Atmospheric Photochemistry

Natural Processes Involving Oxygen

Photochemical reactions have played a determining role in the evolution of the atmosphere and of life on Earth.

Our present survival depends on our being protected by atmospheric ozone from the short-wavelength solar UV radiation, and the absorption of sunlight by ozone is the ultimate source of energy for many reactions occurring in the atmosphere. Much interest is attached, therefore, to the measurement and interpretation of concentration and altitude distributions of ozone in the atmosphere.

The ozone concentration has a sharp maximum at an altitude of around 27 km, so that atmospheric ozone is usually described as consisting of a layer in the stratosphere, centered on 25–30 km above the surface of the Earth.

It is worth pointing out here that ozone is formed by the photodissociation of molecular oxygen with UV light of λ<240 nm:

$O_2 + h\nu \rightarrow O + O$ ----------(1)

$O_2 + O \rightarrow O_3$ ----------(2)

Ozone absorbs light at wavelength λ<300 nm, so that only a small portion of the UV rays coming from the sun reach the Earth, which threatens-life on the surface of the Earth. When light is absorbed, ozone decomposes as shown in equation (3):

$O_3 + h\nu \rightarrow O_2 + O$ ----------(3)

The oxygen atoms then react with ozone to again form molecular oxygen shown in equation (4):

$O_3 + O \rightarrow O_2 + O_2$ ----------(4)

These reactions would maintain equilibrium between the three forms of oxygen**, O, O_2, and O_3**.

However, this equilibrium can be upset by chemical species that are discharged in the atmosphere by human activities, particularly (nitrogen oxides and chlorofluorocarbons (CFCs).

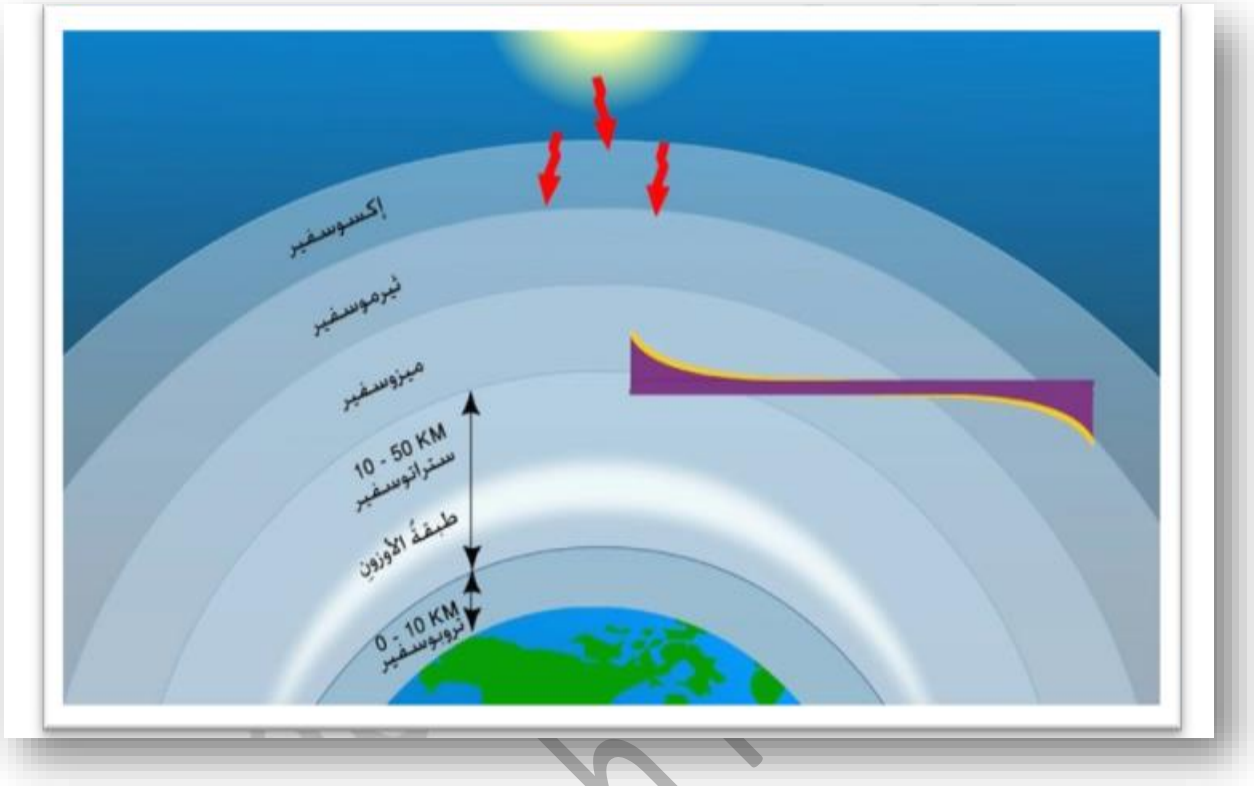

Fig. (14): A schematic explaining the Ozone layer

Ozone Hole

1- Molecular nitrogen (N_2) is a major component of air and it is a very stable and chemically inert species. However, it can form various oxides (N_2O, NO, NO_2), often labeled NOx) by reaction with oxygen.

N_2O comes particularly from agricultural activities, whereas NO and NO_2 are formed at high temperature in internal combustion engines and other combustion processes. Such compounds can undergo several light-induced or thermally induced reactions, for example:

$N_2O + h\nu \rightarrow NO + N$ ----------(5)

$NO_2 + h\nu \rightarrow NO + O$ ----------(6)

$NO_2 + O \rightarrow NO + O_2$ ----------(7)

Reactions (7)and (8) destroy ozone with a chain mechanism:

$NO + O_3 \rightarrow NO_2 + O_2$ ----------(8)

2- Chlorofluorocarbons (CFCs) particularly Freon (CF_2Cl_2), have been widely used for several decades as cooling agents, blowing agents, and propellants in medicinal applications. When released in the atmosphere, they reach eventually high altitudes where they undergo photodissociation reactions with short wavelength UV light available in the upper atmosphere:

$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$ ----------(9)

The halogen atoms (Cl) then destroy ozone in a chain reaction

$Cl + O_3 \rightarrow ClO + O_2$ ----------(10)

$ClO + O \rightarrow Cl + O_2$ ----------(11)

Such a chain reaction is even more dangerous because it consumes oxygen atoms, thereby preventing ozone formation (Reaction 2).

For reasons of atmospheric circulation, ozone depletion is particularly evident in the Antarctic stratosphere (ozone hole).

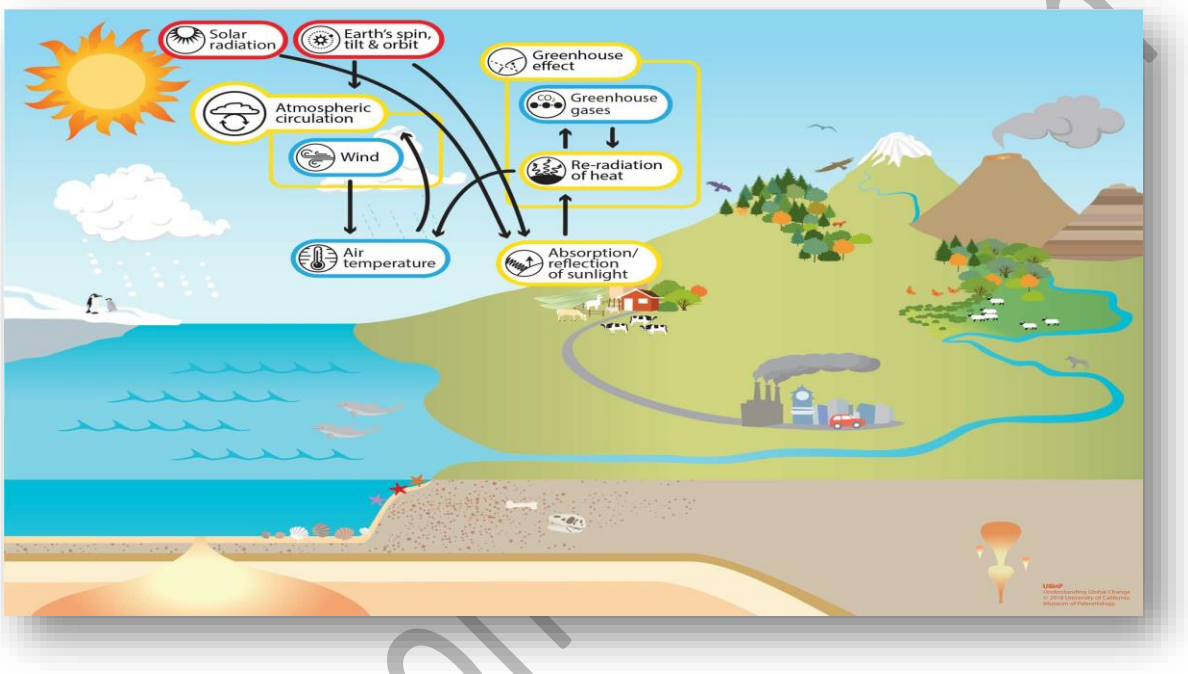

Fig. (15): A schematic explaining the atmospheric circulation

Atmospheric circulation is the large-scale movement of air and together with ocean circulation is the means by which thermal energy is redistributed on the surface of the Earth.

The atmosphere is constantly in motion, the energy for all that movement comes from sunlight that is absorbed and re-radiated by the surface of the Earth and the rotation of the Earth.

Atmospheric circulation, along with ocean circulation, distributes heat across the entire surface of the Earth, bringing us our daily weather and shaping regional climates.

The main public concern regarding the ozone hole has been the effects of increased surface UV radiation on human health, An increase of UV radiation would also be expected to affect important species of crops, such as rice.

After long and difficult international negotiations, production of chlorofluorocarbons (CFCs) has been banned in most countries.

To some extent, (CFCs) have been replaced by the less damaging hydrochlorofluorocarbons (HCFCs),

Therefore, even (HCFCs) have been banned in some developed countries and replaced with substances such as chlorine-free HFCs, which are protected by patents.

CFCs and HCFCs are still used in developing countries because replacement is too expensive.