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Origin and Distribution of the Polyatomic Molecules in the Atmosphere

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Origin and distribution of the polyatomic molecules in the atmosphere

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Introduction

Of those gases which occur in the upper atmosphere and have strong absorption bands in the infra-red part of the spectrum and which must, therefore, be considered when calculating the absorption and radiation of heat in the atmosphere, only carbon dioxide is uniformly mixed with the air at all heights which we are likely to be dealing with; it will not be considered further here. The vertical distributions of water vapour and ozone are of great interest, particularly when considered together. Water vapour, originating at ground level, usually decreases rather rapidly with increasing height, particularly in the lower stratosphere. This leads to extremely low concentrations at a height of about 15 km. On the other hand, ozone, being formed by the action of solar ultra-violet radiation at a height of 30 km or more, decreases in concentration downwards. We find, therefore, ozone diffusing downwards and water vapour diffusing upwards through the same region of the atmosphere, but, as we shall see, with very different lapse rates.

Water vapour

The standard hygrometers which are used to measure the humidity from free balloons are only satisfactory at temperatures above about 235°K, and our knowledge of the humidity at high levels in the atmosphere is almost entirely dependent on measurements made with frost-point hygrometers carried on aircraft. The work of the Meteorological Research Flight of the British Meteorological Office is notable for the very large number of measurements made from Mosquito aircraft to a height of about 12 km and more recently from Canberra aircraft to 15 km. Most unfortunately, hardly any measurements having similar accuracy have been made in other parts of the world. However, at the present time Dr A. W. Brewer is in north Norway making such measurements with the kind co-operation of the Norwegian Air Force and I had hoped that some results might have been available in time to report them at this Discussion (see note at end of paper).

The remarkable accuracy of these measurements has been demonstrated by making simultaneous measurements from two aircraft while flying in close formation (Shellard 1950), the agreement in the frost-points being usually better than ± 1°C. The frost-point hygrometers used can measure the humidity of very dry air better than any other type of hygrometer, but even with these instruments it is not possible to measure frost-points lower than about 190°K owing to the deposit being in a glassy, rather than crystalline, form and therefore invisible. The frost-point may be raised by compressing the air, but with normal compressors the water vapour coming from the surfaces would entirely invalidate the results.

With jet aircraft, however, it is possible to use air from the engine compressor which delivers such very great amounts of compressed air that the water vapour coming from surfaces is negligible. By this method the actual frost-point measured by the instrument may be raised some 12° C above that of the outside air so that frost-points equivalent to 180° K in the free air may be measured accurately. This is very important, since the lowest frost-points measured are about 188° K.

By the kind permission of the Director of the Meteorological Office I am able to show the results of twenty-one ascents by the Meteorological Research Flight in Canberra aircraft over southern England. These are given in figure 24, which gives the frost-points at various pressures relative to the tropopause. The amount of water vapour in grams per cubic metre is also given. I would call attention to two points: (*a*) The extraordinary dryness of the air at about 15 km with less than 1 mg of water vapour/m³. Owing to this dryness, the greatest care has to be taken to ensure that the amount of water vapour coming from the surfaces of the pipes, etc., through which the air must pass is extremely small. (*b*) The fact that the frost-points at 15 km are as low as the lowest air temperatures measured in the upper troposphere near the equator.

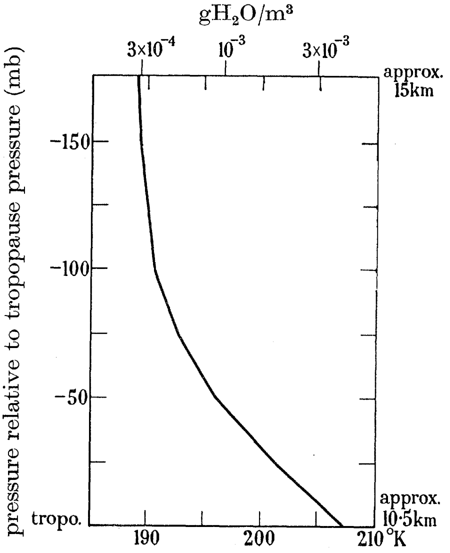


FIGURE 24. Frost-points and water-vapour content of the lower stratosphere. Mean values from twenty-one flights in southern England by the Meteorological Research Flight, Meteorological Office.

OZONE

There is little doubt that the main source of ozone in the atmosphere is due to photochemical processes in the presence of solar ultra-violet radiation in the upper atmosphere. Since no other process such as rising and falling currents or advection can increase the ozone/air ratio, we may safely place the level of the main chemical action at that of the maximum ozone/air ratio, i.e. somewhat above 30 km. The ozone which diffuses to lower levels will be shielded from the effects of sunlight by the ozone above, and it is probably very stable, though that which reaches the surface of the earth will be quickly decomposed by contact with oxidizable material. Thus probably only a small part of the ozone in the atmosphere is in chemical equilibrium under the action of sunlight and much of the variations in total quantity which are found (i.e. the annual variation and the day-to-day variations which are associated so closely with the meteorological conditions) must be due to other causes such as advection and vertical movements of the air in the stratosphere. The chemical measurements which have been made from aircraft indicate that some 8 % of the total ozone is in the troposphere and that this proportion is roughly the same whatever the total amount of ozone.

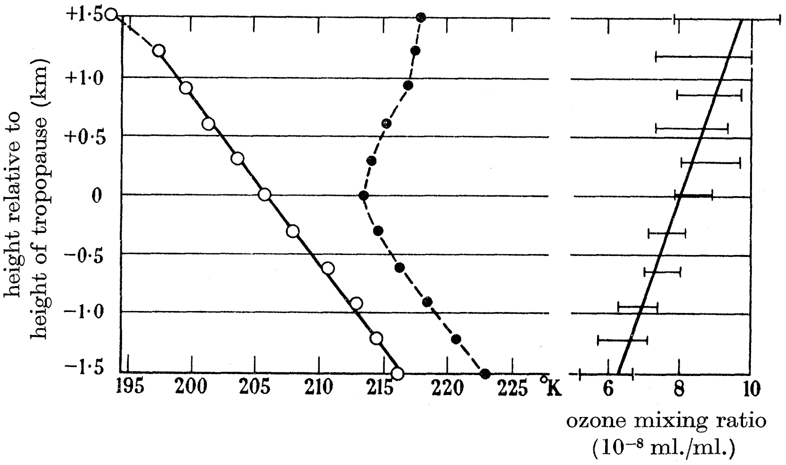


FIGURE 25. Average values of the ozone/air ratio, air temperature (○) and frost-point (●) in the upper troposphere and lower stratosphere. Results from thirteen flights by the Meteorological Research Flight over southern England. After R. H. Kay.

The vertical distribution of ozone has been measured in the following ways:

(1) By chemical methods with apparatus carried on aircraft.

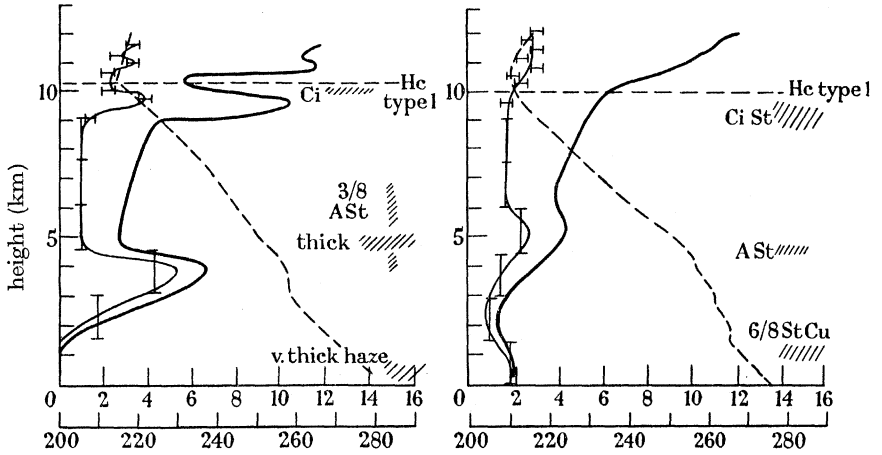
(2) By observations of the earth's shadow on the partially eclipsed moon.

(3) By spectroscopic measurements of sunlight with apparatus carried on free balloons or rockets and which therefore give the amount of ozone above the instrument at any height, from which the concentration at any level must be deduced.

(4) By the Götz method using spectroscopic measurements of the zenith sky light when the sun is low.

Each of these methods has advantages and disadvantages. The Götz method is simple and many measurements can easily be obtained provided the atmosphere is clear, but there is some uncertainty in calculating the distribution from the observations. The lunar eclipse method, of course, suffers from the small number of observations that can be obtained, but allows the distribution to be obtained for various latitudes. A spectroscope carried on a rocket or balloon probably gives the best accuracy for the upper part of the ozone region, but is inaccurate for the lower part since the value depends on small differences between large quantities. The chemical method allows the distribution in the first 15 km to be determined fairly accurately, but has not been used above this level.

As a result of such measurements we now know that there is a maximum ozone concentration about 20 to 25 km, while the maximum ozone/air ratio is about 30 to 35 km. This must also be the level where the production of ozone is greatest. About 8 % of the total ozone is probably in the troposphere in middle latitudes, but this is not uniformly distributed. Figure 26 shows the results of two ascents in which maxima are shown, but it must be remembered that the measurements are taken on aircraft and that there is a large horizontal motion. Figure 25 shows the mean values from all the flights.



12 November 1952
15.00 to 16.00 G.M.T., East Anglia
Oxford $O_3 = 0{\cdot}190$ cm
total O_3 below $11\frac{3}{4}$ km $= 0{\cdot}024$ cm

13 February 1953
14.00 to 15.00 G.M.T., Boscombe Down
Oxford $O_3 = 0{\cdot}294$ cm
total O_3 below $12\frac{1}{2}$ km $= 0{\cdot}018$ cm

upper scale: ——, O_3 (10^{-8} ml./ml.); ——, O_3 (10^{-3} cm/km)
lower scale: – – – –, air temperature (°K)

FIGURE 26. Values of ozone content, ozone/air ratio, air temperature and frost-point over southern England, on 12 November 1952 and 13 February 1953. From ascents by Meteorological Research Flight. After R. H. Kay.

VERTICAL DISTRIBUTION OF WATER VAPOUR AND OZONE IN THE LOWER STRATOSPHERE

The only likely way so far suggested by which the amount of water vapour in the stratospheric air could have been reduced to so low a value is to suppose that this air has all passed at some time through the very cold region of the upper troposphere and lower stratosphere near the equator and that the greater part of the water vapour had been condensed and had fallen out and that little or no water vapour had been able to enter the air since then. The lowest frost-points which have been measured in the stratosphere in middle latitudes up to the present time are just about equal to the lowest air temperatures measured anywhere in the atmosphere. The measurements from Canberra aircraft over England indicate that the further decrease of frost-point with height is small at about 15 km, and it may well be that this is the driest air anywhere in the atmosphere.

It has been suggested that water vapour is decomposed at very great heights in the atmosphere under the action of solar radiation, but it is difficult to see how water vapour could be transported upwards sufficiently quickly through the region of strong positive temperature gradient around 40 km or why the form of the water-vapour curve should be that shown in figure 27.

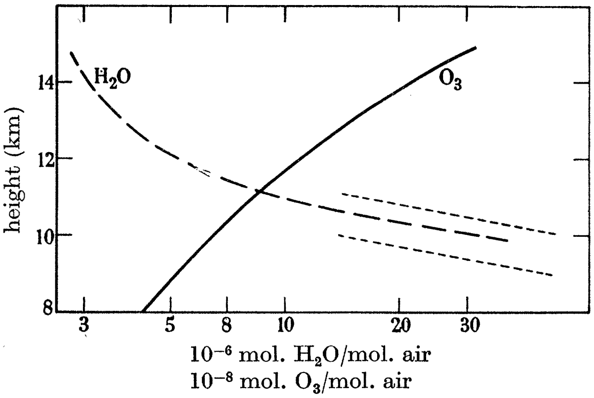


FIGURE 27. Ozone/air ratio and water vapour/air ratio in the lower stratosphere. Average height of the tropopause approx. 10 km. Ozone values after R. H. Kay; water-vapour values after Murgatroyd *et al.* Dashed lines water vapour/air ratio for high and low tropopauses after Bannon, Frith & Shellard (1952).

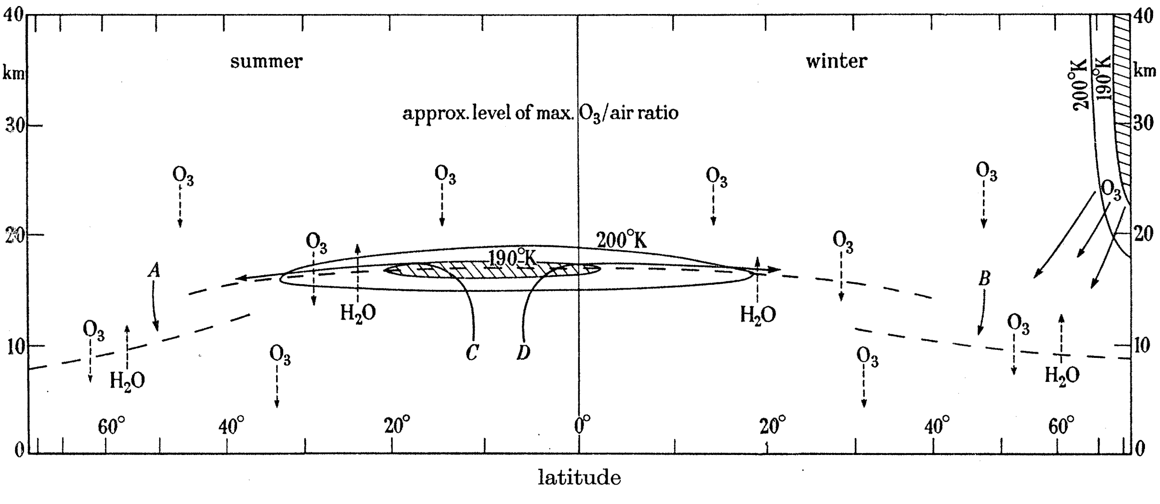


FIGURE 28. Cross-section of the atmosphere, equator to pole for summer and winter, showing regions of lowest air temperature and height of tropopause together with suggested paths of the air entering and leaving the stratosphere and the upward and downward diffusion of water vapour and ozone, respectively.

Figure 28 shows the regions of lowest temperatures in the atmosphere and the average levels of the tropopause. The equatorial belt of very cold air is only a few kilometres thick and is limited to about 20° in latitude. There is a cold pool of air over the winter pole during the late winter months, but it probably plays little part in drying the whole stratosphere though it may well be the cause of the rapid increase in total ozone in early spring in high latitudes by causing sinking of the air which carries ozone-rich air to lower levels.

Water vapour and ozone must be diffusing upwards and downwards respectively in the atmosphere as indicated symbolically by the dotted arrows of figure 28. Within the troposphere the decrease of water vapour upwards is primarily due to condensation and precipitation. Within the stratosphere this cause ceases to act, but we find the water-vapour gradient to be slightly steeper in the lower stratosphere than in the troposphere. It is difficult to explain the form of the water-vapour curve of figure 27 except as the result of upward diffusion of water vapour opposed by a slow sinking of very dry air from above as indicated by the arrows A, B (figure 28). Such a sinking would also account for the great difference in the gradients of ozone and water vapour just above the tropopause.

If there is such a slow sinking of air in middle latitudes from the stratosphere into the troposphere it must be balanced by a reverse current from troposphere to stratosphere elsewhere. The dryness of the stratosphere would indicate that this can only be in the very cold region near the equator. The actual flow might be as indicated by the arrows C, D (figure 28). The flow cannot be along the under side of the tropopause since eddy diffusion would quickly increase the water-vapour content of the air, nor is it likely to move upward rapidly in the region of strong positive temperature gradient immediately above the cold region.

Again it must be emphasized that our knowledge of the humidity of the stratosphere is confined to middle latitudes and that only up to 15 km. Further observations are urgently required.

Figures 24, 25, 26 and 27 are reproduced by the kind permission of the Director of the Meteorological Office from data obtained by the Meteorological Research Flight.

Note added 4 *July* 1955. The first results of the measurements made by Dr A. W. Brewer by chemical means of the amount of ozone in the air in northern Norway, with the generous help of the Norwegian Air Force, have just been obtained, and Dr Brewer has kindly made them available to me. They indicate that the amount of ozone in the troposphere is much the same as in middle latitudes, but a marked increase was found immediately on entering the stratosphere. It will be noticed that this is markedly different from the results given by Dr Kay for southern England which have been used in the foregoing discussion of the circulation of the air in the stratosphere.

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Thermal radiation in the upper atmosphere

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Atmospheric radiation calculations usually assume a Boltzmann distribution of molecules among the vibrational and rotational energy levels. At the low pressures encountered high in the earth's atmosphere, the collision rate is insufficient to maintain such a distribution. An equation of transfer is derived, for a vibration-rotation band, which does not assume a Boltzmann distribution among the vibrational levels. From this is derived an equation for the heating rate due to the band in a plane-stratified atmosphere. It is shown that the heating rate per unit mass tends to zero with the pressure, because of the departure from a Boltzmann distribution, which becomes serious above about 75 km. A method of solving the equation for the heating rate is described, and is applied to a model of the 15μ carbon dioxide band as an example.

The effect of departures from a Boltzmann distribution among the rotational levels is also considered, and it is shown to be unimportant for vibration-rotation bands, but to limit computations on the water-vapour rotation band to heights less than about 90 km.

1. INTRODUCTION

In the lower atmosphere the radiation balance is controlled by direct solar heating and by absorption and emission in the vibration-rotation and rotation bands of minor polyatomic constituents, principally water vapour, carbon dioxide and ozone. Calculations of the radiation balance always make use of Kirchhoff's law, which is equivalent to assuming that the relevant energy levels are populated according to Boltzmann's law. Similar methods have been used by Gowan (1947) up to 55 km and Godfrey & Price (1937) above 100 km, from which it appears that this long-wave absorption and emission will always be important in the atmosphere up to those heights at which the polyatomic constituents are decomposed.

Spitzer (1949, p. 213), in a discussion of upper atmospheric temperatures, has drawn attention to the fact that at low pressures an assumption of Kirchhoff's law is invalid because the collision frequency may be too small to preserve a Boltzmann distribution among the energy levels in the presence of the radiation field, which tends to destroy it. This situation has been investigated by Milne (1930) and subsequent writers for stellar atmospheres, but no quantitative treatment has been given of the consequences in the earth's atmosphere.

In §§ 2 and 3 of this paper we shall develop a method for computing heating rates for a vibration-rotation band without using Kirchhoff's law, but assuming a