Chapter 1

Atmospheric ozone - A brief review

1.1 Introduction

Ozone is one of the most important trace constituents of the earth's atmosphere, found in varying amounts from the surface up to 80 km. It is continuously formed and destroyed in the upper air by the action of sunlight on atmospheric oxygen. At levels above 35 km, in regions which receive direct solar radiation, ozone is in photochemical equilibrium and its existence is only slightly affected by other factors. Below 35 km ozone is rarely at equilibrium concentration and being protected from dissociation by solar radiation, the ozone-to-air mixing ratio becomes practically a conservative property of air and the concentration is mainly governed by air motions. Usually at high levels and over low latitudes, the ozone concentration is below equilibrium level and ozone is continuously produced. As it is produced, it is transported poleward and downward in the winter hemisphere. Consequently the greatest amounts of ozone are found at high latitudes at the end of the winter night. Because of this situation plants, animals and human beings of high latitudes are adjusted to life under lower intensities of ultraviolet radiation than those recorded over the equatorial regions.

Ozone from the stratosphere passes into the troposphere, mainly at the tropopause breaks, and is then slowly destroyed by contact with vegetation at the earth's surface and in other ways.
The total quantity of ozone in the atmosphere compared to the other constituents is extremely small, amounting to a thickness of only 0.2 to 0.5 cm reduced to standard temperature and pressure, or 1 ozone molecule to every million molecules of normal oxygen even at the level where it is a maximum. This extremely small amount of ozone is further spread out in the vertical in a very uneven manner from the ground up to about 80 km and also unevenly over the globe in space and time. Despite its very low concentrations in the atmosphere, ozone has been studied in greater detail than any other atmospheric gas, mainly because of: (a) its absorption properties and the dominant role it consequently plays in the radiative thermal budget of the upper stratosphere and (b) its usefulness as a natural tracer in the study of atmospheric motions in the lower stratosphere.

Ozone absorbs solar radiation in three different parts of the spectrum: (1) in the ultraviolet Hartely bands between 2100 and 3000 A.U. and Huggins band between 3000 and 3600 A.U., (2) in the Chappuis bands of visible spectrum between 4500 and 7000 A.U. and (3) in the infrared region chiefly around 9.6 μ. The absorption in the ultraviolet region is so strong that the entire solar radiant energy in the wavelengths between 2100 and 2900 A.U. is completely depleted by the small amount of ozone present in the atmosphere. The heat liberated by the absorption and exothermic decomposition of ozone leads to the formation of a warm region at a height of about 50 km over the greater part of the earth. This
stable warm region, with a temperature peak of 0° to 20° C, is one of the dominant features of the thermal structure of the earth's atmosphere.

Ozone absorption in the visible region is very weak and in the infrared the absorption band is quite narrow. However, the absorption band in the visible occurs in that part of the spectrum where the intensity of the incoming solar radiation is maximum while the infrared absorption band is nearly coincident with the intensity maximum in the outgoing long wave radiation from the earth and lower atmosphere. Thus the absorption of visible and infrared radiation by ozone, though comparatively less significant than ultraviolet absorption, still gives rise to appreciable warming of the upper atmosphere.

1.2 Historical development of the study of atmospheric ozone

Study of atmospheric ozone commenced about 50 years ago with the pioneering work of Prof. Charles Fabry, the great master of optics, in collaboration with Buisson. They obtained the first ever accurate measurements of the amount of ozone in the atmosphere and their fundamental studies have been the mainstay of most of the later experimental work on atmospheric ozone.

The second major step forward in the study of ozone was taken by Professor G.M.B. Dobson, who developed to a high degree of precision the technique of determining from the earth's surface the total amount of ozone in the air column above the observer. Dobson also planned and directed a measuring programme
which, between 1925 and 1929 revealed the large scale features of the seasonal and geographical distribution of ozone, first over Europe and then over the world.

The method used by Fabry and Buisson and developed by Dobson consists essentially of measuring the intensity of the solar spectrum within a range of wavelengths in which there is no important absorption by other atmospheric gases. Dobson chose the Huggins band for this purpose and used a specially designed spectrograph to make his measurements. Though there were inherent difficulties in this method, he succeeded in determining rather closely the total amount of ozone in the atmosphere. He later designed a spectrophotometer (1931) which was considerably more convenient and sensitive. The Dobson ozone spectrophotometer is even today the basic instrument for all accurate measurements of atmospheric ozone and is regularly used at nearly 100 stations in the world. It is used to confirm the ozone observations from satellites and to check the data obtained by balloon-borne ozonesondes which measure the vertical distribution of ozone.

Dobson's simultaneous observations from six stations in Europe during the years 1925-1929 revealed two largescale features of ozone variability. First, a definite seasonal variation consisting of a maximum of ozone in the spring months and a minimum in the autumn months; second, large day-to-day variations related to the general weather situation, with large ozone amounts in the rear of cyclones and ahead of anticyclones. The
observations also indicated that the total ozone amount increased with latitude. Dobson therefore redistributed his instruments at widely separated latitudes, from Christ Church, New Zealand (44°S) to Spitzbergen (78°N) and the extended observations confirmed the earlier conclusions, the spring maximum and autumn minimum except near the equator and an apparently increasing amplitude in the annual variation with increasing latitude. Dobson's classical measurements formed the basis of all discussions of ozone till the IGY, when ozone observations were again organized systematically on a global basis.

While it was known that the absorption of solar ultraviolet radiation caused the warm region at a height of about 50 km, no information was available on the vertical distribution of ozone in the atmosphere. The maximum was supposed to be at 40-50 km. No accurate knowledge of the formation and decomposition of the ozone in the atmosphere was also available. Paul Götz was responsible for the next important observational advance, in determining the height and vertical distribution of ozone using the Umkehr (reversal) effect, discovered by him during his observations in Spitzbergen. Using light from the clear zenith sky and comparing the intensities of two wavelengths in the Huggins band, Götz found that as the sun went down, the shorter wavelength was relatively less and less absorbed than the longer wavelength. A study of this effect led to the conclusion that the height of the centre of gravity of ozone in the atmosphere was in the neighbourhood of 20 km instead of 35-50 km, as had been thought before, and that
there was some ozone present in the lower layers too. This immediately made it easier to understand the connection that had been observed between ozone changes and weather and brought ozone within the realm of interest of the synoptic meteorologist.

In the meantime important developments were taking place in finding a theoretical explanation to the observed facts regarding ozone. In 1928 McLennan discovered the presence of atomic oxygen at a height of about 100 km and Dobson and Lindemann discovered a hot layer around 50 km above the ground. Based on these observations Chapman, in one of his brilliant contributions of the 1930's proposed, in what has now come to be called the classical theory, that the formation and largely also the destruction of ozone were of photochemical nature. Other mechanisms of production of ozone like aurorae, cosmic rays, electric discharges in thunderstorms etc have also been suggested on several occasions, but contributions from these sources have not been proved to be quantitatively significant and it may be safely assumed that photochemical action together with transport processes determine the three dimensional distribution of ozone in the stratosphere. Wulf and Deming (1936, 1937) for the first time quantitatively investigated the photochemical theory and showed conclusively that ozone is of photochemical origin and calculated the vertical distribution of ozone. They also showed that while above the level of maximum ozone, ozone is in a state of photochemical equilibrium, below, ozone may persist for days together.
Until about 1960, the theoretical knowledge of the vertical distribution of ozone derived from the classical photochemical theory was accepted as adequate. But the intensified observations of the total and vertical distribution of ozone during and after the International Geophysical Year (IGY) brought to light many discrepancies between theory and observations. Some of the main discrepancies are:

1. Over the tropics the total ozone is much less than that over the rest of the earth almost throughout the year, despite the fact that the amount of solar ultraviolet radiation available for photochemical processes is greater in the tropics.

2. The total ozone over the middle and high latitudes is higher during winter and spring than during summer.

3. In the polar regions which are completely cut off from solar radiation during winter an appreciable amount of ozone is found during that period.

These discrepancies between theory and observation were attributed mainly to the uncertainties in the estimation of the concentrations of the various constituent gases and the various reaction and dissociation rates assumed in the theory. The assumption of a pure oxygen atmosphere is also of questionable validity. Another factor which contributed to the differences between theory and observations was the dearth of adequate reliable observations of ozone in the upper stratosphere.
Although the classical theory gave a reasonable explanation for the existence of the ozone layer, its failure to explain correctly the temporal and spatial variations of ozone pointed to the fact that the bulk of the atmosphere cannot be in photochemical equilibrium. This led to the development of the non-equilibrium theory, in which the time of half restoration of ozone when the equilibrium is disturbed, called the relaxation time, varies sharply with decreasing altitude, from about one hour at the stratopause to several months or more, at the level of the ozone maximum and below. The relaxation times at any level are larger in winter than in summer. The non-equilibrium theory has reduced the magnitude of the discrepancies between theory and observations to a slight extent but it became obvious that any photochemical theory has to take into account the transport processes in the atmosphere as well as many other possible reactions involving active radicals produced from water vapour. Though Bates and Nicolet (1950) had suggested the role of the active radicals from water vapour as far back as 1950, and Venkateswaran (1963) had stressed the importance of the reaction of ozone with H to the mesospheric ozone, the full implication of these reactions was brought out only when Hampson (1964) proved that the contribution of these active radicals to the ozone photochemistry is significant throughout the mesosphere, stratosphere and even down to the earth's surface. This formed the basis of the new theory by Hunt in 1966 of ozone photochemistry in a moist atmosphere. When the H radicals (H, OH and HO₂) are taken into account the number of photochemical reactions become manyfold, as we have to deal with 9 variable trace substances (O, O₂, O₃, OH, HO₂, H₂
$H_2O$ and $H_2O_2$) instead of the initial two ($O_3$ and $O$). Thus there are nine interrelated equilibrium equations and this full set can only be solved numerically. Considerable amount of work has since been done on the various aspects of the problem - Ditchburn (1962), Hampson (1964), Hesstvedt (1964, 1968, 1969), Hunt (1966, 1968), Brewer (1968), Dütsch (1968), Reed (1968), Curtze (1969, 1970, 1971), Nicolet (1970), Strobel (1970) - and a complete and critical review of the photochemistry of ozone in a moist atmosphere has been published by Dütsch (1971).

Side by side with these attempts to find a theoretical explanation of the ozone distribution over the globe important developments were also taking place in the observational techniques, particularly of the vertical distribution of ozone. The Umkehr method of Paul Götz, briefly mentioned earlier, continues to yield valuable data on the broad features of the vertical distribution of ozone in the atmosphere. The first ozone sounding with a balloon-borne instrument was made by Regener in 1934 in his classical experiment using an ultraviolet spectrograph. Since then different types of optical and chemical ozonesondes have been developed by various workers - Regener (1934, 1956, 1960, 1964), Paetzold (1955), Vassy (1956), Brewer (1960), Komhyr (1964, 1969), Kobayashi (1965) and Sreedharan (1968) - and have been flown extensively in various parts of the globe. The data collected from these soundings have given a much clearer picture of the vertical distribution of ozone in the atmosphere up to 30 km and its variations with latitude and season. These data have also brought to light the limitations of
the theories of ozone distribution developed so far. The comparatively high resolution of the profiles from soundings encouraged meteorologists to investigate the possibility of using ozone as a tracer of atmospheric air movements. This possibility further accelerated the development of instruments for the measurement of ozone. A number of new ozone sensors have been flown from rockets - Hirasawa and Takeo (1970), Randhawa (1970), Sissens (1970), Hilsenrath (1971), Evans and Carver (1972) and recently from satellites - Hanel (1970), Mateer (1971), Prabhakara (1971), Lovill (1972), Heath (1973), Krueger (1974). The satellites provide an exciting new platform for the measurement of ozone from outside the earth's atmosphere - Twomey (1961) - and have rendered possible the collection of global data on a regular basis for the first time since ozone observations were made in 1920.

With the rapid developments in the theory of atmospheric ozone and increase in the volume of observational data, it became obvious that atmospheric dynamics plays an important role in the distribution of ozone. Extensive investigations made by Reed (1950), Kulkarni (1959, 1962), Godson (1960), Ohring (1960), Boville (1961), Dütsch (1962), Junge (1962), London (1963), Ramanathan (1969), Farkas (1970), Berkofsky (1971), Pittock (1971) and others brought to light the following prominent features of the distribution of ozone in the atmosphere.

1. The maximum ozone density (10 to 25 x 10^{-3} cm NTP km^{-1}) is usually found between 20 and 30 km above which the density decreases very rapidly with height.
2. The troposphere contains 5 to 10% of the total ozone.

3. Over low latitudes the total amount as well as the vertical distribution of ozone remain nearly constant throughout the year; over middle and high latitudes both the total and the vertical distribution are highly variable.

4. Considerable stratification of ozone is observed in the lower stratosphere over middle and high latitudes.

5. In the troposphere ozone appears to be well mixed and does not vary significantly with height.

6. Most of the destruction of ozone takes place when ozone comes into contact with organic matter near the ground.

7. The highest amounts of ozone are found over the middle and high latitudes during winter and spring and not during summer.

8. There is distinct asymmetry between the two hemispheres with regard to ozone distribution. Marked differences are also found in the distribution along a given latitude circle.

9. In the high and middle latitudes the spring rise in ozone is associated with the warming and break up of the polar vortex.

10. A clear, though small biennial variation of atmospheric ozone is found at stations in tropics and middle latitudes.

   It is of interest to note the relative abundance of ozone in the atmosphere vis a vis the other gases. The mole fraction of the different gases expressed as a percentage in dry air up to about 25 km is given below:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>78.09</td>
</tr>
<tr>
<td>Oxygen</td>
<td>20.95</td>
</tr>
<tr>
<td>Argon</td>
<td>0.93</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.03</td>
</tr>
<tr>
<td>Neon</td>
<td>$1.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>Helium</td>
<td>$5.24 \times 10^{-4}$</td>
</tr>
<tr>
<td>Krypton</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>$5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Xenon</td>
<td>$8 \times 10^{-6}$</td>
</tr>
<tr>
<td>Ozone</td>
<td>$1 \times 10^{-6}$</td>
</tr>
<tr>
<td>Radon</td>
<td>$6 \times 10^{-18}$</td>
</tr>
</tbody>
</table>
It may be seen that the concentration of ozone in the lower atmosphere is less than that of all the rare gases barring radon.

The height of the homogeneous atmosphere (constant air density equal to the density at sea level at all elevations) is about 8 km. As already mentioned the total ozone in unit vertical column of the atmosphere would occupy a depth of only 2 to 5 mm at NTP, which shows that the fractional contribution of ozone is less than \(10^{-6}\) to the total mass of air in a unit column. Despite its small abundance the importance of ozone in the physics and dynamics of the atmosphere is fundamental. The thermal structure of the stratosphere and mesosphere is intimately linked with the photochemistry of ozone and its horizontal and vertical transport from its source region by the general circulation of the atmosphere. By its intense absorption of the ultraviolet part of the solar spectrum the ozone in the upper atmosphere acts as a shield protecting the biosphere from the lethal effects of these radiations.

### 1.3 Units used in the measurement of ozone

With the development of various methods for the measurement of ozone, a number of units have been adopted for expressing the quantity of ozone.

The total amount of ozone in the atmosphere is generally expressed as the height of an equivalent column of ozone at standard temperature and pressure (STP). This is usually expressed in units of \(10^{-3}\) cm STP or one milli-atmos centimetre, commonly called a Dobson Unit, the absorption coefficients adopted for the measurement being in accordance with the Vigroux scale. The total amount of ozone
in the atmosphere varies from about 200 to 500 D.U. depending upon
latitude and season. The amount of ozone in the atmosphere deter-
mined by the Umkehr method is expressed in milli atmos cm per
kilometre \((10^{-3} \text{ cm STP})/(\text{km})^{-1}\) and is denoted by symbol \(d_3\).

1.3.2 Another convenient unit is the partial pressure of ozone
\((p_3)\) expressed in micromillibars \((\mu \text{mb})\), a unit which came into
extensive use with the development of ozonesondes. Since an ozone
density of one \(10^{-3} \text{ cm km}^{-1}\) represents a concentration \(10^8\) times
smaller than that of air at S.T.P. the corresponding partial pressure
of ozone is \(\frac{10^{13}}{10^8} = 10.13\ \mu \text{mb}\) at a temperature of \(273^\circ\text{A}\). The partial
pressure at a given concentration of a gas is proportional to its
temperature and hence the conversion factor between \(p_3\) and \(d_3\) is
given by

\[
p_3 = 10.13 \frac{T}{T_0} d_3 \quad (1.1)
\]

1.3.3 In photochemical studies, the unit employed to express
ozone concentration is the number of molecules per cubic centimetre
\((n_3)\). The partial pressure of ozone, \(p_3\), is given by

\[
p_3 = \left(\frac{n_3}{n}\right) p
\]

where \(n_3\) is the number density of ozone, \('n'\) the number density of
air and \('p'\) the total pressure. Since the gram-molecular weight of
ozone is 48 and that of air is 28.96, this can be written as

\[
p_3 (\mu \text{mb}) = 0.603 r_3 (\mu \text{g cm}^{-1}) p \quad (1.2)
\]

In one milli atmos cm, we have \(L/10^8 = 2.7 \times 10^{11}\ \text{mol/cm}^2\),
where \('L'\) is the Loschmidt\'s number. Thus

\[
n_3 = 2.687 \times 10^{11} d_3
\]

\[= 2.652 \times 10^{10} \frac{T_0}{T} p_3 \quad (1.3)\]
1.3.4 The ozone mixing ratio \( r_3 \) is the ratio by mass of ozone to mass of air in a given volume and is expressed by

\[
 r_3 = \frac{\rho_3}{\rho}
\]

(1.4)

It is dimensionless. A convenient unit is \( 10^{-6} \), expressed as 'micrograms per gram' (\( \mu g \text{ gm}^{-1} \)) or sometimes referred to as 'parts per million'. \( r_3 \) is a quasi-conservative property of an air parcel in the lower stratosphere (below 20-25 km) where photochemical reactions are slow. It can, therefore, be used to trace air movements in the lower stratosphere.

\[
r_3 = 2.87 \times 10^{-3} \left( \frac{\mu g \text{ gm}^{-3}}{T^{(\text{OK})} \text{ p}(\text{mb})} \right)
\]

(1.5)

For the study of tropospheric ozone, another unit currently in use is parts per hundred million (pphm), which is \( 10^2 \) times smaller than \( r_3 \).

1.3.5 For expressing ozone concentrations \( (\rho_3) \) near the ground, the unit adopted universally is the microgram per cubic metre \( (\mu g \text{ m}^{-3}) \). From the equation of state for ozone,

\[
\rho_3 = \frac{R_u T}{M_3}
\]

using the appropriate values for the constant

\[
\rho_3 = 0.472 \frac{T}{T_0} \rho_3
\]

\[
= 1.73 \times 10^{-3} \text{ T(\text{OK}) } \rho_3
\]

(1.6)

where \( \rho_3 \) is expressed in \( \mu g \text{ m}^{-3} \) and \( \rho_3 \) in \( \mu \text{mb} \).

A new diagram called the ozonagram devised by Godson (1962) has been universally accepted for representing the vertical distribution of ozone in the atmosphere. The diagram has the
partial pressure of ozone as the X-coordinate and \( \log p \) as the Y-coordinate, with lines of constant mass mixing ratio drawn as sloping curves to the right. The unique feature of the ozonagram is that the integrated amount of ozone between any two pressure levels is proportional to the area enclosed by the ozone curve and the Y-axis. If \( p_0 \) is the pressure at ground level and \( p_{\text{min}} \) that at the top of the sounding the integrated ozone from the ground to the maximum level of the sounding will be equal to

\[
\int_{p_0}^{p_{\text{min}}} p \, d(\log p) = 10.13 \frac{T}{T_0} \int_0^{Z_{\text{max}}} \frac{dM}{R*T} \, dz
\]

\[
= C \int_0^{Z_{\text{max}}} d_2 \, dz = C' X'
\]

(1.7)

where 'M' is the molecular weight of ozone, \( R^* \) is the universal gas constant, \( C \) and \( C' \) are constants and \( X' \) is the total ozone from ground up to the level of termination of sounding \( (Z_{\text{max}}) \).

Another advantage of the ozonagram is that the vertical distribution obtained from an ozone sounding or an Umkehr calculation can be checked graphically with the total ozone amount measured by the Dobson spectrophotometer. The ozonagram thus provides a convenient method for verifying the values obtained by a sounding.
1.4 Photochemistry of atmospheric ozone

1.4.1 The classical photochemical theory in a pure oxygen atmosphere

1.4.1.1 Chapman's theory

Most of the important features of ozone photochemistry and the relationship of ozone with transport processes can be explained by Chapman's theory, discussed below.

Oxygen absorbs radiation of wavelengths 600 to 2425 Å and dissociates into atomic oxygen in accordance with

\[ \text{O}_2 + h\nu (\lambda < 2420 \, \text{Å}) \rightarrow 0 + 0 \]  \hspace{1cm} (1.8)

The oxygen atoms so produced combine with \( \text{O}_2 \), in the presence of a third molecule of \( \text{N}_2 \) or \( \text{O}_2 \) by a collision process, to form ozone as follows:

\[ \text{O}_2 + 0 + M \rightarrow \text{O}_3 + M \]  \hspace{1cm} (1.9)

Ozone, however, has important absorption bands in the ultraviolet, visible and infrared parts of the solar spectrum and on absorption is transformed into \( \text{O}_2 \) and 0 according to

\[ \text{O}_3 + h\nu (\lambda \simeq 11,800 \, \text{Å}) \rightarrow \text{O}_2 + 0 \]  \hspace{1cm} (1.10)

The ozone molecule and oxygen atom can unite to form oxygen molecules in accordance with

\[ \text{O}_3 + 0 \rightarrow 2 \, \text{O}_2 \]  \hspace{1cm} (1.11)
In addition other collisional reactions can also occur

\[ 2 \, O_3 \rightarrow 3 \, O_2 \quad (1.12) \]

\[ O + O + M \rightarrow O_2 + M \quad (1.13) \]

Since in the stratosphere the concentration of atomic oxygen is extremely small, the reaction (1.13) can be neglected. Reaction (1.12) is called the thermal decomposition of ozone and is unimportant for temperatures and ozone concentrations found in the stratosphere. All the reactions detailed above take place side by side in the same environment with the result that a certain equilibrium amount of ozone is formed at each level of the atmosphere when the rate of production equals the rate of destruction.

Let \( n_1, n_2, n_3 \) and \( n_m \) be the number densities respectively of oxygen atoms and of \( O_2, O_3 \) and air molecules. If \( k_{12} \) and \( k_{13} \) be designated as the rate coefficients for reactions (1.9) and (1.11) respectively and \( q_2, q_3 \) be the number of dissociating quanta of solar ultraviolet radiation absorbed by \( O_2 \) and \( O_3 \) respectively per unit volume and per unit time, then the number of ozone molecules formed by reaction (1.9) per unit volume and time is proportional to the product \( (n_1 n_2 n_3) \); on the other hand the number of oxygen atoms (or oxygen molecules) lost as a result of the same reaction per unit volume and time is given by \( (k_{12} n_1 n_2 n_m) \). Due to photochemical processes the rate of change of \( n_1, n_2 \) and \( n_3 \) in unit volume is given by:
\[
\begin{align*}
\frac{dn_1}{dt} &= -k_{12} n_1 n_2 n_m + 2 q_2 - k_{13} n_1 n_3 + a_3 \quad (1.14) \\
\frac{dn_2}{dt} &= -k_{12} n_1 n_2 n_m - q_2 + 2 k_{13} n_1 n_3 + a_3 \quad (1.15) \\
\frac{dn_3}{dt} &= k_{12} n_1 n_2 n_m - k_{13} n_1 n_3 - q_3 \quad (1.16)
\end{align*}
\]

It should be noted that \(q_2\) and \(a_3\) are proportional to \(n_2\) and \(n_3\) respectively. For photochemical equilibrium

\[
\frac{dn_1}{dt} = \frac{dn_2}{dt} = \frac{dn_3}{dt} = 0 \quad (1.17)
\]

But the amount of molecular oxygen is uniform and quite large from the ground up to 80 km and photochemical processes have a negligible effect on the value of \(n_2\). Therefore (1.15) can be ignored and the values of \(n_2\) and \(n_m\) that enter in equation (1.14) and (1.16) may be considered to be constant.

Eliminating \(n_1\) between equations (1.14) and (1.16) the expression for \(n_3\) becomes

\[
n_{3e} = \frac{k_{12} n_2 n_m}{k_{13}} \frac{q_2}{a_3} \quad (1.18)
\]

where \(n_{3e}\) is the equilibrium number density of ozone. Since \(a_3\) involves \(n_3\), the equation (1.18) is quadratic and can be solved
without ambiguity because only one of the two solutions gives a positive value for \( n_{3e} \). It is seen that \( n_{3e} \) depends on the number density of oxygen and air, on the dissociating quanta of oxygen and ozone and through the rate coefficients on temperature.

The computation of \( n_{3e} \) at different levels involves a knowledge of various quantities on the right hand side of equation (1.18). Wulf and Deming (1937) were the first to perform this computation with the data available at their disposal. Later Dütsch (1946, 1956 and 1968), Craig (1950), Paetzold (1953) and Hunt (1966) carried out the computation with improved data. The important parameters that enter into the evaluation of \( n_{3e} \) are the emission spectrum of the sun in the ultraviolet, the absorption spectra of oxygen and ozone, the photochemical factor \( k_{12}/k_{13} \) and the vertical distribution of oxygen and nitrogen in the atmosphere.

In the absence of actual observed data Wulf and Deming (1937) assumed a black body radiation from the sun corresponding to 6000° K to obtain ultraviolet intensities. Craig (1950) used values of ultraviolet intensities measured with the aid of rockets in the U.S.A. in 1946. The actual data showed wide departures from the black body radiation at 6000° K. The ratio of the observed intensity to the assumed black body radiation was observed to decrease irregularly from 70 percent at 3300 - 3400° A to 6 percent at 2200° A. For lower wavelengths,
Craig arbitrarily assumed 5 percent of the black body radiation as valid. Later investigators Paetzold (1953) and Mitsch (1956) used more recent rocket data for ultraviolet intensities and Detwiler et al (1961) computed ultraviolet intensities from rocket measurements. Brewer and Wilson (1961) measured the intensities of solar radiation in the window region around 2100 Å by direct flux measurement using a balloon borne sonde. They obtained values which are almost 3 times smaller than Detwiler's. The data from both measurements are represented in Fig 1.1.

Recent advances in satellite observations of solar variability in the ultraviolet have been reported by Heath (1974). These include the measurements of solar irradiance in the ultraviolet by the Monitor of Ultraviolet Solar Energy (MUSE) experiment and the atmospheric radiance and the solar irradiance by the backscatter ultraviolet (BUV) experiment in Nimbus 3 and Nimbus 4 satellites. It is hoped that these and future experiments will remove the existing uncertainties regarding the absolute value of the intensity of the emission of the sun in the ultraviolet.

The use of Brewer - Wilson values reduces the total amount of ozone computed theoretically by about 20% and lowers the centre of gravity of ozone slightly. The relaxation times are increased by about 20 percent in the middle stratosphere and still more at higher levels; only below the level of ozone maximum are the changes in relaxation times nominal.
Fig. I-I - Absorption coefficients of ozone and oxygen and extra-terrestrial spectral intensity distribution of solar radiation.
1.4.1.2 Absorption spectra of ozone and oxygen

Fig 1.1 also depicts the absorption coefficients of oxygen and ozone as a function of wavelength. While below about 2000 Å the depletion of solar radiation is completely due to the absorption by molecular oxygen, above about 2200 Å ozone is the only important absorber and most of the radiation around 2500 Å is eliminated by the time it reaches the upper stratosphere well above the ozone maximum. Between these two regions of strong absorption, there is a window where photochemically active radiation penetrates relatively deep into the atmosphere, although not to the ground. It is this part of the spectrum which dissociates oxygen below the stratopause and which is thus responsible for the formation of the main ozone layer. The overlapping ozone and oxygen absorption in this window region is an important feature of ozone photochemistry. About 80 - 90% of the potentially ozone forming radiation in that part of the spectrum is absorbed by ozone itself leading to its own destruction. This property along with the nature of variation of the dissociation rate of ozone with height acts as a strong damping mechanism on photochemically produced ozone variations.

According to Dütsch (1971) our knowledge of the ozone absorption coefficients seems at present well established by measurements of Vigroux (1953) and Inn and Tanaka (1953) and
changes which might yet appear in the values of these coefficients will hardly be large enough to have a significant influence on photochemical results except perhaps in the region where ozone and oxygen absorptions overlap (2000-2300 Å).

The most critical absorption coefficients with respect to stratospheric ozone distribution are those of oxygen in the window region. This is clearly shown by the difference between some earlier photochemical computations which assumed the validity of Beer's law for this particular window region and more recent computations which take into account the deviations from Beer's law suggested by Heilpern (1952). Later measurements by Ditchburn and Young (1962) substantiated Heilpern's findings although the numerical values were only slightly changed. Allowances to the deviation from Beer's law lower the centre of gravity of the ozone layer and increases the total amount. The small difference in the absorption coefficients given by Ditchburn and Young, now generally used, produces a notable difference in the photochemical computations and a re-evaluation of these constants, therefore, appears to be necessary.

The ratio of reaction rates $k_{12}/k_{13}$ has been experimentally determined. This ratio which is sensitive to temperature plays an important role in the computation of equilibrium ozone density. Widely different values of $k_{12}$ and $k_{13}$ and their temperature coefficients are mentioned in literature. Campbell and Nudelmann (1960) have discussed in detail the reaction kinetics, thermodynamics
and transport properties in the ozone-oxygen system. Dütsch (1968) and Crutzen (1969) suggest that the best solution would be to determine the ratio of $k_{12}/k_{13}$ by trying to obtain the best fit between theory and observation in the upper stratosphere where ozone concentration can be expected to be close to equilibrium.

1.4.1.3 Relaxation time

Although the simple photochemical theory in a pure oxygen atmosphere gives a reasonable explanation for the existence of the ozone layer, it fails to explain correctly the variations of ozone with latitude and season and the considerable day to day fluctuations observed in the middle and high latitudes. This leads one to the obvious conclusion that the bulk of the atmospheric ozone cannot be in photochemical equilibrium. This is easily proved by investigating the relaxation times at different levels.

The distribution of a gas like ozone which is not uniformly mixed with the main atmospheric constituents is influenced by air motions. In order to estimate the relative importance of photochemical processes and of air motion, it is necessary to know the relaxation time which is the time required for ozone to attain half the equilibrium value if all the ozone were to be removed at any level. This time also indicates whether or not the actual concentration would follow the theoretical variation of the equilibrium content produced by the seasonal changes of solar elevation.
The relaxation time is approximately given by the ratio of the total content of odd oxygen particles \((n_1 n_3)\) divided by their rates of formation (Dütsch, 1968).

\[
t = \frac{n_1 n_3}{2f_2 n_2}
\]

In the stratosphere \(n_1\), \(n_3\) and the relaxation time can be given by

\[
t = \frac{n_3}{2f_2 n_2}
\]

The time of half restoration has been calculated by different workers Dütsch (1956), Craig (1950) and Paetzold (1955). Though the actual values differ slightly they are of the same order of magnitude at different levels.

The relaxation time sharply increases with decreasing altitude from about one hour at the stratopause to several months or more at the level of the ozone maximum and below, with values which are at the same level larger in winter than in summer. This means that equilibrium will never exist in the lower stratosphere. Below the level of the ozone maximum the distribution will largely be determined by air motions and it is obvious to assume that the discrepancy between observed and theoretically computed distribution of the total amount is a result of the redistribution of ozone by general circulation.

To obtain an idea of the interplay of photochemical action and transport processes, the non-equilibrium equation is used to compute
the time cross section of the vertical distribution of ozone. Fig 1.2 shows the results of such computations compared with those obtained from the equilibrium theory for 45°N. The considerable asymmetry shown in the seasonal variation in the middle stratosphere and just above the level of the ozone maximum is the result of a relaxation time of the order of a few months; still higher values around 20 km and below lead to ozone concentrations which are almost independent of season. It can be seen from Fig 1.3 that the discrepancy between theory and observation with respect to worldwide distribution of the total amount remains although its magnitude is slightly reduced.

For the whole earth, the average value of total ozone is fairly in agreement with theory but in regard to seasonal and latitudinal variations complete disagreement is found. Theory predicts maximum ozone values near the equator, while observations show a pronounced minimum there in all seasons. For middle latitudes, theory indicates a summer maximum of small magnitude whereas observations show a pronounced maximum in late winter/spring. These discrepancies are well illustrated in Fig 1.4 which shows the observed and the theoretically calculated values for different latitudes and seasons—after Dütsch (1961).

About the level of maximum ozone concentration, the observed values agree well with the theoretical ones.
FIG. 1.2 - Computed time cross-sections of vertical ozone distribution at 45° N

A - Classical equilibrium theory
B - Classical non-equilibrium theory

(Dütsch 1971)
FIG 1-3 - Variation of total ozone with season and latitude from photochemical theory

- **Equilibrium theory**
- **Non-equilibrium theory**

(Dutsch 1971)
FIG. I.4 - OBSERVED AND THEORETICALLY CALCULATED TOTAL OZONE DISTRIBUTION COMPARED AT DIFFERENT LATITUDE AND SEASON.
(AFTER DÜTSCH 1961)
1.4.2 **Photochemistry in a moist atmosphere**

As early as 1950 Bates and Nicolet had suggested that reactions involving hydroxyl groups produced by the dissociation of water vapour could be important in the photochemical reactions in the mesospheric region. Venkateswaran (1963) was the first to point out the importance of the reaction of ozone with hydrogen in deciding the mesospheric ozone concentration.

In 1964 Hampson, on the basis of laboratory measurements of McGrath and Norrish (1960) suggested that the water molecule might also be split by the reaction with excited oxygen atoms. Such excited atoms are produced by photodissociation of ozone by wavelengths shorter than about 3100 Å and also by absorption of oxygen in the Shumann – Runge continuum (1749 Å) and even at still shorter wavelengths. Photodissociation in the upper stratosphere above 35 km predominantly results in the production of excited oxygen atoms. Though the production of excited O atoms decreases rapidly below 35-40 km, their contribution is still significant in the lower stratosphere and to a certain extent even down to the earth's surface.

Pettersen and Kretchmer (1960), Reeves et al (1960), Clyne and Thrush (1963), Benson (1965) and Schofield (1967) have discussed in detail the rate coefficients of the various possible reactions in a moist atmosphere and Schiff (1969) and Hesstvedt (1969) the possible reactions in an atmospheric model containing oxygen, nitrogen and hydrogen. From detailed laboratory investigations Kaufman (1964) assessed the various reactions involving
hydrogen in a moist atmosphere. Based on the investigations of these workers Dütsch (1971) listed 44 possible reactions which may be of significance to the photochemistry in a moist atmosphere. He has also listed separately 22 reactions which are of importance to the ozone photochemistry below the stratopause. These are reproduced in Table 1.1.

The basic reaction schemes showing the interplay of the O and H systems in the stratosphere is shown in Fig 1.5.

Let \( x, y \) and \( z \) represent the concentrations of \( \text{H}, \text{OH} \) and \( \text{HO}_2 \) radicals and \( W_1, W_2 \) and \( W_3 \) represent the concentrations of \( \text{H}_2\text{O}, \text{H}_2 \) and \( \text{H}_2\text{O}_2 \). The equilibrium between \( x \) and \( y \) is determined by reactions 9, 12, 14 (Table 1.1).

\[
\frac{k_{11} n_3 x + k_{18} n_2^2}{x} = \frac{k_{15} n_1}{y}
\]

and

\[
\frac{x}{y} = \frac{k_{15} n_1}{k_{18} n_2^2} = \frac{k_{15} f_3 n_3}{k_{18} n_2^2 (k_{11} n_3 + k_{18} n_2^2)}
\]

which means that

\[
\frac{x}{y} < \frac{n_1}{n_3}
\]

\( x \) is thus decreasing very rapidly with decreasing altitude and reactions with hydrogen atoms become of only marginal importance for stratospheric ozone contents.

The equilibrium between \( y \) and \( z \) is given by reactions 9, 10, 11, 12 and 13 (Table 1.1).
### Table 1.1

**Important reactions relating to ozone photochemistry below stratopause in a moist atmosphere**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Reaction</th>
<th>Rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$O_2 + O + M \rightarrow O_3 + M$</td>
<td>$k_{26} \text{cm}^{-3} \text{sec}^{-1}$</td>
</tr>
<tr>
<td>2.</td>
<td>$O_3 + h\nu \rightarrow O^* + O_2$</td>
<td>$k_{27} \text{sec}^{-1}$</td>
</tr>
<tr>
<td>3.</td>
<td>$O_3 + h\nu \rightarrow O + O_2$</td>
<td>$(1 - \frac{\alpha}{\beta}) k_{28} \text{sec}^{-1}$</td>
</tr>
<tr>
<td>4.</td>
<td>$O^* + M \rightarrow O + M$</td>
<td>$k_{29} \text{cm}^3 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>5.</td>
<td>$O_2 + h\nu \rightarrow O + O$</td>
<td>$f_2 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>6.</td>
<td>$O_3 + O \rightarrow 2 O_2$</td>
<td>$k_3 \text{cm}^3 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>7.</td>
<td>$O_3 + O^* \rightarrow 2 O$</td>
<td>$k_6 \text{cm}^3 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>8.</td>
<td>$O + O + M \rightarrow O_2 + M$</td>
<td>$k_1 \text{cm}^6 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>9.</td>
<td>$O_3 + H \rightarrow OH + O_2$</td>
<td>$k_{11} \text{cm}^3 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>10.</td>
<td>$O_3 + OH \rightarrow HO_2 + O_2$</td>
<td>$k_{12} \text{cm}^3 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>11.</td>
<td>$O_3 + HO_2 \rightarrow OH + 2 O_2$</td>
<td>$k_{13} \text{cm}^3 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>12.</td>
<td>$O + OH \rightarrow H + O_2$</td>
<td>$k_{15} \text{cm}^3 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>13.</td>
<td>$O + HO_2 \rightarrow OH + O_2$</td>
<td>$k_{16} \text{cm}^3 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>14.</td>
<td>$H + O_2 + M \rightarrow HO_2 + M$</td>
<td>$k_8 \text{cm}^6 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>15.</td>
<td>$H_2O + h \rightarrow H + OH$</td>
<td>$f_1 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>16.</td>
<td>$O^* + H_2O \rightarrow 2 OH$</td>
<td>$k_{21} \text{cm}^3 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>17.</td>
<td>$O^* + H_2 \rightarrow OH + H$</td>
<td>$k_{22} \text{cm}^3 \text{sec}^{-1}$</td>
</tr>
<tr>
<td>18.</td>
<td>$OH + OH \rightarrow H_2O + O$</td>
<td>$k_{23} \text{cm}^3 \text{sec}^{-1}$</td>
</tr>
</tbody>
</table>

...... contd.
Table 1.1 (contd)

19. \[
\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2
\]

20. \[
\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2
\]

21. \[
\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2
\]

22. \[
\text{H}_2\text{O}_2 + \text{h}^+ \rightarrow 2 \text{OH}
\]

\[k_{24} \text{ cm}^3 \text{ sec}^{-1}\]

\[k_{25} \text{ cm}^3 \text{ sec}^{-1}\]

\[k_{26} \text{ cm}^3 \text{ sec}^{-1}\]

\[k_{27} \text{ cm}^3 \text{ sec}^{-1}\]

\[k_{28} \text{ cm}^3 \text{ sec}^{-1}\]

\[k_{29} \text{ cm}^3 \text{ sec}^{-1}\]

\[k_{30} \text{ cm}^3 \text{ sec}^{-1}\]
Fig. 1.5 — Reaction scheme of the interplay of the $\tilde{O}$- and $\tilde{H}$-systems in the stratosphere (Dütsch 1971)
\[ k_{11} n_1 x + k_{16} n_1 x + k_{15} n_3 z = k_{12} n_3 y + k_{15} n_1 y \]  
(1.20)

The ratio between 0 and \( O_3 \) is given by

\[ \frac{n_1}{n_3} = \frac{f_3}{k_2 n_2^2} \]  
(1.21)

Combining \( x \) and \( y \) it can be shown that

\[
\frac{x}{y} = \frac{k_{12} + \frac{k_{15} f_3}{k_2 n_2^2} \left( \frac{1}{k_{11} n_3} \right)}{k_{13} + k_{16} \left( \frac{f_3/k_2 n_2^2}{k_{11} n_3 + k_{16} n_2} \right)}
\]  
(1.22)

For most levels this relation can be simplified as

\[ R = \frac{z}{y} \approx \frac{k_{12}}{k_{13}} \approx 35 \]  
(1.23)

Below about 35 km where the destruction of \( O_3 \) predominates \( n_1 \) \( n_3 \) and

\[ R = \frac{z}{y} \approx \frac{k_{15}}{k_{16}} \approx 5 \]  
(1.24)

The actual numbers may yet differ from those shown here because of the uncertainties about the reaction rates involved, especially about \( k_{13} \). Crutzen (1970) and Kaufman (1964) have questioned the very possibility of reaction 11 (Table 1.1).
If reaction 20 (Table 1.1) which is only one-tenth as effective in destroying H particles than reaction 19 (Table 1.1) is discarded, \( y \) can be computed easily from the equilibrium assumption for the formation and destruction of H particles. Thus it can be shown that

\[
y = \frac{n_3}{n_2} \frac{w_1}{k_{21} n_2 f_3} \frac{k_{21} n_3 f_3}{k_{24} k_4 R}
\]

(1.25)

whereby \( \frac{w_1}{n_2} \) is 4.75 times the number mixing ratio of water vapour.

It can be shown that the concentration of \( H_2O_2 \) is given by

\[
W_3 = R \frac{n_3 f_3}{f_4} \frac{k_{21} k_{26}}{k_4 k_{24}} \frac{w_1}{n_2} n_3
\]

(1.26)

The concentration of \( H_2O_2 \) is thus proportional to the concentration of both \( O_3 \) and water vapour mixing ratio.

The equilibrium concentration of ozone can be obtained by balancing the odd oxygen particle production through photodisso-ociation of oxygen, with the destruction through reactions 6, 10, 11, 12 and 13 (Table 1.1).

Thus

\[
2 f_2 n_2 = n_3 \left[ \frac{2 f_3}{k n_2} n_3 + \frac{f_3}{k_2 n_2} (k_{15} \gamma + k_{16}) \right] n_3 + k_{12} \gamma + k_{13} \gamma
\]

(1.27)
Because \( k_{15}y \) and \( k_{16}z \) above 45 km and \( k_{12}y \) and \( k_{13}z \) below 35 km this may be further simplified to

\[
f_2n_2 = n_3 \left\{ \frac{3}{f_3} + (B + C) n_3^{1/2} \right\} \quad (1.28)
\]

where

\[
A = \frac{f_3}{kn_2^2}
\]

\[
B = \frac{f_3}{k_2n_2^2} \left\{ \frac{\rho_3^2f_3 k_{21} w_1}{R k_4 k_{24} n_2} \right\}^{1/2}
\]

and

\[
C = \frac{n_3 f_3 k_{21} w_1}{R k_4 k_{24} n_2}^{1/2}
\]

Equation (1.28) throws considerable light into the relative importance of the different processes.

The first term in equation (1.28) represents the destruction of atomic oxygen \( O \) in a pure oxygen atmosphere. The second and third terms represent the reactions of water vapour derivatives with atomic oxygen and ozone respectively.

With reaction rates compiled by Hunt (1971) the first term in equation (1.28) becomes negligible, the destruction of \( O \) particles is fully dominated by the reaction with \( H \) radical, whereby the term with \( B \) predominates in the upper stratosphere, the term with \( C \) below 30 - 35 km. The theoretically computed ozone concentration below 25 - 30 km becomes very much reduced by these high additional contributions to \( O \) particle destruction and is far below the observed values.
Fig 1.6 represents the comparison between the observed vertical distribution and theoretical computed values from classical as well as moist atmosphere photochemical theories. The two sets of curves A and B represent respectively Detwiler's and Brewer's values for ultraviolet intensities. Theoretically computed values using reaction rates after both Hesstvedt and Hunt are also represented in the figure.

It can be seen that there is reasonably good agreement between theory and observation at the levels where the photochemical influence predominates when Hesstvedt's rate coefficients are used. The best fit is obtained with the Brewer-Wilson ultraviolet radiation data and the agreement might still be improved by a $k_{13}$ value somewhat lower than that assumed by Hesstvedt and Hunt (1966), but not zero. While comparing the observed and theoretical distribution it has to be borne in mind that the observed vertical distribution is based mainly on Umkehr measurements which have their own limitations. It is likely, therefore, that part of the remaining differences between theory and observation can be explained by uncertainties in the observation and that the photochemical theory in moist atmosphere may be able to account for the observed ozone distribution.

1.4.3 **Night time processes in a moist stratosphere**

All photochemical processes are terminated right after sunset when all atomic oxygen is converted into ozone within a minute after sunset. Also in a moist stratosphere atomic oxygen is removed rapidly and the production of atomic oxygen by
Fig. 1-6 A and B - Vertical ozone distribution at 45° lat. (theory and observation) A, Radiation 1, summer; B, Radiation 2, summer. Curve (a) reaction rates after Hesstvedt, mixing ratio $5 \times 10^{-6}$; (b) reaction rates after Hesstvedt, but $k_{13} = 0$; mixing ratio $5 \times 10^{-6}$; (c) classical theory; (d) reaction rates after Hunt; (e) observed

(Dűtsch 1971)
reaction 18 (Table 1.1) is too small to be of any importance. Nevertheless the destruction of ozone continues by reactions with H particles as long as H particles are present. It can be shown that the relative loss of ozone during the night is represented by

\[
\frac{\Delta n_3}{n_3} = -\frac{k_{13}}{k_{26}} \ln \left( 1 - 2k_{26}n_0(t - t_0) \right)
\]

This predicts about 2 percent reduction in stratospheric ozone content during a 12 hour night. This is a value which could be observable with a Dobson spectrophotometer if a sufficiently long series of observations are taken.

1.4.4 Ozone in the mesosphere

In the mesosphere the recombinative reaction

\[ O + O + M \rightarrow O_2 + M \]

cannot be neglected as was done in the stratosphere since the relative combination of atomic oxygen is large. This with equations (1.8) to (1.11) leads to a third order equation for equilibrium concentration.

\[
o_3 = (o_2)^2 \left( \frac{(\phi_2 f_2/2 \phi_3 f_3) k S}{(k_1/k_2 k_3) \phi_3 f_3 o_2} \right)^{1/3}
\]

where \( \phi_2, \phi_3 \) are the quantum yields for oxygen and ozone dissociation, \( f_2 \) the number of quanta (\( \lambda < 2425 \text{ A} \)) absorbed per oxygen molecule/sec, \( f_3 \) the number of quanta (\( \lambda < 11800 \text{ A} \)) absorbed per ozone molecule/sec, \( k = k_{12}/k_{13} \) and \( S \) a parameter introduced to take into account the oxygen molecules.
\[ S = (O_2) + \gamma (N_2)/O_2 \]

\( \gamma \) having the effectiveness of \( N_e \) relative to \( O_2 \) as a third body in the reaction. \( k_1, k_2 \) and \( k_3 \) are reaction constants for the reactions (1.13), (1.9) and (1.11) respectively. The above equation reduces to the conventional equation

\[ 0_3 = (O_2)^{\frac{3}{2}} (\frac{\varphi_2}{\varphi_3}) \left( \frac{f_2}{f_3} \right) k S \left( \frac{k_1}{k_2 k_3} \right) \]

where

The day time equilibrium value falls off very rapidly with height. The number of oxygen atoms which is small in the main ozone layer becomes equal to that of ozone at about the stratopause level and increases rapidly with height throughout the mesosphere. Further the total number of odd oxygen particles becomes a minimum near 55 km at which level the photochemical period of half restoration is the least. This time interval does not decrease at higher levels, as it happens in the stratosphere, since there is no instantaneous adjustment of atomic oxygen to ozone concentration. Rather, in the day time, the small amount of ozone adjusts itself to the concentration of atomic oxygen.

During the night when there is no solar radiation, a transformation of atomic oxygen to ozone takes place at any height by the three body collision

\[ O + O_2 + M \rightarrow O_3 + M. \]
In the main ozone layer, where \( O = O_3 \), this leads to a rapid depletion of \( O \) without any appreciable increase in \( O_3 \). Thereafter the concentration of \( O_3 \) remains constant throughout the night. In the mesosphere, on the other hand, where the concentration of \( O \) is very large a proportionately large increase of \( O_3 \) can occur during the night. Above 55 km the transformation of \( O \) to \( O_3 \) can proceed until all \( O \) is used up or until an equilibrium is reached between the ozone production by three body collision and destruction of ozone by the reaction \( O + O_3 \rightarrow 2 O_2 \).

From these theoretical considerations, a secondary ozone maximum can be expected at night near about 70 km.

As early as 1953, Ramanathan and Ramanamurthy made a series of observations of day and night values of total ozone at Mount Abu. On each occasion the total ozone amount was found to be higher at night than during the day, the excess at night being of the order of 0.20 to 0.40 mm. The increase appeared to take place within an hour after sunset and the change from night to day took place soon after sunrise. The night increase of ozone concentration was attributed to recombination of odd oxygen atoms with oxygen molecules above the level of maximum ozone concentration. According to theoretical calculations of Dütsch (1954) the night increase of total ozone would be between 1 and 7 percent.
1.5 Seasonal and latitudinal variation of ozone

1.5.1 Total ozone

Dobson had established in the early thirties the variability of total ozone with latitude and season. A clearer picture of the latitudinal and seasonal variation of total ozone emerged from the extended observations during and after the IGY. The observed dependence on latitude and season is shown in Fig 1.7. The ozone maximum is reached in early spring and its occurrence is delayed from March or even late February in the Arctic to almost May in sub-tropics. Whether the polar maximum really occurs as early as indicated is a question still to be answered satisfactorily (Dütsch, 1969).

Seasonal changes in the tropics are insignificant. The difference between the maximum and minimum values increases steadily poleward reaching 50 percent of the annual mean in the Arctic. Therefore the latitudinal gradient is quite pronounced at the time of the spring maximum but it almost vanishes when the ozone minimum is reached in the autumn. In the middle latitudes the rather flat maximum occurs in October; it is again delayed towards the equator. While the maximum in the Arctic is apparently reached at the same time or even earlier than in middle latitudes, the minimum seems to occur rather later.
FIG.1.7-TOTAL OZONE DISTRIBUTION WITH SEASON AND LATITUDE

A - Northern hemisphere
B - Southern hemisphere
(Dütsch 1969)
There are also considerable differences between the northern and southern hemispheres regarding the seasonal and latitudinal variations. According to Dutsch all these differences may not be real as the picture of the mean distribution is based on scanty data, something less than 10 percent of its northern counterpart. The main differences between the two hemispheres are discussed below. While in the north the highest ozone values are observed in subpolar regions around 60-65°N latitude and the poleward decrease from these latitudes is not very marked, the maximum is observed in the south near 50°S. The ozone amounts in the Antarctic are considerably lower than in the Arctic, especially in winter and spring. The surplus in the southern mid-latitudes, however, is highest in the autumn. The seasonal variation in the southern hemisphere is also only about 60 percent of that found north of the equator. The autumn minimum of the middle and low latitudes occurs earlier in the south, while in the polar regions the maximum is delayed until late spring or even early summer.

Lovill (1974) reported the average distribution of total ozone for the northern and southern hemispheres for the period April to July 1969 (Fig 1.8) based on the Nimbus 3 infrared interferometer (IRIS) data. The broad features of average global total ozone distribution revealed by the Dobson spectrophotometer measurements are confirmed by this IRIS data. The data reveals a large region of low total ozone (less than 240 D.U.), 10 to 20
Fig. 1.8 - The average distribution of total ozone (m atm cm), 19 April to 21 July 1969. Shading represents total ozone values less than 240 m atm cm from IRIS (Lovill 1974).
degrees on either side of equator extending from south east Asia eastward to central Pacific. A region of anomalously high total ozone in the tropics is seen to extend from the western Atlantic eastward to western Indian Ocean.

Prabhakara (1971) reported similar findings from the Nimbus 3 IRIS data.

More recently Krueger (1974) published zonally averaged total ozone amounts derived from the back scatter ultraviolet measurements from the Nimbus 4 satellite (Fig 1.9). The results obtained are in close agreement with the average total ozone values observed with the Dobson spectrophotometer.

1.5.2 Longitudinal dependence of total ozone

London (1963) analysed all the available data upto 1963 in order to determine the longitudinal variation of total ozone (Fig 1.10). The longitudinal dependence is most pronounced at high latitudes and again during winter and spring. During this period ridges of high ozone values are associated with major quasi-stationary upper air troughs over eastern America, eastern Asia and over middle and eastern Europe.

1.5.3 Vertical distribution of ozone

Mean vertical distributions have been computed mainly from Umkehr data as extensive data from the ozone soundings are still not available for all latitudes. Fig 1.11 depicts the spring distribution for various latitudes. The rather sharp and high
Fig. 1-9 - Zonally averaged total ozone amounts (m atm cm) from Nimbus 4 B.U.V. system for the period April 10, 1970 to April 9, 1971 adapted from Krueger 1974
FIG. 110 - LONGITUDINAL DISTRIBUTION OF TOTAL OZONE
ANNUAL MEAN IN DOBSON UNITS (LONDON 1963)
FIG 1-2 - MEAN VERTICAL OZONE DISTRIBUTIONS AT DIFFERENT LATITUDES IN SPRING

A - Umkehr  B - Chemical sondes

(Dütsch 1969)
lying maximum of the tropical and sub-tropical ozone (Leopoldville, Mt Abut and Balboa respectively) becomes broader with increasing latitude and the centre of gravity is correspondingly lowered. There can be little doubt that the pronounced increase of ozone with latitude observed in spring is entirely due to the accumulation of ozone in the lower stratosphere, where photochemical reactions are comparatively unimportant. It is also significant to note that the latitudinal gradient is reversed in the upper part of the ozone layer where we can find the equatorward increase which is predicted by photochemical theory. Its contribution to the total amount is, however, not strong enough to compensate for the ozone deficiency found between 8-22 km at low latitudes. The ozone deficit, however, extends too far into the stratosphere over the low latitudes. A strong decrease in ozone content in the lower stratosphere at middle and high latitudes from spring to autumn (Fig 1.12) is the most obvious feature when Figs 1.11 and 1.12 are compared. It can be seen that over most of the middle latitudes the ozone distribution is similar to that over the tropics, except for a somewhat lower position of the maximum. In the polar and sub-polar regions, however, the stratospheric ozone content at lower levels is still comparatively high. At these high latitudes the observed loss of ozone through summer
FIG 1.12—MEAN VERTICAL OZONE DISTRIBUTIONS AT DIFFERENT LATITUDES IN AUTUMN

A - Umkehr  B - Chemical sondes
(Dütsch 1969)
does not completely clear away the surplus ozone accumulated during winter. The decrease of ozone concentration with latitude in the upper part of the ozone layer is considerably more pronounced in autumn than in spring. The latitudinal increase at lower levels is just about balanced at this time of the year by the decrease in the upper levels and the total amount becomes almost independent of latitude except for a slight drop towards the tropics.

Krueger (1974) computed the vertical distribution of ozone in the middle and upper stratosphere for individual days using the backscatter ultraviolet data from Nimbus 4 satellite. From analysis of selected cross-sections he finds that the zonally symmetric patterns of mid summer begin to be distorted before the end of summer. By the beginning of the northern winter increase of total ozone a bridge of high mixing ratio air is formed between the tropics and high levels near the pole. Total ozone increases seem to be associated with projections of the tropical high mixing ratio core to higher latitudes.

1.5.4 Latitudinal cross sections

Dutsch (1969) has constructed latitudinal cross sections of the vertical distribution of ozone using Umkehr data as well as data from ozonesondes from the north American network. The ozonesonde data are somewhat sparse particularly at high latitudes. Fig 1.13 shows the vertical cross sections
Fig. 1-13 - Latitudinal cross section of ozone concentration with height
A - January/February compared to July/August.
B - March/April compared to September/October
C - May/June compared to November/December

(Dütsch 1969)
for different months compiled from data for the northern hemisphere. The right hand half of the cross sections represent data with a six month phase shift. The main features are as follows:

The level of ozone peak has its highest position over the tropical region (around 25 km) and slopes down towards the poles. This slope is most pronounced in spring when the height difference from the equator to 70° latitude is of the order of 9 km and least strong at the end of summer when it is not more than half of that value. During the first 4 months of the year the equatorial peak looks like a southward extension of the much stronger polar maximum, but it has quite a different origin. The tropical peak which varies very little over the year is predominantly a photochemical feature, although its steep lower edge is certainly shaped by circulation influences. The polar maximum however, with its strong seasonal variation in strength and also in altitude can only be explained by ozone redistribution through circulation effects. This maximum starts building up sometime in November and is strongest, at least in middle latitudes in December and January. About a month after the initial rise in the 25–50 mb layer in the middle latitudes the well known very strong ozone fluctuations in the lower stratosphere reach their full development and the final buildup of the main polar maximum at about 100 mb is observed.
During summer the polar ozone maximum gradually weakens and the almost ozone-free area, which persists around 100 mb extends more into the middle latitudes. Below the sloping surface of the level of ozone maximum there is a positive gradient of ozone in the poleward direction; it is strongest in early spring. Above the ozone maximum the poleward gradient is negative reaching a maximum in autumn between 30-50 mb and in early winter above these levels.

3.5.5 Biennial variations in atmospheric ozone

The existence of biennial variations in atmospheric ozone over the Australian latitudes was found by Funk and Garnham (1962). They attributed the biennial feature to changes in the subsidence pattern of ozone-rich stratospheric air. Ramanathan (1963) showed that there were similar variations in the subtropics and lower middle latitudes, up to 40°N, in the northern hemisphere and that over the equatorial latitudes there were corresponding variations with an inversion of phase. Ramanathan pointed out that changes in phase of the biennial oscillation of the ozone content over the equator as shown by the ozone records of Kodaikanal (10°N) were connected with the biennial changes of the zonal winds over equatorial latitudes. The changes in the zonal winds could cause a change in the relative ozone amounts and consequently the temperatures in the lower stratosphere (18 to 30 km) between the equator and lower middle latitudes. This agency could also produce an ozone flux.
between the tropics and the middle latitudes. Further investigations by Angreji (1967) showed that a 24 month cycle exists at all latitudes from Spitzbergen (78°N) to Kodaikanal (10°N) and the period was found to be remarkably constant up to about 55°N latitudes. He also observed that a phase change occurred every 11 years e.g. in 1941, 1952 and 1963 the amount of phase shift being \( \pi \) radians each time, the same phase repeating after 22 years.

1.6 Ozone and general circulation

It has become clear that the ozone-to-air mixing ratio below 20-25 km is very nearly a conservative property of an air parcel. Ozone has thus become a useful tracer and it is mainly for this reason that considerable effort has been put into measuring vertical ozone distributions over the globe. A fairly clear picture of the ozone distribution and ozone budget has since emerged and Dütsch (1969) has given a tentative model for large scale ozone fluxes and for the seasonal ozone cycle. This is reproduced in Fig 1.14.

The equatorial stratosphere is the main region of production of atmospheric ozone. A poleward flux transports ozone from this source region towards the winter hemisphere where it descends to the lower levels. This leads to the observed winter time increase in ozone content, which cannot be explained by in situ photochemical production. In the lower stratosphere, the ozone is effectively shielded from photochemical destruction, leading to concentrations
FIG. 1-14: MODEL OF LARGE SCALE OZONE TRANSPORT (AFTER DÜTSCH)
far above photochemical equilibrium in this region. The transfer of ozone to the troposphere is facilitated by the high concentrations just above the tropopause. Once in the troposphere the ozone mixes rapidly downward. At the ground continuous destruction by a number of mechanisms is in progress, especially by contact with organic material. The northward flux and combined with it the downward flux are apparently shut off in spring when the westerly circulation of the winter time circumpolar vortex is replaced by summer easterlies above about 20 km. However, transfer of ozone into the troposphere and its destruction near the ground continue. This destruction is probably a maximum in late spring or early summer when, due to the phase lag with height, the ozone concentration near the ground reaches its maximum and increased temperature also presumably speeds up the destruction processes. This leads to the observed net loss of ozone in the lower stratosphere in late spring and through summer. The extent to which photochemical destruction of surplus ozone in the region around 25 km contributes to the loss has yet to be determined. Due to the much decreased mixing in summer, horizontally as well as vertically, the middle stratosphere is quite isolated from this development and ozone concentrations are determined by photochemical processes. During winter, however, circulation influences reach well into the middle stratosphere and a considerable part of the northward flux probably occurs at these levels.
The amplitude of the annual variation of the integrated ozone, polewards from about 20° latitude, suggests that the net yearly production in the tropical stratosphere is of the order of about 30 - 40 percent of the total hemispheric ozone content of the atmosphere.

Though the general validity of the system proposed above cannot be doubted, the actual transport mechanisms are still not clear. Meridional circulation cells have been proposed in the past. Ramanathan and Kulkarni (1960) suggested that in winter and spring there is an ozone regenerating cycle due to a meridional circulation in stratosphere of the tropical and middle latitudes, which carries air from the lower equatorial stratosphere to the lower levels in the stratosphere of middle latitudes and puts back some of this accumulated air to higher levels in the equatorial stratosphere above 25 km. The more vigorous this circulation, the greater will be the rate of ozone storage in the lower stratosphere of extra-tropical latitudes. Newell (1961, 1964) has convincingly shown that for dynamical reasons this meridional circulation theory is unacceptable and that large-scale exchange along quasi-horizontal surfaces must be the predominant mechanism. The very pronounced sandwich structure of vertical ozone distribution which is observed over middle latitudes gives strong support to this argument. Such a structure can only be explained through the action of large scale mixing processes, certainly not an organised sinking motion. A poleward
flux by mixing with a concentration increasing northward in the lower part of the stratosphere is only possible if northward motion is positively correlated with downward motion. Improved knowledge of the variation with time of vertical ozone distribution at all latitudes will indicate at which level the main northward flux occurs. The question is whether the main ozone flow from tropical stratosphere to the subtropics is accomplished solely by large scale mixing. The considerably reduced stratifications observed in the tropical stratosphere seem to indicate that we may have to consider an extension of the Hadley cell into the tropical stratosphere with ascending motion over the equatorial region and descending motion over the sub-tropics of the winter hemisphere.
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