

# Atmospheric chemistry

R. P. Wayne

*This paper reviews some topics in atmospheric chemistry that have aroused interest or in which substantial progress has been made recently. In order to place the material in context, the earlier sections of the paper present the underlying principles of atmospheric physics and chemistry. Amongst the subjects treated are ozone in the stratosphere, and the possibility that man's activities might interfere with the amount present. The Antarctic ozone 'hole' seems to be a consequence of man's release of chlorine-containing compounds, and current interpretations of the phenomenon are presented. Tropospheric chemistry involves the oxidation of organic and inorganic 'fuels'. Pollution of the troposphere provides more of these fuels; photochemical smog results from enhanced oxidation of organic compounds, while acid rain is a consequence of the oxidation of inorganic nitrogen and sulphur compounds. Combustion processes involving fossil fuels are implicated in many of the worst kinds of pollution that man inflicts on the atmosphere. Increased radiation trapping by additional burdens of trace gases makes up the 'greenhouse effect' that is currently the*

*subject of much debate. In this review, the question of greenhouse heating is briefly considered in relation to the more general aspects of atmospheric chemistry.*

*Certain threads run through the whole of this paper. An attempt is made to present a unified view of atmospheric chemistry, in which a few basic principles are common to many of the processes. Radicals such as OH and HO<sub>2</sub>, and atoms such as O, are important intermediates, and the oxides of nitrogen play key roles. Biological processes release many of the trace gases that make the Earth's atmospheric chemistry so rich. Concentrations of trace gases in the atmosphere are increasing on a relatively short time-scale, and the overall oxidizing capacity of the atmosphere seems to be changing. Particles in the atmosphere play an important part in atmospheric chemistry that must not be neglected just because of our ignorance of the details of the processes. The paper ends with an illustration of how the biota could even influence cloudiness through a combination of many of the processes previously explained, including oxidation steps and chemistry within cloud droplets.*

## Introduction

Knowledge of the atmospheres of Earth and the planets has improved dramatically over recent decades. Investigations of the compositions of the atmospheres, including the trace gases present, has been greatly facilitated by the use of satellites, rockets, balloons and aircraft to take instruments to remote regions of our own atmosphere and to other planets of the solar system. Alongside this work, laboratory investigations of the mechanisms and rates of chemical transformations has enabled quantitative interpretation of atmospheric chemistry. Linking the atmospheric measurements and the laboratory studies are the so-called models, which provide numerical simulation of the chemistry and physics of the real atmosphere. The speed and power of modern computers has permitted the development of sophisticated models that can be used diagnostically to understand the atmospheric observations and to predict prognostically what future changes the atmosphere might undergo.

Recent developments in atmospheric chemistry include the startling discovery<sup>6,24,30</sup> of the 'Antarctic ozone hole', a heightened awareness<sup>10</sup> of the importance of surface phenomena in the Earth's atmospheric chemistry, and a growing emphasis<sup>5,13</sup> on the way in which the composition of the Earth's atmosphere is changing. The Voyager 2 spacecraft completed its proposed odyssey through the solar system by visiting Uranus and Neptune, and our understanding of the atmospheres of the outermost planets and their satellites (including Triton) improved immeasurably<sup>28</sup> with the encounters. Comet Halley was investigated in 1986 by an 'Armada' of spacecraft and studies of the 'atmospheric' gases in the coma and tail of the comet provided much new insight<sup>28</sup> into the composition and chemistry of primitive bodies in the solar system. Atmospheric science in general, and atmospheric chemistry in particular, has never been more exciting.

This article cannot hope to cover all the new discoveries and all the new interpretations. A fuller account can be found in a recent book<sup>28</sup> by the present author. I shall concentrate here on some aspects of the changing composition of the Earth's atmosphere. Man's activities, in particular, appear to be leading to an increase in concentration of trace gases in the atmosphere. The changes are occurring not on geological time-scales, but at rates reaching the order of 1% annually. Important gases in this respect include methane (CH<sub>4</sub>), carbon monoxide (CO), nitrous oxide (N<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), chlorofluorocarbons (CFCs) and some sulphur compounds such as sulphur dioxide (SO<sub>2</sub>). Some of the species are a consequence of industrial production or release (e.g. the CFCs), or the burning of fossil fuels (e.g. CO<sub>2</sub> and SO<sub>2</sub>). However, changes in land use and agricultural practice are also important causes of increases of gases such as CH<sub>4</sub> and N<sub>2</sub>O. Biomass burning is another very important contributor to the atmosphere of a variety of trace species.

The effects of the changing composition on atmospheric behaviour encompass a considerable range. The oxidizing capacity of the atmosphere may itself be changing,<sup>5</sup> and with it the capability of the lower atmosphere to 'process' materials released even by natural biological and geological phenomena. As we shall see shortly, the molecule ozone (O<sub>3</sub>) plays a central role

in the atmosphere of the Earth. Ozone at altitudes ranging roughly from 15 to 35 km, in the so-called 'ozone layer', shields living organisms on the surface of the Earth from solar ultraviolet radiation. Much concern exists at present<sup>15,28</sup> about the possible damage to the ozone layer that might follow the release of chemical species such as the CFCs. Ozone nearer the ground<sup>3,4</sup> is less clearly a friend to the biosphere. It is undoubtedly present in relatively unpolluted atmospheres, and is an important component of the oxidizing system that attacks most species which are released from the surface of the continents and the oceans. However, it is a toxic and noxious substance, harmful to animal and vegetable life. Elevated concentrations are produced in photochemical reactions<sup>1,3,4,21,22,28</sup> that follow the release of oxides of nitrogen and unburned hydrocarbons from automobile engines and industrial combustion processes, and ozone is thus a key component of 'photochemical smog'. Many of the chemical compounds that we will discuss are 'greenhouse gases', i.e. they trap solar infra-red radiation<sup>19</sup> in the lower atmosphere, and so increase temperatures. Carbon dioxide is particularly important in this context, but other trace gases<sup>17</sup> act synergistically with it in trapping infra-red radiation. There is a very real risk<sup>18</sup> that the global climate could alter significantly, probably with adverse social and economic consequences. A further complication arises in that gases that trap radiation near the ground and lead to a warming may radiate radiation at greater altitudes and produce cooling. Reduced temperatures in the ozone layer may, in turn, modify the chemistry and extent of ozone destruction. It is evident that the multiple feedbacks between chemical composition, temperature, and the rates of chemical change must be taken into account.

In this article, I shall explore recent progress and discoveries in some of the areas just described. To put the ideas in context, I present first a simplified view of the basic ideas of atmospheric physics and chemistry that underlie the interpretations.

## Basic ideas of atmospheric physics and chemistry<sup>4,21,28</sup>

Throughout the altitude regions that concern us in this review—from the Earth's surface to approximately 50 km—the major gases of the Earth's atmosphere show a constant composition, and are well mixed. Nitrogen makes up 78.1% of the mixture in dry air, oxygen 20.9%, and argon 0.93%, all percentages being expressed by volume. Carbon dioxide makes up 0.035% by volume of the contemporary atmosphere, having increased from about 0.032% in 1960 and 0.028% in the pre-industrial atmosphere. Water vapour is obviously a variable component of the atmosphere, concentrations ranging from near-zero to as much as 4% in the humid tropics: a typical concentration is 1%. The quantities of gases in the atmosphere are often expressed as volume *mixing ratios*, which are equivalent to the chemists' mole fractions: for example, the present-day carbon dioxide mixing ratio is about 350 parts per million by volume (p.p.m.v.).

The oxygen in the Earth's atmosphere is something of a surprise. The atmospheres of Venus, Earth and Mars appear all to be formed from gases

released from within the planets, and they might be expected to be rather similar. In reality, the atmospheres of our neighbours are made up of 95–97% CO<sub>2</sub>. The differences between Earth and the other two planets are a consequence of life on Earth. Photosynthesis is able to convert carbon dioxide and water to carbohydrate and oxygen. So long as the carbohydrate is buried (and thus does not oxidize), free oxygen can be liberated. No inorganic process is known that could produce more than a tiny fraction of the oxygen in the Earth's present-day atmosphere, yet photosynthesis is able to generate all the oxygen in the geologically insignificant time of about 3000 years. The effects of photosynthesis are evident in diurnal and seasonal fluctuations in atmospheric carbon dioxide concentrations about a mean level: for example, over continental areas there are seasonal fluctuations, with concentrations reaching a peak in winter when photosynthetic activity is weakest. The existence of liquid water on the surface of the Earth, probably throughout the period that life has been present, means that carbonate rocks have been laid down in which much of the initial carbon dioxide inventory has been tied up; the oceans constitute another important reservoir. On hot and dry Venus, where there is no liquid water, most of the carbon dioxide is in the atmosphere, at a total pressure of about 90 Earth atmospheres. On cold Mars, much of the carbon dioxide has condensed on to the surface, and the atmospheric pressure may be controlled by the vapour pressure of carbon dioxide at the temperature of the planetary surface.

One further remark is required concerning the unusual composition of the Earth's atmosphere. Along with the major gases are dozens of minor trace gases, particularly in the lower atmosphere, which are of biological or geological (e.g. volcanic) origin. Many of these gases are organic or reduced inorganic compounds that should be readily oxidized<sup>11</sup> by the large quantities of oxygen present. That the disequilibrium is sustained is also a consequence of biological activity; microbiological processes, in particular, are capable of generating methane (CH<sub>4</sub>), hydrogen sulphide (H<sub>2</sub>S), dimethyl sulphide ((CH<sub>3</sub>)<sub>2</sub>S) and many other reduced compounds. The disequilibrium corresponds to an entropy reduction which is driven by solar energy and which is mediated by the biota.

While some aspects of the chemical composition of the Earth's atmosphere appear at first sight not to respect the laws of physics and chemistry, those laws can nevertheless be applied without difficulty<sup>28</sup> to explain the physical behaviour of the atmosphere. Two particular features require our attention here, the pressure and temperature structure of the atmosphere. The variation of pressure with altitude follows the Boltzmann distribution law, thermal randomization competing with the tendency for gravitational settling of the air molecules. If temperature were constant, the pressure would drop in a simple exponential manner with altitude (the acceleration due to gravity and the effective molecular mass of the well-mixed air are essentially constant in the altitude regions being considered). Temperature changes lead to small deviations from pure exponential behaviour. The characteristic distance over which the pressure drops by a factor  $1e$  is known as the scale height, and it varies from about 8.5 km for a temperature of 290 K (typical of the surface) to 6 km at 210 K (typical of an altitude of about 20 km).

Atmospheric temperature structure is more complex than the pressure structure, but is extremely important in interpreting some aspects of chemical behaviour; the structure itself turns out to be partially dependent on chemistry.

The first problem concerns the temperature at the surface of the planet. A simple thermal equilibrium calculation can be carried out in which the Stefan–Boltzmann  $T^4$  radiation law is used to determine the rate at which energy is radiated to space, and the rate at which energy is received from the Sun is obtained from the incoming solar flux and the overall reflectivity (the albedo) of the planet's surface, atmosphere and clouds. For the Earth, the calculation would suggest a surface temperature of about 256 K. However, the mean surface temperature is measured to be about 288 K. The discrepancy is explained by the existence of radiation trapping in real atmospheres, a phenomenon somewhat imprecisely termed<sup>19</sup> the greenhouse effect. The incoming radiation from the Sun is very roughly characteristic of a black body with a temperature of about 5780 K, and peaks in the fairly short infra-red region where the atmospheric gases are relatively transparent. On the other hand, the Earth's surface, at a temperature of 250–300 K, emits radiation at much longer wavelengths, and various components of the atmosphere, especially water vapour and carbon dioxide, are strong absorbers in this wavelength region. Radiation re-emitted by the absorbers is immediately absorbed by other molecules in the vicinity. As a result, infra-red energy is trapped in the lower atmosphere, and the atmosphere is warmed. Water vapour or carbon dioxide on its own would be a much less efficient trapping medium than the two gases together. The absorption spectrum of each species consists of a series of discrete bands; radiation could escape to space through the non-absorbing spectral 'window' regions. However, the absorption bands of CO<sub>2</sub> match many of the windows in H<sub>2</sub>O, and *vice versa*, so that the windows are effectively stopped up in a synergistic process. The true significance to the greenhouse effect of other trace gases<sup>17</sup> whose atmospheric concentration is increasing (e.g. CH<sub>4</sub>, N<sub>2</sub>O, the CFCs) is that they have further absorptions that stop up the remaining windows, and thus exert a disproportionate effect on greenhouse heating of the lower atmosphere. As pointed out in the Introduction, the radiatively active gases have a rather different effect at high altitudes, where the gases are less dense and are thus optically thin. Emission of radiation from an infra-red-active molecule is now no longer likely to be absorbed by a neighbouring molecule, but rather to be radiated to space. Under these circumstances, there is a cooling of the atmospheric region in which the gases are present.

With the surface temperature explained, it is now necessary to examine the altitude dependence of temperature in the atmosphere. If a hypothetical air packet is lifted to higher altitudes, it will expand and do work on its surroundings. Accordingly, its temperature must fall, and application of simple thermodynamics suffices to calculate the magnitude of the decrease with altitude, the adiabatic lapse rate. For a dry atmosphere, this lapse rate would be 9.8 K km<sup>-1</sup>. The presence of condensable vapours in the atmosphere reduces the lapse rate, because of the latent heat released to the hypothetical air parcel. The lapse rate for air saturated with water vapour near the surface is as low as 4 K km<sup>-1</sup>; in fact, the average lapse rate on Earth is about 6.5 K km<sup>-1</sup>.

Although it is common experience that the air gets colder the higher the altitude, the temperature does not fall indefinitely. At some altitude, usually around 15–20 km, the temperature begins to increase again. This increase is a consequence of absorption of solar ultraviolet radiation by processes that destroy and generate ozone, and that are intimately bound up with the formation of the ozone layer. I shall consider the chemistry involved in the next section. Here I explore the physical consequences of the temperature change.

Near the surface, temperature decreases with increasing altitude, and colder air lies on top of warmer. This is the situation for convection currents to be set up, and the atmospheric region is named the troposphere ('*tropos*' is Greek for 'turning'). The ordinary atmospheric wind and weather systems are set up within the troposphere, and the region is characterized by strong vertical mixing. However, where the temperature begins to rise again with altitude, warmer air lies on top of colder, a situation referred to as a temperature inversion. The atmosphere here is therefore stable, and is characterized by very small vertical mixing. The region is called the stratosphere ('*stratus*' is Latin for 'layered'). The hypothetical boundary between the troposphere and the stratosphere is the tropopause. Figure 1 shows a typical temperature–altitude profile for the Earth's atmosphere, in which the two lowest regions are those just discussed. Above about 50 km, the atmospheric heating becomes too weak to sustain the temperature inversion, and cooling is once again observed in the mesosphere; as the figure shows, temperatures finally increase again at yet higher altitudes. These higher regions are not relevant to this

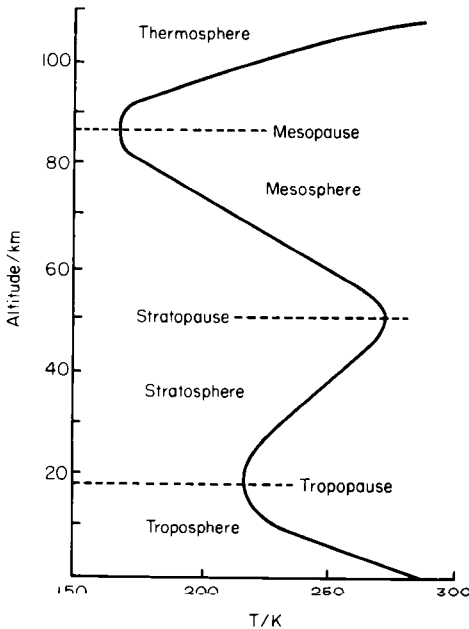


Fig. 1. Temperature–altitude profile for the Earth.<sup>28</sup> The curve shown represents the mean structure for latitude 40°N during June.

review, and will not be discussed further here. The real importance to us of the different regions is the vertical transport of trace compounds. Within the troposphere, individual molecules can traverse the entire depth in periods ranging from minutes to days, while in the stratosphere, the time-scale for transport is of the order of years. Thus compounds that are injected into the stratosphere, or that reach it from the troposphere, are not quickly removed physically, and they can remain available for long periods to participate in chemical changes. An interesting feature of the transport of chemical substances to the stratosphere from the troposphere is that they must pass the lowest temperature point of the tropopause, which thus acts as a 'cold trap' and can remove condensable materials. This cold-trap behaviour is of paramount importance for water vapour; the stratosphere is relatively dry, and much of the water vapour found there is the product of *in-situ* oxidation of non-condensable precursors such as methane.

Chemical changes in the Earth's atmosphere are generally driven by the absorption of ultraviolet (and, to a lesser extent, visible) radiation from the Sun. The atmosphere is often regarded as a giant photochemical reactor. The photon energy of electromagnetic radiation is inversely proportional to the wavelength. In general, the shorter wavelength radiation is absorbed highest in the atmosphere, so that the highest altitudes are also characterized by the highest energy processes. Ion formation, for example, is very important in all regions above the stratopause (c. 50 km). Below the stratopause, photodissociation of molecules to smaller fragments, including atoms and free radicals, becomes the dominant photochemical process. Molecular oxygen,  $O_2$ , is of special interest because it absorbs ultraviolet radiation at much longer wavelengths than any other major constituent of the atmosphere: it absorbs quite strongly for wavelengths ( $\lambda$ ) shorter than 220 nm, and continues to absorb more weakly at longer wavelengths. Oxygen thus plays a very important role in determining the penetration of the shorter wavelength radiation through the stratosphere and below. As we shall see in the next section, the absorption of ultraviolet radiation by oxygen is also the critical step in the formation of ozone ( $O_3$ ) which itself absorbs ultraviolet radiation strongly in the wavelength region 200–300 nm. The atoms and radicals formed by various photodissociation processes in the stratosphere and the troposphere are able to initiate further (thermal) secondary chemical reactions, and it is this suite of processes<sup>26</sup> that effects the important atmospheric chemical transformations.

Although the picture of the atmosphere as a giant photochemical reactor is a useful one, it is also essential not to forget the part that atmospheric dynamics and transport play in redistributing chemical species. Horizontal motions can transport chemical species over large distances from where they are released from the surface or produced in the atmosphere, and vertical motions not only allow substances released from the surface to mix with the bulk atmosphere, but they also transport photochemical products and intermediates from those altitude regions in which they are formed. The weak vertical motions in the stratosphere mean that this redistribution is relatively slow, although still important, in that region. Transport across the tropopause is inhibited. Nevertheless, species from the troposphere do reach the stratosphere, and,

conversely, some stratospherically generated species, such as ozone, can be transported down to the troposphere.

One further general feature of atmospheric chemistry is that many of the processes are cyclic. Production and loss of atmospheric constituents have to be balanced if concentrations are not to vary. To a first approximation, the system of land, sea and air is a closed one (although a small amount of material enters the atmosphere from space and other material escapes to space).

The conservation of the quantities of each chemical element means that if a species appears in the atmosphere (at a rate which must be matched by its disappearance to maintain the balance), then the elements must be passing through a series of cyclic chemical (or physical) transformations. The major elements such as carbon, oxygen, nitrogen and sulphur each have their own balanced cycle. For example, one step in the carbon cycle is the uptake of  $\text{CO}_2$  by photosynthetic plants and micro-organisms, and the release of  $\text{CO}_2$  as a result of fermentation, respiration and decay. Ozone chemistry in the stratosphere is another example of a cyclic process: ozone ( $\text{O}_3$ ) is formed photochemically from  $\text{O}_2$ , while destruction of  $\text{O}_3$  ultimately yields  $\text{O}_2$ . As we shall see shortly, the details of the process may be complex, but it is still cyclic. Greater insight into the chemistry of the atmosphere can always be gained by examining the changes to find out which parts are cyclic.

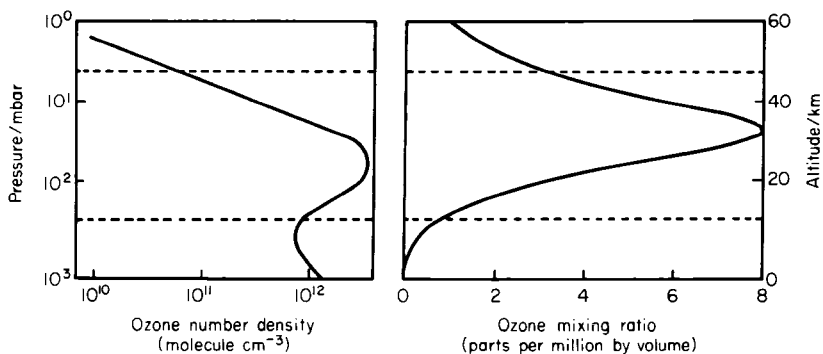
## Ozone in the stratosphere<sup>26</sup>

If compressed to the pressure at sea level, the ozone in the stratospheric layer would make up a column only 3 mm thick, but our existence on Earth, and our survival here, depend on that ozone. Living cells all contain proteins and nucleic acid, and these compounds would be destroyed by ultraviolet radiation from the Sun. Ozone is the only atmospheric filter for much of this radiation, although oxygen itself is effective at the shorter wavelengths. Without oxygen there would be no ozone, so that the oxygen in our atmosphere is critical to life because of the filtering of damaging ultraviolet radiation. One present concern is that man's activities might jeopardize the amount of ozone present in the stratosphere, and that the increased penetration of ultraviolet radiation to the Earth's surface might have untoward consequences,<sup>28</sup> such as an increased incidence of skin and other cancers, and the suppression of the immune systems of living creatures. Figure 2 shows typical measured concentrations of ozone in the atmosphere, expressed both as absolute concentrations and as mixing ratios. Bearing in mind that the ordinate is a logarithmic scale, the sharply layered structure becomes very evident.

The basic ideas of the chemistry of ozone in the Earth's atmosphere were suggested by Sydney Chapman in 1930. The essential chemical steps in Chapman's scheme were







*Fig. 2. Variation of atmospheric ozone concentration with altitude, expressed as an absolute number density and as a relative mixing ratio. (From Stratospheric Ozone 1988, HMSO, London 1988.)*

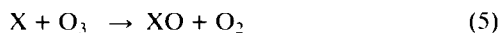
In these equations, the symbol ' $h\nu$ ' represents a photon of ultraviolet radiation, in accordance with normal chemical nomenclature. The first of these steps is the dissociation of oxygen by sunlight to form atomic oxygen, while the second is the addition of atomic oxygen to molecular oxygen to form ozone (a 'third body', not shown in the equation, is needed to stabilize the newly formed molecule). Reaction (3), which is the photodissociation of ozone, converts ozone back to atomic and molecular oxygen, and is thus essentially the reverse of reaction (2). Reaction (4) destroys an oxygen atom and an ozone molecule. Because reactions (2) and (3) interconvert O and O<sub>3</sub> (rapidly in much of the stratosphere), it is often convenient to consider the two species as making up the 'family' of 'odd' oxygen (i.e. O<sub>1</sub>, O<sub>3</sub>, but not O<sub>2</sub>). Odd oxygen is formed only in reaction (1), and destroyed only in reaction (4), and it is these two reactions that determine the balance between production and loss of ozone, and thus the amount of ozone in the atmosphere, in Chapman's scheme.

The existence of ozone as a layer in the atmosphere is readily understood. Reaction (1) requires the presence both of photons of ultraviolet radiation and of molecular oxygen to be dissociated. High up in the atmosphere, there are plenty of photons (i.e. there is a high intensity of radiation) from the Sun, but little oxygen. Low down, there is much oxygen, but the radiation has already been filtered out by the absorbing oxygen that lies in between. In neither the very high nor the very low altitude regions, therefore, is ozone production favoured. At some intermediate altitude, which turns out to lie between 15 and 40 km, there is a compromise between solar ultraviolet flux and molecular oxygen density, and the ozone layer is formed in this region. It is also the solar energy absorbed in the photochemical reactions (1) and (3), and liberated in the exothermic processes (2) and (4), that is largely responsible for the heating that gives rise to the temperature inversion characterizing the stratosphere.

The simple 'oxygen-only' scheme of Chapman explains why a layer of ozone should be formed, and generally predicts the right shape for the altitude profiles shown in Fig. 2. However, laboratory data on the rates of the production and loss processes can be used to predict the absolute concentrations

of ozone expected, and if these calculations are performed, it is found that the predicted concentrations exceed those actually measured by a factor of roughly five. It is as though the rate of reaction (4) must be five times greater than the laboratory determinations say it is.

The key to the apparent discrepancy in calculated and measured ozone concentrations is the occurrence of reactions that destroy ozone in addition to reaction (4). The processes are chain reactions that are propagated by atoms and radicals derived from trace constituents of the atmosphere. The chain carriers are regenerated, and the overall change still corresponds to the removal of one O atom and one O<sub>3</sub> molecule, so that we are dealing with a catalytic destruction of O<sub>3</sub>. The idea is summarized by the scheme



For the purposes of writing this scheme, the catalyst has been called simply 'X'. But what is 'X' in reality? Several catalytic families have been identified. Some of the most important cases are X = OH, the hydroxyl radical, in which case XO = HO<sub>2</sub>, the hydroperoxyl radical; X = NO, nitric oxide, so that XO = NO<sub>2</sub>, nitrogen dioxide; and X = Cl, atomic chlorine, with XO = ClO, the chlorine monoxide radical. Side reactions break, or terminate, the chains, but even so, one 'X' can destroy up to 100,000 O<sub>3</sub> molecules. All three cycles, and especially the first two, occur in the natural atmosphere, dominating the loss of ozone, and controlling its concentration in the stratosphere. Precursor molecules are converted into the catalytically active radicals: for example, methane and water vapour can be converted to OH, and nitrous oxide, N<sub>2</sub>O, can be converted to NO. Both methane and nitrous oxide are produced in enormous quantities by micro-organisms, so we see how the biota can control both production and loss of ozone. Natural precursors of Cl and ClO do exist, but they are dominated by man's contribution of chlorine in the form of the CFCs. Later in this review, I shall examine the possibility that man's activities can release significant quantities of catalytically active compounds, and thus thin the protective ozone layer. For the present, I shall turn to the fundamentals of chemistry in the troposphere.

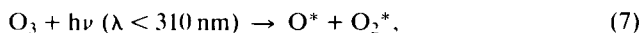
## Tropospheric chemistry<sup>1,3,4</sup>

About 90% of the total atmospheric mass resides in the troposphere, and the bulk of the minor trace gas burden is also found there. Literally hundreds of chemical species are present<sup>1</sup> in the troposphere. Chemical change in the troposphere usually involves the conversion of fully or partially reduced substances to more oxidized forms, and, in many cases, the chemistry resembles that of a low-temperature combustion system. The oxidant is ultimately oxygen, of course, and the fuels are the reduced compounds that are released from the biosphere or from volcanic and other emanations from within the Earth itself. Methane, for example, is produced by enteric fermentation in ruminant animals, in emissions from swamps, bogs and rice paddies, by termites, and

so on. Higher hydrocarbons, and especially terpenes, are released by trees and plants. Hydrogen sulphide ( $\text{H}_2\text{S}$ ) is liberated by volcanic activity, and is also formed by anaerobic biological activity, while dimethyl sulphide ( $\text{DMS}$ ,  $(\text{CH}_3)_2\text{S}$ ) is released by the oceans as a consequence of metabolic processes in certain algae. To these, and a host of other natural compounds, man adds<sup>7,21,22</sup> his own contribution. Some compounds, such as sulphur dioxide ( $\text{SO}_2$ ) and the oxides of nitrogen (nitric oxide,  $\text{NO}$ , and nitrogen dioxide,  $\text{NO}_2$ ) have natural sources, but man provides a major part of the budget. Other substances, such as methyl chloroform (trichloromethane,  $\text{CH}_3\text{CCl}_3$ ) and the chlorofluorocarbons (e.g.  $\text{CF}_2\text{Cl}_2$ ) are solely man-made ('anthropogenic'). The ultimate oxidation products of the compounds are carbon dioxide, water, and fully oxidized acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ), and so on. However, the troposphere contains a wide variety of partially oxidized species such as carbon monoxide ( $\text{CO}$ ), aldehydes, organic peroxides and acids, all of which play a part in the rich chemistry of the atmosphere's lowest region.

Hydroxyl radicals,  $\text{OH}$ , dominate the day-time chemistry of the troposphere in the same way that oxygen atoms and ozone dominate the chemistry of the stratosphere. High reactivity<sup>1</sup> of the  $\text{OH}$  radical with respect to a wide range of species leads to oxidation and chemical conversion of most trace constituents that have an appreciable physical lifetime in the troposphere. It has recently become apparent<sup>29</sup> that, at night, the nitrate radical,  $\text{NO}_3$ , takes over from  $\text{OH}$  as the dominant oxidant in the troposphere. The diurnal impact of  $\text{OH}$  and  $\text{NO}_3$  is complementary, because  $\text{OH}$  is generated photochemically, as we shall see, while  $\text{NO}_3$  is readily photolysed, and thus can survive only at night. Species that survive both chemical conversion in the troposphere and physical loss, such as suffering 'rain-out' (discussed briefly in the final section), or being deposited to surfaces, can be transported across the tropopause to the stratosphere. Some important compounds that are transported in this way include  $\text{N}_2\text{O}$ , some  $\text{CH}_4$ , and  $\text{CH}_3\text{Cl}$ , and they yield the  $\text{NO}_x$ ,  $\text{HO}_x$  and  $\text{ClO}_x$  radicals that destroy ozone in the catalytic cycles introduced in the last section.

Ozone is a critical compound in both daytime ( $\text{OH}$ -initiated) and night-time ( $\text{NO}_3$ -initiated) tropospheric oxidation. Some ozone can be generated within the troposphere, at least when  $\text{NO}_x$  is present, but some ozone is also transported down from the stratosphere. The day-time oxidation of the most important natural hydrocarbon,  $\text{CH}_4$ , is now traced making the assumption that ozone is already present in the troposphere. Photolysis of ozone at wavelengths shorter than about 310 nm leads to formation of electronically excited fragments

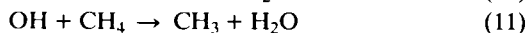
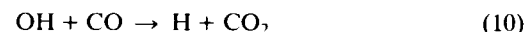


as represented by the asterisks on  $\text{O}$  and  $\text{O}_2$  in equation (7). From our point of view, the interest lies in the potentially different reactivity of the excited species. Specifically, the two reactions

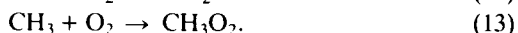


are possible, which they are not for ground-state oxygen atoms. The point is an important one, because these two reactions are dominant contributors to

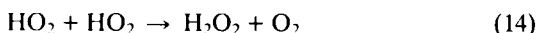
OH production in 'clean' atmospheres, and  $O_3$  is the only precursor that can yield excited  $O^*$  at the solar ultraviolet wavelengths that penetrate to the troposphere. Once the hydroxyl radicals are formed, the oxidation of hydrocarbons can be initiated. Roughly 70% of the OH radicals react with CO and 30% with  $CH_4$



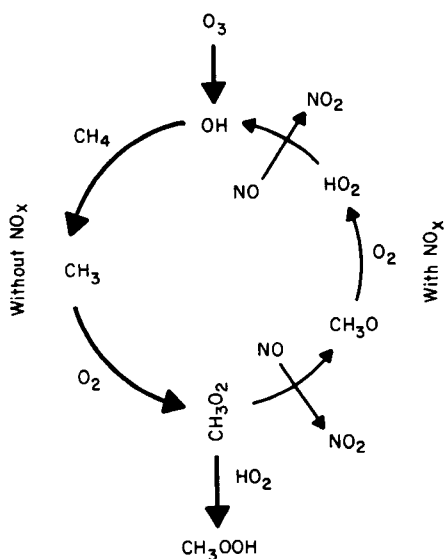
and the product H atom or  $CH_3$  radical adds oxygen to form an  $HO_2$  (hydroperoxyl) or a  $CH_3O_2$  (peroxymethyl) radical. These processes require a third body to stabilize the newly formed product in the same way as reaction (2), but we shall represent them by the bimolecular equations



Assuming, for the present, that  $NO_x$  concentrations are very low (which they might be over remote oceanic regions), the main reactions of the  $HO_2$  and  $CH_3O_2$  radicals lead to the formation of hydrogen peroxide ( $H_2O_2$ ) and methyl hydroperoxide ( $CH_3OOH$ )



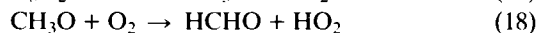
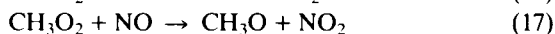
One fate of the peroxides is that they can dissolve in cloud droplets and be removed from the troposphere in the form of rain. The left-hand semicircle of Fig. 3 illustrates the essential steps of methane oxidation that I have



**Fig. 3.** Essential steps in methane oxidation in the troposphere. The heavier arrows show the steps possible in the absence of  $NO_x$ , while the lighter arrows indicate

how the process becomes cyclic when  $NO_x$  is present. (From a diagram devised by M. E. Jenkin.)

discussed so far. Alternative fates of the peroxides, such as photolysis, regenerate radicals and thus permit a cyclic chain oxidation to occur. Of much greater importance for the occurrence of a chain oxidation, however, is the presence of  $\text{NO}_x$ , and especially of  $\text{NO}$ , in the troposphere. These oxides of nitrogen have natural sources, such as forest fires, anaerobic processes in soil, oxidation of biogenic ammonia ( $\text{NH}_3$ ), and electrical storms; and man makes a further large contribution as a result of the 'fixation' of atmospheric  $\text{N}_2$  and  $\text{O}_2$  in high-temperature combustion. The importance of  $\text{NO}$  is that it reacts rapidly with the  $\text{HO}_2$  and  $\text{CH}_3\text{O}_2$  from reactions (12) and (13), with the net result of regenerating  $\text{OH}$ . These processes are illustrated by the right-hand semicircle of Fig. 3, and because the processes now complete the full circle, a true cyclic chain oxidation of  $\text{CH}_4$  is occurring. In this chain, termination involves the loss of  $\text{HO}_2$  and  $\text{CH}_3\text{O}_2$  radicals through peroxide formation, and the termination is balanced by new initiation steps involving ozone photolysis. The chemical equations corresponding to the new steps on the right-hand semicircle of Fig. 3 are:



The outstanding feature of these equations is the direct or indirect formation of  $\text{HO}_2$  in reactions (18), (19) and (20), and the regeneration of  $\text{OH}$  from  $\text{HO}_2$  in reaction (16). However, there are other features of the scheme that are relevant to our enquiry, including the formation of the methoxy radical ( $\text{CH}_3\text{O}$ ), formaldehyde ( $\text{HCHO}$ ), and carbon monoxide ( $\text{CO}$ ). The last of these compounds, it will be remembered, is often the main sink for  $\text{OH}$  in reaction (10), and leads to the final oxidation product,  $\text{CO}_2$ .

Both Fig. 3 and reactions (16) and (17) in the scheme demonstrate that  $\text{NO}$  is converted to  $\text{NO}_2$ . This leads to another central topic in tropospheric chemistry. Nitrogen dioxide is photolysed by the wavelengths that reach the troposphere, and the photodissociation yields atomic oxygen that can add to  $\text{O}_2$  to give  $\text{O}_3$

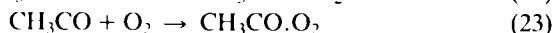


This pair of reactions is the only established *in-situ* source of ozone in the troposphere, and is thus of paramount importance. Below a certain critical value of the ratio  $[\text{NO}]/[\text{O}_3]$ , ozone loss through reaction with  $\text{HO}_2$  radicals dominates over the generation sequence. Regions of the Earth characterized by extremely low concentrations of  $\text{NO}$ , such as the remote Pacific, are thus likely to be a net sink for odd oxygen, while over the continents at mid-latitudes, where  $[\text{NO}]$  is relatively high, there is likely to be a net source of odd oxygen. As long as  $\text{NO}_x$  is available, the supply of  $\text{CO}$ ,  $\text{CH}_4$ , and other hydrocarbons ultimately limits the production of ozone. It has been estimated that as many as 3.5 molecules of  $\text{O}_3$  could be formed from the oxidation of

each CH<sub>4</sub> molecule. Ozone abundances are, of course, determined not only by the *in-situ* production rate, but also by the rate of injection from the stratosphere and by loss to the surface. Recent estimates put the last two rates roughly equal, so that tropospheric ozone concentrations are largely dependent on the *in-situ* production processes just outlined. The tropospheric abundance of ozone is obviously critical in determining the oxidizing capacity of the troposphere. Ozone is not only an oxidizing species in its own right, but, more important, it is the primary source of OH radicals. It should already be evident that hydroxyl radical chemistry in the troposphere provides an efficient chemical scavenging mechanism for both natural and anthropogenic trace constituents, and the oxidizing capacity of the troposphere thus determines the ability of the lower atmosphere to 'purify' itself as well as the extent to which tropospheric compounds will be transferred to the stratosphere. Future trends<sup>5</sup> of tropospheric oxidizing capacity are evidently tied to future atmospheric burdens of NO<sub>x</sub>, CO, CH<sub>4</sub>, and other hydrocarbons.

The complexities of even hydrocarbon oxidation in the troposphere should have become apparent from this simplified discussion. Field observations of the concentrations of key compounds is an essential feature<sup>28</sup> of the validation of models of the atmosphere that are based on the chemical ideas just outlined. One obvious candidate for study is the OH radical itself, because it is so central to tropospheric oxidation chemistry. Reliable values for OH concentrations are also needed to estimate tropospheric lifetimes for many trace gases, including CO and CH<sub>4</sub> whose sources are extremely difficult to quantify. Some indirect methods for the estimation of [OH] exist, but recently direct spectroscopic techniques have begun to be employed for the time-resolved measurement of local hydroxyl radical concentrations. Both laser-induced fluorescence (LIF) and long-path absorption spectroscopy have been employed for these experiments. The work is still in its infancy, but its development and wide application seem likely to bring considerable rewards.

Measurements of NO<sub>x</sub> in remote regions have, until fairly recently, been thought to be representative of the 'natural' atmosphere. However, the situation is more complex than it at first appears, because NO<sub>x</sub> can be transported over long distances<sup>23</sup> in the form of the compound of formula CH<sub>3</sub>CO.O<sub>2</sub>NO<sub>2</sub>. The compound is usually called peroxyacetyl nitrate, or PAN (its proper systematic name might be ethane peroxyacetic nitric anhydride) and it is an adduct of the peroxyacetyl radical and NO<sub>2</sub>. Many hydrocarbons, both saturated and unsaturated, produce aldehydes as oxidation intermediates. Attack of OH on these compounds yields acyl radicals, to which oxygen adds to give the peroxyacyl radical, behaviour which is analogous to that of alkanes and alkyl radicals. To this peroxyacyl radical, NO<sub>2</sub> can add in a reversible process. For example, with acetaldehyde (ethanal, CH<sub>3</sub>CHO) the sequence of steps is

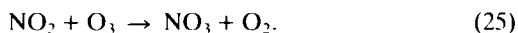


The importance of PAN is that it is in thermal equilibrium with its precursors, as implied by equation (24), and that the equilibrium is shifted to the right-hand side at lower temperatures. Well away from the planetary surface, temperatures

are sufficiently low for PAN to be relatively stable, but the molecule becomes unstable at the higher temperatures found close to the surface. PAN is thus able to transport  $\text{NO}_x$  from cooler to warmer regions, possibly over very large distances, and to regions remote from local sources. In view of the importance of  $\text{NO}_x$  in ozone production, and thus in determining  $[\text{OH}]$  and the oxidizing capacity of the atmosphere, this mode of transport to remote regions may prove<sup>23</sup> to be of great significance.

## The nitrate radical<sup>29</sup>

Until fairly recently, it was thought that tropospheric oxidation processes initiated by radicals became quiescent at night, because the photochemical source of OH was absent. It has now emerged that another free radical, the nitrate radical ( $\text{NO}_3$ ), can have considerable importance in the night-time troposphere. Although the  $\text{NO}_3$  radical has been known for over 100 years (and may therefore qualify as the first free radical to be detected directly), its involvement in atmospheric chemical processes has only slowly become apparent. In the Earth's atmosphere,  $\text{NO}_3$  is formed by the reaction between nitrogen dioxide ( $\text{NO}_2$ ) and ozone



Generation of the radical thus demands the presence both of  $\text{NO}_x$  and of ozone. That is, the oxidizing power of the radical really derives from the energy stored in ozone formed photochemically during the day.

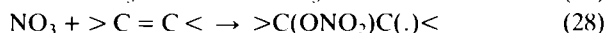
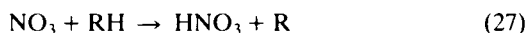
One of the most important reactions of  $\text{NO}_3$  is with  $\text{NO}_2$  to yield dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ )



This process is another three-body association (cf. reactions (2), (12) and (13)), and its rate is pressure dependent. Furthermore,  $\text{N}_2\text{O}_5$  is itself thermally unstable, redissociating to yield  $\text{NO}_3$  and  $\text{NO}_2$ . However,  $\text{N}_2\text{O}_5$  is the acid anhydride of nitric acid ( $\text{HNO}_3$ ), and it can react heterogeneously with  $\text{H}_2\text{O}$  to yield the acid. It can thus contribute to atmospheric acidification,<sup>14</sup> which will be discussed briefly in the next section.

Although the nitrate radical is, in general, much less reactive than OH towards the many organic compounds present in the troposphere, it is also present at night in concentrations up to three orders larger than those of OH during the day. As a result, attack of  $\text{NO}_3$  during the night can provide a comparable extent of oxidation to that effected by day through attack of OH. For some species, such as dimethyl sulphide (DMS,  $(\text{CH}_3)_2\text{S}$ ) and some naturally occurring terpenes, the reactions with  $\text{NO}_3$  are particularly rapid, so that the night-time  $\text{NO}_3$  processes dominate.

Two main types of initial step occur in the reaction of  $\text{NO}_3$  with organic substrates. They are hydrogen abstraction and addition to unsaturated bonds



The molecule RH on the left-hand side of equation (27) represents any organic

species with a removable hydrogen atom, so that the species R is an organic radical. The radical R can subsequently add oxygen to form  $\text{RO}_2$ , and enter into the sequence of reactions exemplified for  $\text{R} = \text{CH}_3$  in Fig. 3 and reactions (13), (15) and (17)–(20). Note also that nitric acid is a direct product of the reaction. Addition to unsaturated bonds, as in reaction (28), probably accounts for more atmospheric oxidation than the abstraction process. The initial adduct formed in the reaction can eliminate  $\text{NO}_2$  to yield an epoxide. However, the adduct is a radical, and in the presence of air it can be expected to add oxygen, and several products can subsequently be formed. For example, with propene as the unsaturated compound, and in the presence of  $\text{O}_2$  and  $\text{NO}_x$ , the products observed include  $\text{HCHO}$ ,  $\text{CH}_3\text{CHO}$ , 1,2-propanediol dinitrate (PDDN), nitroxyperoxypropyl nitrate (NPPN), and  $\alpha$ -(nitroxy)acetone. The sequence of reactions involves the liberation of the radical  $\text{HO}_2$ , which can react with  $\text{NO}$  in reaction (16) to provide a night-time source of  $\text{OH}$  that itself can attack organic substrates. The possibility thus exists of a night-time chain oxidation of organic compounds initiated by production of organic radicals in either the abstraction or the addition steps. Attack of  $\text{NO}_3$  on aldehydes can produce acyl radicals, so that the chemistry is set up for the formation of PAN in reactions (23) and (24). Furthermore, all the nitrates discussed, such as PDDN, NPPN, and PAN itself are toxic and noxious, and  $\alpha$ -(nitroxy)acetone has been shown to be a mutagen. It is evident that the contribution of the  $\text{NO}_3$  radical to tropospheric chemistry is considerable, and future work should help to strengthen the quantitative understanding of the chemistry of the radical and to elucidate the mechanistic details of the interactions.

## Tropospheric pollution<sup>4,7,14,21,22,28</sup>

It is not the purpose of this article to delve into the myriad facets<sup>7</sup> of air pollution, even though an understanding of atmospheric chemistry is the key to control of pollution. However, it is appropriate here to review very briefly some aspects of pollution of the lower atmosphere that relate to the overview of tropospheric chemistry that has been presented.

Combustion of fossil fuels in one way or another seems to be responsible for some of the most serious types of pollution. Of course, the soot and other particles produced by inefficient combustion are all too apparent, and they were an important component of the London 'smog' (a word coined to mean 'smoke + fog') that used to afflict the city before the burning of bituminous coal was prohibited. Sulphur dioxide was another component, and its presence was a consequence of relatively high levels of sulphur compounds in the coal. Release of sulphur dioxide is still a major problem, in particular from electricity generating plants that use fossil fuels such as coal or oil, and internal combustion engines are also a significant source of the gas. Sulphur dioxide is an irritant gas; it is toxic and damages buildings, amongst other effects. However, the gas may be of more importance as a precursor of sulphuric acid, which is a component<sup>14</sup> of 'acid rain', and which poses a threat to living organisms, especially trees and fish. Nitric acid is another contributor to acid rain, and its precursors are the oxides of nitrogen  $\text{NO}$  and  $\text{NO}_2$  that we call



collectively  $\text{NO}_x$ . These oxides are mainly a result of the conversion to  $\text{NO}$  at high temperatures of the  $\text{N}_2$  and  $\text{O}_2$  of the air used for combustion. Power plants and other industrial combustion sources, and emissions from internal combustion engines (especially of automobiles in urban areas) all contribute to the anthropogenic  $\text{NO}_x$ . However,  $\text{NO}_x$  is implicated not only in the production of acid rain, but it is also one precursor<sup>4</sup> of 'photochemical smog' (often called Los Angeles smog after the city where it was first identified, and where it is still a serious problem). Automobile exhaust, and other combustion sources, are also responsible for another essential component of the mixture of pollutants that leads to photochemical air pollution. Unburnt, or partially burnt, hydrocarbons are essential for the photochemical changes that lead to the secondary pollutants, which include  $\text{O}_3$ ,  $\text{NO}_2$ , and PAN. All the pollutants mentioned, and perhaps especially the acids and the oxidants, are damaging to human and other life, and have other untoward and undesirable effects.

It may be, however, that all these effects pale into insignificance in comparison with the release of carbon dioxide as a result of the combustion of fossil fuels. Fossil carbon, whose burial over millions of years was an essential condition<sup>28</sup> for the build-up of atmospheric oxygen, has been dug up over a span of a few hundred years, and oxidized deliberately to  $\text{CO}_2$ . Concentrations of  $\text{CO}_2$  have risen since the industrial revolution because the loss processes (solution and transport to the deep ocean, and formation of carbonate deposits and rocks) are much too slow to keep up with the rate of release. Ultimately, an excess of  $\text{CO}_2$  could be removed by the slow loss mechanisms, but it may be that  $\text{CO}_2$  levels will build up sufficiently that the increased greenhouse trapping will have a marked effect<sup>18</sup> on our climate. There is much current debate about whether there is already evidence for a global increase in mean temperatures. A temperature rise in the future seems very likely. Consequences of a climate change include redistribution of the fertile and arid areas of the Earth, and, perhaps most serious of all, an increase in sea levels as the Antarctic ice sheets melt, leading to flooding of many of the most densely populated parts of the globe. The greenhouse problem is compounded by other anthropogenic releases of greenhouse gases<sup>17</sup> such as  $\text{N}_2\text{O}$  (from increased use of nitrate fertilizers, and some contribution from combustion sources),  $\text{CH}_4$  (from rearing of domestic ruminants that make the gas in their digestive systems, from cultivation of rice paddies, from termites, and from released natural gas), and the CFCs (long-lived compounds solely of anthropogenic origin).

Let us now turn to some of the types of pollution described, and see how the general principles of tropospheric oxidation chemistry explain the changes that occur. First, we consider photochemical smog.<sup>4,21,22</sup> The observations are typified by the results shown in Fig. 4. Nitric oxide ( $\text{NO}$ ) builds up during the night and during the early morning period of heavy commuter traffic. After dawn,  $\text{NO}$  is replaced by  $\text{NO}_2$ , and oxidants (in particular  $\text{O}_3$ ) appear. A brown haze is evident by noon because there are substantial numbers of particles in the air, and the eyes water because PAN, a powerful lachrymator, is present in the atmosphere. All the substances described are components of the normal tropospheric oxidation system outlined in the last section, and in some ways photochemical smog is a grotesquely exaggerated version of

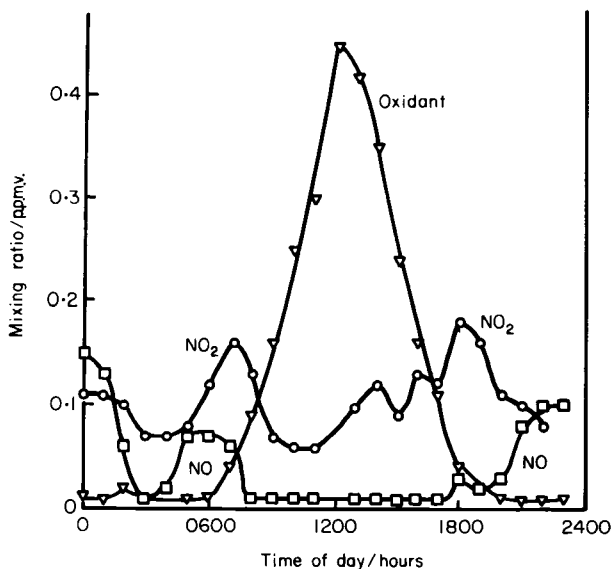
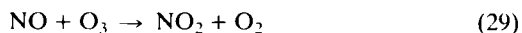


Fig. 4. Variations in concentration of oxidant (mainly ozone) and oxides of nitrogen during the course of a smoggy day.<sup>28</sup>

the natural atmosphere, although the concentrations of all species is greatly elevated over the background levels. The large quantities of NO and incompletely oxidized hydrocarbons spewed out by motor vehicles are responsible, but the chemistry is the same as that described earlier. The methane that probably dominates the 'fuel' of the natural atmosphere is replaced by higher hydrocarbons, and especially unsaturated species, and aromatic compounds, as well as partially oxidized compounds such as aldehydes and ketones that present an even greater potentiality for participation in radical-chain oxidation. Surrogate mixtures of alkene, NO and air illuminated in a test chamber ('smog chamber') by real or artificial sunlight show production with the same temporal dependence of materials similar to those seen in the real atmosphere. Ozone can, once again, be produced only via the photolysis of NO<sub>2</sub> to yield O atoms in reaction (21), followed by the addition of O to O<sub>2</sub> in reaction (2). Conversion of the NO first released to NO<sub>2</sub> cannot just involve reaction with O<sub>2</sub>, as that reaction is much too slow at the concentrations of NO present. Rather, it is the reactions of NO with HO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub>, and other organic peroxy radicals in reactions (16), (17), and their analogues, that effect the conversion. Hydroxyl radicals are key species in the transformation steps just as they are in the natural troposphere. They are the agent of initial attack on hydrocarbons and other primary organic pollutants, and they are one of the chain-carrying intermediates. Ozone photolysis, followed by reaction (8) and the analogues of reaction (9), is still an important source of the radicals, but supplementary sources are to be found in the photolysis of formaldehyde (a component of automobile exhaust) in reaction (19) followed by the conversion steps (12) and (16), and also in the photolysis of nitrous acid (HONO), a compound that is formed by the reaction of NO, NO<sub>2</sub> and water.

Control measures must involve reduction both of unburnt or partially oxidized hydrocarbons and of  $\text{NO}_x$ . A so-called 'lean burn' strategy reduces hydrocarbon emissions, but leads to large increases in  $[\text{NO}_x]$ . This strategy appears to reduce pollution in the immediate vicinity of the emission sources, partly because the hydrocarbon levels are reduced, but partly also because  $\text{NO}$  reacts rapidly with ozone in the reaction

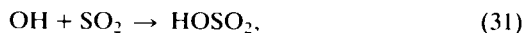


and the enhanced  $[\text{NO}]$  thus reduces  $[\text{O}_3]$ . Smog-chamber experiments confirm this finding, and show that under conditions of relatively high  $[\text{NO}]$ , a reduction of  $[\text{NO}]$  increases  $[\text{O}_3]$  production. Indeed, the importance of reaction (29) is shown by the normal diurnal variation of pollutant concentrations displayed in Fig. 4. Ozone does not build up in the atmosphere until virtually all the  $\text{NO}$  has been consumed. Downwind of the emission sources,  $\text{NO}_2$  is photolysed in reaction (21), providing an additional source of  $\text{O}$  and thus of  $\text{O}_3$ . Greatly increased oxidant pollution is thus seen in these downwind areas when excess  $\text{NO}$  is released. The correct control strategy must therefore be to reduce both hydrocarbon and  $\text{NO}_x$  emission at the same time. Lowered combustion temperatures to reduce  $[\text{NO}]$  and efficient catalytic converters to remove the hydrocarbons seem to be reasonably effective. Even here, some caution must be exercised, because inefficient or poisoned converters may only partially oxidize the exhaust hydrocarbons, to yield compounds like aldehydes which are more reactive than the parent hydrocarbons in initiating and promoting smog formation.

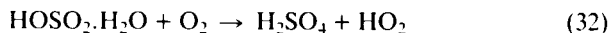
I shall now turn to a very brief examination of the conversion<sup>2</sup> of the primary pollutants  $\text{NO}_x$  and  $\text{SO}_2$  to the acids  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  that are the major culprits in acidification<sup>7</sup> of rain-water. Hydroxyl radicals and ozone are yet again implicated. It was seen in the last section that  $\text{N}_2\text{O}_5$ , the acid anhydride of  $\text{HNO}_3$ , can be formed by the reaction of  $\text{NO}_3$  with  $\text{NO}_2$ ; the conversion of  $\text{N}_2\text{O}_5$  to  $\text{HNO}_3$  is probably a heterogeneous process<sup>4,21</sup> occurring on surfaces or in water droplets. Direct abstraction by  $\text{NO}_3$  of  $\text{H}$  from organic compounds was shown earlier to be a source of  $\text{HNO}_3$ . However, the major source of  $\text{HNO}_3$  is probably the (three-body) addition of  $\text{OH}$  to  $\text{NO}_2$



Sulphuric acid production from  $\text{SO}_2$  in the gas phase also seems to involve addition of  $\text{OH}$  as the first step



again in a three-body process. The  $\text{HOSO}_2$  radical is further oxidized to  $\text{H}_2\text{SO}_4$ , although the mechanism is probably more complex than just the addition of a further  $\text{OH}$  radical. One suggestion is that hydrated  $\text{HOSO}_2$  reacts with  $\text{O}_2$



although alternative mechanisms have also been proposed. Heterogeneous oxidation of  $\text{SO}_2$  in the aqueous droplets that constitute rain, fogs, clouds and aerosols may be more important<sup>2,4</sup> than the purely homogeneous processes.

Solution of  $\text{SO}_2$  in water yields the ions  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$ . Both hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ozone dissolved from the gas phase can oxidize  $\text{HSO}_3^-$  to the  $\text{SO}_4^{2-}$  ion. Free radicals in the liquid phase, such as OH and  $\text{HO}_2$ , scavenged from the gas phase or formed by reactions in droplets, may also play a part in the oxidation. For example, aqueous OH reacts with  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  to yield  $\text{SO}_4^{2-}$ , and the  $\text{H}_2\text{O}_2$  just presented as an oxidant of  $\text{HSO}_3^-$  can be formed from the self-reaction of two  $\text{HO}_2$  radicals in droplets. This section thus ends with a hint of the importance of droplet and aerosol chemistry to which I shall return towards the end of this review.

## Man's interference with the stratosphere<sup>6,13,16,25,26,30</sup>

In this section, the question of ozone in the stratosphere is reconsidered, in order to examine the possible ways that man could upset the natural balance between production and removal of ozone, and to look for evidence that man's activities have already altered ozone concentrations. In this latter context, the discovery<sup>6,24,25,30</sup> of the 'Antarctic ozone hole' is of particular importance.

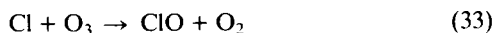
Catalytic cycles involving trace amounts of atoms and radicals were shown earlier to dominate the loss of ozone in the natural stratosphere, and thus are largely responsible for determining the steady-state concentration of the gas. In the natural stratosphere, the most important cycles are those based on  $\text{NO}_x$  (NO and  $\text{NO}_2$ ) and  $\text{HO}_x$  (OH and  $\text{HO}_2$ ); the  $\text{NO}_x$  cycle contributes most in the lower stratosphere (c. 75% of ozone loss at 30 km), while the  $\text{HO}_x$  cycle virtually dominates  $\text{O}_3$  loss in the upper stratosphere (c. 90% at 60 km). A chain in which  $\text{ClO}_x$  compounds (Cl and ClO) act as carriers is responsible for a destruction cycle that removes a maximum of c. 30% of the ozone at an altitude of 40 km in the ordinary stratosphere. Much of the chlorine loading in the stratosphere is a result of man's release of CFCs, and this will be a theme that runs through the present section.

As suggested earlier, there has been increasing speculation<sup>6,16,28</sup> since the 1970s that man's activities could release catalytically active species that add to those already present in the atmosphere, and thin the ozone layer on which we depend for our protection. One of the first potential sources of interference with stratospheric ozone to be proposed was the SST, or Stratospheric Super-sonic Transport, of which the Concorde is an example. All aircraft produce quite large quantities of nitric oxide, NO, because of the high temperature of combustion in air containing both  $\text{N}_2$  and  $\text{O}_2$ . For aircraft flying lower down, in the troposphere, the oxides of nitrogen get well mixed, and ultimately converted to soluble compounds that are rained out to the surface of the Earth; extra ozone may even be produced, as discussed in the last section. However, injection into the stratosphere could be potentially dangerous. Because of the stability of the stratosphere, the lifetime against physical removal could be several years, by which time chemical reaction would be likely to occur, especially because the injection is into that region where the ozone layer is found. If natural oxides of nitrogen catalyse ozone destruction, so will man-made nitric oxide. Initial calculations of ozone depletion were

greatly in error, both because the future Concorde fleet size was grossly over-estimated and because there were substantial errors or omissions in the chemistry. However, the question has again become one of active debate<sup>9</sup> because plans for a second-generation SST fleet have begun to be considered seriously. It is now recognized that both NO<sub>x</sub> and HO<sub>x</sub> cycles must be considered, because aircraft produce huge quantities of H<sub>2</sub>O in addition to the NO<sub>x</sub>.

Another source of the oxides of nitrogen, more significant perhaps than the small Concorde fleet, was seen to be the rising levels of nitrous oxide, N<sub>2</sub>O, from increased use of nitrogen-rich fertilizers. The N<sub>2</sub>O, produced microbially at ground level, could make its way to the stratosphere and there enter the NO<sub>x</sub> catalytic cycle to increase the destruction of ozone over natural rates.

A much more serious threat to the atmospheric ozone layer was identified from 1974 onwards. The culprit catalytic cycle this time was the one involving Cl atoms and ClO radicals. In view of the importance of the reactions in the material that follows, it is now appropriate to write out the cycle of reactions (5) and (6) explicitly for X = Cl.

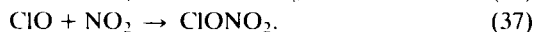


The main source of the catalytic species in the stratosphere is the release by man of chlorofluorocarbons (CFCs) at the surface of the Earth. A typical CFC is the molecule CF<sub>2</sub>Cl<sub>2</sub>, or dichlorodifluoromethane. The CFCs had been introduced in 1930 by General Motors in the U.S.A. for use mainly as coolants for refrigerators and air conditioning systems, aerosol propellants, blowing agents, and so on. Nearly 10<sup>9</sup> kg yr<sup>-1</sup> of the CFCs are produced annually at present. The great perceived virtue of the CFCs is their almost complete chemical inertness and lack of toxicity. In the early 1970s, Professor James Lovelock had been able to measure quite high concentrations of the CFCs in ordinary tropospheric air, and the concentrations suggested that almost all the CFCs ever produced had accumulated in the lower atmosphere. Since that time, repeated measurements have demonstrated that the CFCs have continued to build up in the troposphere. In 1974, Molina and Rowland, at the University of California at Irvine, showed what the real problem was concerning these compounds. Because the CFCs are so inert in the troposphere, substantial amounts will eventually enter the stratosphere. However, at stratospheric altitudes, the CFCs are not so inert, because they can be split by the relatively short wavelength ultraviolet radiation present there



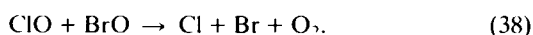
A chlorine atom is formed in the process, and it can thus initiate the ClO<sub>x</sub> ozone catalytic destruction chain. Millions of tonnes of the CFCs are released to the atmosphere every year, and each chlorine atom can destroy as many as 100,000 ozone molecules before it is inactivated. There is thus great potentiality for damage to the ozone layer. Indeed, were it not for another

very important piece of atmospheric chemistry, the effect would be much greater. Much of the chlorine released from the CFCs is not in the immediately available catalytic form—that is chlorine atoms and chlorine monoxide—but is bound up in reservoir compounds, of which hydrogen chloride (HCl) and chlorine nitrate (ClONO<sub>2</sub>) are the most important. The reservoir species are formed from Cl and ClO in reactions with methane and in a three-body reaction with nitrogen dioxide



It is worth noting that the reactants that form the reservoir species are themselves important in other catalytic cycles, thus clearly illustrating interactions between the cycles, and showing the complexity of atmospheric chemistry. Yet other reactions release the chlorine from the reservoirs. The important point, though, is that these reactions are slow in the normal atmosphere, so that most of the atmospheric chlorine is bound up and not available for ozone destruction.

Bromine seems to be even more active<sup>15,24</sup> than chlorine in destroying ozone in catalytic cycles. Man releases substantial amounts of brominated CFCs (compounds called 'halons', and used, for example, as fire retardants). The species CF<sub>2</sub>BrCl is three to four times more destructive towards ozone than is CF<sub>2</sub>Cl<sub>2</sub>, and CF<sub>3</sub>Br is nearly ten times more destructive. For the time being, release rates are less than one-hundredth of the non-brominated CFCs, but the dangers of the compounds must not be underestimated. The peculiar activity of bromine compounds once they reach the stratosphere seems to be partly associated with a synergism with respect to chlorine. The oxide radicals ClO and BrO react with each other to release free halogen atoms in one branch of the interaction



Both chlorine and bromine atoms can attack ozone (in reaction (33) and its bromine analogue), but note that the free atoms become released from the oxide without the intervention of atomic oxygen in the usual reaction (34). This point will turn out to be of significance in interpreting the behaviour of polar stratospheric ozone.

The demonstrated increasing trend of CFC concentrations in the troposphere together with the strong scientific evidence that destruction of stratospheric ozone was likely, at least in the future, finally led to the political will to limit production. The most wide-ranging control is embodied in the 'Montreal Protocol' that was agreed in September 1987 and entered into force in January 1990. Subsequently, further amendments to the 1987 Protocol have been enacted. The intention is to freeze at 1986 levels, and then cut back on, production and consumption of an agreed list of CFCs and halons. Model calculations may be performed to predict how tropospheric concentrations of the CFCs will change with time according to various scenarios. The results of some such calculations for CF<sub>2</sub>Cl<sub>2</sub> are shown in Fig. 5. The most striking result is immediately evident. Although adherence to the Montreal Protocol will alleviate the problem, it would require a much larger reduction (of 85%)

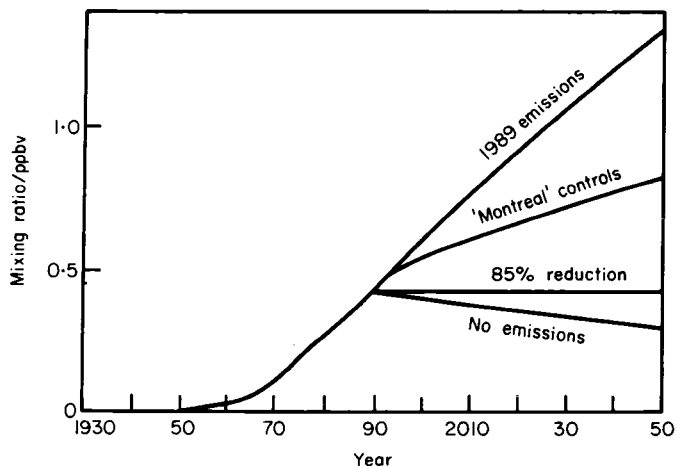


Fig. 5. Model predictions of future average atmospheric concentrations of  $CF_2Cl_2$  resulting from four different emission scenarios. (From *Stratospheric Ozone 1988*, HMSO, London 1988.)

to stabilize concentrations at their 1989 level. Even if release of CFC ceases completely now, it will be well into the twenty-second century before atmospheric concentrations return to the levels they were at in 1960.

Other chemical models of the stratosphere can be used to predict how the increased CFC concentrations in the future might translate to depletions of ozone. A complication arises because changing concentrations of other trace gases such as  $N_2O$ ,  $CH_4$  and  $CO_2$  also influence the altitude distribution and total amount of stratospheric ozone through chemical interactions and temperature feedback effects. The results of a typical calculation, from the University of Oslo, that allows for the effects is shown in Fig. 6. It is evident that,

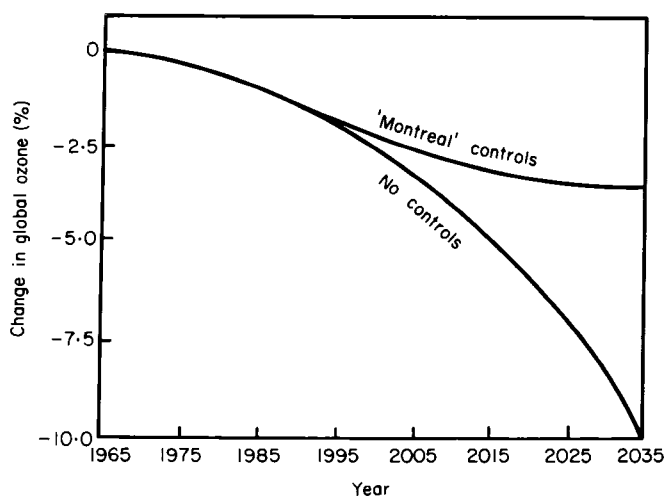


Fig. 6. Model predictions of changes in global mean ozone column. Allowance is made for the growth of  $CO_2$ ,  $N_2O$  and  $CH_4$ . (From *Stratospheric Ozone 1988*, HMSO, London 1988.)

even with the Montreal Protocol in place, ozone depletions of several percentage points might be expected by the middle of the next century, and without the Protocol depletions would exceed 10%.

Figure 6 suggests that some depletion of ozone might already be apparent, and the models indicate that there might be substantial seasonal and latitudinal fluctuations that are not revealed by the averages represented in the figure. So is there any experimental evidence for ozone depletion? An elaborate analysis<sup>27</sup> was undertaken by the NASA/WMO Ozone Trends Panel in 1988, in which an attempt was made to allow for changes resulting from natural phenomena (such as variations over the solar cycle) and for increases in tropospheric ozone. The results do seem to show a significant downward trend. For example, in comparing the pairs of years 1986/87 with 1979/80, there seem to be depletions polewards in excess of 5% throughout the year, and depletions exceeding 6% are found at northern high latitudes during the winter months. However, the outstanding feature is a change of more than 30% over the Antarctic during the (austral) spring. This ozone loss, and the even more precipitous fall between August and October each year, mark changes so unequivocal that there is little room for argument about the statistical significance of the observations. It is to these enormous and deepening seasonal depletions of polar ozone that we must now turn. A quirk of fate meant that the Montreal Protocol was based on scientific evidence that was just about to be questioned. In the weeks following the Montreal meeting, the most dramatic decline ever in ozone concentrations in the Antarctic was observed, and this depletion in ozone was not predicted by any of the atmospheric models then current.

Scientists of the British Antarctic Survey (BAS) have been measuring ozone concentrations at their base at Halley Bay (76°S) for many years. In 1982 they believed that they had detected a decline in springtime ozone since 1977, and by October 1984 they were sure, with something like 30% total ozone loss. The BAS team published their findings in *Nature* in 1985, and the phenomenon of springtime ozone depletion<sup>6,25,30</sup> has become known as the 'Antarctic ozone hole'. Each subsequent spring has seen a repetition of the phenomenon, with total column losses reaching up to 50% in some years. Satellite measurements, which map ozone over most of the Earth's atmosphere confirm and extend the BAS observations. At some altitudes, almost all the ozone that is present in early spring has disappeared a few weeks later, as Fig. 7 illustrates for the austral spring of 1989. There really is a 'hole' at an altitude of 15 km!

The explanation that has emerged<sup>24,25,30</sup> for the formation of the ozone holes depends on some special features of polar stratospheric meteorology and dynamics as well as on anomalous chemistry. The temperatures in the winter Antarctic stratosphere are exceptionally low (below -80°C); they are associated with a vortex with very high westerly wind speeds that isolates the air over the Antarctic. At the very low temperatures, clouds form even in the dry stratosphere. These polar stratospheric clouds (PSCs), together with the isolation of air within the vortex, seem central to the peculiar chemical behaviour. Large-scale campaigns, especially in 1987, have helped to establish the chemical composition of the stratosphere at high latitudes. Figure 8 shows one of the most important results, obtained by instrumented aircraft flying



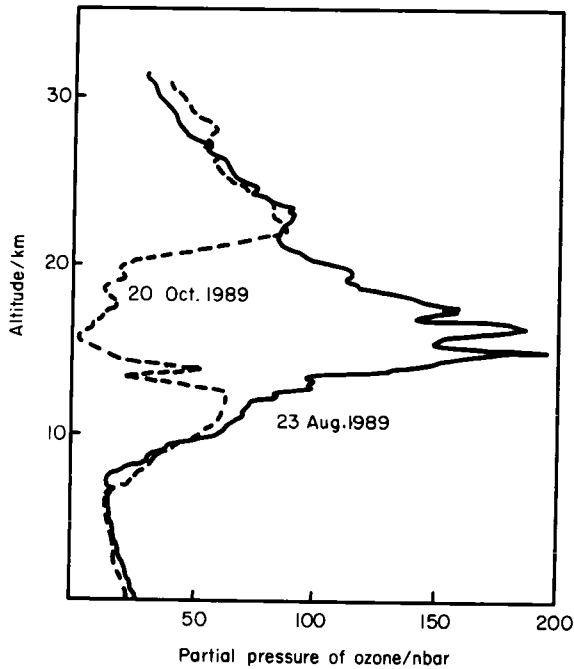


Fig. 7. Ozone concentrations over McMurdo station in August and September 1989. (from Deshler T., Hoffman D.J., Hereford J.V. & Sutter C.B. (1990) *Geophys. Res. Letters* 17, 151).

into the vortex region. In late August 1987 (Fig. 8a), before the hole had developed, ozone concentrations were 'normal', and did not change greatly on flying into the vortex. Concentrations of the radical ClO, on the other hand, increased by a factor of up to 400 over those outside the vortex. After the Sun had returned in mid-September (Fig. 8b), the situation had altered dramatically. Now the ozone concentrations dropped sharply on entering the vortex. There is a strong anticorrelation between  $[O_3]$  and  $[ClO]$ , both on the large scale and with regard to the smaller, more detailed, changes, leaving

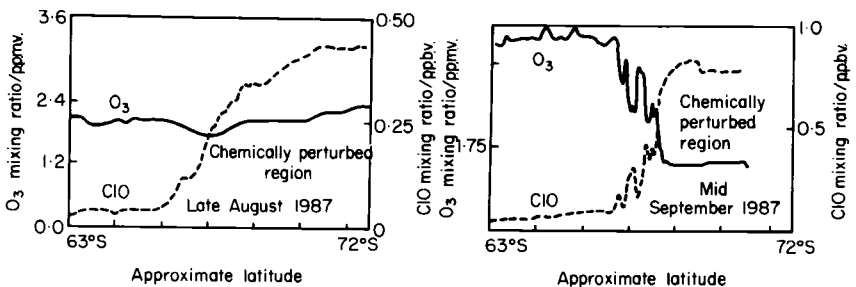
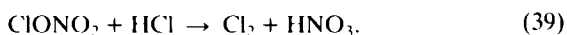


Fig. 8. Latitude dependence of  $O_3$  and ClO concentrations on entering the chemically perturbed region: (a) late August 1987;

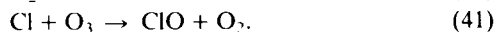
(b) mid-September 1987. (From *Stratospheric Ozone 1988*, HMSO, London 1988.)

little doubt that enhanced [ClO] is implicated in ozone depletion. Other measurements showed that the stratosphere within the disturbed region was abnormally dry (dehydrated), and that it was highly deficient in the oxides of nitrogen (denitrified). One explanation for these phenomena is that water condenses, and the oxides of nitrogen are converted to nitric acid, to make up the polar stratospheric clouds. The smaller cloud particles, which condense at  $-80^{\circ}\text{C}$  are, in fact, composed of nitric acid trihydrate ( $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ ), and the larger cloud particles are more dilute nitric acid. Sinking of the larger particles through the stratosphere thus removes both  $\text{H}_2\text{O}$  and  $\text{NO}_x$ , and it is the removal of  $\text{NO}_x$  that appears to lead to the anomalous chlorine chemistry.

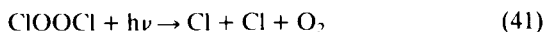
It will be remembered that, in the ordinary (i.e. non-polar) stratosphere, much of the inorganic chlorine is sequestered in the form of the reservoir compounds  $\text{HCl}$  and  $\text{ClONO}_2$ , as a result of the occurrence of reactions (36) and (37). Recent research has shown that these two compounds react together on the surface of the PSCs in the heterogeneous step



The nitric acid dissolves in the PSC, and is ultimately removed from the stratosphere, while free molecular chlorine is released in the gas phase. Because the vortex isolates the air within it, this part of the stratosphere can be 'pre-conditioned', with release of  $\text{Cl}_2$ , throughout the long polar night. As soon as the Sun rises in spring, this  $\text{Cl}_2$  is dissociated to atoms, which then react with ozone to form ClO



The conditions for enhanced [ClO] accompanying depleted [ $\text{O}_3$ ] thus seem to be established. As yet, however, we have not written any chain decomposition, an essential condition for appreciable ozone depletion. In the non-polar stratosphere, it is reaction of ClO with O in reaction (34) that regenerates Cl atoms, but when the Sun has just risen there are not yet enough O atoms present for the normal chain to have much influence. We must look, instead, for some process that regenerates Cl without needing atomic oxygen. One such process has already been presented, that of the reaction of BrO with ClO in reaction (38). Indeed, measurements show anomalously high levels of BrO within the chemically perturbed region, and a chain based on reactions (33) and (38) is thought to account for about 30% of the ozone depletion. The major proportion of ozone depletion, however, seems to depend on a 'new' piece of chemistry whose significance has only been apparent since the discovery of the ozone holes. At the low temperatures within the vortex, two ClO radicals can form a dimer, ClOOCl, that is photochemically active. Solar radiation can split this molecule to yield products that can be represented by the equation



although the liberation of two chlorine atoms is probably a two-step process. The important point is that Cl atoms have been regenerated, and can therefore destroy further molecules of ozone.

With this understanding<sup>24</sup> of the anomalous chemistry, which depends in turn on low temperatures, and the existence of PSCs and a 'containment vessel' in the form of the vortex, we must now ask where the chlorine (and bromine) come from in the polar regions. The answer, of course, is that they derive once again from man's release of the CFCs and the halons at lower latitudes. Over many months, and even years, photolysis of the anthropogenic substances that have reached the non-polar stratosphere from the troposphere yields free halogen atoms, halogen oxide radicals, and then the reservoir compounds like HCl, ClONO<sub>2</sub> (and, probably, BrONO<sub>2</sub>). Transport of these reservoirs brings them to the polar regions, where they can be trapped in the vortex during the winter. Details of the dynamics and transport thus determine, in large measure, how 'deep' the hole will become in any subsequent spring. Denitrification of the stratosphere, incidentally, prevents re-formation of the reservoir ClONO<sub>2</sub>.

Perturbed chemistry very similar to that found in the Antarctic is evident in the Arctic stratosphere. The winter stratosphere is generally warmer over the Arctic than over Antarctic regions, and PSCs are less abundant and persistent. An Arctic airborne campaign in the winter and early spring of 1989 showed, however, that PSCs were frequently present. Concentrations of ClO were up to 50 times greater than predicted for a 'normal' stratosphere (that nevertheless contains anthropogenic chlorine), and BrO concentrations were also elevated. The excess active chlorine species were associated with the presence of nitric acid-water clouds, and provide further evidence that the PSCs offer a surface on which release of active chlorine can occur. Extensive denitrification occurred, with losses of up to 80% of the reactive nitrogen expected to be present. Somewhat surprisingly, the dehydration associated with denitrification in the Antarctic was not observed in the Arctic, which implies that denitrification can occur at higher temperatures (and thus over wider areas) than had hitherto been supposed. The denitrification and enhanced active halogen concentrations suggest that local ozone losses of several tens of per cent would occur. In fact, no unequivocal ozone loss was found in the air masses sampled by the aircraft. Balloon-borne instruments found notches in the ozone profiles resembling those found during the onset of hole formation in the Antarctic. One interpretation of the results is that a 10–25% loss of ozone had occurred at altitudes between 20 and 25 km by the end of January 1989. Even if there is, as yet, no fully developed Arctic ozone hole, it is clear that the potentiality exists for hole formation, especially as chlorine loadings increase in future years.

The Antarctic ozone holes are important in several ways. One very significant aspect is the clearcut evidence that polar hole formation provides for destruction of stratospheric ozone resulting from man's release of CFCs and similar compounds. The depletion is not projected for some time in the future, but already occurs each year, and the quantities involved are not just barely detectable, but can be up to 97% of the normal ozone concentrations at some altitudes. The discovery of the Antarctic holes has also focused scientific attention on the role played by heterogeneous chemistry in the Earth's atmosphere. Atmospheric scientists had a rude awakening from a period of complacency when a phenomenon was discovered that had not been

remotely predicted by the most sophisticated models and theories then current! The environmental impacts of polar ozone depletion are harder to assess. Springtime biologically active UV irradiances over the Antarctic are greatly enhanced, and can even exceed those normally experienced in the Antarctic midsummer. A threat may thus be posed to indigenous organisms: one area of particular concern is the possible sensitivity of the spring bloom of phytoplankton living in the surface waters around Antarctica. Another question to be asked is whether the processes occurring within the chemically perturbed region can affect ozone concentrations at lower latitudes. The vortex is somewhat leaky, and ozone-deficient and chemically processed air can be transported to lower latitudes. When the vortex breaks up in late spring, more extensive mixing takes place. Export of ozone-poor air (and of processed air rich in active chlorine) from polar regions to middle latitudes might lead to dilution and ozone depletion that could last from one spring to the next, and thus produce a cumulative, permanent depletion of ozone. There is already some observational evidence<sup>27</sup> to support these concepts, with relatively large losses of ozone at 50–60°S throughout the year, and suggestions that ozone-poor air reached as far as 32°S in the Australia–New Zealand area a few months after the enormous Antarctic depletions of September–October 1987. If extensive, fully developed Arctic ozone holes begin to appear in the future, then a comparable dilution effect in the Northern Hemisphere could have very serious consequences.

## Chemistry on particles and in clouds<sup>4,10,21,28</sup>

Most of the chemistry discussed in this review has involved homogeneous interactions between reactants in the gas phase. There has been some discussion of processes that may loosely be called heterogeneous, in connection with the oxidation<sup>2</sup> of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>, and especially with regard to the involvement of polar stratospheric clouds<sup>24</sup> in the anomalous chemistry of the ozone hole. Because dusts and particles, clouds, and other aerosols are found widely<sup>28</sup> throughout the atmosphere, there is a strong probability that important chemical transformations take place on the surfaces of such aerosols, or within liquid droplets. Chemists are well aware of the importance of such processes, but they are very hard to study directly in the laboratory under conditions that really mimic those of the atmosphere. The detailed understanding of heterogeneous chemistry is thus less well developed than that of gas-phase processes. Nevertheless, it seems appropriate to finish this review with a few remarks about the involvement of particles and clouds in atmospheric chemical change.

Sulphuric acid and sulphate aerosol is found throughout the stratosphere. Recent laboratory experiments have shown that reactions can proceed on H<sub>2</sub>SO<sub>4</sub> particles in a manner analogous to the way that processes occur on the surfaces of PSCs. Ozone destruction in non-polar regions might thus have a component involving the H<sub>2</sub>SO<sub>4</sub> aerosol. Volcanic eruptions sometimes inject large quantities of material that penetrates into the stratosphere. For example, the eruption of El Chichón in the spring of 1982 spewed vast amounts of SO<sub>2</sub> into the stratosphere<sup>8</sup> that subsequently have undergone conversion to H<sub>2</sub>SO<sub>4</sub>.

droplets. Physical effects, such as a hemispheric cooling of the Earth, are evident. However, there are probably chemical effects as well, and ozone depletion is one of them. Winter trends of stratospheric ozone concentrations in middle-to-high latitudes are hard to explain by gas-phase mechanisms, but could be accounted for if heterogeneous loss occurred on the sulphate aerosol from El Chichón. Record lows in  $[O_3]$  were recorded in late 1982 and throughout 1983. Total column  $NO_2$  abundances also showed a marked decrease in a manner reminiscent of the denitrification seen in the Antarctic as a result of chemical processing on PSCs.

Reactions involving condensed-phase species are obviously of great importance within the troposphere. Not only may chemical change occur on or in particles and droplets, but secondary particulate matter may be formed as aerosols of solids or liquids. This latter type of process is clearly at work in photochemical smog. The hazes that are a characteristic<sup>4</sup> of this type of pollution are often largely a result of secondary organic aerosols, probably resulting from the ozone-mediated oxidative polymerization of hydrocarbons. Another type of secondary aerosol particle is found in the reaction of  $NO_2$  or  $HNO_3$  with sea-salt particles to form  $NaNO_3$  aerosol. Reactive condensation of gas-phase molecules on pre-existing particles ('aerosol scavenging') can have an impact on bulk atmospheric chemistry by providing a sink for a variety of species, and removal of soluble species from the atmosphere by cloud and rain drops followed by precipitation has a major effect on concentrations in the troposphere.

Simple chemical processes occurring in aqueous aerosols and droplets include the hydrolysis of  $N_2O_5$  to  $HNO_3$ , and cloud reactions also further influence the oxides of nitrogen by removal of  $NO_3$  radicals. The oxidation of  $SO_2$  to  $SO_4^{2-}$  is more complex, as I explained earlier. Yet another kind of cloud process involves radicals such as  $HO_2$  in the aqueous phase. It has recently become apparent<sup>10</sup> that cloud reactions in radicals can strongly influence the overall oxidizing capacity of the troposphere. Various processes can remove  $HO_2$  and  $OH$ , and  $HCHO$  (which is a photochemical source of  $HO_x$  in the gas phase) can also be hydrated and removed in cloud droplets. There are even aqueous-phase reactions that destroy ozone itself. The disproportionate influence of the aqueous-phase reactions, given that clouds occupy only about 15% of the volume of the lower troposphere, is in part a consequence of the enhanced concentration of reagents in solution. Activation energies are also often lower in solution than in the gas phase for the corresponding reaction. However, a special feature of aqueous-phase chemistry seems to be the high solubility of certain key species such as  $HO_2$  and  $N_2O_5$  so that partitioning into the aqueous phase is strongly favoured. Interestingly,  $NO$  is relatively insoluble, so that  $HO_2$  and  $NO$  are separated, and reaction (16) between them is prevented. Thus the reaction that converts  $NO$  to  $NO_2$  and allows  $O_3$  formation in the gas phase is inhibited.

This review ends by reporting a proposal<sup>20</sup> that particles play a part in an ecosystem regulation of cloudiness. It is evident that atmospheric composition has important effects on biological activity. The supply of oxidants and nutrients, the intensity and wavelength distribution of solar radiation, and the temperature of the Earth all play a part. Conversely, the biota release gases

that determine in large part the composition and detailed chemistry of our atmosphere, a concept that has run as a linking thread throughout this review. Some workers, notably James Lovelock<sup>11,12</sup> in his Gaia Hypothesis, see the feedback systems as constituting a closed loop, with the biota maintaining atmospheric composition, temperatures, and so on, within bounds favourable to the living organisms themselves. Regulation of cloudiness by the biota would provide Gaia with yet another control mechanism. Yet even without the closed feedback loops of Gaia, the alteration of cloudiness by life forms is of interest, because ecological changes, whether natural or imposed by man, might have unexpected meteorological consequences. The underlying idea of the regulatory mechanism that has been proposed<sup>20</sup> is that condensation of water vapour to form cloud droplets is thermodynamically unfavourable in the initial stages, and condensed-phase nuclei ('cloud condensation nuclei') are needed to start the process. Sulphate aerosols are very efficient cloud condensation nuclei, for example. The reduced sulphur compound dimethyl sulphide (DMS) is produced by metabolic processes in certain algae, and is released in substantial quantities from the oceans. If the atmospheric oxidation of DMS leads to SO<sub>2</sub>, then SO<sub>4</sub><sup>2-</sup> can be formed in the aqueous phase, and the activity of the marine biota could influence cloud cover. The feedback aspect of the system is provided by the backscattering of sunlight by clouds, which influences both illumination and temperature at the surface, and thus indirectly controls the rate at which DMS is generated.

This review has concentrated on some of the more important chemical processes that occur in the troposphere and the stratosphere. The information often comes from laboratory studies of the chemical systems, but the motivation derives from measurements of the concentrations of primary trace gases, reaction intermediates, and final products; from the quantitative identification of sources, sinks, and budgets of the trace materials; and from the hypotheses and models that seek to interpret the measurements. Atmospheric chemistry is a rich science that calls on the concepts and techniques of older disciplines, especially those of chemistry and physics. In turn, it contributes to the parent sciences, and offers much that is truly original at the most fundamental level.

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