The Ozone Layer : Source and Depletion

The **ozone layer** refers to a region of Earth's stratosphere that absorbs most of the Sun's ultraviolet (UV) radiation. It contains high concentrations of ozone (O_3) relative to other parts of the atmosphere, although still very small relative to other gases in the stratosphere. The ozone layer contains less than 10 ppm of ozone, while the average ozone concentration in Earth's atmosphere as a whole is only about 0.3 ppm. The ozone layer is mainly found in the lower portion of the stratosphere, from approximately 20 to 30 kilometers. The ozone layer absorbs 97–99% of the Sun's medium-frequency ultraviolet light (from about 200 nm to 315 nm wavelength), which otherwise would potentially damage exposed life forms near the surface.

The United Nations General Assembly has designated September 16 as the International Day for the Preservation of the Ozone Layer.

Source of Ozone :

Ozone in the Earth's stratosphere is created by ultraviolet light striking ordinary oxygen molecules containing two oxygen atoms (O_2), splitting them into individual oxygen atoms (atomic oxygen); the atomic oxygen then combines with unbroken O_2 to create ozone, O_3. The ozone molecule is unstable (although, in the stratosphere, long-lived) and when ultraviolet light hits ozone it splits into a molecule of O_2 and an individual atom of oxygen, a continuing process called the ozone-oxygen cycle. Chemically, this can be described as:

The Chapman Cycle

The ozone layer is created when ultraviolet rays react with oxygen molecules (O_2) to create ozone (O_3) and atomic oxygen (O). This process is called the **Chapman cycle**.
An oxygen molecules is photolyzed by solar radiation, creating two oxygen radicals:

$$h\nu + O_2 \rightarrow 2O.$$

Oxygen radicals then react with molecular oxygen to produce ozone:

$$O_2 + O. \rightarrow O_3$$

Ozone then reacts with an additional oxygen radical to form molecular oxygen:

$$O_3 + O. \rightarrow 2O_2$$

Ozone can also be recycled into molecular oxygen by reacting with a photon:

$$O_3 + h\nu \rightarrow O_2 + O.$$

About 90% of the ozone in our atmosphere is contained in the stratosphere. Ozone concentrations are greatest between about 20 and 40 kilometres), where they range from about 2 to 8 ppm.

Depletion of Ozone:

The ozone layer can be depleted by free radical catalysts, including nitric oxide (NO), nitrous oxide (N_2O), hydroxyl (OH), atomic chlorine (Cl), and atomic bromine (Br). While there are natural sources for all of these species, the concentrations of chlorine and bromine increased markedly in recent decades due to the release of large quantities of man-made organohalogen compounds, especially chlorofluorocarbons (CFCs) and bromofluorocarbons. These highly stable compounds are capable of surviving the rise to the stratosphere, where Cl and Br radicals are liberated by the action of ultraviolet light. Each radical is then free to initiate and catalyze a chain reaction capable of breaking down over 100,000 ozone molecules. Nitrous oxide was the largest ozone-depleting substance (ODS) emitted through human activities.

The breakdown of ozone in the stratosphere results in reduced absorption of ultraviolet radiation. Consequently, unabsorbed and dangerous ultraviolet radiation is able to reach the Earth's surface at a higher intensity. Ozone levels have dropped by a worldwide average of about 4% since the late 1970s. For approximately 5% of the Earth's surface, around the north and south poles, much larger seasonal declines have been seen, and are described as "ozone holes".

Chemistry of Ozone Depletion

CFC molecules are made up of chlorine, fluorine and carbon atoms and are extremely stable. This extreme stability allows CFC's to slowly make their way into the stratosphere (most molecules decompose before they can cross into the stratosphere from the troposphere). This prolonged life in the atmosphere allows them to reach great altitudes where photons are more energetic. When the CFC's come into contact with these high energy photons, their individual components are freed from the whole. The following reaction displays how Cl atoms have an ozone destroying cycle:

$Cl + O_3 \rightarrow ClO + O_2$ (step 1)

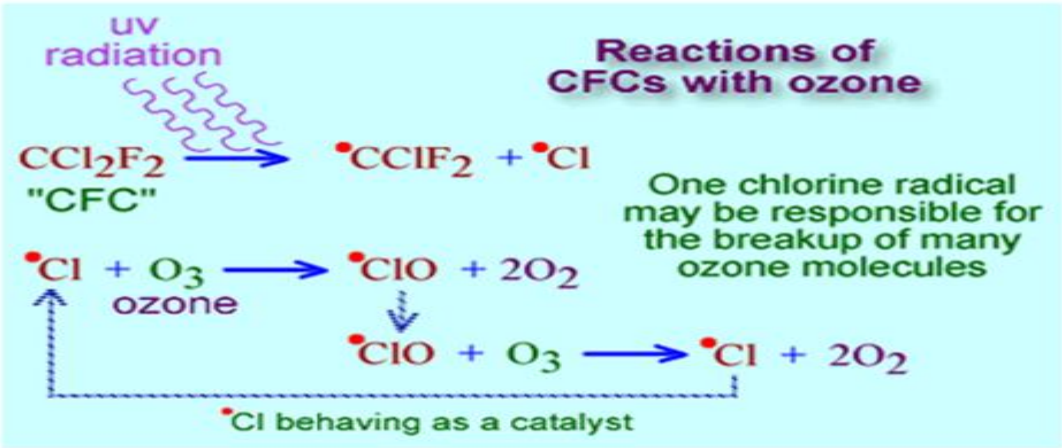
$ClO + O. \rightarrow Cl + O_2$ (step 2)

$O_3 + O. \rightarrow 2O_2$ (Overall reaction)

Chlorine is able to destroy so much of the ozone because it acts as a catalyst. Chlorine initiates the breakdown of ozone and combines with a freed oxygen to create two oxygen molecules. After each reaction, chlorine begins the destructive cycle again with another ozone molecule. One chlorine atom can thereby destroy thousands of ozone molecules.

Because ozone molecules are being broken down they are unable to absorb any ultraviolet light so we experience more intense UV radiation at the earths surface.

Low-temperature surface reactions on polar stratospheric clouds (PSCs) significantly increase reactive halogen gases and thereby cause severe ozone loss in polar regions in late winter and early spring.



General Questions

- What are the causes of the depletion of our ozone layer?
  - the release of free radicals, the use of CFC's, the excessive burning of fossil fuels
- What is the chemical reaction that displays how ozone is created?
  - UV + O_2 -> 2O + heat, O_2 + O -> O_3, O_3 + O -> $2O_2$
- Which reactions demonstrate the destruction of the ozone layer?
  - Cl + O_3 ------> ClO + O_2 and ClO + O ------> Cl + O
- How do CFC's destroy the ozone layer?
  - the atomic chlorine freed from CFC reacts in a catalytic manner with ozone and atomic oxygen to make more oxygen molecules
- Why should regulations be enforced now in regards to pollution and harmful chemicals?
  - without regulation, the production and use of chemicals will run out of hand and do irreversible damage to the stratosphere
- What type of atom in the CFC molecule is most destructive to the ozone?
  - chlorine
- In which layer of the atmosphere does the ozone layer?
  - the stratosphere, the second closest to the Earth's surface
- What cycle is responsible for ozone in the stratosphere?
  - the Chapman cycle
- What factor is responsible for breaking up stable molecules?
  - ultraviolet rays from the sun

The Smog:

Under the right conditions, the smoke and sulfur dioxide produced from the burning of coal can combine with fog to create **industrial smog**. In high concentrations, industrial smog can be extremely toxic to humans and other living organisms. London is world famous for its episodes of industrial smog. The most famous London smog event occurred in December, 1952 when five days of calm foggy weather created a toxic atmosphere that claimed about 4000 human lives.

Smog is a common form of air pollution found mainly in urban areas and large population centers. The term refers to any type of atmospheric pollution—regardless of source, composition, or concentration—that creates a significant reduction in atmospheric visibility . It is a particular type of smog that resulted from a combination of dense fog and soot from coal combustion.

the burning of fossil fuels like gasoline can create another atmospheric pollution problem known as **photochemical smog**. Photochemical smog is a condition that develops when **primary pollutants** (oxides of nitrogen and volatile organic compounds created from fossil fuel combustion) interact under the influence of **sunlight** to produce a mixture of hundreds of different and hazardous chemicals known as **secondary pollutants**.

Photochemical Smog

Photochemical smog, as commonly seen in the Los Angeles Basin, is mainly composed of ozone and nitrogen dioxide. During the formation of ozone, nitrogen dioxide from vehicle exhaust is photolyzed by incoming solar radiation to produce nitrogen oxide and an unpaired oxygen atom. The lone oxygen atom then combines with an oxygen molecule to produce ozone. Under normal conditions, the majority of ozone molecules oxidize nitrogen oxide back into nitrogen dioxide, creating a virtual cycle that leads to only a very slight build up of ozone near ground level. However, when volatile organic compounds (VOCs) are present in the atmosphere, the equation changes entirely. Highly reactive VOCs oxidize nitrogen oxide into nitrogen dioxide without breaking down any ozone molecules in the process. This leads to a proliferation of ozone near ground level and dense smog formation.

Composition of Photochemical Smog

The following substances are identified in photochemical smog:

1. Nitrogen Dioxide (NO_2) from vehicle exhaust, is photolyzed by ultraviolet (UV) radiation (hv) from the sun and decomposes into Nitrogen Oxide (NO and an oxygen radical:

$NO_2+hv \rightarrow NO+O.$ (1)

2. The oxygen radical then reacts with an atmospheric oxygen molecule to create ozone, O_3:

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

3. Under normal conditions, O_3 reacts with NO, to produce NO_2 and an oxygen molecule:

$O_3 + NO \rightarrow O_2 + NO_2$ (3)

This is a continual cycle that leads only to a temporary increase in net ozone production. To create photochemical smog on the scale observed in Los Angeles, the process must include Volatile organic compounds (VOC's).

$NO + RO_2$ »»» NO_2 + other products

Nitrogen dioxide (NO_2) can also react with radicals produced from volatile organic compounds in a series of reactions to form toxic products such as **peroxyacetyl nitrates** (PAN).

$NO_2 + R$ »»» products such as PAN

It should be noted that ozone can be produced naturally in an unpolluted atmosphere. However, it is consumed by **nitrogen oxide** as illustrated in the first reaction. The introduction of **volatile organic compounds** results in an alternative pathway for the **nitrogen oxide**, still forming **nitrogen dioxide** but not consuming the **ozone**, and therefore ozone concentrations can be elevated to toxic levels.

4. VOC's react with hydroxide in the atmosphere to create water and a reactive VOC molecule:

$RH + OH. \rightarrow R. + H_2O$ (4)

5. The reactive VOC can then bind with an oxygen molecule to create an oxidized VOC:

$R. + O_2 \rightarrow RO_2$ (5)

6. The oxidized VOC can now bond with the nitrogen oxide produced in the earlier set of equations to form nitrogen dioxide and a reactive VOC molecule:

$RO_2 + NO \rightarrow RO-. + NO_2$ (6)

In the second set of equations, it is apparent that nitrogen oxide, produced in equation 1, is oxidized in equation 6 without the destruction of any ozone. This means that in the presence of VOCs, equation 3 is essentially eliminated, leading to a large and rapid build up in the photochemical smog in the lower atmosphere.

In the morning, NO and VOC concentrations are high, as people fill their cars with gas and drive to work. By midmorning , VOC's begin to oxidize NO into NO_2, thus reducing their respective concentrations. At midday, NO_2 concentrations peak just before solar radiation becomes intense enough to photolyze the NO_2 bond, releasing an oxygen atom that quickly gets converted into O_3. By late afternoon, peak concentrations of photochemical smog are present.

London Smog

London-type smog is mainly a product of burning large amounts of high sulfur coal. Clean air laws passed in 1956 have greatly reduced smog formation in the United Kingdom; however, in other parts of the world London-type smog is still very prevalent. The main constituent of London-type smog is soot; however, these smogs also contain large quantities of fly ash, sulfur dioxide, sodium chloride and calcium sulfate particles. If concentrations are high enough, sulfur dioxide can react with atmospheric hydroxide to produce sulfuric acid, which will precipitate as acid rain.

$SO_2 + OH. \rightarrow HOSO_2$ (1)

$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$ (2)

$SO_3 + H_2O \rightarrow H_2SO_4$ (3)