

Werk

Jahr: 1936

Kollektion: fid.geo

Signatur: 8 GEOGR PHYS 203:12

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Werk Id: PPN101433392X_0012

PURL: http://resolver.sub.uni-goettingen.de/purl?PPN101433392X_0012

LOG Id: LOG_0073

LOG Titel: Aufsätze

LOG Typ: section

Übergeordnetes Werk

Werk Id: PPN101433392X

PURL: <http://resolver.sub.uni-goettingen.de/purl?PPN101433392X>

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Aufsätze

Ozone and Water Vapor in the Atmosphere

by Sydney Chapman, London

Prof. K. Wegener's recent suggestion that atmospheric ozone is formed from water vapor is examined, and found to be unlikely. The diffusion of ozone is considered, and also the ways in which ozone is likely to be destroyed in the troposphere.

1. This note was prompted by the recent brief communication „Die Ozonfrage“ by Prof. K. Wegener, in this Journal*) [pp. 124, 125 (1936)], though the subjects here treated are not confined to those he dealt with.

2. *Oxygen in the stratosphere.* The main point raised by Prof. Wegener is that ozone may be primarily due to the dissociation of water vapor, and not (as is commonly supposed) of molecular oxygen, by ultraviolet light. He considers, in fact, that the assumption of great quantities of O_2 permanently present in the stratosphere (and not merely temporarily formed and dispersed) is contrary to Dalton's law. This law, however, refers to a *static* mixture of gases, a condition not present either in the troposphere (where Dalton's law is obviously not operative) or in the stratosphere, at least up to the considerable heights attained by balloons. The Russian scientists Prokofiev, Godunov and Birnbaum**) found no appreciable difference between the O_2 concentration at 18.5 km and at ground level. The recent work on the helium content of the stratosphere by Paneth and Glückauf***), though in some cases suggesting a slight increase in the helium content at about 20 km., implies that the O_2 -content there is practically the same as at ground level. Regener†) has directly confirmed this, and has also shown that at 28 or 29 km the air still contains over 20% of oxygen (by volume). Thus we may be sure that up to at least 50 km. (below which level most of the atmospheric ozone is situated) there is a substantial proportion of O_2 in the stratosphere.

3. *Water vapor in the stratosphere.* On the other hand, owing to the low temperature — say 219° K — in the stratosphere (up to at least 30 km.) the H_2O

*) In paragraph 2 Prof. Wegener states that ozone decays quickly, and must therefore be confined to the day hemisphere of the earth and be absent over the night hemisphere. This is, of course, a misapprehension, since Barbier, Chalonge and Vassy [Rev. d'Optique 13, 199 (1934) and Compt. Rend. 198 2139 (1934)] have shown that there is no substantial systematic difference between the amounts of ozone present by day or by night.

**) Nature 133, 15 (London 1934).

***) Nature 136, 717 (1935).

†) Nature 138, 544 (1936).

vapor content is likely to be far less than that of O_2 . It is very desirable to have actual measurements of the water vapor content in the stratosphere; the important question to decide is whether at, or not much above, the base of the stratosphere — say 12 km. — the air is saturated, less than saturated, or super-saturated.

4. The distribution of water vapor in the ozone layer in the stratosphere will first be discussed on the supposition that super-saturation does *not* occur there. In this case, since the density of water vapor in equilibrium with water (or rather ice) at 219° K is $2.5 \cdot 10^{-8}$ g./ccm., this is an upper limit to the H_2O density at 12 km. At this level the O_2 density is $7 \cdot 10^{-5}$ g./ccm., or about 3,000 times as great. If Dalton's law were fully operative above 12 km., the ratio H_2O/O_2 would steadily increase with height; but the level h at which the H_2O density becomes equal to the O_2 density would not be less than about 120 km., even supposing $T = 219^{\circ}$ K up to the height h ; if $T > 219^{\circ}$ K over part of this range of height (as is suggested by the abnormal propagation of sound to great distances), the estimate of h would have to be increased. Moreover if, as is indicated by the appreciably uniform concentration of O_2 up to 20 km., there is some convective mixing up to this level, the H_2O/O_2 ratio will be kept at about $1/3000$ up to 20 km., and h would need to be still further increased. Hence this ratio would certainly be very small up to 40 or even 50 km., that is, throughout the stratospheric part of the ozone layer. Moreover the percentage humidity of the air would steadily decrease upwards even if $T = 219^{\circ}$ K at all heights, while in any region where T much exceeds 219° K the percentage humidity would be considerably lessened.

5. These remarks will be modified, but scarcely to a degree which is important for the ozone problem, if super-saturation occurs in the stratosphere. The saturation density of water vapor increases rapidly with temperature in the neighbourhood of 220° , and any convective mixing which brings normally humid air from the upper tropospheric levels just into the stratosphere must tend to raise the stratospheric humidity to or above the saturation point. In the absence of sufficient condensation-nuclei in the clean air at those heights above the ground, appreciable super-saturation may well occur, and may increase until a limit is reached at which the vapor condenses to water or ice, and clouds are formed such as Störmer and others have observed. Presumably these cloud particles descend to the troposphere where they vaporize. The stratosphere, on account of its low temperature, thus acts like a trap to catch any water vapor from below which might otherwise travel to hotter layers above; the effectiveness of the trap is impaired by the possibility of super-saturation*).

6. *Dissociation of O_2 and H_2O in the stratosphere.* We proceed, therefore, on the basis that the H_2O/O_2 ratio is small throughout the ozone layer. Prof.

*) Brunt: Q. J. Roy. Met. Soc. 60, 279 (1934) has shown that convection in the stratosphere itself must tend to an upward decrease in relative humidity.

Wegener's suggestion that the dissociation of H_2O , instead of O_2 , is the primary cause of ozone formation, is based on a contrary opinion as to the value of this ratio; but his suggestion might still be tenable if, nevertheless, H_2O molecules were dissociated in much greater numbers than O_2 molecules. This would depend on the absorption coefficients of the two gases, for the radiations that dissociate them. Above 12 km. level, the amount of H_2O is (on the assumptions of § 4) equivalent to a layer about 50 cm. thick at n. t. p., and the corresponding layer of O_2 above 12 km. would have a thickness of the order 5.000 cm. According to Flory*) O_2 molecules can be dissociated by radiation of about 2.000 Å and less. In this region both H_2O and O_2 absorb, H_2O rather the more strongly except in certain bands where the reverse is true; the absorption coefficient**) α (on the scale of 10) for both gases ranges about $5 \cdot 10^{-4}$ to $2 \cdot 10^{-3}$ in the region 1900—2050. Ninety per cent of such radiation would be absorbed by a layer of thickness $1/\alpha$, or from 2.000 to 500 cm., at n. t. p. Clearly only a small fraction of this radiation could be absorbed by the 50 cm. of H_2O proper (at n. t. p.) lying above 12 km., even if it were all situated above the oxygen, thus getting the first „bite“. Actually O_2 is present in considerable excess of the H_2O , and hence will be responsible for most of the absorption and dissociation. Consequently I conclude that the usual hypothesis, ascribing ozone-formation to O_2 -dissociation, is substantially correct.

7. *The dissociation of H_2O .* It is not unlikely, of course, that H_2O dissociation contributes, very slightly, to the ozone formation. But so far as I am aware it is not certain that ultraviolet radiation dissociates H_2O into H_2 and O, as Prof. Wegener suggests. The dissociation, if it occurs, may be into $\text{H} + \text{OH}$, though by further absorption some of the OH may be further dissociated into $\text{H} + \text{O}$. Atomic hydrogen formed in either of these ways would tend to rise, and might well escape from the atmosphere altogether, if at high levels the temperature is at times very high, (up to 800° K or more) as many writers have suggested. This may be an alternative way in which water vapor is removed from the stratosphere.

8. *The diffusion of ozone.* In my memoir on atmospheric ozone***) I briefly considered its molecular diffusion, but the subject deserves more detailed consideration, and the treatment now to be given supersedes that of my former paper.

It is sufficient for this purpose to regard the atmosphere as merely a binary mixture, all the constituents other than ozone being lumped together as a simple gas having the mean molecular weight 29, as against 48 for O_3 . Let suffix 1 refer to ozone, and 2 to the rest of the air. Let n_1, n_2 be the number of molecules per cm.

*) Flory: Journ. Chem. Soc. 4, 23 (1936).

**) Granath: Phys. Rev. 34, 1046 (1929).

***) Mem. Roy. Meteor. Soc. 3, 115 (1930).

of each kind, m_1, m_2 the molecular masses, and u_1, u_2 their mean velocities in the upward vertical (x) direction. Let

$$n_0 = n_1 + n_2, \quad n_0 u_0 = n_1 u_1 + n_2 u_2 \dots \dots \dots (1)$$

so that u_0 is the mean velocity of the mixture. Let X_1, X_2 be the external forces per molecule, so that in the present case, where the forces are purely gravitational,

$$X_1 = m_1 g, \quad X_2 = m_2 g \dots \dots \dots (2)$$

These appear explicitly in the equation of diffusion only through X'_0 , given by

$$X'_0 = \frac{n_1 n_2 m_1 m_2}{n_0 (n_1 m_1 + n_2 m_2)} \left(\frac{X_1}{m_1} - \frac{X_2}{m_2} \right) \dots \dots \dots (3)$$

in the present case X'_0 clearly vanishes.

Let p, ρ, T denote the atmospheric pressure, density and temperature, D_{12} the coefficient of diffusion, and D_T that of thermal diffusion. Then writing

$$D_T = k_T D_{12} \dots \dots \dots (4)$$

the equation of vertical diffusion may be written

$$u_1 - u_0 = D_{12} \left\{ - \frac{\partial \log (n_1/n_0)}{\partial x} + \frac{n_0}{k n_1 T} X'_0 + \frac{n_2 (m_1 - m_2)}{n_1 m_1 + n_2 m_2} \frac{\partial \log p}{\partial x} - \frac{n_0 k_T}{n_1} \frac{\partial \log T}{\partial x} \right\} (5)$$

In our case $X'_0 = 0$, and n_1/n_2 is very small, so that practically $n_2 = n_0$; also p , which is equal to $k (n_1 + n_2) T$ (k being Boltzmann's constant), may be written $p = k n_2 T$, so that

$$\frac{\partial \log n_2}{\partial x} = \frac{\partial \log p}{\partial x} - \frac{\partial \log T}{\partial x} \dots \dots \dots (6)$$

Furthermore,

$$k_T = \frac{n_1 n_2}{n_0^2} k'_T \dots \dots \dots (7)$$

where k'_T is of order unity, or, since n_1/n_2 is small, k_T is approximately n_1/n_2 . Hence the equation of diffusion may be written in the approximate form, appropriate to the present case,

$$u_1 - u_0 = D_{12} \left\{ - \frac{\partial \log n_1}{\partial x} + \frac{m_1}{m_2} \frac{\partial \log p}{\partial x} - (1 + k'_T) \frac{\partial \log T}{\partial x} \right\} \dots \dots (8)$$

If T were uniform and a steady state had been attained in which $u_1 - u_0 = 0$, that is, without diffusion, this would reduce to $n_1 \propto p^{m_1/m_2}$, corresponding (so long as n_1/n_2 is small) to Dalton's law; the ozone density would decrease with increasing height much more rapidly than the air density.

In the stratosphere T is approximately constant, but below the level of maximum ozone density n_1 increases with increasing height, so that $u_1 - u_0$ cannot be zero. On the right of the last equation the first two terms correspond to a downward diffusion of ozone; the last term, in the troposphere where T decreases upwards, represents an upward diffusion of ozone.

So far as I know, D_{12} (and D_T) for an ozone-air mixture has not been determined, but it may be estimated with sufficient accuracy for our purpose as $0.2 (\rho_0 T / \rho T_0)$, where the suffixes 0 refer to ground level. In the troposphere at Arosa n_1 is nearly constant, and the upward increase of n_1 does not become important till about 12 km. height is reached; the maximum value of $\partial \log n_1 / \partial x$, which is about $5 \cdot 10^{-7} \text{ cm}^{-1}$, is attained at 20 km. or so. At this height D_{12} will be about 23, so that the mean downward speed of the ozone molecules due to their density gradient at 20 km. is about 10^{-5} cm./sec. , rather less than 1 cm. per day. The value of $\partial \log p / \partial x$ in the troposphere is about $1.3 \cdot 10^{-6} \text{ cm}^{-1}$, and slightly more in the lower part of the stratosphere; at 20 km. height the second (pressure) term in the diffusion velocity is about $23 \times (48/29) \times 1.3 \cdot 10^{-6}$ or $5 \cdot 10^{-6} \text{ cm./sec.}$, or about 0.4 cm. per day. The diffusion velocity due to the temperature gradient (in the troposphere) is less than this, and upward. Thus at 20 km. height the „molecular“ diffusion of ozone is downward, at the rate of about 1 cm. per day, or $3\frac{1}{2}$ m. per year. It will be more than this at higher levels, and less at lower levels, in rough proportion to the air density, though above the level of maximum n_1 the first two terms in the expression (8) for $u_1 - u_0$ will not reinforce but counteract each other.

The significance of molecular diffusion for the ozone equilibrium in the stratosphere can be roughly illustrated as follows. Let us suppose that the ozone is formed mainly between say 10 and 35 km. height, and that it is diffusing downwards across the lower boundary with a velocity of $\frac{1}{2}$ cm. per day, and upwards across the upper boundary with a velocity of $1\frac{1}{2}$ cm. per day. The ozone densities of these levels are approximately equal, at Arosa, the value being 0.005 cm. of ozone (at n. t. p.) per km. height. The loss of ozone to this 25 km. layer per day is equal to the amount contained in a layer ($\frac{1}{2} + 1\frac{1}{2}$) or 2 cm. thick, that is $2 \cdot 10^{-5} \times 0.005 \text{ cm. at n. t. p.}$ or $10^{-7} \text{ cm. at n. t. p.}$ In half a year the loss would be $1.8 \cdot 10^{-5} \text{ cm. at n. t. p.}$; this is quite negligible in comparison even with the slow seasonal variation of ozone at Arosa, which is of the order $10^{-1} \text{ cm. (or 1 mm.)}$ at n. t. p., from spring to autumn or vice versa.

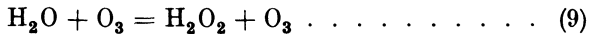
9. Actually, by air convection, ozone is probably transferred downwards into the troposphere at a rate considerably greater than that due to molecular diffusion. The actual rate of convective transfer cannot be calculated, but may be as much as 1000 times the rate of molecular transfer. Convective transfer will carry ozone downwards wherever the ratio ozone/air decreases downwards (that is, at Arosa, throughout the layer below 35 km.). At 35 km., where the ozone/air ratio has its maximum, any convection will not transfer ozone, because the ozone/air ratio there has zero gradient. Hence the 10 to 35 km. layer considered at the end of § 9 would be losing ozone (by convection) only at its lower boundary, at a rate say $1000 \times \frac{1}{2} / (\frac{1}{2} + 1\frac{1}{2})$ or 250 times the „molecular“ rate, amounting, in half a year, to about $4.5 \cdot 10^{-3} \text{ cm. at n. t. p.}$ Even this is small compared with the seasonal variation of the ozone content.

10. Since ozone is supplied to the troposphere from above, at some such rate, and since probably little or no ozone is actually formed in the troposphere itself, this amount of ozone must be destroyed in some way in the troposphere. Since the ozone/air ratio steadily decreases downwards in the troposphere, convection must steadily transfer ozone downwards the ground. The question arises whether the ozone is destroyed partly in transit, or mainly at or near the ground.

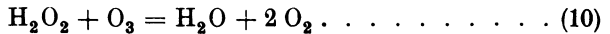
The ozone even in the lowest layers of the atmosphere will (weakly) absorb solar radiation in the Chappuis bands, which seems capable of dissociating the ozone. But in the troposphere and lower stratosphere this dissociation has very slight power of really destroying the ozone; it merely interrupts the life of the ozone molecules, by temporarily detaching the odd oxygen atom; this, however, in nearly all cases, at once re-forms an ozone molecule by attachment to another oxygen molecule. Even in the main ozone layer, where dissociation by absorption in the Hartley band is active during the day-time, the ozone is very permanent and long-lived; only a small proportion of the O atoms and O₃ molecules combine to re-form O₂, representing a permanent destruction of ozone. Thus we must look to other processes than photo-dissociation to explain the disappearance of the ozone brought downwards by convection from the ozone-forming layer.

In the lowest kilometre or two of the atmosphere the ozone will doubtless partly disappear by oxidizing organic matter (and possibly also H₂S) carried up by convection from the ground. But this may not be the main process of ozone destruction in the troposphere, and particularly over the large ocean area of the earth, where such oxidizable matter may be very scarce.

11. It seems quite possible that the chief ozone-destroying agent in the troposphere is water and water vapor; certainly no other atmospheric constituent seems so likely as water to react with the ozone. Water itself dissolves ozone*), and doubtless some ozone is thus taken into solution, both at water surfaces at ground level, and in the clouds; such ozone will ultimately combine with organic substances in the water, or at the ground when ozonized rain descends. But perhaps more potent will be the direct gaseous interactions between ozone and water vapor, first yielding hydrogen peroxide according to the formula



(a two-body reaction), and in a second two-body reaction reducing the peroxide again to water, e. g.



We may hope in time to be able to discuss these processes quantitatively, but at present we are far from having the necessary data for this.

*) About 4.5 ccm. of ozone can be dissolved in 1000 ccm. of water, according to Newth, *Inorganic Chemistry*.