been accomplished mainly by people interested in the biological effects of radiation. The most extensive effort of this type, and also the most recent, is that of Loevinger, whose paper contains a fairly complete summary of experimental work with beta-ray sources.¹ From a more

basic standpoint the problem is essentially new, since few attempts—and those in unrealistic schematization—have been made to calculate electron spatial distributions taking into account both energy loss and direction changes, although both effects have a strong influence.^{2,3} Many contributions have been made to

² For efforts to apply age diffusion theory to electron penetration problems see Bethe, Rose, and Smith, Proc. Am. Phil. Soc. **78**, 573 (1938) and W. C. Roesch, Hanford Report No. HW-32121, May 24, 1954 (unpublished). There can be hardly any doubt that this simple model gives better than an order-of-magnitude estimate of the distance electrons travel "on the average." However, two important features of the penetration are given wrongly: (a) The initial transient stage of the penetration when electrons move directly away from the source, which is particularly important for high-energy sources or for low-*Z* scattering materials; and (b) the deep-penetration trend. The results of this paper indicate that there is hardly any region of penetration in which age diffusion theory can be expected to provide a reasonable description.

³ For calculations of electron backscattering see J. W. Weymouth, Phys. Rev. **84**, 766 (1951). Weymouth took into account energy losses as well as deflections, but only in the approximation of an energy-independent scattering cross section. He did not attempt to calculate electron spatial distributions.

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¹ R. Loevinger (private communication).