MODULE 3.1

The Atmosphere And atmospheric chemistry

MODULE 3.1

The Atmosphere And atmospheric chemistry

Importance Of The Atmosphere:

As outlined in the introduction, the atmosphere plays a vital role in the survival of life in this planet by absorbing most of the harmful cosmic rays from outer space and most of the electromagnetic radiation from the sun.

By reabsorbing much of the infrared radiations re emitted by the earth to space, the atmosphere stabilises the earth's temperature, preventing temperature extremes.

The atmosphere is a source of carbon dioxide for plant photosynthesis and of oxygen for respiration. It provides nitrogen for nitrogen -fixing bacteria and ammonia-manufacturing plants to produce chemically bound nitrogen, which is an essential component of life molecules.

The atmosphere transports water from ocean to land, thus acting as the condenser in a vast solar powered still. Unfortunately,due to increase in industrial activity the atmosphere is used as dumping place for many pollutant materials, and this is causing damage to vegetation and materials, shortens human life, and alters the characteristics of the atmosphere itself.

The following pages will give a brief description of major regions of the atmosphere and some of the very important reactions that take place in the atmosphere.

Physical Characteristics Of The Atmosphere:

The components of our earth's atmosphere may be divided broadly as major, minor and trace constituents. For pollution –free dry air at ground level, the components may be expressed as percent by volume, as follows.

Major Constituents:	• Nitrogen, 78.08% (by volume) • Oxygen, 20.95%
Minor Constituents:	• Argon, 0.934% • carbondioxide, 0.035%
Trace constituents:	• Neon, 1.818 x 10^{-3} % • Helium, 5.24 x 10^{-4} % • Krypton, 1.14 x 10^{-4} % • Xenon, 8.7 x 10^{-6}%

- Methane, 2 x 10^{-4} %
- Nitrous oxide , 2.5 x 10^{-5}%
- Hydrogen 5 x 10^{-5} %
- Sulphur dioxide 2 x 10^{-8} %
- Ozone (trace)
- Ammonia 1 x 10^{-6} %
- Carbon monoxide 1.2 x 10^{-5} %
- Nitrogen dioxide1x 10^{-5} %
- Iodine (trace)
- H_2O_2 10^{-8}- 10^{-6}%
- HO• 10^{-13}- 10^{-10} %
- HO_2• 10^{-11}- 10^{-8} %
- H_2CO 10^{-8}- 10^{-7} %

Atmospheric air may contain 0.1 % to 5% water by volume, with a normal range of 1 to 3%

The density of the atmosphere decrease sharply with increasing altitude. More than 99% of the total mass of the atmosphere is found with in approximately 30 km of the earth's surface. The total masses of the global atmosphere is approximately 5 x 10^{15} metric tones which is roughly one millionth of the earth's total mass.

The characteristics of the atmosphere vary greatly, with altitude, time (season), location (latitude), and even solar activity. Temperature in the atmosphere may vary from as low as the -92^{o} C to over 1200^{o} C. Atmospheric pressure drops from 1 atm. at sea level to 3.0 x 10^{-7}atm at 100 km above sea level. Due to these variations, the chemistry of atmosphere varies greatly with altitude. In addition to temperature differences the mean free path of species in the atmosphere (the mean distance traveled before collision with another particle) increases over many orders of magnitude with increasing altitude. A particle with a mean free path of 1 x10^{-6} cm at sea level has a mean free path exceeding 2 x 10^{6} cm at an altitude of 500 km, when the pressure is lower by many orders of magnitude.

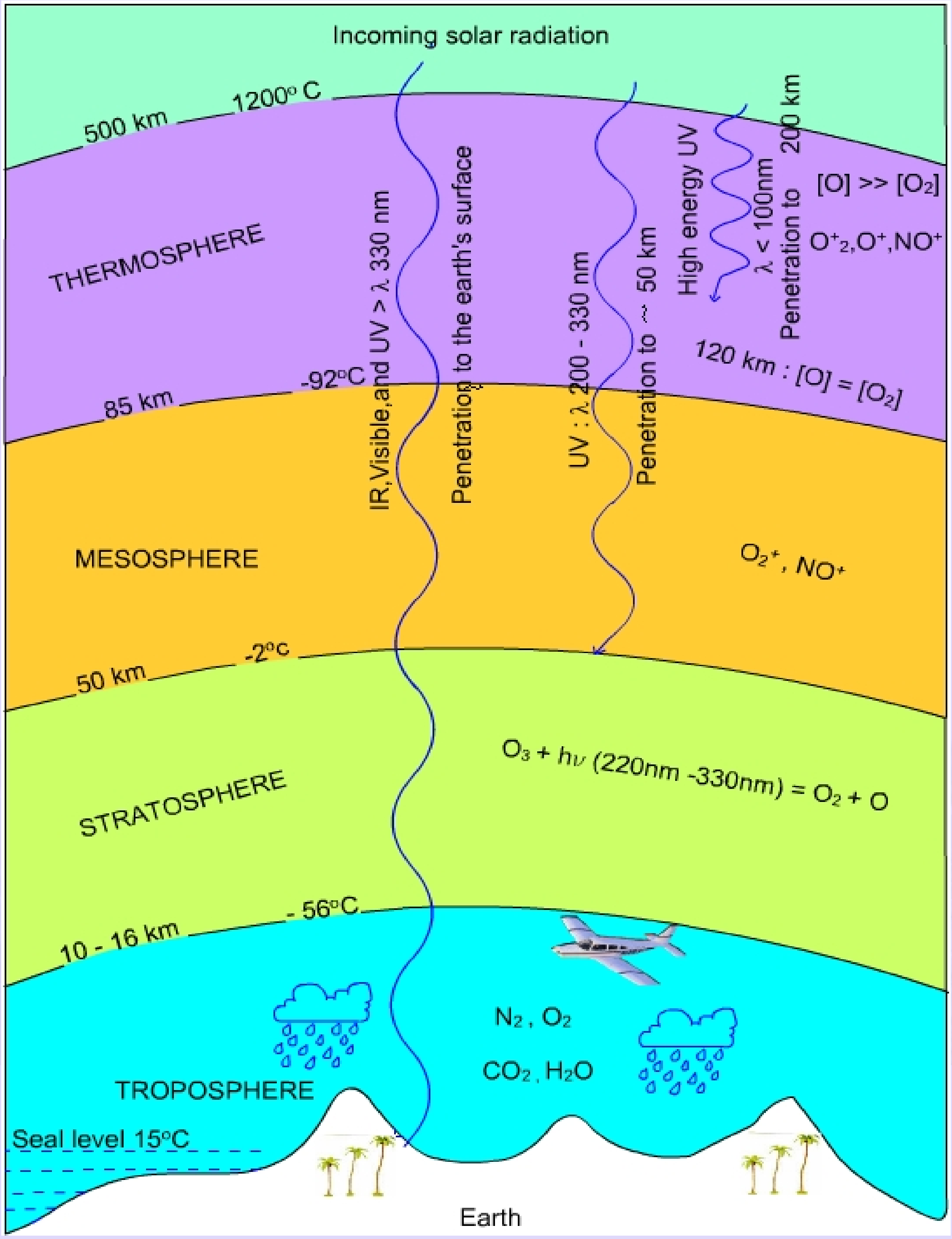

Fig 1 Major regions of the atmosphere

(Redrawn by permission of Lewis Publishers, Chelsea, Michigan 48118, USA from Fundamentals of Environmental Chemistry, S.E.Manahan, p.549,1993)

Major Regions Of The Atmosphere:

The atmosphere is broadly divided in to four regions as shown in fig.1 above and table 1 below . It extends upto 500km and the temperature may vary from as low as -92^{o}C to over 1200^{o}C .

Table-1 Major regions of atmosphere and their characteristics

Region	Altitude range Km	Temperature range ^{o} C	Significant chemical species
Troposphere	0 – 11	15 to -56	N_2, O_2, CO_2, H_2O
Stratosphere	11 – 50	-56 to –2	O_3
Mesosphere	50 -85	-2 to –92	O_2^+, NO^+
Thermosphere	85 -500	-92 to 1200	O_2^+, O^+, NO^+

Troposphere:

The lowest layer of earth from sea level to an altitude of 10 to 16 km is called the troposphere. In this region the composition of the atmosphere is more less uniform in the absence of air pollution mainly due to the constant circulation of air masses in this region.

However air is far from uniform with respect to density and temperature in this region. Density decreases exponentially with increasing altitude. The water content also varies because of cloud formation, precipitation, and evaporation of water from terrestrial water bodies.

The very cold layer at the top of troposphere is known as tropopause. Its low temperature and resulting condensation of water to ice particles prevents water from reaching altitudes at which it would photo dissociate through the action of intense UV light. If this happens, the hydrogen produced would escape the earth's atmosphere.

Stratosphere:

The atmospheric layer directly above the troposphere is called the stratosphere. In this layer the temperature increases with increase in altitude, with a maximum of -2^{o} C at the upper limit of stratosphere.

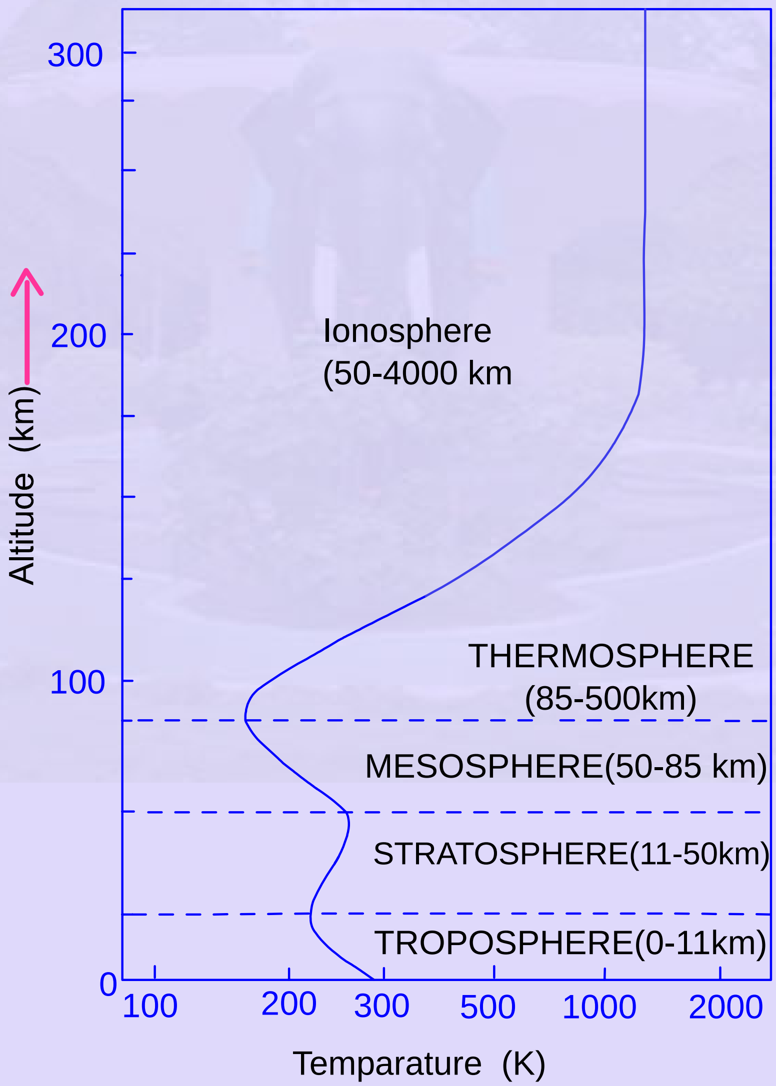

Fig 2 Major regions of the atmosphere with temperature profile

This temperature increase is due to the presence of ozone, O_3, which may reach a level of around 10 ppm by volume in the mid-range of the stratosphere.

The heating effect is caused by the absorption of ultraviolet radiation energy by ozone. The ozone layer in the stratosphere thus acts as a protective shield for life on earth from the injurious effects of sun's ultraviolet rays and at the same time supplies heat source.

The residence times of molecules or particles in the stratosphere are quite long because of slow mixing. If the pollutants can some how reach the stratosphere, they pose long-term global hazards compared to their impact in the much denser troposphere.

Mesosphere:

The mesosphere on the top of the stratosphere extends roughly to 85 km. In this region the temperature falls with increase in altitude, resulting in a temperature decrease to about -90^{o}C. This is due to the absence of high levels of radiation absorbing species, particularly ozone. The principal chemical species in this region are O_2^+ and NO^+.

Thermosphere:

The far outer reaches of the atmosphere above mesosphere is called thermosphere. In this region the temperature reaches to as high as 1200^{o}C . Here the atmospheric gases, particularly oxygen and nitric oxide, split into atoms and also undergo ionisation by the absorption of very high energy radiation of <200nm.

Evolution Of The Atmosphere:

It is widely accepted that the present state of earth's atmosphere is quite different and the present changes were brought about by biological and accompanying chemical reactions. Approximately 3.5 billion years ago, when the first primitive life molecules were formed, the atmosphere was chemically reducing, coexisting primarily of methane, ammonia, water vapor and hydrogen.

Due to bombardment by intense high energy uv radiation accompanied by lightning and radiation from radionuclides. Chemical reactions were brought about which resulted in the production of relatively complicated molecules, including even amino acids and sugars. Life molecules evolved from the rich chemical mixture in the sea. These life forms drew their energy arising from chemical and photochemical processes. Ultimately they were capable of producing organic matter $[CH_2O]$ by photosynthesis:

$$CO_2 + H_2O + h\upsilon \rightarrow [CH_2O] + O_2 \uparrow \text{ .... } \textbf{\textit{(1)}}$$

These massive biochemical transformations had ultimately resulted in the production of almost all the atmospheric oxygen

The oxygen initially produced by photosynthesis was presumably quite toxic to primitive life forms. However bulk of this oxygen was converted to iron oxides by reaction with soluble iron (II), yielding Fe_2O_3.

$$4Fe^{2+} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+ \text{ .... } \textbf{\textit{(2)}}$$

The existence of iron oxide provides major evidence for the liberation of free oxygen in the primitive atmosphere.

In course of time enzyme systems developed which enabled organisms to mediate the reactions of waste product O_2 with oxidizeable organic matter in the sea. Gradually O_2 accumulated in the atmosphere, which helped the formation of an ozone shield in the stratosphere. The ozone shield in the stratosphere helped in protecting the life forms from the destructive effect of high energy ultraviolet radiations. As a result the earth was converted in to a much more hospitable environment for life, and life forms were enabled to move from sea to land.

Earth's Radiation Balance

Out of a very large amount of radiation energy received from the sun, the earth absorbs radiation mainly in the visible region but emits radiation at the same rate in the infrared region.(2 - 40µm with maximum at 10µm). The average surface temperature of the earth is maintained at relatively comfortable 15^{o}C due to the atmospheric green house effect, in which water vapors and to a lesser extent carbon dioxide, reabsorb much of the outgoing radiation and reradiate about half of it back to the surface. If this were not to be the case the surface temperature of the earth would have been averaged around –18^{o}C. Most of the absorption of the infrared radiation is done by water molecules in the atmosphere.Carbon dioxide though present at a much lower concentration than water vapor, absorbs strongly between 12µm and 16.3µm contributing in a major way in maintaining the heat balance. There is concern that an increase in the carbon dioxide level in the atmosphere would prevent sufficient energy loss from the earth's surface. This would cause a perceptible and damaging increase in the earth's temperature, which is known as green house effect.

Carbon Dioxide In the atmosphere:

Carbondioxide is the major contributor to greenhouse warming. Eventhough the concentration of carbondioxide is only 0.035% of the earth's atmosphere, it along with watervapour is mainly responsible for the increase in surface temperature of the earth. It absorbs in the 14-19 µm range and completely blocks the radiative flux between 15 and 16 µm ; it also absorbs between 4 and 4.5 µm.

There are many natural sources of carbondioxide including animal and plant respiration and decay, combustion through forest and grassland fires and volcanic activity. Human activities have a significant effect on the global carbon cycle. The anthropogenic sources of atmospheric carbondioxide include combustion of fossil fuels and forest destruction and burning. Besides releasing carbondioxide into the atmosphere burning trees eliminates their contribution to carbondioxide removal by photosynthesis reactions. Current studies reveal that the global CO_2 levels will double by the middle of the next century, thereby increasing the mean surface temperature of the earth by 1.5^{o}C to 4.5^{o}C.

Water vapour in the atmosphere:

Water is the important component of the atmosphere. Its physical properties are a major factor responsible for controlling climate. The atmospheric concentration of water in time and space is highly variable. The water vapour content in troposphere normally ranges from 1-3% by volume. The percentage of water in the atmosphere decreases rapidly with increasing altitude. Watervapour is actually the most important of all greenhouse gases and it absorbs IR radiation in the ranges 2.5 to 3.5 µm, 5-7 µm, as well as over a broad range above 13 µm.

Condensed water vapour in the form of very small droplets is of considerable concern in atmospheric chemistry.

For example the harmful effects of some air pollutants- for instance the corrosion of metals by acid forming gases - requires the presence of water which may be available in the atmosphere. The main source of water in the stratosphere is the photochemical dissociation of methane which involves many steps.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \text{.......(3)}$$

The participation of water vapour in atmospheric chemical reactions is not appreciable, but the photochemical reaction of water vapour is appreciable.

$$H_2O + h\upsilon \rightarrow H + OH \quad \text{.......(4)}$$

and presence of atomic hydrogen in the atmosphere is mainly due to the above reactions.

Ions And Radicals In The atmosphere:

The upper atmosphere has significant levels of electrons and positive ions (eg, O_2^+, O^+, NO^+,etc) and ultraviolet radiation is primarily responsible for the production of ions in this region. Because of the rarefied conditions, these ions may exist in the atmosphere for long periods before recombining to form neutral species. These ions are prevalent at altitudes of approximately 50 km and above and hence this region is called **ionosphere**.

This globe-enveloping band of ions reflects the outgoing radio waves back to earth, making radio transmission possible over long distances.

Besides ions, free radicals are generated by electromagnetic radiation. They consist of atoms or group of atoms with unpaired electrons. The upper atmosphere is so rarefied that at very high altitudes, radicals may have half-lives of several minutes, or even longer. Radicals can take part in chain reactions in which one of the products of each reaction is a radical. Eventually, through processes such as reaction with another radical, one of the radicals in a chain is destroyed and the chain ends.

$$RH + O + O_2 \rightarrow ROO\bullet + HO\bullet$$ ***...(5)***

(where RH = aliphatic hydrocarbon.)

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + h\upsilon \rightarrow H_3C\bullet + HCO\bullet$$ ***...(6)***

$H_3C\bullet + H_3C\bullet \rightarrow C_2H_6$ ***(Chain termination reaction) ....(7)***

Free radicals play an important role in photochemical smog formation.

A totally isolated free radical or atom would be quite stable. Therefore, free radicals and single atoms from diatomic gases tend to persist under the rarefied conditions of very high altitudes because they can travel long distances before colliding with another reactive species. However, electronically excited species have a finite, generally very short, life time because they can lose energy through radiation without having to react with another species.

Reactions involving hydroxyl And hydroperoxyl radicals:

A variety of radical species are encounted in the atmospheric chemical reactions. The most important radical species among them is the hydroxyl free radical (•OH). It plays a central role in many atmospheric chemical reactions. It is formed in the troposphere by a variety of means but the most important is a four-step process (including two photochemical steps)

$$NO_2 + h\upsilon \rightarrow NO + O \qquad \textbf{(8)}$$

$$O + O_2 + M \rightarrow O_3 + M \qquad \textbf{(9)}$$

The formation of O_3 takes place as represented in the equation (5) takes place in the presence of a third body M, which is mostly N_2 or O_2 which are the most common species.

Ozone undergoes photolysis in the troposphere as per the following equation

$$O_3 + h\upsilon(\lambda < 315nm) \rightarrow O^* + O_2 \qquad \textbf{(10)}$$

The fraction of the excited (O*) oxygen react with water molecules to give rise to hydroxyl radicals.

$$O^* + H_2O \rightarrow 2 \bullet OH \qquad \textbf{(11)}$$

Hydroxyl radicals are also formed in the atmosphere by the photolysis of water

$$H_2O + h\upsilon \rightarrow HO\bullet + \bullet H \qquad \textbf{(12)}$$

Hydroxyl radical is most frequently removed from the troposphere by reaction with carbon monoxide

$$CO + HO\bullet \rightarrow CO_2 + \bullet H \qquad \textbf{(13)}$$

or with methane $CH_4 + HO\bullet \rightarrow H_3C\bullet + H_2O$ ***..(14)***

The highly reactive methyl radical $H_3C\bullet$, reacts with O_2

$H_3C\bullet + O_2 + M \rightarrow H_3COO\bullet + M$ (third body) ***............................ ……………....(15)***

to form **methylperoxyl radical**, $H_3COO\bullet$.

Hydrogen radicals produced in reaction 8 & 9 react with O_2 to produce **hydroperoxyl radical** an intermediate in some important chemical reactions:

$H\bullet + O_2 + M \rightarrow HOO\bullet + M$ (third body) ***..(16)***

The hydroperoxyl radical can undergo chain termination reactions, such as

$HOO\bullet + HO\bullet \rightarrow H_2O + O_2$ ***...(17)***

$HOO\bullet + HOO\bullet \rightarrow H_2O_2 + O_2$ ***...(18)***

or reactions that regenerate hydroxyl radical:

$HOO\bullet + NO \rightarrow NO_2 + HO\bullet$ ***...(19)***

$HOO\bullet + O_3 \rightarrow 2O_2 + HO\bullet$ ***...(20)***

The global concentration of hydroxyl radical, averaged diurnally and seasonably, is estimated to range from 2×10^5 to 1×10^6 radicals per cm^3 in the troposphere.

Atmospheric Reactions Of Oxygen:

In the upper atmosphere, due to extremely rarefied conditions, oxygen exists in some forms, which are quite different from those stable at lower levels. In addition to molecular oxygen, O_2, the upper atmosphere is having oxygen atoms, O; excited oxygen molecules, O_2^*, and ozone O_3.

ultraviolet radiation causes photochemical dissociation of molecular oxygen as shown below.

$$O_2 + h\upsilon \xrightarrow[240-260\,nm]{135-176\,nm} O + O \quad \text{.........(21)}$$

The atomic oxygen is stable in the rarified upper atmosphere and three body collisions are necessary for the chemical reaction of atomic oxygen which seldom occur.

It is because of photochemical dissociation, O_2 is virtually non-existent at very high altitudes.

Oxygen atoms in the atmosphere can exist in the ground state (0) and in the excited states (0*). Excited oxygen atoms are produced by the photolysis of ozone, which has relatively weak bond energy of 26 kcal/mole at wavelengths below 308 nm,

$$O_3 + h\upsilon\ (\lambda < 308\ nm) \rightarrow O^* + O_2 \quad \text{.........(22)}$$

In intermediate regions of the ionosphere, the species O^+, O_2^+, are formed by absorption of ultraviolet radiation.

$$O + h\upsilon \rightarrow O^+ + \bar{e} \quad \text{.........(23)}$$

$$O_2 + h\upsilon \rightarrow O_2^{+} + \bar{e} \text{ ....} \textbf{\textit{(24)}}$$

Ozone O_3, is the important species in the stratosphere acting as protective radiation shield for living organisms on earth. The maximum ozone concentration is around 10 ppm in stratosphere at an altitude of 25-30 km. It is formed by the photochemical reaction by a three body collision as shown below.

$$O_2 + h\upsilon \rightarrow O + O \text{ ....} \textbf{\textit{(25)}}$$

$$O + O_2 + M \rightarrow O_3 + M \text{ ....} \textbf{\textit{(26)}}$$

in which M is another species like a molecule of N_2 or O_2, which absorbs excess energy given off by the reactions and enable the ozone molecule to stay together.

Absorption of electromagnetic radiation by ozone, converts the radiant energy into heat which is responsible for the temperature maximum encountered at the boundary between the stratosphere and the mesosphere at an altitude of approximately 50 km.

Thermodynamically, the overall reaction

$$2O_3 \rightarrow 3O_2 \text{ ....} \textbf{\textit{(27)}}$$

is favored so that ozone is inherently unstable. The mechanism of ozone removal is not well understood. It is believed that ozone decomposition is catalysed by NO, NO_2, H, HO•, HOO•, ClO, Cl, Br, and BrO.

Atmospheric Reactions Of Nitrogen:

The nitrogen cycle and nitrogen fixation by micro organisms were already discussed in section 1.1. A small amount of nitrogen is thought to be fixed in the atmosphere by lightning and some is also fixed by combustion processes, as in the internal combustion engine.

The molecular nitrogen is not readily dissociated unlike oxygen by ultraviolet radiation in the higher regions of thermosphere. However at altitudes exceeding approximately 100 km, atomic nitrogen is produced by photochemical reactions:

$$N_2 + h\upsilon \rightarrow N + N \qquad \textbf{(28)}$$

Nitric oxide in the stratosphere is probably responsible for most of the ozone from this layer. The reaction of NO with O_3 can be shown as follows.

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad \textbf{(29)}$$

$$NO_2 + O \rightarrow NO + O_2 \qquad \textbf{(30)}$$

Pollutant NO is regenerated as shown by the above equation. NO_2, is the key species involved in air pollution and the formation of photochemical smog. The most important photochemical process involving NO_2 is its facile photochemical dissociation to NO and reactive atomic oxygen.

$$NO_2 + h\upsilon \rightarrow NO + O \qquad \textbf{(31)}$$

And this is the most important primary photochemical process that initiates smog formation.