Chemistry of Ozone

Ozone is triatomic oxygen, O_3. (Ozone is from the Greek ozein, "to smell.")
It is a form of oxygen in which the atoms combine in threes, (correct IUPAC name: trioxygen, O_3), rather than the usual twos, (dioxygen, O_2).
If we breathe in trioxygen, it's a poison, it's measured as an air pollutant at ground level.
Both trioxygen and dioxygen forms play a role in protecting life on the Earth's surface from the harmful ultraviolet radiation.

Ozone is an allotrope or a polymorph of oxygen.

Definition: Polymorph: compounds or elements which can exist in more than one solid form, in which the particles are arranged in different ways.

Definition: Allotrope

Lewis structure of: ozone, O_3 O_2

Molecular geometry of ozone, O_3

Explain the following terms: resonance, resonance hybrid, delocalisation

What is the bond order of the O_3 and O_2 molecule?

Is O_3 a polar or non-polar molecule?

Is O_3 a diamagnetic or paramagnetic molecule?

What type of intermolecular forces are expected for the O_3 molecule?

What are the expected physical properties of O_3 ?

The ozone, O_3, molecule has a bent geometry, bond angle of ~ 117 ^{0}, and is a hybrid of two resonance structures, bonds intermediate between single and double, bond order of 1 ½ .

Ozone is a diamagnetic, unstable blue gas with a characteristic pungent odour.
Ozone condenses at low temperatures to give a deep blue liquid and is violet-black as a solid; however both forms are dangerously explosive, decomposing to oxygen gas.
(Note: gaseous ozone also decomposes to oxygen but more slowly.)

Ozone, O_3, is much less abundant in the atmosphere than the other polymorph - dioxygen, $O_{2(g)}$

The Ozone Cycle in the Stratosphere

The stratosphere is the zone of the atmosphere lying just above the troposphere (upper atmosphere- where we live), and is between 16 and 40 km in altitude, and one of its gases is trace amounts of ozone; it contains much more UV radiation than the radiation which reaches the surface of the Earth, protecting us from the harmful radiation.

There is more naturally occurring ozone gas in the stratosphere than in the rest of the atmosphere.

Ozone in the stratosphere is beneficial because it prevents most of the short-wavelength, high-energy ultraviolet radiation from reaching the Earth's surface.

What is the relationship between wavelength, frequency and energy? ($\Delta E = hf = hc / \lambda$)

In the table below, is oxygen gas or ozone more susceptible to break the bond?

	bond length (nm)	**bond enthalpy (kJ mol^{-1})**	**wavelength of UV needed (nm)**	**absorption frequency (10^{14} Hz)**	**bond type**
oxygen, O_2	0.121	498	< 242	12.4	double, bond order of 2
ozone, O_3	0.128	302	< 330	10.1	'one and a half', 1½

The bonds in O_2 and O_3 can both be broken when they absorb ultraviolet radiation of sufficient energy.
However the double bond in O_2 is stronger than the 1.5 bond in O_3.
Energy, with a wavelength of 300 nm – 330 nm is insufficient to break the double bonds in O_2 but sufficient to break the bonds in O_3

The temperature of the atmosphere decreases with increasing height, but at 12 km above the Earth's surface, the temperature begins to rise because the ultraviolet radiation is absorbed in a number of photochemical reactions.

Ultraviolet radiation is involved in producing the ozone layer. The first step in the formation of the ozone, $O_{3\,(g)}$, is the dissociation fo oxygen molecules, $O_{2\,(g)}$ by UV light.

In the upper stratosphere, O_2 is bombarded with ultraviolet radiation from the sun.
The double bond in the O_2 molecule requires a shorter wavelength, < 242 nm, ultraviolet radiation, (i.e. higher energy), this can break the covalent double bonds in the oxygen molecule, O_2, by the photochemical reaction and generate oxygen free radicals:

$$O = O_{(g)} \xrightarrow{\lambda < 242\ nm} 2\ O\bullet_{(g)}$$

[Definition: free radical: is a species with an unpaired electron.]

The oxygen free radicals, $O\bullet_{(g)}$, then react with the oxygen molecules, $O_{2\,(g)}$, to form ozone, $O_{3\,(g)}$

$$O\bullet_{(g)} + O_{2(g)} \longrightarrow O_{3(g)}$$

This reaction is exothermic because bonds are formed and hence the temperature of the stratosphere rises, compared to the atmospheric levels immediately above and below it.

The ozone, $O_{3(g)}$, bond is weaker than the O_2 bond, thus less energy is required to break it, the ozone, $O_{3(g)}$ molecules also absorb UV radiation and decompose to oxygen free radicals and oxygen molecules:

$$O_{3(g)} \xrightarrow{\lambda < 330\text{ nm}} O\bullet_{(g)} + O_{2(g)}$$

The oxygen free radical then reacts with another ozone, $O_{3(g)}$ molecule to form oxygen gas, $O_{2(g)}$

$$O_{3(g)} + O\bullet_{(g)} \longrightarrow 2O_{2(g)}$$

This bond forming reaction is again an exothermic reaction and continues to maintain the high temperature of the stratosphere. There is a net energy conversion from UV to heat energy.

Through the process of formation and decomposition of ozone, almost all of the harmful UV radiation is absorbed.

The rate of formation of $O_{3(g)}$ is balanced by its rate of removal , a natural steady state equilibrium exists. This process is known as the Chapman Cycle.

Hence, a natural dynamic equilibrium exists between O_2 and O_3 in the stratosphere:

The natural formation of ozone in the stratosphere:

$$O_2 \longrightarrow 2O\bullet$$
$$O\bullet + O_2 \longrightarrow O_3$$

The natural depletion of ozone in the stratosphere

$$O_3 \longrightarrow O\bullet + O_2$$
$$O_3 + O\bullet \longrightarrow 2O_2$$

The natural equilibrium between $O_{2(g)}$ and $O_{3(g)}$ in the stratosphere allows the absorption of ultraviolet radiation.

Before photosynthetic bacteria released oxygen into the atmosphere and purged it of CO_2 the sun's UV light reached the Earth's surface, thus stopping life from existing onto land as the exposed DNA can be ripped to shreds by the UV radiation.
However, once the oxygen rich atmosphere was established, then a concentration of ozone, O_3, built up around the stratosphere where the UV radiation impacted and this $O_2 - O_3$ equilibrium acted as a shield against the high energy UV radiation; thus allowing the Earth's surface to be conducive to life: plants, dinosaurs, and of course humans.

If there is little ozone in the stratosphere, then UV radiation is able to reach the surface, resulting in the damage of the DNA, leading to skin cancer, eye cataracts. It can also cause genetic mutations and destroy vegetation.

Ozone is used in the treatment of water rather than chlorine to kill microorganisms, (pathogens,

germs or bacteria).
The advantages of ozone over chlorine are that it is more effective than chlorine against viruses, leaves no taste, does not produce harmful by-products, (no poisonous chlorine compounds); and further it can be produced on site.

One of the cause of the depletion of the ozone is known to be chemicals called CFCc, (chlorofluorocarbons); these are volatile, readily liquefied, relatively inert and non-toxic, noncombustible; they have been used as propellants in aerosol cans, used as blowing agents in plastics and used as coolants in refrigerators and air conditioners.
Because they are inert, CFCs remain unchanged in the atmosphere and eventually diffuse to the stratosphere, where UV radiation causes them to decompose.

Bond energy: C – F = 452 kJ mol^{-1} Bond energy: C – Cl = 346 kJ mol^{-1}

The relatively weak C – Cl bond is an easy target for the UV radiation and free radicals are produced, which then go on to attack ozone, $O_{3(g)}$

Chlorine free radicals can form via homolytic fission of the C – Cl bond, from the chlorofluorocarbon organic compounds which can then react with the ozone, O_3.

Equations for the depletion of ozone by CFCs:

$$CF_2Cl_2 \xrightarrow{hf} CF_2Cl\bullet + Cl\bullet$$

$$Cl\bullet + O_3 \longrightarrow ClO\bullet + O_2$$

$$ClO\bullet + O_3 \longrightarrow Cl\bullet + 2O_2$$

overall reaction: $$2\,O_3 \longrightarrow 3O_2$$

Note that the chlorine free radical is reformed and in fact is acting as a homogeneous catalyst.

Definition: homogeneous catalysis

One chlorine free radical can stay in the stratosphere for years destroying huge numbers of ozone molecules; since the free radical Cl• is regenerated therefore it can continue to deplete O_3 molecules. CFCs lower the concentration of ozone in the ozone layer.

The chloro-compounds have been replaced by the hydroflurocarbon compounds as the C–F bond is much stronger so fluorine free radicals do not form and thus do not pose the same threat to ozone.

Following the 1987 Montreal Protocol, the use of CFCs is being phased out.

Two alternatives to CFCs are HCFCs, (e.g. chlorodifluoromethane, CHF_2Cl) and hydrocarbons, (e.g. 2-methylpropane, C_4H_{10}).

The C – H bond is stronger than a C – Cl bond, thus the hydrocarbons do not react with ozone

and do not form free radicals in UV light.
(Bond energy: Bond energy: $C - H = 414\ kJ\ mol^{-1}$ $C - Cl = 346\ kJ\ mol^{-1}$)

Apart from being less harmful to the ozone layer, these two alternatives generally have low boiling point, are non reactive, non toxic.

They do not form free radicals in ultraviolet light and do not react with ozone.

However, they are flammable and less efficient as solvents than CFCs; and contribute to global warming.

Lewis structures:

NO $\qquad\qquad\qquad\qquad$ NO_2

Note that both • NO and • NO_2 are already free radicals, i.e. odd number of electrons - one unpaired electron.

Some natural activities and some caused by industrial activities can affect the ozone cycle also. The primary pollutant are nitrogen oxides known as NO_x , (e.g., $N_2O_{(g)}$, $NO_{(g)}$, $NO_{2(g)}$, $N_2O_{4(g)}$).

Nitrogen monoxide, $NO_{(g),}$ is produced whenever fuel is burned in air at high temperature, for example in an internal combustion engine; and like CFCs works its way up into the stratosphere.

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$$

When released into the atmosphere, the colourless nitrogen monoxide reacts rapidly with oxygen to form nitrogen dioxide, a reddish-brown gas - a toxic smog-forming gas-the brownish colour of the air in a smog-bound city.

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

• NO, • NO_2, act as catalysts, (homogeneous catalysis), in the depletion of ozone:

$$\bullet NO + O_3 \longrightarrow \bullet NO_2 + O_2$$

$$\bullet NO_2 + O_3 \longrightarrow \bullet NO + 2O_{2(g)}$$

•NO is acting as a catalyst because it is regenerated during the destruction of O_3

Catalytic converters significantly reduce the level of NO_x emitted by automobile engines.
In a catalytic converter the exhaust gases pass over a surface containing beads of rhodium, palladium and platinum, which reduce the $NO_{(g)}$ to $N_{2(g)}$, (and oxidize $CO_{(g)}$ to $CO_{2(g)}$). This is an example of heterogeneous catalysis

However ozone depletion does not take place evenly throughout the world or at even times of the year.

This is because tiny ice crystals in the stratospheric clouds provide the surface upon which the reactions take place.

Cl• and NO_x react at the surface of the ice particles in the arctic winter because ice surface acts as a heterogeneous catalyst, (define: heterogeneous catalysis).

These icy clouds in the stratosphere form in very cold region and climate, i.e. in the polar regions and in the winter months.

So the Antarctic ozone hole is much worse than the Arctic and is seasonal- opening up in September and closing during the course of November.
This mirrors the temperature variation in the Southern Hemisphere region.

Ozone depletion is greatest during the Arctic Spring because ice particles melt releasing the pollutants, the returning sunlight -UV light triggers the photochemical reaction to break the bonds producing the Cl• free radicals.

Ozone depletion can also be catalysed by droplets of sulphuric acid aerosol in the stratosphere. This occurs during sulphur rich volcanic eruption - this causes a short term effect in the ozone levels and is not confined to the poles.