The chemistry of the stratosphere and its pollution

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In recent years, there has been growing concern about the possible consequences—for health and climate—of the depletion of the ozone in the atmosphere by the cumulative effects of aerosol propellents and the exhaust fumes of supersonic aircraft. This review shows that while the basic chemical reactions involved are relatively simple, the assessment of their consequences demands fuller knowledge of atmospheric processes and of the biological effects of prolonged exposure to intensified ultraviolet radiation.

In the last few years, concern about air pollution has extended from the more obvious effects at ground level to consideration of the stratosphere, and particularly to possible depletion of the ozone that is concentrated in this region. This interest stems partly from possible consequential climatic changes, but mainly from the increased amounts of ultraviolet light with wavelengths between 290 and 320 nm (uv-B) which would reach ground level as a result of ozone depletion. Uv-B causes sunburn and prolonged exposure can produce skin cancer, particularly in fair-skinned people [1].

The potential pollutants discussed to date in this context are: (i) nitrogen oxides released directly into the stratosphere by supersonic aircraft; (ii) chlorofluoromethanes (CFMs) released at ground level from aerosol sprays, refrigerators, and foam blowing; and (iii) greatly increased use of nitrate fertilisers.

The accurate assessment of ozone depletion by these substances—which is fundamental to a critical assessment of their potential hazard—requires a detailed understanding of the chemistry of the stratosphere and of the transport processes in the atmosphere. Until the last decade, interest in meteorology and in ionospheric physics had caused atmospheric chemistry to be a relatively neglected subject. This neglect must now be made good.

The Earth's atmosphere

Our atmosphere is conventionally divided into regions, the boundaries of which correspond to temperature minima or maxima (figure 1). The troposphere extends from ground level to an altitude of about 16 km (50 000 ft) in the tropics and 8 km (25 000 ft) near the poles, its upper boundary being the tropopause at which temperature has fallen to about 210°K (−80°F). Above this is the stratosphere, in which the temperature rises to a maximum value of about 280°K (45°F) at the stratopause. Between this and the ionosphere is the mesosphere, another region of falling temperature, extending from approximately 50 to 80 km (30 to 50 miles), above which ionic rather than neutral chemical processes predominate.

The atmospheric pressure decreases approximately exponentially with increasing altitude, falling to about 1/10th atm. at the tropopause and 1/1000th atm. at the top of the stratosphere (figure 2). Up to this altitude, gases are transported predominantly by movement of air masses (eddy mixing) rather than by molecular diffusion; gravitational settling-out is negligible.
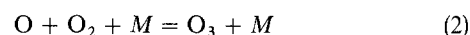
In the troposphere, this mixing is rapid because warmer air tends to rise and be replaced by cooler air from above. Gases are redistributed along the lines of latitude in a matter of months, and between the Northern and Southern hemispheres over period of about two years. Vertical circulation in the stratosphere is much slower because the cooler, denser air is below. This situation resembles the temperature inversions near

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ground level which can produce fogs and smogs over London, Los Angeles, and other natural basins. The tropopause and the region a few kilometres above it can be regarded as a barrier where the rate of vertical transport drops by more than an order of magnitude. Unlike the troposphere, from which rain rapidly removes water soluble substances, the stratosphere is virtually cloudless.
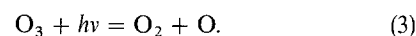
Ozone chemistry

Almost all the ozone is in the stratosphere (figure 2), but although it is customary to speak of an ozone layer, the concentration of ozone in fact never exceeds a few parts per million. The total amount of ozone in a vertical column corresponds to only about 3 mm of pure ozone at STP (figure 3).

The basic mechanism of the formation of ozone from oxygen was suggested by S. Chapman in 1930 [2]. Molecular oxygen is photolysed by light of wavelength less than 242 nm to yield oxygen atoms; this occurs mainly in a region of very weak absorption by oxygen. The oxygen atoms then combine rapidly with molecular oxygen to form ozone, a process which requires the presence of a third body (M) to remove excess energy.

$$O_2 + h\nu = O + O \tag{1}$$

$$O + O_2 + M = O_3 + M \tag{2}$$

Ozone is very rapidly photolysed, both in the region of the strong continuum which prevents ultraviolet light below 290 nm from reaching ground level, and by visible light.

$$O_3 + h\nu = O_2 + O. \tag{3}$$

Ozone is also removed by reaction with atomic oxygen to regenerate molecular oxygen

$$O + O_3 = O_2 + O_2. \tag{4}$$

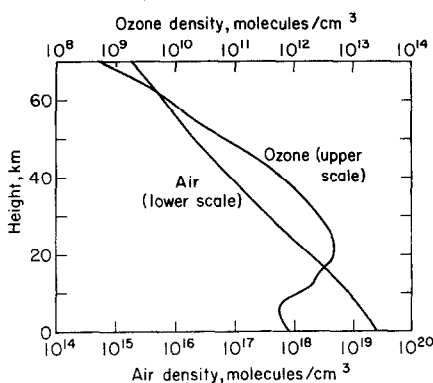Figure 1 The temperature of the atmosphere as a function of altitude [1].

Figure 2 The air density and ozone density in mid-latitudes as a function of altitude. Note that the density scales differ by a factor of 10^6 and would be the same for 1 ppm of ozone [1].

If we group O_3 and O together as 'odd oxygen', it can be seen that the rapid processes (2) and (3) merely interconvert the two forms of odd oxygen, whereas the much slower processes (1) and (4) form and remove odd oxygen. In the stratosphere, the balance between (2) and (3) is achieved within a minute or less, whereas the time-scale for (1) and (4) is typically months. The solar energy absorbed by ozone in process (3) heats the stratosphere, giving the temperature inversion responsible for its stability.

Reaction (4) is unusually slow for a highly exothermic reaction ($\Delta H = -390\,\text{kJ mol}^{-1}$) involving a free atom; it has an activation energy of 19 kJ mol^{-1}. A comparison of the calculated rate of process (1) with the observed ozone densities shows that reaction (4) accounts for only one-fifth of the odd oxygen removal in the atmosphere [3]. The remaining four-fifths is largely accounted for by catalytic cycles in which a species X abstracts an oxygen atom from ozone and is then regenerated in a reaction with atomic oxygen

$$X + O_3 = XO + O_2 \qquad (5)$$

$$XO + O = X + O_2 \qquad (6)$$

$$\overline{O + O_3 = O_2 + O_2.} \qquad (5) + (6)$$
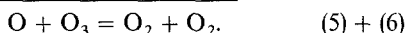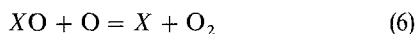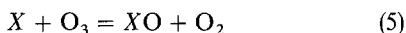
Such cycles have been recognised for $X = $ H, HO, NO, Cl, and Br. They achieve the same result as reaction (4) but with smaller activation energies.
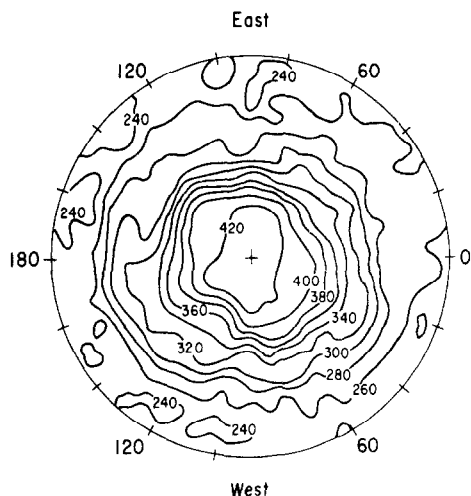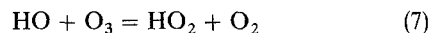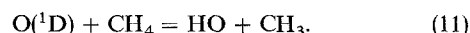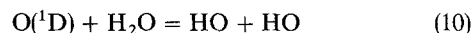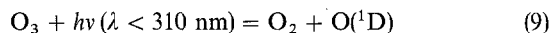

Figure 3 Total ozone cover in the northern hemisphere May 1969, measured from Nimbus IV satellite. Units are 10^{-5} m ozone at STP [15].

In 1950, D. R. Bates and M. Nicolet [4] recognised the importance of the H, HO, and HO$_2$ radicals. For instance, with $X = $ HO we have

$$HO + O_3 = HO_2 + O_2 \qquad (7)$$

$$HO_2 + O = HO + O_2 \qquad (8)$$

$$\overline{O + O_3 = O_2 + O_2.} \qquad (7) + (8)$$
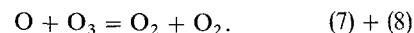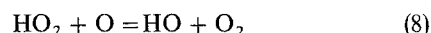
These radicals are formed in the stratosphere by the photolysis of water vapour and by the attack on water vapour and methane by electronically excited oxygen atoms (O(^{1}D)) from the short-wavelength photolysis of ozone:

$$O_3 + hv\,(\lambda < 310\text{ nm}) = O_2 + O(^1D) \qquad (9)$$

$$O(^1D) + H_2O = HO + HO \qquad (10)$$

$$O(^1D) + CH_4 = HO + CH_3. \qquad (11)$$

Hydrogenous radicals are destroyed predominantly by the process

$$HO + HO_2 = H_2O + O_2. \qquad (12)$$
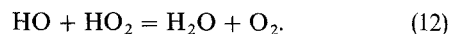
Such radicals account for about 15 per cent of the ozone removal.

In 1970, P. J. Crutzen [5] first pointed out the importance of natural nitrogen oxides in the destruction of odd oxygen ($X = $ NO). The oxides involved are nitric oxide (NO), and nitrogen dioxide (NO$_2$).

$$NO + O_3 = NO_2 + O_2 \qquad (13)$$

$$NO_2 + O = NO + O_2 \qquad (14)$$

$$\overline{O + O_3 = O_2 + O_2.} \qquad (13) + (14)$$
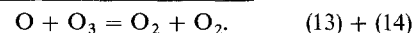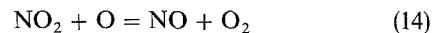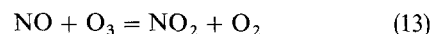
This effect is reduced by day because ultraviolet light rapidly decomposes NO$_2$, giving the 'do nothing' cycle:

$$NO_2 + hv = NO + O \qquad (15)$$

$$NO + O_3 = NO_2 + O_2 \qquad (13)$$

$$O + O_2 + M = O_3 + M. \qquad (2)$$
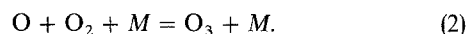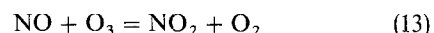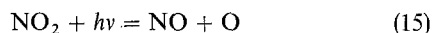
The main source of NO in the stratosphere is nitrous oxide; this is produced at the surface by denitrifying bacteria and rises to the stratosphere. There most is photolysed by ultraviolet light to yield nitrogen:

$$N_2O + hv = N_2 + O \qquad (16)$$
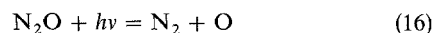
but about 1 per cent reacts with O(^{1}D) from the ozone photolysis, where one path yields nitric oxide

$$O(^1D) + N_2O = NO + NO \qquad (17)$$

$$= N_2 + O_2. \qquad (18)$$
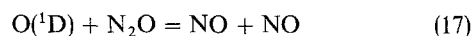
Ion-molecule reactions in the higher atmosphere provide a minor source of nitrogen oxides.

Nitrogen dioxide combines with hydroxyl radicals to form nitric acid, from which it is slowly regenerated by photolysis:

$$HO + NO_2 + M = HNO_3 + M \qquad (19)$$

$$HNO_3 + hv = HO + NO_2. \qquad (20)$$
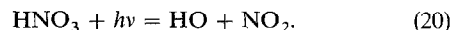
Nitric acid is transported slowly downwards towards the troposphere, where it is removed in rain, thereby returning nitrate to the soil. It is currently believed that the natural nitrogen oxide cycle removes about 60 per cent of the ozone [1,3].

Nitrogen oxide pollution

The projected ten-fold increase in the use of nitrate fertilisers by the year 2000 might, if realised, generate enough additional N$_2$O to reduce the ozone cover significantly. Figures between 1 and 20 per cent have been suggested at conferences. This wide range stresses our poor knowledge of the natural N$_2$O cycle; for instance, whether the oceans are a major source.
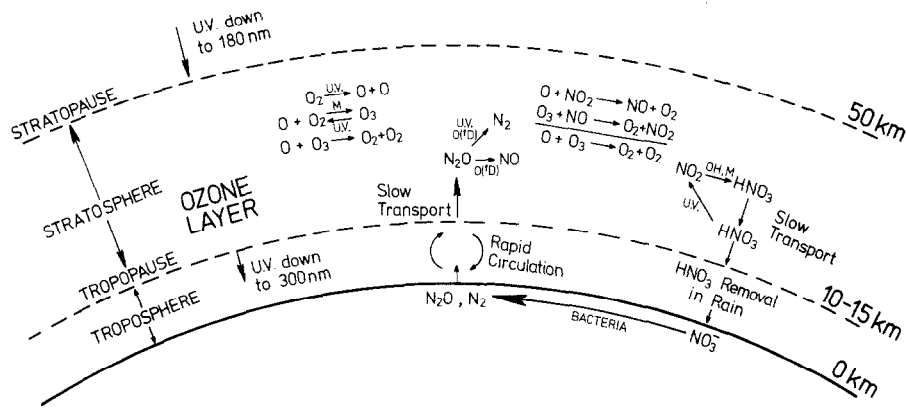
Figure 4   Ozone formation and removal processes in the unperturbed atmosphere.

NO and NO_2 released at ground level or in the troposphere do not reach the stratosphere in significant amounts, because NO_2 is efficiently removed by 'rain out'. However, supersonic aircraft and some subsonic aircraft using polar routes in winter, enter the stratosphere; their exhausts release NO and NO_2 directly into the stratosphere, where the residence time is several years. The Climatic Impact Assessment Program in the United States and the Committee on the Meteorological Effects of Supersonic Aircraft in the United Kingdom examined the consequences of this in detail. They deduced respectively that 100 Concordes flying 7 hr/day would deplete the ozone cover by 1 and 0·2 per cent.

Halogen pollution

It has been known for several years [6] that the chlorofluoromethanes (CFMs) $CFCl_3$ (or F-11) and CF_2Cl_2 (or F-12)—which are extensively used as aerosol propellants, refrigerants, and foam-blowing agents—are accumulating in the atmosphere at rates close to their release rates. No significant destruction processes for these compounds on land, in the oceans, or in the troposphere have been discovered. In 1974, F. S. Rowland and M. J. Molina [7] pointed out that these compounds would be transported upwards through the stratosphere to altitudes above 25 km; there they would be decomposed by far ultraviolet light (between 180 and 220 nm) or by reaction with $O(^1D)$ to yield chlorine atoms which can destroy ozone. The proposed aluminium powder-ammonium perchlorate propellent of the American Space Shuttle and natural chlorine sources (volcanoes, salt spray) would not remove significant amounts of ozone [8].

$$Cl + O_3 = ClO + O_2 \qquad (21)$$

$$ClO + O = Cl + O_2 \qquad (22)$$

$$O + O_3 = O_2 + O_2. \qquad (21) + (22)$$
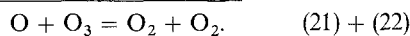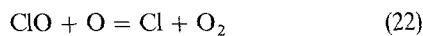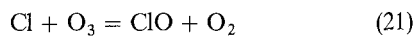
Chlorine atoms are rendered inert by reaction with methane to form HCl, which is eventually transported downwards to the tropopause where it is removed in rain. During this period, chlorine atoms are regenerated many times by attack of hydroxyl radicals.

$$Cl + CH_4 = HCl + CH_3 \qquad (23)$$

$$OH + HCl = H_2O + Cl. \qquad (24)$$
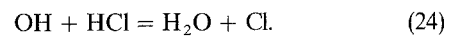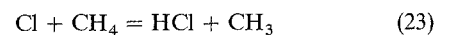
Comparison of figures 4 and 5 brings out the similarity to the nitrogen oxide cycle. A more detailed examination shows that these cycles interact, both by the rapid reaction

$$ClO + NO = Cl + NO_2 \qquad (25)$$
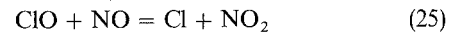
and by a combination reaction (26) to form chlorine nitrate, which is only slowly decomposed by ultraviolet light or attack by free atoms:

$$ClO + NO_2 + M = ClNO_3 + M. \qquad (26)$$

Both these reactions reduce the effect of stratospheric chlorine, the latter by 'tying up' the active species of two destruction cycles.

The calculated stratospheric residence times for F-11 and F-12 are about 5 and 10 years respectively. As the greater air density at lower altitudes means that only 10 per cent of these compounds would be in the stratosphere at steady state, their total atmospheric residence times would be 50–100 years in the absence of other removal processes. For this reason the exponential growth in the release of F-11 and F-12 from 5 and 49 million lbs respectively in 1948 to 666 and 844 million lbs in 1973 [9] gave cause for concern. More recent figures suggest a slight fall in demand, but current calculations indicate that continued release of CFMs at the 1973 rate would eventually produce about 7 per cent depletion in the ozone cover. During this time their tropospheric concentrations would rise from the present levels of c. 1 in 10^{10} to about 1 in 10^9 [10].
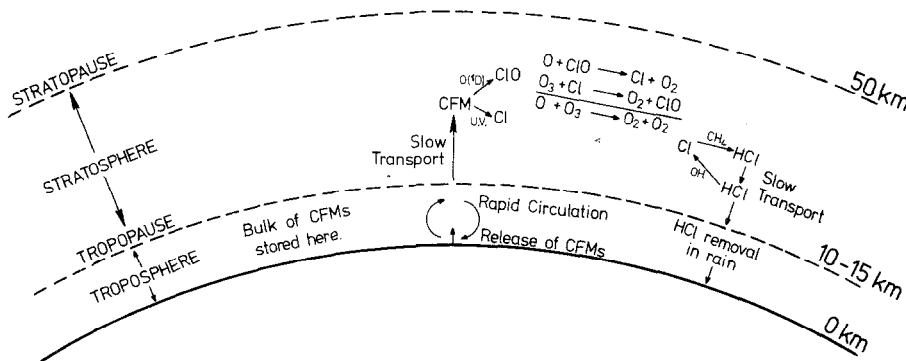
Figure 5   Simplified atmospheric behaviour of the chlorofluoromethanes.

Atmospheric modelling

So far, we have considered the stratosphere in terms of a steady-state system of chemical reactions. This is a fair approximation for altitudes between 30 and 50 km, but at lower altitudes the rates of many chemical processes become comparable with transport. The solution of the combined equations for chemical reaction and transport involves extensive computing, as can be seen from the number of species and the limited set of reactions given here. To carry out a full calculation on a three-dimensional basis—using altitude, latitude, and longitude as variables—would be prohibitively complex, and the few two-dimensional calculations made to date (in which longitude is omitted) use only a limited set of chemical reactions. Most of the calculations have therefore been one-dimensional, with altitude as the sole variable.

In addition to laboratory data on photochemistry and reaction rates at the appropriate temperature, modelling calculations require solar irradiances and eddy transport coefficients. Both are normally determined from balloon or rocket flights, the latter by grab sampling or cryo-trapping to determine vertical profiles of methane or nitrous oxide. Both these compounds are generated at ground level and are removed by photolysis or reaction in the stratosphere [11]. The spread of debris from nuclear tests in the atmosphere has also provided data on transport processes.

Infra-red spectroscopy (using the setting sun as a source) and chemiluminescence techniques, have provided in situ measurements of NO, NO_2, and HNO_3 which show relative proportions of these species in fair agreement with modelling calculations [12]. The predicted decrease in CFM concentrations above the tropopause, as they are transported up to altitudes where they are decomposed, has also been observed.

The active species O and HO have been measured in the stratosphere by resonance fluorescence [13] but, as with other experiments cited above, it is hard to know how far measurements at one or two places are characteristic of the atmosphere as a whole. HO is an important species because an increase in its concentration decreases the effect of NO and NO_2 by reaction (19), but increases the effect of Cl and ClO by reaction (24).

Ozone measurements

There are extensive data on the distribution and fluctuations of the stratospheric ozone. These come from ground-based [14] or satellite [15] measurements of its absorption spectrum; they are mainly of total layer thickness but give some information about its vertical distribution. Vertical profiles can be measured in situ with an electrochemical probe.

Although the bulk of the ozone is formed in tropical latitudes at altitudes between 25 and 35 km, the largest layer thicknesses are found near the poles (figure 3). The average ozone cover over Northern Scotland is 5 per cent more than over Southern England. Except near the tropics, the ozone burden shows large annual fluctuations 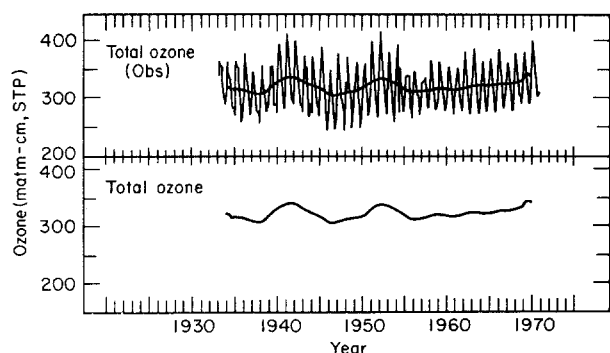on which are superimposed longer term variations which are believed, but not proved, to be related to the sunspot cycle. Examination of figure 6 shows that many years of careful measurement will be needed to detect slow changes in the ozone cover.

Effects of ozone depletion

Most concern about the effects of ozone depletion have centred on skin cancer, which can arise from exposure to uv-B over long periods of time, typically 25 years. A 1 per cent decrease in ozone cover would give a 2 per cent increase in uv-B radiation. Statistics based on the dependence of skin cancer incidence on latitude in the United States suggest that this would cause a corresponding increase in skin cancer [1] amounting to 10000 additional cases per year in the United States [3]. These figures refer to basal-cell and squamous-cell skin cancers, which are very rarely fatal. The more dangerous, but fortunately rare, malignant melanoma also increases towards the tropics, but a link with uv-B is not clearly established. Very little is known about other biological effects of uv-B radiation.

With each successive year seeming to break some long-standing weather record, concern about climatic effects is natural. The accumulation of CFMs will move the ozone layer to lower altitudes, but it is unlikely that this will have much effect on the denser lower layers. The CFMs also have strong infrared transitions which could give a 'greenhouse' effect, but this is likely to be small compared with the trapping of solar energy by the vastly greater amounts of carbon dioxide released from combustion processes.

Conclusion

We have seen that excessive use of chlorofluoromethanes as aerosol propellents, or a great increase in stratospheric flying, could cause a depletion of the ozone layer. It must be stressed, however, that these calculated depletions involve considerable uncertainties, probably a factor of four, due to our limited understanding of circulation processes and atmospheric chemistry, and the limited precision of laboratory data [10]. More research is needed in particular areas to narrow these limits to the point where well-founded decisions can be taken as to the need to limit stratospheric pollution. The biological and climatological effects of ozone depletion are far from adequately understood, and much effort is needed here to establish what would be an acceptable level of ozone depletion.

Figure 6   Long-term variation in total ozone cover in the Northern hemisphere. The lower diagram is an 11-year running mean [16].

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